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Article

The Role of Mineral Matter in Concentrating Uranium and Thorium in Coal and Combustion Residues from Power Plants in Poland

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Abstract: Based on the results of tests on feed coal from the Lublin Coal and Upper Silesian Coal Basin and its fly ash and slag carried out using X-ray diffraction and X-ray fluorescence analysis, atomic emission spectroscopy, and scanning electron microscopy, it was found that in feeds, coal Th is associated with phosphates and U with mineral matter. The highest Th content was found in anhedral grains of monazite and in Al-Si porous particles of fly ash of <0.05 mm size; whereas in the slag, Th is concentrated in the massive Al-Si grains and in ferrospheres. U is mainly concentrated in the Al-Si surface of porous grains, which form a part of fly ash of <0.05 mm size. In the slag, U is to be found in the Al-Si massive grains or in a dispersed form in non-magnetic and magnetic grains. Groups of mineral phase particles have been identified that have the greatest impact on the content of Th and U in whole fly ash and slag. The research results contained in this article may be important for predicting the efficiency of Th and U leaching from furnace waste storage sites and from falling dusts to soils and waters.

Keywords: Th and U in minerals; feed coal; combustion residues; environment pollution

1. Introduction

The identification of groups of minerals that have the greatest influence on trace elements content in coal makes it easier to forecast the efficiency of various chemical and mechanical procedures for purging ecotoxic elements (e.g., refs. [1–3]); it also has an influence on more conscious forecasts concerning the quantities of elements released into the environment following coal combustion [4–8]. Combustion of hard coal in thermo-electric power stations provides people with electricity and heat, but also raises concerns about the possibility of environmental pollution. Dust from the thermo-electric power stations (TPS), as well as the combustion residues generated and remaining at these plants, are a threat to the environment, due to the ecotoxic trace elements present in them. The highest content of trace elements in combustion residues is recorded in the smallest particles of fly ash (e.g., refs. [1,9–12]). On the surface of the fly ash particles, there are condensed elements of high volatility, which include As, Cd, Cu, Pb, Sb, Sn, and Zn; and in the slag grains, elements of low volatility predominate, such as: Mn, Mo, Ni, and Fe (e.g., refs. [8,13–15]).

As of yet, there are no enforced limitations for ecotoxic element (including Th and U) emissions into the atmosphere from coal-fired industrial plants in Poland and the European Union. There are also no legal regulations concerning the content of these elements in the combusted fuel and in the eluates from combustion residue dumps [16,17].

In order to assess the impact of the industrial process of hard coal combustion on the environment, it is necessary to know the content and distribution of trace elements in the feed coals and in combustion

residues. The elements, associated with the organic matter or sulfides in the feed coals, undergo evaporation and condensation in fine particles of fly ash easier than when they are associated with, for example, oxides, silicates and aluminosilicates [1,8,18,19]. In turn, knowing the distribution and forms of the binding of the elements in the combustion residues will make the prediction of the speed of the possible leaching of elements to the soil and waters more accurate.

The leached concentrations expressed in terms of absolute value may certainly differ, but the leaching behaviour appears to follow relatively common patterns. This suggests that the factors that control the leaching of elements from fly ash do not differ significantly regardless of the composition and characteristics of the ash [20]. The trace element mobility in water is heavily pH-dependent. The concentration ratio of Ca and S in fly ash probably determines the pH of the water-ash system and plays a key role in the assessment of the elution capability of the majority of elements in fly ash. Volatiles concentrated on the surface of fly ash particles are the easiest to elute, whereas the alkalinity contributes to the reduction of the leachability of a large number of heavy metals, which simultaneously increase the mobility and elution of several types of oxyanions. The majority of the elements (Be, Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, REE, Si, Sn, Th, Tl, U, and Zn) are most easily eluted in an acidic environment [20–22].

Among the ecotoxic elements, U and Th pose a threat to the environment and people not only because of the toxicity of some of their chemical compounds (especially U) which are soluble in water and acids, but also because of the recorded radioactivity of the feed coal and the several times higher radioactivity of the combustion residues than the feed coal. The combustion of coal causes an enrichment of naturally occurring radioactive materials in coal combustion residuals that correlates with the U and Th concentrations and ash content of the parent coals [23]. By way of example, combustion residues have total Ra activities typically 7–10 times higher than the activities of coal and 3–5 times higher than the activities of average soil. Radionuclides in the U and Th decay series in combustion residues older than 27 days may be approximately in radioactive secular equilibrium with the exception of certain radionuclides that become volatile during combustion.

The aim of the article is to identify the petrographic components of feed coal and the fly ash and slag particles with the highest content of Th and U together with the determination of the group of mineral particles that have the greatest impact on the content of Th and U in combustion residues. This research goal has not been achieved so far. The authors have studied coal from Lublin Coal (LCB) and Upper Silesian Coal Basin (USCB)—probably the most frequently burnt coal in the countries of Central Europe—and its combustion products in power plants in Poland.

2. Materials and Methods

The object being tested was the feed coal which was, as well as fly ash and slag resulting from the combustion of the feed coal in pulverized steam boilers, at an average temperature of 1340 °C in TPS in Poland (Figure 1). The flue gas desulfurization methods used in the TPS did not lead to the contact of fly ash and slag with a sorbent. The following were submitted for testing:

- six samples of feed coal from the LCB, as well as six samples of fly ash, and nine samples of slag, resulting from the combustion of feed coal in two steam boilers in two TPS;
- nine samples of feed coal from the USCB, as well as nine samples of fly ash, and nine samples of slag, resulting from the combustion of feed coal in nine steam boilers, in seven TPS.

The feed-coal samples were obtained from the samplers located at the coal feeder of the boilers, just before burning. Fly-ash samples were taken from the hoppers of the electrostatic precipitators and slag samples from the slag collectors.

The samples of whole feed coal and whole slag, which were dried in air, were ground into grains of <0.2 mm diameter. The samples of whole fly ash were separated by sieves into four size grain classes, i.e., >0.5 mm, 0.5–0.2 mm, 0.2–0.05 mm, and <0.05 mm. The samples of the whole feed coal, the samples of fly ash grain classes, and the samples of the total slag were separated by a manual

magnetic separator into magnetic and non-magnetic fractions. The yield of fractions and grain classes are given in Table 1.



Figure 1. Location of the coal basins and thermo-electric power station in which samples were taken. 1—Area of the Lublin (LCB) and Upper Silesian Coal Basin (USCB), 2—thermo-electric power station.

The petrographic composition and degree of coalification of feed coal organic matter were determined using a Zeiss Axio Imager D1m microscope (40×objective, 10×oculars, 546-nm interference filters, non-polarized reflected light, oil immersion with the refractive index $n = 1.5176$ at 23 °C). The applied microscopic analysis procedures were in accordance with the procedures described in ISO 7404-3 [24] and ISO 7404-5 [25]. The mineral composition of the feed coal mineral matter was verified using the D8 Discover X-ray diffractometer (irons filtered $\text{CoK}\alpha$ radiation, Ni-filter and Lynxeye detector). The results are shown in Table 1 (see Table S1).

The grains of feed coal (separated into magnetic and non-magnetic fractions), fly ash grains (separated into grain classes and magnetic and non-magnetic fractions), and slag grains (separated into magnetic and non-magnetic fractions), were transformed at 815 °C into ashes which were free from organic matter. The following was determined in the obtained ash samples:

- the content of the main elements (Si, Al, Fe, Ca, Mg, Na, K, S, Ti, and P) using an X-ray fluorescence selective spectrometer (WDXRF) type ZSX Primus II (Rh anode tube power = max 4 kW, 50 kV/60 mA, and analytical crystals: PET, LiF1, Rx25, Ge). Results of the analysis were converted into oxide contents (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO, MgO, Na_2O , K_2O , SO_3 , TiO_2 , and P_2O_5) in the ash;
- the content of Th and U, using the method of inductively coupled plasma atomic emission spectroscopy (0.25 g of the sample was heated with HNO_3 , HClO_4 and HF to fuming and brought to dryness. The residue was dissolved in HCl).

Table 1. Petrographical characteristics of feed coal from the Lublin (LCB) and Upper Silesian Coal Basin (USCB), and yield fraction of the feed coal, fly ash, and slag.

Characteristics	LCB	USCB
Vitrinite (vol %)	58.0	57.6
Liptinite (vol %)	5.3	5.1
Inertinite (vol %)	9.7	22.2
Mineral matter (vol %)	27.1	15.2
Sulfide minerals (vol %)	2.9 (Py) *	3.3 (Py) *
Magnetite + hematite (vol %)	<0.1 (Mh) *	0.2 (Mh) *
Quartz + feldspar (vol %)	<0.1 (Q) *	0.4 (Q) *
Clay minerals (vol %)	21.2 (Ka) *	5.5 (Ka) *
Carbonate minerals (vol %)	3.0 (Sd) *	5.8 (Do) *
Sulphate minerals (vol %)	<0.1 (G) *	<0.1 (G) *
Vitrinite reflectance (%)	0.74	0.76
Ash yield (wt %)	24.72	23.49
Feed coal	0.47	0.48
Fly ash sizes (mm)		
Yield of magnetic fraction (wt %)		
>0.50	0.54	0.14
0.50–0.20	4.71	1.92
0.20–0.05	9.79	8.02
<0.05	3.95	8.97
Slag	16.08	17.96
Feed coal	99.53	99.52
Fly ash sizes (mm)		
Yield of non-magnetic fraction (wt %)		
>0.50	1.90	0.18
0.50–0.20	12.78	5.03
0.20–0.05	32.71	30.59
<0.05	33.62	45.21
Slag	83.92	82.04

* Main minerals identified by X-ray: Do—dolomite, G—gypsum, Ka—kaolinite, Mh—magnetite, Py—pyrite, Q—quartz, Sd—siderite.

The results are shown in Table 2 (see Table S2).

Table 2. The average content of Th and U in the feed coal from the Lublin (LCB) and Upper Silesian Coal Basin (USCB) and in fly ash and slag, and enrichment factor values (EF).

Component	LCB					USCB				
	Feed Coal Content	Fly Ash Content	EF	Slag Content	EF	Feed Coal Content	Fly Ash Content	EF	Slag Content	EF
In whole component (g/Mg, ppm)										
Th	5.2	18.2	3.5	22.1	4.3	3.0	13.6	4.5	12.4	4.1
U	16.5	17.2	1.1	92.0	5.6	5.8	20.7	3.6	2.5	0.4
In whole ash of the component (wt %)										
SiO ₂	57.35 *	56.76	1.0	59.85	1.0	54.27 *	55.23	1.0	60.20	1.1
Al ₂ O ₃	27.47 *	25.72	0.9	26.55	1.0	21.67 *	22.10	1.0	20.89	1.0
Fe ₂ O ₃	7.12 *	7.66	1.1	6.53	0.9	7.96 *	7.37	0.9	7.11	0.9
CaO	1.11 *	1.55	1.4	1.04	0.9	4.05 *	5.33	1.3	3.39	0.8
MgO	1.17 *	0.95	0.8	1.07	0.9	2.85 *	2.70	0.9	2.59	0.9
Na ₂ O	0.49	0.59	1.2	0.43	0.9	1.15	1.16	1.0	0.88	0.8
K ₂ O	2.63	2.57	1.0	2.52	1.0	2.90	3.43	1.2	3.18	1.1
SO ₃	0.63	0.02	<0.1	0.00	0.0	3.74	1.12	0.3	0.40	0.1
TiO ₂	1.24	1.32	1.1	1.34	1.1	0.98	1.01	1.0	0.96	1.0
P ₂ O ₅	0.79	2.86	3.6	0.67	0.8	0.43	0.55	1.3	0.40	0.9

* The quotient of content SiO₂ + Al₂O₃ to CaO + MgO + Fe₂O₃ = 9.0 for feed coal from LCB and 5.1 for feed coal from USCB.

In micro-areas of feed coal (done on cross section), fly ash and slag (done on whole particles), the Th and U content were determined using the method of scanning an electron microscope with an energy dispersive X-ray (SEM/EDS), whilst maintaining the standard conditions of determination (acc. voltage = 15.0 kV, bse-comp = 30 Pa, image resolution = 1024 × 768, image pixel size = 0.04–0.27 μm, magnification = 90–5000). The results of the SEM/EDS analysis are shown in Figure 2 and Table 3 (see Table S3).

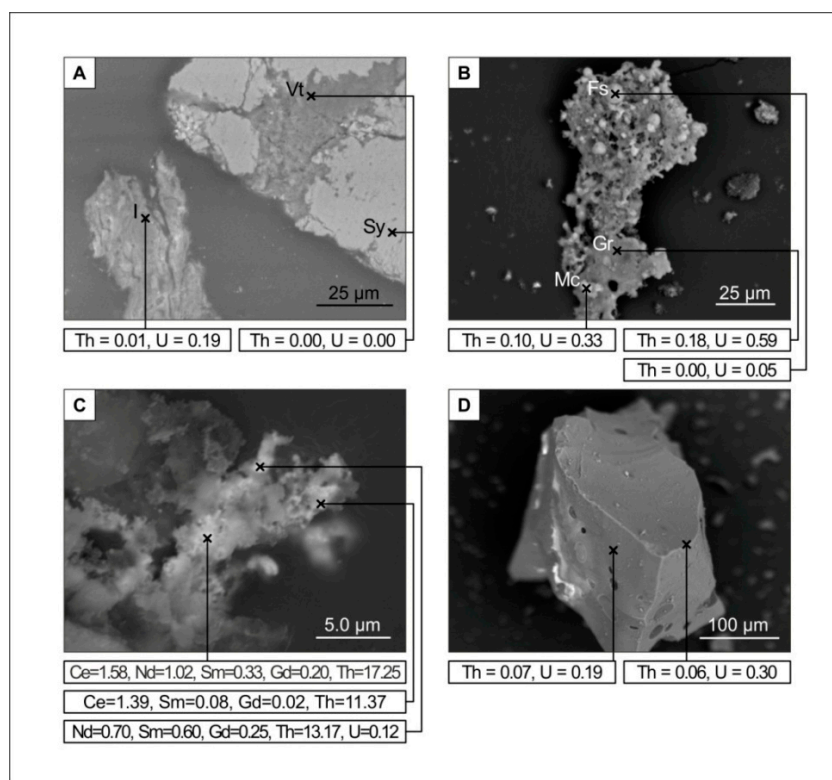


Figure 2. Sample results of the SEM/EDS analysis of U and Th content in: (A) inertinite (I), vitrinite (Vt) and siderite (Sy) in feed coal; (B) ferrosphere (Fs), Al-Si porous grain (Gr) and magnetite microcrystal (Mc) in fly ash <0.05 mm; (C) monazite in fly ash <0.05 mm; (D) Al-Si massive grain in slag.

The hypothesis concerning the normal distribution of measurements was analyzed using the Chi-square Pearson test, Kolmogorov-Smirnov test, and Shaphiro-Wilk test (with a significance level of $\rho = 0.05$). The hypothesis concerning the existence of correlation between petrographic component values and elements content values was verified by the analysis of a student's t-distribution, by calculating the level of significance of the correlation coefficient. The values of the correlation coefficient ($r \geq 0.35$) are shown in Table 4 (see Table S4).

Table 3. Maximum content (wt %) of U and Th in the feed coal from the Lublin (LCB) and Upper Silesian Coal Basin (USCB) and in the fly ash and slag obtained by SEM/EDS methods.

Element	LCB Content	Component	Fraction	USCB Content	Component	Fraction
Feed coal						
U	0.19	inertinite	nonmagnetic	nd *	not found	nonmagnetic
	<0.01	siderite	magnetic	0.12	siderite	magnetic
Th	0.01	inertinite	nonmagnetic	nd *	not found	nonmagnetic
	<0.01	siderite	magnetic	0.02	quartz with maceral inclusions	magnetic
Fly ash						
U	0.12	anhedral monazite grain	<0.05 nonmagnetic	0.16	surface of Al-Si microspheres	<0.05 nonmagnetic
	0.59	surface of Al-Si porous grain	<0.05 magnetic	0.25	surface of Al-Si microspheres with magnetite?	<0.05 magnetic
Th	17.25	anhedral monazite grain	<0.05 nonmagnetic	0.06	Al-Si microsphere	<0.05 nonmagnetic
	0.18	Al-Si porous grain with ferrosphere	<0.05 magnetic	0.14	Al-Si microsphere	<0.05 magnetic
Slag						
U	0.50	Al-Si massive grain	nonmagnetic	<0.01	not found	nonmagnetic
	0.30	Al-Si massive grain with magnetite?	magnetic	<0.01	not found	magnetic
Th	0.11	Al-Si massive grain	nonmagnetic	0.07	Al-Si massive grain	nonmagnetic
	0.13	Al-Si massive grain with magnetite?	magnetic	0.22	ferrosphere	magnetic

* no data.

Table 4. The role of organic and inorganic matter in the concentration of Th and U in the feed coal from Lublin and Upper Silesian Coal Basin, resulting from the results of the CD function solution and the value of the correlation coefficient between the content of Th and U and the content of major element oxides in feed coal and feed coal ash.

Element	Lublin Coal Basin				Upper Silesian Coal Basin			
	Organic Matter		Mineral Matter		Organic Matter		Mineral Matter	
	%	g/Mg (ppm)	%	g/Mg (ppm)	%	g/Mg (ppm)	%	g/Mg (ppm)
CD Function								
In feed coal ash								
Th	0.0	0.0	40.3	100.0	0.0	0.0	16.3	100.0
U	0.0	0.0	228.2	100.0	0.0	0.0	55.4	100.0
In Feed Coal								
Th	0.0	0.0	10.8	100.0	0.0	0.0	4.1	100.0
U	0.0	0.0	61.2	100.0	0.0	0.0	13.8	100.0
Correlation Coefficient (<i>r</i>)								
Th	$r_{Al_2O_3} = 0.813, r_{CaO} = 0.878,$				$r_A = 0.816, r_{Al_2O_3} = 0.888,$			
	$r_{MgO} = 0.681, r_{P_2O_5} = 0.836$				$r_{TiO_2} = 0.804, r_{P_2O_5} = 0.653$			
U	No correlation				No correlation			

Investigated trace element affinity to organic and inorganic coal fraction was found with the concentration distribution (CD) function of Marczak [26] as presented below. Significant geochemical information can be received from the data given by a solution of the CD function.

$$CD = C_A = C_o \frac{1-A}{A} + KA + C_m \quad (1)$$

where: *A*—ash content expressed as a mass fraction; *C_A*—a trace element concentration in ash (g/Mg); *C_o*—average trace element concentration in organic coal substance (g/Mg); *K*—a proportionality factor expressing a concentration increase (g/Mg) for ash unit; and *C_m*—a trace element concentration in coal ash for a limit value *A* = 0 (g/Mg).

The value *A* is determined empirically as the content of ash in coal. The values of *C_o*, *K*, and *C_m* are determined mathematically by solving a system of three equations with three unknowns. The first expression "*C_o·1 - A/A*" in the above equation determines the part of the content of the element in the coal ash which is related to organic matter. The sum of the two remaining expressions, i.e., "*KA + C_m*", includes the part that results from the presence of the element in mineral matter. The usefulness of the CD function for determining which part of a given trace element concentration is associated with the organic one and which with the inorganic coal fraction, has been confirmed in earlier publications [27–29]. The results obtained by this method are shown in Table 4 (see Table S5).

In order to determine the elements that were enriched in the furnace wastes, as a result of the combustion of feed coal, the enrichment factor (EF) was calculated, which is the quotient of the element content in fly ash or slag in relation to feed coal. The results of the calculations are presented in Table 2. Then, the influence of fly ash grains (divided into grain classes, and into a magnetic and non-magnetic fraction) and slag grains (divided into a magnetic and non-magnetic fraction) on the content of Th and U in the whole fly ash and slag was determined. For this purpose, the percentage share of each component of the weighted average was calculated. This component is the product of the element's content (in each class of grains, in each fraction of fly ash, and in each fraction of slag grains), the percentage share of the mass of each class, and the fraction of grains in the composition of whole fly ash and slag. The sum of the components of the weighted average is 100%. The results of the calculations are shown in Figure 3.

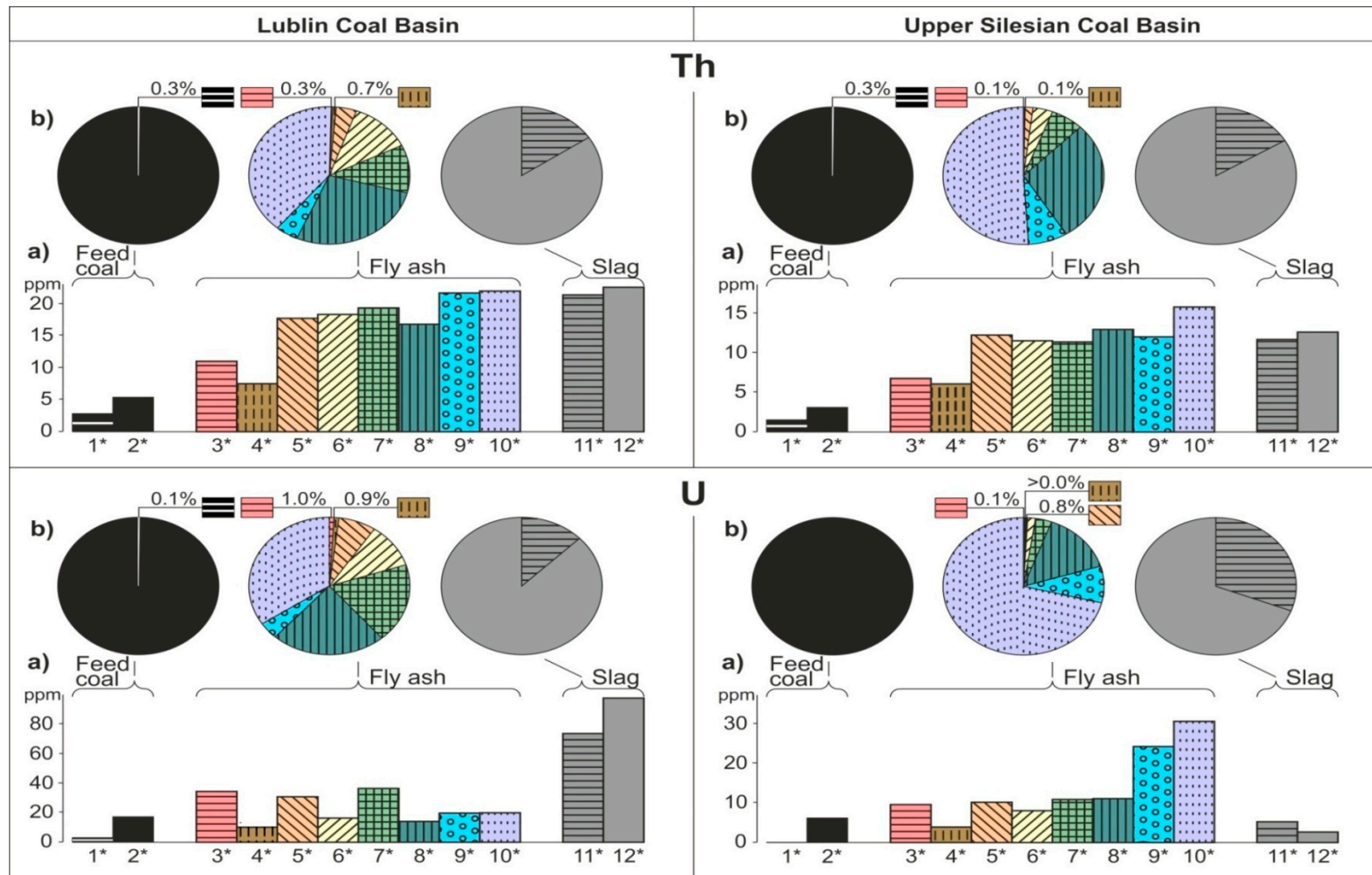


Figure 3. The distribution of U and Th content in the feed coal from the Lublin (LCB) and Upper Silesian Coal Basin (USCB) and in the fly ash and slag, (a) and their proportions in determining the average element concentration in fly ash and slag (b) (Table S6). *1—magnetic and 2—nonmagnetic fraction of the feed coal, 3–10 fly ash: (3—magnetic and 4—nonmagnetic fraction >0.5 mm, 5—magnetic and 6—nonmagnetic fraction 0.5–0.2 mm, 7—magnetic and 8—nonmagnetic fraction 0.2–0.05 mm, 9—magnetic and 10—nonmagnetic fraction <0.05 mm), 11—magnetic and 12—nonmagnetic fraction of the slag.

3. Results and Discussion

3.1. Geochemical Characteristics of Feed Coal

From the reflectance of vitrinite (Table 1), feed coals from the LCB and USCB were classified as ortho-bituminous coal. The feed coals from the LCB contain more mineral matter and less inertinite than the feed coals from the USCB. The composition of the mineral matter of the feed coals from the LCB most often contains kaolinite, and the feed coals from the USCB contain dolomite and kaolinite. There was no presence of Th or U minerals in the feed coals. The average ash yield of feed coal from the LCB amounts to 24.72% and 23.49% from the USCB.

In the chemical composition of the ash from the feed coals, there is a clear advantage of the sum of SiO_2 and Al_2O_3 contents over the sum of Fe_2O_3 , CaO , and MgO contents (Table 2). Due to the content of SiO_2 , Al_2O_3 , CaO , and SO_3 , the fly ash studied, which is generated by the combustion of feed coals from the LCB and the USCB, is classed as silicate ash according to Polish standards [30]. The average P_2O_5 content in feed coal ash from the USCB (0.43%) and especially from the LCB (0.79%) is greater than the average P_2O_5 content in hard coal from worldwide deposits (0.344 ± 0.022) [31]. The high phosphorus content, found multiple times in LCB coal, is a result of the presence of phosphate minerals (most likely apatite and crandallite) in kaolinite aggregates in tonsteins (in coal seam 382, 385, 387, and 391). The secondary source of phosphorus in these coal seams and main source of phosphorus in these coal deposits that do not contain mineral matter of the pyroclastic origin (378, 389, 394) may be clay minerals which absorbed phosphorus compounds derived from organic matter released during coalification [32].

The average Th and U content in feed coals from the LCB (Th = 5.2 ppm, U = 16.5 ppm; Table 2) and uranium in feed coals from the USCB (U = 5.8 ppm) is higher than the hard coal Clarke values (Th = 3.2 ppm, U = 1.9 ppm; Table 5) [31], and the average thorium content in the feed coals from the USCB (Th = 3.0 ppm) is lower. In the feed coals from the LCB, higher Th and U contents are present than in feed coals from the USCB. With regard to the Th and U contents in the feed coal, the Th and U contents in USCB coal (for Th and U) and LCB coal (for Th) are similar to raw coal from Bulgaria, China and the USA [33–35], while, with regard to the U content in the LCB feed coal, it is similar to the U content in feed coal from Europe, Turkey and the USA [36,37]. Bituminous coal (raw coal and/or feed coal) combusted over the last decade in Poland is characterized by low Th and U content, which is significantly different from the maximum content of, for example, uranium observed in coal from the Xijiang province in China (7207 ppm; Table 5).

From the SEM/EDS analysis results, it was found that in the feed coals from the LCB, the highest content of Th and U was recorded in inertinite (Table 3). For this reason, the content of Th and U is clearly higher in the non-magnetic fraction of the feed coals than in the magnetic fraction (Figure 3). Due to the large share in whole coal (Table 1), the non-magnetic fraction also has the greatest impact on the average content of Th and U in the whole feed coal from the LCB (Figure 3). In turn, in the USCB feed coal, the highest content of Th was found in quartz, with inclusions or in adhesions with organic matter, and the highest content of U was found in siderite, which are components of the magnetic fraction (Table 3). This fraction, due to its small share in the composition of feed coals (Table 1), has a negligible effect on the average Th and U content in feed coals from the USCB (Figure 3). The non-magnetic fraction has a significant influence on the content of Th and U in feed coals from the USCB, in the composition of which macerals and minerals are characterized by low content of U (Table 3).

Table 5. U and Th in the selected world’s bituminous coal/feed coal, fly ash, bottom ash, slag and eluates, and leaching efficiency (in brackets).

Materials	Type of Material	Area	Thorium g/Mg	Uranium g/Mg	Reference *
Coal	raw	World	3.2 ± 0.1	1.9±0.1	Ketris and Yudovich [31]
	feed coal	Europe	5.6	6.1	Querol et al. [38]
	feed coal	Europe	17–65	5.0–29.0	Moreno et al. [36]
	feed coal	Brazil	14.09–17.04	6.12–7.67	Silva et al [39]
	raw	Bulgaria	6.0	5.0	Yossifova [33]
	raw (background)	China	5.84	2.43	Dai et al. [34]
	raw (significant)	China	nd	0.75–7207	Chen [40]
	raw, LCB	Poland	3.2	1.9	Parzentny [41]
	raw, USCB	Poland	2.3	1.9	Bojakowska et al. [42]
	feed coal	Poland	1.1–2.6	0.2–0.8	Smolka-Danielowska [43]
	feed coal	Spain	5.6	6.1	Llorens et al. [44]
	feed coal	Turkey	9	14	Vassilev et al. [37]
	raw	USA	3.2 ¹	2.1 ¹	Finkelman [45] ¹
raw	USA	1.5–5.9 ²	1.2–3.9 ²	Bragg et al [35] ²	
Fly ash		Europe	22.1	22.9	Querol et al. [38]
		Brazil	33.5–42.0	14.5–24.8	Silva et al. [39]
		China	5.8–50	2.6–51.9	Dai et al. [46]
	USCB	Poland	23.0	10.6	Ratajczak et al. [47]
	USCB	Poland	7.6–19.3	3.3–10.6	Smolka-Danielowska [43]
		Spain	22.1	22.9	Llorens et al. [44]
		Turkey	22	34	Vassilev et al. [45]
		USA	14.0–28.0 ²	6.9–12.7 ²	Affolter et al. [48] ²
		USA	11.8–21.6	6.72–10.4	Jones et al. [49]
Bottom ash/slag		Europe	20.6	19.0	Querol et al. [38]
		Australia	15–42	5.0–9.7	Ilyushechkin et al. [50]
		Brazil	25.8–42.9	9.3–16.7	Silva et al. [39]
		China	19.1–25	8.5–379.2	Dai et al. [46]
		Spain	20.6	19	Llorens et al. [44]
		Turkey	15	19	Vassilev et al. [37]
		USA	14.9–25.3 ²	0.9–9.7 ²	Affolter et al. [48] ²
Leachate **		USA	13.0–25.3	5.87–9.83	Jones et al. [49]
	fly ash ^a	Europe	7.0–18.0	<1–12	Moreno et al. [36]
	fly ash ^a	Brazil	<0.01	<0.01	Silva et al. [39]
	fly ash ^a	Spain	0	0	Querol et al. [51]
	fly ash ^a	Spain	0.7 × 10 ⁻³	1.6 × 10 ⁻³	Llorens et al. [44]
	fly ash ^b	USA	nd	0.003–0.015	Jones et al. [49]
			nd	(0.6%–5.3%)	
	fly ash ^c	USA	nd	0.004–0.007	Jones et al. [49]
			nd	(0.8%–2.1%)	
	Slag ^a	Australia	0–0.6 ⁻⁵ (0%–0.8 ⁻³ %)	0–2.0 ⁻⁵ (0%–0.8 ⁻³ %)	Ilyushechkin et al. [50]
bottom ash ^a	Brazil	<0.01	<0.01–0.20	Silva et al. [39]	
Slag ^a	Spain	0	0	Querol et al. [51]	
bottom ash ^a	Spain	0.1 × 10 ⁻³	1.7 × 10 ⁻³	Llorens et al. [44]	
bottom ash ^b	USA	nd	<0.001–0.001	Jones et al. [49]	
		nd	(0.2%)		
bottom ash ^c	USA	nd	<0.001–0.001	Jones et al. [49]	
		nd	(0.2%)		

* Citation after: ¹ Dai et al. [34], ² Hower et al. [19]; ** Analytical procedure: ^a with distilled water (µg/kg), ^b synthetic groundwater leaching procedure (mg/L), ^c toxicity characteristic leaching procedure (mg/L); nd—no data.

The solution of the CD function made it possible to determine that the average Th and U content in feed coals from the LCB and the USCB is affected by mineral matter (Table 4). The analysis of the value of the correlation coefficient between the content of the main elements in the feed coal ash and the content of Th in coal, indicates the important role of phases containing Al_2O_3 , P_2O_5 , CaO, and MgO (probably apatite or crandallite) in concentrating Th in feed coals from the LCB, and the major role of phases rich in Al_2O_3 , P_2O_5 , and TiO_2 (probably phosphates), in concentrating Th in the feed coals from the USCB. Which group of macerals or minerals has the greatest impact on the U content in feed coals from the LCB and USCB is not yet known.

It is assumed that Th and U in low rank caustobiolites are found in humic compounds and, as a result of the catagenesis of organic matter, these elements co-create autogenic inorganic compounds [52]. However, the above average Th and U contents in bituminous coal are of volcanic and/or epigenetic origin. Thorium occurrences in coal are generally linked to assemblages of detrital minerals. Zircon, monazite, apatite, xenotime, and clay minerals are among the minerals that are most common and most abundant in Th. Uranium can have both organic and inorganic associations in coal. In the organic matter of bituminous coal, uranium concentrates most often in vitrinite, while when it comes to mineral matter components, it is more common in uraninite, coffinite, anatase, guadarramite, brannerite, kaolinite, and pyrite, which are predominantly carriers of U in coal [19,38,40,52–56]. Although Th and U minerals were not found in the feed coal investigations (Table 1), these minerals were often identified in raw coal from the LCB and USCB (e.g., [32,35,43,51,57–59]). The mode of binding Th, U, and other trace elements in feed coals is probably an individual feature of each coal feed and may be different than the specific mode of their binding in raw coal. As it was noted for chalcophile elements, the mode of binding of Th and U in coal is probably not a permanent identification feature of raw coal for the entire deposit or basin. It may be different in raw coal from the individual lithostratigraphic members of a given seam and may even differ in individual parts of a single coal bed [5,27,40,60,61]. In addition, the content and mode of binding elements in feed coal may be different before and after removal in the plant for the enrichment of mineral matter from coal.

The distribution of Th and U found above in the investigated coal feeds was assessed as unfavorable for the creation of clean Th and U-free energy fuel. The removal of Th and U from macerals and sub-microscopic Th and U minerals from coal using gravity separation and flotation is generally considered ineffective, because the Th and U concentration in the cleaned coal is still much higher than the average value for world hard coals [40,55,62]. It is best to avoid the combustion of coal rich in Th and U, with prior monitoring of their contents in the raw coal or the feed coal. Though the Th and U contents in the studied feed coal are minor and, simultaneously, similar to those found most often in worldwide raw coal, it is nevertheless possible for coal deposits with high uranium content to be present in the LCB and USCB (e.g., 2660 ppm, as found by Sałdan [63] in the USCB). Care must be taken so that no coal with high uranium and other ecotoxic element contents are combusted. This goal has already been achieved in the USA [64].

3.2. Content and Distribution of Th and U in Fly Ash and Slag

Non-magnetic particles of <0.05 mm size are the most common component of fly ash generated by the combustion of feed coal from the LCB (33.6%) and USCB (45.1%; Table 1). Non-magnetic grains are also most commonly found in slag composition (83.9% and 82.0%, respectively). The contents of Th and U in the fly ash and slag resulting from the combustion of feed coal from the LCB and USCB is of 1.1–5.6 times higher than in feed coal (Table 2). Only the content of uranium in the slag, resulting from the combustion of feed coals from the USCB, is smaller than the content of uranium in the feed coals. The average thorium content in the fly ash from the LCB and USCB is lower, and the uranium content is higher than in fly ash, which is generated in combusted coal in Poland (according to reference [43]: content of Th = 25.9 ppm, U = 8.6 ppm; according to reference [47]: content of Th = 23.0 ppm, U = 10.6 ppm; shown in Tables 2 and 3). Compared to the combustion residues generated in other power plants (Tables 2 and 3), the Th and U contents in the studied fly ash are

similar to fly ash from power plants in the USA (for Th) [48,49] and power plants in Brazil and China (for U) [39,46]. The Th content in the studied slag is similar to the Th content in the slag from other cited power plants, and the uranium content in the slag from the USCB feed coal is the same as in the slag from the Figueira power plant in Australia and Brazil [49,50], whereas from the LCB it is similar to the U content in the slag from power plants in China. It is assumed that the Th and U contents in combustion residues are proportional or similar to their contents in feed coal [8,19]. This arises from the assumption that Th and U constitute non-volatile or slightly volatile elements during the coal combustion process [19], particularly when they are bound with mineral matter. Yet, other authors claim that U is a volatile element [18,65] or an element with intermediate qualities, i.e., it is both non-volatile (concentrating in slag and large fly ash particles) and volatile (easily evaporating and condensing on fine fly ash particles) [10]. The results presented in Table 2 demonstrate Th and U enrichment in the fly ash and slag compared to the feed coal. Taking into account the fact that the combustion temperature of the studied feed coal (1340 °C) was lower than the melting point of thorium (1750 °C) and higher than the melting point of uranium (1132 °C), it is assumed that a part of the Th and U bound with organic matter in the feed coal (Table 3) evaporated and condensed mainly on the surface of the fine fly ash particles. Meanwhile, as a result of coal combustion, the Th and U which was bound with mineral matter (including phosphorus compounds) in the feed coal remained concentrated in simple phosphates (monazite) and Al-Si glass which formed in the fly ash as well as in Al-Si glass (mostly USCB) and magnetite (mostly LCB) in the slag.

On the basis of the results of the Th and U content in grain classes and fractions of fly ash and slag, it was found that the highest contents of thorium were found in the non-magnetic fraction of fly ash particles of <0.05 mm size and in the non-magnetic fraction of the slags (Figure 3a). The largest contents of uranium are found in the magnetic fraction of fly ash particles of 0.05–0.2 mm size, in the non-magnetic slag fraction generated by the combustion of feed coal from the LCB, in the non-magnetic group of fly ash particles of <0.05 mm size, and in the magnetic fraction of slag resulting from the combustion of feed coal from the USCB. Considering the share (wt %) of grains in the composition of the whole fly ash and whole slag (Table 1), it was found that a group of non-magnetic particles of <0.05 mm size has the largest influence on the average Th and U content in the fly ash, and non-magnetic grains have the largest impact on Th and U content in the slag (Figure 3b).

Based on the results of the SEM/EDS analyses in micro-areas of the grains of fly ash and slag, it was found that the highest content of Th was found in anhedral monazite grains, which are included in the fraction of non-magnetic fly ash of <0.05 mm size (Table 3, Figure 2) and were generated as a result of the combustion of feed coals from the LCB and in the Al-Si microspheres, which are part of the magnetic fraction of fly ash of <0.05 mm, resulting from the combustion of feed coals from the USCB. In turn, the highest content of U was found on the surface of the Al-Si porous grains, which are included in the magnetic fraction of fly ash with grain size <0.05 mm, resulting from the combustion of feed coals from the LCB and USCB. The highest content point of thorium was found in the Al-Si grains and in ferrospheres in the magnetic fraction of slag, resulting from the combustion of feed coals from the LCB and USCB. The highest content point of U was found in the massive Al-Si grains, resulting from the combustion of feed coals from the LCB. In the slag, resulting from the combustion of feed coal from the USCB, uranium probably occurs in a dispersed form (i.e., <0.01%). The aforementioned morphological forms of the phase-minerals of fly ash and slag belong to the most common of the combustion residues, resulting from the combustion of feed coal in Poland and the world (e.g., refs. [6,37,47]). These phases often have a high content of trace elements, as already demonstrated by studies of the concentrates of phase-minerals groups, the concentrates of morphological forms of furnace waste, and studies of technogenic magnetic particles [9,37,66,67]. The finest ferrospheres and Al-Si particles from Fe dendritic crystals emitted to the atmosphere, together with Th and U, can enrich the collection of technogenic magnetic particles in the topsoil, thereby increasing the magnetic susceptibility of the soil. Therefore, high magnetic susceptibility is still observed in Poland in the vicinity of metallurgical and power plants (e.g., refs. [68,69]).

Eluates generated as a result of the influence of lentic or rainwater on fly ash particles deposited on the surface of the soil and eluates from combustion residue dumps may be hazardous to the environment. Th and U are equivocally considered to be slightly eluting elements [20,70]. This is reflected in the low Th and U concentrations in the eluates and the low values (%) of the efficiency of their elution (Table 5). With the use of water and acids, U and Th are first eluted from the several-micron surface layer of the fly ash particles. Th and U present within the Al-Si particles of the combustion residues are eluted more slowly, due to the limited availability of the solutions [53,71–73]. The increased elution of heavy metals and, perhaps, of Th and U from the combustion residue particles, can occur when the elements are concentrated on the surface of alkaline particles, when they are in an acidic environment of groundwater, and also when the elements are on the surface of acidic particles in a neutral or slightly alkaline environment of surface or rain water [20]. The elution of U and Th from monazite with the use of non-concentrated inorganic acids or humic acid and carboxylic acids is negligible (content in eluates of approximately 1 ppb), while elution with the use of water has not been observed [74,75]. Greater efficiency of Th and U extraction from monazite can be obtained only by using complex industrial sintering methods or applying concentrated bases, acids or salts at high temperatures to ground monazite [76]. To summarize, it can be assumed that under the influence of rainwater or groundwater, Th and U, from furnace waste particles generated as a result of the combustion of feed coals from the LCB and the USCB, will undergo slight and slow leaching. Th and U will most likely be first eluted from the surface of the fly ash particles, next from within the Al-Si grains of the fly ash, and then from the Al-Si grains of the slag and finally from the monazite. However, even small concentrations of trace elements in aqueous effluents penetrating the groundwater are in the surface layers of the bioavailable soil and can reach the plants and food chain of humans and animals.

Through these studies of coal from two coal basins differing in genesis (LCB is of platform origin and USCB of geosynclinal origin; more information can be found in refs. [77,78]), burnt in 8 large power plants, and producing combustion residues that have been geochemically characterized, perhaps it has been made possible to better understand the modes of occurrence of Th and U in combustion residues. The observed variation in the phase composition of particles, their size, and thus the surface of particles; and the content of Th and U in the particles of the combustion residues (Table 3, Figure 3), raises suspicion of the different impacts of individual groups of particles on the course and yield of elution of these elements. Little attention has thus far been paid to the diversity of U and Th contents in microareas of the coal combustion residue particles. In the microareas of the particles there may be mineral phases of different size, specific surface area and the method of binding Th and U next to each other. These particles in contact with water can change its pH in a different way, and ecotoxic elements can be washed out at different rates. Perhaps more accurately it will be possible to predict the course and efficiency of leaching of the ecotoxic elements from the particles of the combustion residues, when the chemical and phase composition of the individual particles will be known in greater detail. This issue will be dealt with by the authors in the near future.

4. Conclusions

1. Feed coal and fly ash are characterized by increased phosphorus content compared to hard coal Clarke, which is concentrated most likely in apatite and crandallite (for feed coal) and in monazite (for fly ash). The average Th and U content in feed coals from the LCB and U in feed coals from the USCB is higher, and the average Th content in the USCB feed coals is lower than the hard coal Clarke values. In feed coals from the LCB, higher Th and U contents are present than in feed coals from the USCB. The highest content of Th and U was found in inertinite, in feed coals from the LCB. The highest content of Th was recorded in the quartz association with organic matter, and the highest content of U was recorded in siderite in feed coals from the USCB. In feed coals from the LCB and USCB, Th is probably connected with apatite and/or crandallite, and U generally with mineral matter.

2. The highest Th contents are found in the non-magnetic class of fly ash particles of <0.05 mm size and in the non-magnetic fraction of slag, resulting from the combustion of the whole feed coal from the LCB and USCB. Th in fly ash is mainly concentrated in the anhedral monazite grains (LCB) and in the Al-Si microspheres (USCB), whereas in the slag, Th is concentrated in the massive Al-Si grains and in ferrospheres. The greatest U contents were found in the magnetic fraction of fly ash particles of 0.05–0.2 mm size and in the non-magnetic fraction of slag, resulting from the combustion of whole feed coal from the LCB, in the non-magnetic fraction of fly ash particles of <0.05 mm size, and in the magnetic fraction of slag resulting from combustion of feed coal from the USCB. U is mainly concentrated on the Al-Si surface of porous grains and microspheres. In the slag, U occurs mainly in Al-Si massive grains (LCB) or in a dispersed form in non-magnetic and magnetic grains. Considering the share (wt %) of specific groups of particles in the composition of fly ash and grain groups in the composition of the slag, it was found that a fraction of non-magnetic particles of <0.05 mm size has the largest influence on the Th and U content in whole fly ash, and non-magnetic grains have the largest impact on Th and U content in the slag.
3. It is assumed that under the influence of ground or rain water, Th and U will undergo slight and slow elution from combustion residue particles generated as a result of LCB and USCB feed coal combustion. The Th and U will most likely be first eluted from the surface of fly ash particles, next from within the Al-Si grains of the fly ash, then from the Al-Si grains of the slag, and finally from the monazite. The monitoring of Th and U contents in coal, combustion residues and eluates should result in no combustion of coal with a high content of these elements or in the appropriate management of its combustion residues.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/9/5/312/s1>, Table S1: Data for Table 1, Table S2: Data for Table 2, Table S3: Data for Table 3; Table S4: Correlation data for Table 4; Table S5: CD function data for Table 4, Table S6: Data for Figure 3.

Author Contributions: H.R.P. developed the concept of the article and strategy of the experiment, guaranteed the analysis of Th and U content in samples by atomic emission spectroscopy, developed the results, and wrote the manuscript in the part concerning the occurrence of Th and U in coal feeds and furnace wastes. L.R. performed petrographic analysis, X-ray diffraction, X-ray fluorescence analysis, and scanning electron microscopy of samples, developed the results, and wrote the manuscript in the part concerning the petrographic composition of the samples.

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References

1. Bhangare, R.C.; Ajmal, P.Y.; Sahu, S.K.; Pandit, G.G.; Puranik, V.D. Distribution of trace elements in coal and combustion residues from five thermal power plants in India. *Int. J. Coal Geol.* **2011**, *86*, 349–356. [[CrossRef](#)]
2. Pan, J.; Zhou, C.-C.; Zhang, N.-N.; Liu, C.; Tang, M.-C.; Cao, S.-S. Arsenic in coal: modes of occurrence and reduction via coal preparation—A case study. *Int. J. Coal Prep. Util.* **2018**, *38*, 1–14. [[CrossRef](#)]
3. Zhou, C.-C.; Liu, C.; Zhang, N.; Cong, L.-F.; Pan, J.-H.; Peng, C.-B. Fluorine in coal: The modes of occurrence and its removability by froth flotation. *Int. J. Coal Prep. Util.* **2018**, *38*, 149–161. [[CrossRef](#)]
4. Finkelman, R.B. Potential health impacts of burning coal beds and waste banks. *Int. J. Coal Geol.* **2004**, *59*, 19–24. [[CrossRef](#)]
5. Parzenty, H.R.; Lewińska-Preis, L. The role of sulphide and carbonate minerals in the concentration of chalcophile elements in the bituminous coal seams of a paralic series (Upper Carboniferous) in the Upper Silesian Coal Basin (USCB), Poland. *Geochem.* **2006**, *66*, 227–247. [[CrossRef](#)]
6. Parzenty, H.R.; Róg, L. Distribution of heavy metals in fly ash originating from burning coal of Upper Silesian Coal Basin. *Prz. Gor.* **2001**, *57*, 52–60. (In Polish)
7. Parzenty, H.; Róg, L. Potentially hazardous trace elements in ash from combustion of coals in Limnic Series (Upper Carboniferous) of the Upper Silesian Coal Basin (USCB). *Gor. Geol.* **2007**, *2*, 81–91.
8. Xu, M.; Yan, R.; Zheng, C.; Oiao, Y.; Han, J.; Sheng, C. Status of trace element emission in a coal combustion process: a review. *Fuel Process. Technol.* **2003**, *85*, 215–237. [[CrossRef](#)]

9. Dai, S.; Zhao, L.; Peng, S.; Chou, C.-L.; Wang, X.; Zhang, Y.; Li, D.; Sun, Y. Abundances and distribution of minerals and elements in high-alumina coal fly ash from the Jungar Power Plant, Inner Mongolia, China. *Int. J. Coal Geol.* **2010**, *81*, 320–332. [[CrossRef](#)]
10. Vejahati, F.; Xu, Z.; Gupta, R. Trace elements in coal: Associations with coal and minerals and their behaviour during coal utilization—A review. *Fuel* **2010**, *89*, 904–911. [[CrossRef](#)]
11. Koniecznyński, J.; Zajusz-Zubek, E. Distribution of selected trace elements in dust containment and flue gas desulphurisation products from coal-fired power plants. *Arch. Environ. Prot.* **2011**, *37*, 3–14.
12. Wierońska, F.; Makowska, D.; Strugała, A. Assessment of the content of arsenic in solid by-products from coal combustion. *Energy Fuels* **2016**, *14*, 1–5. [[CrossRef](#)]
13. Yan, R.; Gauthier, D.; Flamant, G. Volatility and chemistry of trace elements in a coal combustor. *Fuel* **2001**, *80*, 2217–2226. [[CrossRef](#)]
14. Vassilev, S.V.; Eskenazy, G.M.; Vassileva, C.G. Behaviour of elements and minerals during preparation and combustion of the Pernik coal, Bulgaria. *Fuel Process. Technol.* **2001**, *72*, 103–129. [[CrossRef](#)]
15. Vassilev, S.V.; Menendez, R. Phase-mineral and chemical composition of coal fly ashes as a basis for their multicomponent utilization. 4. Characterization of heavy concentrates and improved fly ash residues. *Fuel* **2005**, *84*, 973–991. [[CrossRef](#)]
16. Drobek, L.; Michalik, B. Monitoring of the properties of energy waste subjected to recovery in underground excavations. *Wiad. Gor.* **2008**, *59*, 349–360. (In Polish)
17. Makowska, D.; Wierońska, F.; Dziok, T.; Strugała, A. Ecotoxic elements emission from the combustion of solid fuels due to legal regulations. *Polityka Energetyczna Energy Policy J.* **2017**, *20*, 89–102. (In Polish)
18. Zhang, J.; Han, C.-L.; Xu, Y.-Q. The release of the hazardous elements from coal in the initial stage of combustion process. *Fuel Process. Technol.* **2003**, *84*, 121–133. [[CrossRef](#)]
19. Hower, J.C.; Dai, S.; Eskenazy, G. Distribution of Uranium and Other Radionuclides in Coal and Coal Combustion Products, with Discussion of Occurrences of Combustion Products in Kentucky Power Plants. *Coal Comb. Gasif. Prod.* **2016**, *8*, 44–53.
20. Izquierdo, M.; Querol, X. Leaching behaviour of elements from coal combustion fly ash: An overview. *Int. J. Coal Geol.* **2012**, *94*, 54–66. [[CrossRef](#)]
21. Singh, R.K.; Gupta, N.C.; Guha, B.K. pH dependence leaching characteristics of selected metals from coal ash and its impact on ground water quality. *Int. J. Chemical Environ. Eng.* **2014**, *5*, 218–222.
22. Sliva, E.B.; Li, S.; Oliveira, L.M.; Gress, J.; Dong, X.; Wilkie, A.C.; Townsend, T.; Ma, L.Q. Metal leachability from coal combustion residues under different pHs and liquid/solid ratios. *J. Hazard. Mater.* **2018**, *341*, 66–74. [[CrossRef](#)] [[PubMed](#)]
23. Lauer, N.; Hower, J.C.; Hsu-Kim, H.; Taggart, R.K.; Vengosh, A. Naturally occurring radioactive materials in coal and coal combustion residuals in the United States. *Environ. Sci. Technol.* **2015**, *49*, 11227–11233. [[CrossRef](#)] [[PubMed](#)]
24. ISO 7404-3. *Methods for the Petrographic Analysis of Bituminous Coal and Anthracite—Part 3: Method of Determining Maceral Group Composition*; International Organization for Standardization: Geneva, Switzerland, 2009; pp. 1–7.
25. ISO 7404-5. *Methods for the Petrographic Analysis of Bituminous Coal and Anthracite—Part 5: Method of Determining Microscopically the Reflectance of Vitrinite*; International Organization for Standardization: Geneva, Switzerland, 2009; pp. 1–14.
26. Marczak, M. Genesis and regularities of the trace elements occurrence in the Chelm coal deposit at Coal Basin of Lublin. *Sci. Work Silesian Univ.* **1985**, *748*, 1–111. (In Polish)
27. Parzenty, H. Lead distribution in coal and coaly shales in the Upper Silesian Coal Basin. *Geol. Q.* **1994**, *38*, 43–58.
28. Lewińska-Preis, L.; Fabiańska, M.J.; Ćmiel, S.; Kita, A. Geochemical distribution of trace elements in Kaffiovrå and Longyearbyen coals Spitsbergen Norway. *Int. J. Coal Geol.* **2009**, *80*, 211–223. [[CrossRef](#)]
29. Parzenty, H.R.; Róg, L. Modes of occurrence of ecotoxic elements in coal from the Upper Silesian Coal Basin, Poland. *Arabian J. Geosci.* **2018**, *11*, 790. [[CrossRef](#)]
30. BN-79/6722-09. *Fly Ash and Slag from Boilers Fired with Hard Coal and Lignite. Division, Names and Terms*; Normalization Publishers in Warsaw: Warsaw, Poland, 1979. (In Polish)
31. Ketris, M.P.; Yudovich, Y.E. Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals. *Int. J. Coal Geol.* **2009**, *78*, 135–148. [[CrossRef](#)]

32. Parzenty, H.R. The role of mineral matter in the concentration of phosphorus in bituminous coal seams from the Lublin Formation in the Lublin Coal Basin in Poland. *Gospod. Surowcami Min.* **2018**, *34*, 53–70.
33. Yossifova, M.G. Petrography, mineralogy and geochemistry of Balkan coals and their waste products. *Int. J. Coal Geol.* **2014**, *122*, 1–20. [[CrossRef](#)]
34. Dai, S.; Ren, D.; Chou, C.-L.; Finkelman, R.B.; Seredin, V.V.; Zhou, Y. Geochemistry of trace elements in Chinese coals: A review of abundances, genetic types, impacts on human health, and industrial utilization. *Int. J. Coal Geol.* **2012**, *94*, 3–21. [[CrossRef](#)]
35. Bragg, L.J.; Oman, J.K.; Tewalt, S.J.; Oman, C.L.; Rega, N.H.; Washington, P.M.; Finkelman, R.B. *U.S. Geological Survey Coal Quality (COALQUAL) Database; Version 2.0*; Open-File Report 97–134; U.S. Geological Survey: Reston, VA, USA, 1998.
36. Moreno, N.; Querol, X.; Andrés, J.M.; Stanton, K.; Towler, M.; Nugteren, H.; Janssen-Jurkovicová, M.; Jones, R. Physico-chemical characteristics of European pulverized coal combustion fly ashes. *Fuel* **2005**, *84*, 1351–1363. [[CrossRef](#)]
37. Vassilev, S.V.; Vassileva, C.G.; Karayigit, A.I.; Bulut, Y.; Alastuey, A.; Querol, X. Phase-mineral and chemical composition of composite samples from feed coals, bottom ashes and fly ashes at the Soma power station, Turkey. *Int. J. Coal Geol.* **2005**, *61*, 35–63. [[CrossRef](#)]
38. Querol, X.; Fernández-Turiel, J.; López-Soler, A. Trace elements in coal and their behaviour during combustion in a large power station. *Fuel* **1995**, *74*, 331–343. [[CrossRef](#)]
39. Silva, L.F.O.; Ward, C.R.; Hower, J.C.; Izquierdo, M.; Waanders, F.; Oliveira, M.L.S.; Li, Z.; Hath, R.S.; Querol, X. Mineralogy and leaching characteristics of coal ash from a major Brazilian power plant. *Coal Comb. Gasif. Prod.* **2010**, *2*, 51–65. [[CrossRef](#)]
40. Chen, J.; Chen, P.; Yao, D.; Huang, W.; Tang, S.; Wang, W.; Liu, W.; Hu, Y.; Zhang, B.; Sha, J. Abundance, distribution, and modes of occurrence of uranium in Chinese Coals. *Minerals* **2017**, *7*, 239. [[CrossRef](#)]
41. Parzenty, H.R. Variability of La, Sc, Th and U contents in bituminous coals of Lublin Formation in Lublin Coal Basin (LCB). *Trans. VŠB Tech. Univ. Ostrava* **2008**, *7*, 203–211.
42. Bojakowska, I.; Lech, D.; Wołkowicz, S. Uranium and thorium in hard coal from polish deposits. *Gospod. Surowcami Min.* **2008**, *24*, 53–65. (In Polish)
43. Smółka-Danielowska, D. *The X-ray Structure Analysis of Amorphous and Nanocrystalline Materials*; Jankowski, A., Ed.; University of Silesia, Printing House WW: Katowice, Poland, 2013; pp. 1–112. (In Polish)
44. Llorens, J.F.; Fernández-Turiel, J.L.; Querol, X. The fate of trace elements in a large coal-fired power plant. *Environ. Geol.* **2001**, *40*, 409–416. [[CrossRef](#)]
45. Finkelman, R.B. Trace and minor elements in coal. In *Organic Geochemistry*; Engel, M.H., Macko, S., Eds.; Plenum: New York, NY, USA, 1993; pp. 593–607.
46. Dai, S.; Seredin, V.V.; Ward, C.R.; Jiang, J.; Hower, J.C.; Song, X.; Jiang, Y.; Wang, X.; Gornostaeva, T.; Li, X.; Liu, H.; Zhao, L.; Zhao, C. Composition and modes of occurrence of minerals and elements in coal combustion products derived from high-Ge coals. *Int. J. Coal Geol.* **2014**, *121*, 79–97. [[CrossRef](#)]
47. Ratajczak, T.; Gawęł, A.; Górniak, K.; Muszyński, M.; Szydłak, T.; Wyszomirski, P. Characteristics of fly ash from combustion of some hard and brown coals. *Mineral. Soc. Poland Spec. Pap.* **1999**, *15*, 1–34. (In Polish)
48. Affolter, R.H.; Groves, S.; Betterton, W.J.; Benzel, W.; Conrad, K.L.; Swanson, S.M.; Ruppert, L.F.; Clough, J.G.; Belkin, H.E.; Kolker, A.; Hower, J.C. *Geochemical Database of Feed Coal and Coal Combustion Products (CCPs) from Five Power Plants in the United States*; Data Series 635; U.S. Geological Survey: Reston, VA, USA, 2011; p. 19.
49. Jones, K.B.; Ruppert, L.F.; Swanson, S.M. Leaching of elements from bottom ash, economizer fly ash, and fly ash from two coal-fired power plants. *Int. J. Coal Geol.* **2012**, *94*, 337–348. [[CrossRef](#)]
50. Ilyushechkin, A.; Roberts, D.; Harris, D.; Riley, K. Trace element partitioning and leaching in solids derived from gasification of Australian coals. *Coal Comb. Gasif. Prod.* **2011**, *3*, 8–16. [[CrossRef](#)]
51. Querol, X.; Juan, R.; Lopez-Soler, A.; Fernandez-Turiel, J.L.; Ruiz, C.R. Mobility of trace elements from coal and combustion wastes. *Fuel* **1996**, *75*, 821–838. [[CrossRef](#)]
52. Yudovich, Y.E.; Ketris, M.P. Toxic trace elements in coals. Russian Academy of Sciences: Ekaterinburg, Russia, 2005. (In Russian)

53. Brownfield, M.E.; Cathcart, J.D.; Affolter, R.H.; Brownfield, I.K.; Rice, C.A.; O'Connor, J.T.; Zielinski, R.A.; Bullock, J.H.; Hower, J.C.; Meeker, G.P. *Characterization and Modes of Occurrence of Elements in Feed Coal and Coal Combustion Products from a Power Plant Utilizing Low-Sulfur Coal from the Powder River Basin, Wyoming*; Scientific Investigations Report 2004-5271; U.S. Geological Survey: Reston, VA, USA, 2005; p. 36. Available online: <http://pubs.usgs.gov/sir/2004/5271/> (accessed on 18 April 2019).
54. Papastefanou, C. Escaping radioactivity from coal-fired power plants (CPP) due to coal burning and associated hazards: a review. *J. Environ. Radio.* **2010**, *101*, 191–200. [[CrossRef](#)]
55. Duan, P.; Wang, W.; Sang, S.; Tang, Y.; Ma, M.; Zhang, W.; Liang, B. Geochemistry of toxic elements and their removal via the preparation of high-uranium coal in Southwestern China. *Minerals* **2018**, *8*, 83. [[CrossRef](#)]
56. Finkelman, R.B.; Palmer, C.A.; Wang, P. Quantification of the modes of occurrence of 42 elements in coal. *Int. J. Coal Geol.* **2018**, *185*, 138–160. [[CrossRef](#)]
57. Jeczalik, A. Uranium geochemistry in uranium-based hard coals in Poland. *Newsl. Geol. Inst.* **1970**, *224*, 103–195.
58. Michalik, B. Natural radioactivity in hard coal and solid products of its combustion. *Karbo* **2006**, *1*, 2–12. (In Polish)
59. Kokowska-Pawłowska, M.; Nowak, J. Phosphorus minerals in tonstein: coal seam 405 in Sośnica-Makoszowy coal mine, Upper Silesia, southern Poland. *Acta Geol. Pol.* **2013**, *63*, 271–281. [[CrossRef](#)]
60. Parzenty, H. Differences in content and bonding pattern of certain elements in coal of the Upper Silesian Coal Basin throughout a single seam profile. *Prz. Gor.* **1989**, *45*, 4, 17–21. (In Polish)
61. Hill, P.A. Vertical distribution of elements in Deposit No. 1, Hat Creek, British Columbia: A preliminary study. *Int. J. Coal Geol.* **1990**, *15*, 77–111. [[CrossRef](#)]
62. Duan, P.; Wang, W.; Sang, S.; Qian, F.; Shao, P.; Zhao, X. Partitioning of hazardous elements during preparation of high-uranium coal from Rongyang, Guizhou, China. *J. Geochem. Explor.* **2018**, *185*, 81–92. [[CrossRef](#)]
63. Sałdan, M. Uranium methalogenesis in carboniferous formations. *Bull. Geol. Inst.* **1965**, *193*, 111–163. (In Polish)
64. Finkelman, R.B. Health Impacts of Coal: Facts and Fallacies. *J. Hum. Environ.* **2007**, *36*. [[CrossRef](#)]
65. Clarke, L. The fate of trace elements during coal combustion and gasification: an overview. *Fuel* **1993**, *72*, 731–736. [[CrossRef](#)]
66. Vassilev, S.V.; Menedez, R.; Diaz-Somoano, M.; Martinez-Tarazona, M.R. Phase-mineral and chemical composition of coal fly ashes as a basis for their multicomponent utilization. 2. Characterization of ceramic cenosphere and salt concentrates. *Fuel* **2004**, *83*, 585–603. [[CrossRef](#)]
67. Vassilev, S.V.; Menedez, R.; Borrego, A.G.; Diaz-Somoano, M.; Martinez-Tarazona, M.R. Phase-mineral and chemical composition of coal fly ashes as a basis for their multicomponent utilization. 3. Characterization of magnetic and char concentrates. *Fuel* **2004**, *83*, 1563–1583. [[CrossRef](#)]
68. Magiera, T.; Strzyszczyński, Z.; Rachwał, M. Mapping particulate pollution loads using soil magnetometry in Urban forests in the Upper Silesia Industrial Region, Poland. *Forest Ecol. Manag.* **2007**, *248*, 36–42. [[CrossRef](#)]
69. Magiera, T.; Parzenty, H.; Róg, L.; Chybiorski, R.; Wawer, M. Spatial variation of soil magnetic susceptibility in relation to different emission sources in southern Poland. *Geoderma* **2015**, *255–256*, 94–103. [[CrossRef](#)]
70. Ukwattage, N.L.; Ranjith, P.G. Accelerated carbonation of coal combustion fly ash for atmospheric carbon dioxide sequestration and soil amendment: an overview. *J. Pollut. Eff. Control* **2018**, *6*, 210. [[CrossRef](#)]
71. Zielinski, R.A.; Finkelman, R.B. *Radioactive Elements in Coal and Fly Ash—Abundance, Forms, and Environmental Significance*; Fact Sheet 163-97; U.S. Geological Survey: Reston, VA, USA, 1997; p. 4.
72. Kukier, U.; Ishak, C.F.; Sumner, M.E.; Miller, W.P. Composition and element solubility of magnetic and non-magnetic fly ash fractions. *Environ. Pollut.* **2003**, *123*, 255–266. [[CrossRef](#)]
73. Seferenioglu, M.; Paul, M.; Sandström, Å.; Köker, A.; Toprak, S.; Paul, J. Acid leaching of coal and coal-ashes. *Fuel* **2003**, *82*, 1721–1734. [[CrossRef](#)]
74. Selvig, L.K.; Inn, K.G.W.; Outola, I.M.J.; Kurosaki, H.; Lee, K.A. Dissolution of resistate minerals containing uranium and thorium: Environmental implications. *J. Radioanal. Nucl. Chem.* **2005**, *263*, 341–348. [[CrossRef](#)]
75. Lapidus, G.T.; Doyle, F.M. Selective thorium and uranium extraction from monazite: I. Single-stage oxalate leaching. *Hydrometallurgy* **2015**, *154*, 102–110. [[CrossRef](#)]
76. Borai, E.H.; Abd El-Ghany, M.S.; Ahmed, I.M.; Hamed, M.M.; Shahr El-Din, A.M.; Aly, H.F. Modified acidic leaching for selective separation of thorium, phosphate and rare earth concentrates from Egyptian crude monazite. *Int. J. Miner. Process.* **2016**, *10*, 34–41. [[CrossRef](#)]

77. Jureczka, J.; Kotas, A. Coal deposits—Upper Silesian Coal Basin. In *The Carboniferous System in Poland*; Zdanowski, A., Żakowa, H., Eds.; Polish Geological Institute: Warsaw, Poland, 1995.
78. Porzycki, J.; Zdanowski, A. Coal deposits, Lublin Coal Basin and Soudtheastern Poland (Lublin Carboniferous Basin). In *The Carboniferous System in Poland*; Zdanowski, A., Żakowa, H., Eds.; Polish Geological Institute: Warsaw, Poland, 1995.



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