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.
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, Ti, 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 $23 \, ^\circ C$). 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 CoKα 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 $815 \, ^\circ C$ 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 ($\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, CaO, MgO, Na$_2$O, K$_2$O, SO$_3$, TiO$_2$, and P$_2$O$_5$) 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     |

Yield of magnetic fraction (wt %)

| Feed coal                          |           |
|------------------------------------|-----------|
| >0.50                              | 0.54      |
| 0.50–0.20                          | 4.71      |
| 0.20–0.05                          | 9.79      |
| <0.05                              | 3.95      |
| Slag                               | 16.08     |

Yield of non-magnetic fraction (wt %)

| Feed coal                          |           |
|------------------------------------|-----------|
| >0.50                              | 1.90      |
| 0.50–0.20                          | 12.78     |
| 0.20–0.05                          | 32.71     |
| <0.05                              | 33.62     |
| Slag                               | 83.92     |

* 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 %)    |           |           |     |             |     |           |           |     |             |     |
| SiO₂     | 57.35     | 56.76     | 1.0 | 59.85       | 1.0 | 54.27     | 55.23     | 1.0 | 60.20       | 1.1 |
| Al₂O₃    | 27.47     | 25.72     | 0.9 | 26.55       | 1.0 | 21.67     | 22.10     | 1.0 | 20.89       | 1.0 |
| Fe₂O₃    | 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 |
| Na₂O     | 0.49      | 0.59      | 1.2 | 0.43        | 0.9 | 1.15      | 1.16      | 1.0 | 0.88        | 0.8 |
| K₂O      | 2.63      | 2.57      | 1.0 | 2.52        | 1.0 | 2.90      | 3.43      | 1.2 | 3.18        | 1.1 |
| SO₃      | 0.63      | 0.02      | <0.1| 0.00        | 0.0 | 3.74      | 1.12      | 0.3 | 0.40        | 0.1 |
| TiO₂     | 1.24      | 1.32      | 1.1 | 1.34        | 1.1 | 0.98      | 1.01      | 1.0 | 0.96        | 1.0 |
| P₂O₅     | 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).

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 CoK\textsubscript{α} 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 4kW, 50 kV/60 mA, and analytical crystals: PET, LiF1, Rx25, Ge). Results of the analysis were converted into oxide contents (SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, CaO, MgO, Na\textsubscript{2}O, K\textsubscript{2}O, SO\textsubscript{3}, TiO\textsubscript{2}, and P\textsubscript{2}O\textsubscript{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\textsubscript{3}, HClO\textsubscript{4} and HF to fuming and brought to dryness. The residue was dissolved in HCl).

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

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).
| Element | LCB Content | Component | Fraction | USCB Content | Component | Fraction |
|---------|-------------|-----------|----------|--------------|-----------|----------|
| Feed coal | | | | | | |
| | 0.19 | inertinite | nonmagnetic | nd * | not found | nonmagnetic |
| U | <0.01 | siderite | magnetic | 0.12 | siderite | magnetic |
| Th | 0.01 | inertinite | nonmagnetic | nd * | not found | nonmagnetic |
| &lt;0.01 | siderite | magnetic | 0.02 | quartz with maceral inclusions | magnetic |
| Fly ash | | | | | | |
| U | 0.12 | anhedral monazite grain | &lt;0.05 nonmagnetic | 0.16 | surface of Al-Si microspheres | &lt;0.05 nonmagnetic |
| &lt;0.05 | surface of Al-Si porous grain | &lt;0.05 magnetic | 0.25 | surface of Al-Si microspheres with magnetite? | &lt;0.05 magnetic |
| Th | 17.25 | anhedral monazite grain | &lt;0.05 nonmagnetic | 0.06 | Al-Si microsphere | &lt;0.05 magnetic |
| &lt;0.05 | Al-Si porous grain with ferrosphere | &lt;0.05 magnetic | 0.14 | Al-Si microsphere | &lt;0.05 magnetic |
| Slag | | | | | | |
| U | 0.50 | Al-Si massive grain | nonmagnetic | &lt;0.01 | not found | nonmagnetic |
| &lt;0.01 | Al-Si massive grain with magnetite? | magnetic | &lt;0.01 | not found | magnetic |
| Th | 0.11 | Al-Si massive grain | nonmagnetic | 0.07 | Al-Si massive grain | nonmagnetic |
| &lt;0.01 | 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           | g/Mg (ppm) | % g/Mg           | g/Mg (ppm) |
| CD Function |                          |                          |                          |
| In feed coal ash |                          |                          |                          |
| Th       | 0.0              | 40.3           | 0.0              | 16.3           |
| U        | 0.0              | 228.2          | 0.0              | 55.4           |
| In Feed Coal |                          |                          |                          |
| Th       | 0.0              | 10.8           | 0.0              | 4.1            |
| U        | 0.0              | 61.2           | 0.0              | 13.8           |
| Correlation Coefficient (r) |                          |                          |                          |
| Th       | rAl₂O₃ = 0.813, rCaO = 0.878, rMgO = 0.681, rP₂O₅ = 0.836 | rA = 0.816, rAl₂O₃ = 0.888, rTiO₂ = 0.804, rP₂O₅ = 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.

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

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 “\(C_o - A/A\)” 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$_2$O$_3$ contents over the sum of Fe$_2$O$_3$, CaO, and MgO contents (Table 2). Due to the content of SiO$_2$, Al$_2$O$_3$, 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$_2$O$_5$ content in feed coal ash from the USCB (0.43%) and especially from the LCB (0.79%) is greater than the average P$_2$O$_5$ 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] |
| Coal - feed coal           | Europe      | 5.6          | 6.1          | Querol et al. [38] |
| Coal - feed coal           | Europe      | 17–65        | 5.0–29.0     | Moreno et al. [36] |
| Coal - raw (background)    | Brazil      | 14.09–17.04  | 6.12–7.67    | Silva et al [39] |
| Coal - raw (significant)   | Bulgaria    | 6.0          | 5.0          | Yossifova [33] |
| Coal - raw, LCB            | China       | 5.84         | 2.43         | Dai et al. [34] |
| Coal - raw, USCB           | Poland      | 3.2          | 1.9          | Parzentny [41] |
| Coal - feed coal           | Europe      | 1.1–2.6      | 0.2–0.8      | Moreno et al. [36] |
| Coal - feed coal           | Poland      | 5.6          | 6.1          | Llorens et al. [44] |
| Coal - feed coal           | Brazil      | 2.3          | 1.9          | Vassilev et al. [37] |
| Coal - raw                 | USA         | 3.2 ± 1      | 2.1 ± 1      | Finkelman [45] |
| Fly ash - raw              | Europe      | 22.1         | 22.9         | Querol et al. [38] |
| Fly ash - USCB             | Brazil      | 33.5–42.0    | 14.5–24.8    | Silva et al. [39] |
| Fly ash - USCB             | China       | 5.8–50       | 2.6–51.9     | Dai et al. [46] |
| Fly ash - USCB             | Poland      | 23.0         | 10.6         | Ratajczak et al. [47] |
| Fly ash - USCB             | Poland      | 7.6–19.3     | 3.3–10.6     | Smolka-Danielowska [43] |
| Fly ash - Spain            | Spain       | 22.1         | 22.9         | Llorens et al. [44] |
| Fly ash - Turkey           | Turkey      | 22           | 34           | Vassilev et al. [45] |
| Fly ash - USA              | USA         | 14.0–28.0    | 6.9–12.7     | Affolter et al. [48] |
| Fly ash - USA              | USA         | 11.8–21.6    | 6.72–10.4    | Jones et al. [49] |

Bottom ash/slag

| Bottom ash/slag - raw       | Europe      | 20.6         | 19.0         | Querol et al. [38] |
| Bottom ash/slag - Australia | 15–42       | 5.0–9.7      | Ilyushechkin et al. [50] |
| Bottom ash/slag - Brazil    | 25.8–42.9   | 9.3–16.7     | Silva et al. [39] |
| Bottom ash/slag - China     | 19.1–25     | 8.5–379.2    | Dai et al. [46] |
| Bottom ash/slag - Spain     | 20.6        | 19           | Llorens et al. [44] |
| Bottom ash/slag - Turkey    | 15          | 19           | Vassilev et al. [37] |
| Bottom ash/slag - USA       | 14.9–25.3   | 0.9–9.7      | Affolter et al. [48] |
| Bottom ash/slag - USA       | 13.0–25.3   | 5.87–9.83    | Jones et al. [49] |

Leachate

| Leachate - Slag - raw       | Australia   | 0.0–0.6    | 0.0–0.6    | Ilyushechkin et al. [50] |
| Leachate - bottom ash - raw | Brazil      | <0.01      | <0.01      | Moreno et al. [36] |
| Leachate - Slag - Spain     | 0           | 0          | Silva et al. [39] |
| Leachate - bottom ash - raw | Spain       | <0.01      | <0.01      | Querol et al. [51] |
| Leachate - bottom ash - raw | Spain       | 0.1×10^{-3} | 1.7×10^{-3} | Llorens et al. [44] |
| Leachate - bottom ash - raw | USA         | <0.001     | <0.001     | Jones et al. [49] |
| Leachate - bottom ash - raw | USA         | <0.001     | <0.001     | Jones et al. [49] |

* Citation after: 1 Dai et al. [34], 2 Hower et al. [19]; ** Analytical procedure: * 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 Al₂O₃, P₂O₅, CaO, and MgO (probably apatite or crandallite) in concentrating Th in feed coals from the LCB, and the major role of phases rich in Al₂O₃, P₂O₅, and TiO₂ (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 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 USCB. 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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