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Author: Henryk R. Parzenty, Leokadia Róg

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HENRYK R. PARZENTNY^{1*}, LEOKADIA RÓG²**DEPENDENCES BETWEEN CERTAIN PETROGRAPHIC, GEOCHEMICAL
AND TECHNOLOGICAL INDICATORS OF COAL QUALITY IN THE LIMNIC SERIES
OF THE UPPER SILESIA COAL BASIN (USCB), POLAND**

This article aims to assess the values of the most often measured petrographic, geochemical and technological indicators of coal quality and to identify probable dependences between them in the USCB coal. The following can also be observed: high content of Cd and Co in carbonate minerals separated from coal, in clay minerals – Cr and Zn, and in sulfide minerals – Cu, Ni and Pb. Nevertheless, it is organic matter which has the greatest influence on the average content of trace elements in coal. Correlations between the values of some of the indicators of coal quality were also observed. It has been observed that the increase in vitrinite content in coal is accompanied by a decrease in, while an increase in the content of liptinite and inertinite in coal is accompanied by an increase in the content of CaO, MgO, and SO₃ in coal ash. An increase in the carbonization of organic matter is accompanied by an increase in the content of Cu and Ni in coal, and a decrease in the content of Pb and S in coal and the content of Fe₂O₃ in coal ash.

Keywords: Coal quality, major and trace elements, correlations, bituminous coal, USCB

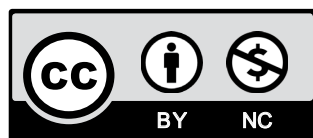
1. Introduction

The dependence between an increase in the average vitrinite reflectance, and an increase in the content of carbon, heating value and, usually, a decrease in the content of volatiles in coal is a commonly known fact which facilitates the cursory assessment of coal quality. The dependence between an increase in the content of SiO₂, Al₂O₃, K₂O, TiO₂, a decrease in the content of Fe₂O₃, CaO and MgO in coal, and a decrease in the ash melting temperature is applied when coal is selected for combustion. The dependence between a decrease in the content of Cl, K, Na, P, and S in coal, and improvement in the quality of products of coal gasification and coking is

¹ UNIVERSITY OF SILESIA, 12 BANKOWA STR., 40-007 KATOWICE, POLAND

² CENTRAL MINING INSTITUTE, 1 GWARKÓW SQ., 40-166 KATOWICE, POLAND

* Corresponding author: hr.parzentny@vp.pl



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essential for selecting coal for thermal processing. In turn, mutual dependences between technological indicators of coal quality are crucial for selecting optimal conditions of coal pyrolysis and for the efficient removal of ecotoxic elements from coal (e.g. Dziok et al., 2014; Porada et al., 2017; Rozwadowski & Strugała, 2006). Thus, it supports the conclusion that coal quality indicators and mutual dependences between them provide important data which facilitate, for example, the selection of coal for processing.

The aforementioned dependences have already been studied in different bituminous coal basins around the world, including the USCB (Bytnar & Burmistrz, 2013; Hamala & Róg, 2004; Kong et al., 2014; Marcisz, 2014; Micek et al., 2013; Porada et al., 2014; Probierz et al., 2012; Róg, 2003; Strugała, 1998; Świetlik, 2000). The search for other dependences, such as between the petrographic composition of coal, its carbonization and the values of technological indicators of its quality, and the content of major and trace elements in coal, may enable the better understanding of the issue of coal quality. A attempt has already been made to find dependences between the quality indicators of coal from the Paralic Series (Parzentny & Róg 2017). The observed dependences led to significantly greater understanding of coal quality in the USCB and improved the for a casting of the suitable use of coal from other deposits.

This article aims to assess the value of the most commonly applied petrographic, geochemical and technological indicators of coal quality, and to identify probable dependences between the indicators by analysing coal from the seams in the Limnic Series of the USCB. Most of the coal produced and combusted in Poland comes from this series, therefore, taking into account ecological issues, it is important to ascertain its geochemical properties.

2. Study area

The research area is the Limnic Series of the USCB (Fig. 1). The series is a thick complex of continental clastic rocks between the Upper Namurianian A and the Stephanian within the Pennsylvanian. The floor of the Limnic Series is adjacent to the coal-bearing complex of the clastic rocks of the Paralic Series. The roof is adjacent to a complex of Permian, Triassic, Jurassic, Miocene and Quaternary rocks. The Limnic Series includes three coal-bearing lithostratigraphic formations (i.e. the Cracow Sandstone Series, Mudstone Series, and Upper Silesian Sandstone Series) among which approximately 150 economic coal seams, nearly all bituminous, were identified (Fig. 2). A representative part of the seams was studied in the research presented in this article. Jureczka and Kotas (1995) and Jureczka et al. (2005) presented detailed geological characteristics of the USCB limnic formation.

3. Materials and methods

We tested 75 coal samples of nearly constant thickness, which were collected from throughout the thickness of 33 coal seams, and a vast lateral profile within the Limnic Series of the USCB. The coal samples were collected following standard PN-G-04501:1998, from coal seams in mining areas 1-6 of USCB coal mines (Fig. 1, 2).

The coal samples were used to prepare representative samples for petrographic tests (following PN-ISO 7404-2:2005) and representative analytical coal samples (following PN-G-04502:2014-11). The values of the petrographic indicators of coal quality, i.e. the content of

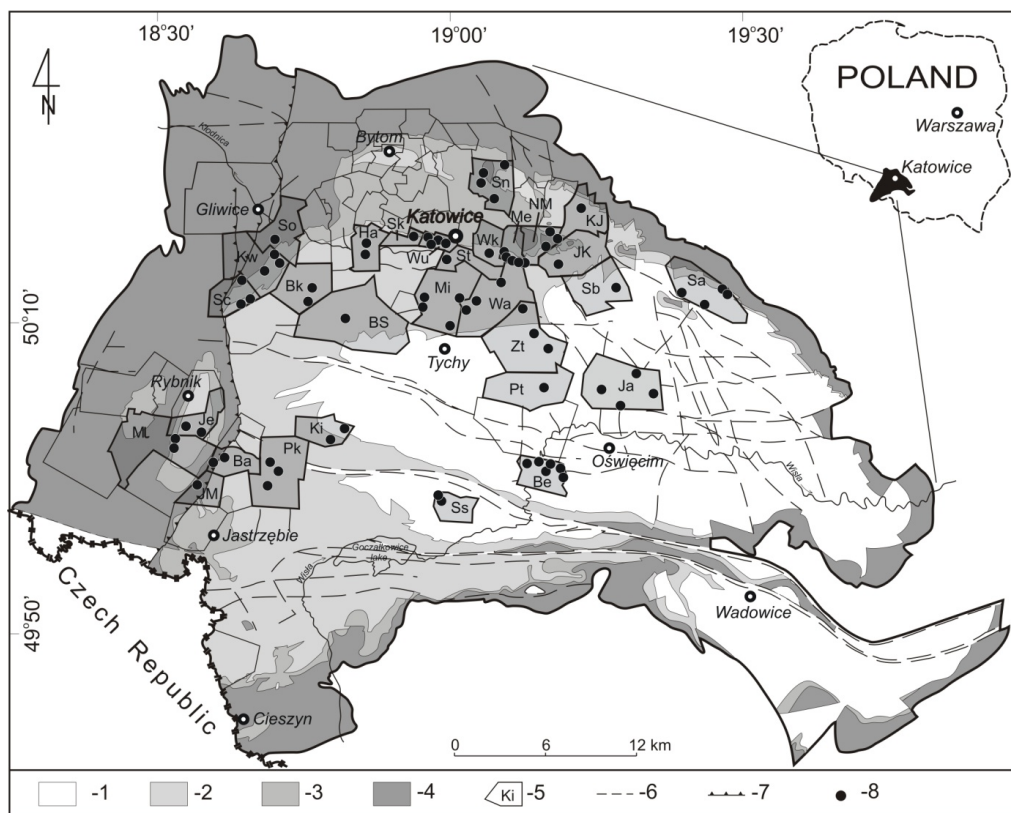


Fig. 1. The geological structure of the USCB (after Jureczka et al., 2005) and location of the coal sampling points

- 1 – Cracow Sandstone Series, 2 – Mudstone Series, 3 – Upper Silesian Sandstone Series, 4 – Paralic Series, 5 – active and closed coal mine areas (Ba – Borynia, Be – Brzeszcze, Bk – Budryk, BS – Bolesław Śmiały, Ha – Halemba, Ja – Janina, Je – Jankowice, JK – Jan Kanty, Jt – Jastrzębie, KJ – Kazimierz-Juliusz, Ki – Krupiński, Kw – Knurów, Me – Mysłowice, Mi – Murcki, Ml – Marcel, NM – Niwka-Modrzejów, Pk – Pniówek, Pt – Piast, Sa – Siersza, Sb – Sobieski, Sc – Szczygłowice, Sk – Śląsk, Sn – Saturn, So – Sośnica, Ss – Silesia, St – Staszic, Wa – Wesoła, Wk – Wieczorek, Wu – Wujek, Zt – Ziemowit), 6 – thrusts, 7 – fault, 8 – sampling places

vitrinite (Vt), liptinite (L), inertinite (I), and mineral matter (MM) in coal and vitrinite reflectance (R_r), were determined with a Zeiss Axio Imager D1m microscope. The applied procedures of microscopic analysis followed the standards set by the International Committee for Coal and Organic Petrology as well as the procedures described in PN-ISO 7404-3 (2009a) and PN-ISO 7404-5 (2009b). Mineral composition of the MM was determined with the D8 Discover diffractometers with iron filtered $\text{CoK}\alpha$ radiation, Ni-filter, and Lynxeye detector. Following the International Code System for Medium and High-Rank Coals (ECE Geneva, 1988), the technological indicators of coal quality were determined, i.e. the content of volatile matter (V^{daf}); the heating value (Q_s^{daf}); the content of the major elements (carbon (C^{daf}), hydrogen (H^{daf}), nitrogen (N^{daf}), and, with the computational method, also of oxygen ($O^a = 100 - (W^a + A^a + C^a + H^a + N^a + S^a)$));

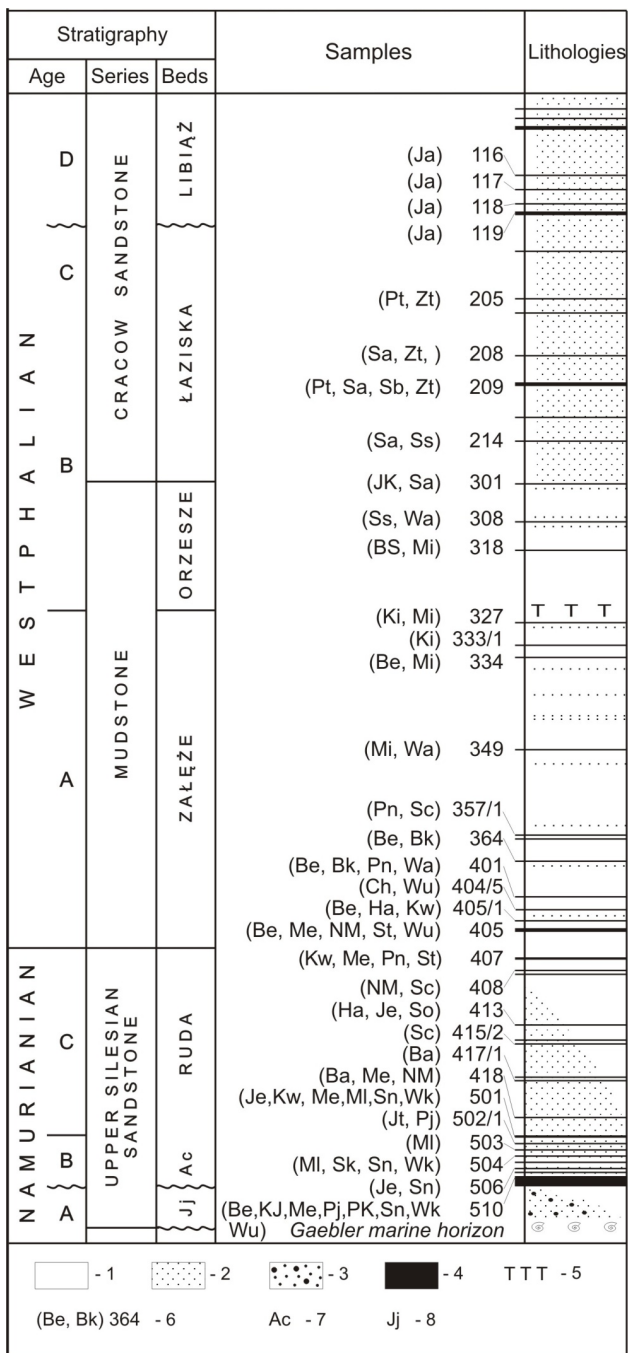


Fig. 2. Location of samples in the lithological profile of the USCB (after Jureczka et al., 2005)
 1 – mudstone, 2 – sandstone, 3 – conglomerate with sandstone, 4 – coal, 5 – tuffite, 6 – mining area code
 (like for Fig. 1) and coal seam numbers, 7 – Anticlinal Beds, 8 – Jejkovice Beds

the content of total sulphur (S_t^a), pyritic sulphur (S_p^a), organic sulphur (S_o^a) and sulphate sulphur (S_s^a); the value of coking strength (Roga Index, RI); and the value of the free swelling index (SI). The ash yield in coal was determined at the temperature of 815°C, following PN-ISO 1171:2002. The value of the geochemical indicators of coal quality, i.e. the content of major trace elements (Si, Al, Fe, Ca, Mg, Na, K, S, Ti, P) and certain trace elements (Cd, Co, Cr, Cu, Ni, Pb, Zn) in ash was determined with the Wavelength Dispersive X-ray Fluorescence method (WDXRF). The content of major elements in coal ash was converted into the content of oxides of the elements in coal ash (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO, MgO, Na_2O , K_2O , SO_3 , TiO_2 , P_2O_5), and the content of trace elements in coal ash was converted into their content in coal. The trace elements were selected for research by choosing those of the highest content and the most common in USCB coal (Ptak & Rózkowska, 1996) and in solid combustion waste (Wierońska et al., 2019; Parzenty & Róg, 2020), as well as those associated with ecotoxic elements (Duffus, 2002). Then, the arithmetic mean values of all the petrographic, geochemical and technological indicators of coal quality in the coal samples, representing the whole Limnic Series and its given beds (i.e. Anticlinal Beds, Ruda Beds, Załęże Beds, Orzesze Beds, Łaziska Beds, and Libiąż Beds, see Fig. 2) were calculated. The results of the calculations are presented in Table 1.

The probable mode of occurrence of trace elements in coal was determined in two ways.

1. The method of weighted mean and percentage share (wt.%) of its components. The weighted mean is a total of its components, i.e. the total of products of the content of a given element in each of the petrographic component groups of coal and the percentage share of the weight of each of the groups in the entire body of coal. Petrographic groups of coal components (organic matter, carbominerites, clay minerals + quartz, carbonate minerals and sulfide minerals) were obtained through the 3-fold separation of ground coal samples (~50 μm) in a mixture of dimethyl benzene, tetrachloromethane and tribromomethane, following the procedure described by Parzenty (1995). In each of the groups, the content of trace elements (Cd, Co, Cr, Cu, Ni, Pb, Zn) was measured using the WDXRF method. Then, the amount (wt.%) of the weighted mean of each of the components' elements was calculated. The content of elements in given petrographic groups of coal components (Fig. 3A) and the percentage share of each of the groups (wt.%) in the weighted mean of the content of the elements in the coal (Fig. 3B) is presented in Fig. 3.
2. The correlation method. Through applying Pearson's chi-squared test (χ^2) and the Kolmogorov-Smirnov test ($p = 0.05$), it was observed that the values of coal quality indicators have a normal or nearly normal distribution and the best assessment of the average value of the measured indicators was obtained with the arithmetic mean (Tab. 1-3). The value of the Pearson correlation coefficient was calculated to discover the dependence between the content of maceral groups and mineral groups in coal, ash yield, vitrinite reflectance, the content of fixed carbon and volatile matter in coal, the heating value, coking strength (Roga Index), the value of swelling index, and the content of sulphur and trace elements in coal together with the oxide content of major elements in coal ash. The model of linear regression was verified with the F-Snedecor test ($\alpha < 0.05$), and the significance of the correlation coefficients was verified with the Student's t-test. The values of the Pearson correlation coefficient (Table 4) ($r \geq \pm 0.35$ at $p < 0.05$) were interpreted as significant, indicating the occurrence of statistically significant dependences between the analysed indicators of USCB coal quality

4. Results and discussion

4.1. Petrographic and geochemical indicators of coal quality

The data in Table 1 show that the petrographic composition of the tested coal is similar to the petrographic composition of Palaeozoic coals in the North Atlantic macroregion of Europe ($V_t = 68\%$, $L = 12\%$, $I = 20\%$), determined by Vasconcelos (1999). The average content of vitrinite in the tested coal (64.4%) is similar to the content of the maceral group in the coal of the USCB Limnic Series (67.4%), determined by Jurczak-Drabek (1996). The content of vitrinite and inertinite in coal in the profile of the USCB is diverse. In the coal of the Libiąż Beds, the highest content of vitrinite (72.0%) was observed, and in the coal of the Saddle Beds the highest content of inertinite (34.0%) was observed. This is a specific feature of the USCB coal, resulting from differences in the facies development and carbonization of coal (Gabzdyl, 1987; Jurczak-Drabek, 1996; Kruszewska & Dybova-Jachowicz, 1987). The content of mineral matter in coal is low (5.8%) and in some coal seams in the Saddle Beds there is no mineral matter whatsoever. This is a favourable feature for coking coal, gasification, hydrogenation and combustion (e.g. Porada et al., 2014; Strugała et al., 2014). The above-average content of vitrinite and liptinite, measured in the coal from a few seams located in the Łaziska Beds, Orzesze Beds and Ruda Beds, is, in turn, a favourable feature in coal for hydrogenation. The mineral matter is made up of 2.5% of sulphide minerals and 1.7% of carbonate minerals. According to vitrinite random reflectance (0.74%), the tested USCB coal is orthobituminous (according to the International Classification of Seam Coals). The range of carbonization is wide, from subbituminous coal type A (in Łaziska Beds, $R_r = 0.45\%$), to metabituminous coal (in Ruda Beds and Saddle Beds, $R_r = 1.22\%$). According to ash yield average (11.37%), the tested coal is of medium-rank (International Classification 1995), and, according to the criteria by Chou (2012), the content of total sulphur (1.09%) is medium-high.

In comparison with the average content of oxides of major elements in the ash of coal from deposits around the world ($\text{SiO}_2 = 10\text{--}45\%$, $\text{Al}_2\text{O}_3 = 1\text{--}11\%$, $\text{Fe}_2\text{O}_3 = 1.5\text{--}5.5\%$, $\text{CaO} = 2\text{--}45\%$, $\text{MgO} = 1\text{--}20\%$, $\text{Na}_2\text{O} = 0.2\text{--}5.0\%$, $\text{K}_2\text{O} = 0.1\text{--}2.5\%$, $\text{SO}_3 = 5\text{--}20\%$ by Bouška 1980; $\text{TiO}_2 = 0.88 \pm 0.03\%$ and $\text{P}_2\text{O}_5 = 0.344 \pm 0.022\%$ by Ketris and Yudovich 2009), the tested coal has above-average content of Al_2O_3 (22.15%), Fe_2O_3 (17.03%), and P_2O_5 (0.70%; Table 2). The high content of Al_2O_3 and P_2O_5 in the Limnic Series of the USCB, especially in the coal from the Orzesze Beds, Załęże Beds and Ruda Beds is probably caused by tonstein partings and intrusive vulcanites in the coal seams and/or their vicinity (Kokowska-Pawłowska & Nowak, 2013; Łapot, 1992). In the USCB, as there are few signs of volcanic activity, phosphorus in coal is probably of syngenetic origin (Marcisz, 2014; Rózkowska & Parzenty, 1990). In turn, the high content of Fe_2O_3 in coal is likely caused by the frequent occurrence of different forms of sulphides, ankerite and siderite, mostly of dia- and epigenetic origin, in the coal seams of the USCB Limnic Series (e.g. Chodyniewska, 1973; Parzenty, 1999, 2003; Parzenty & Róg, 2018). The relatively high content of Fe_2O_3 in the ash of the tested coal is a favourable feature of coal for liquefaction; as Fe_2O_3 increases the liquefaction rate and lowers slag viscosity (Kong et al., 2014; Porada et al., 2014). The above-average content of P_2O_5 in coal is an unfavourable feature of coal for coking (Bytnar & Burmistrz, 2013; Diez et al., 2002; Michalik & Bronny, 2001; Morga, 2005; Strugała, 1998). The approximately average content of CaO in coal was considered to be a favourable feature in coal used for gasification. The increased content of Ca in coal

TABLE 1

Petrographic and technological quality indicators of coal

Indicator*	Arithmetic mean / Range							
	Li**	La**	Oi**	Za**	Ru**	Si**	Total**	
I	2	3	4	5	6	7	8	
Ro (%)	0.54	0.56	0.62	0.76	0.91	0.85	0.74	
RI	0.51-0.56	0.45-0.63	0.53-0.69	0.62-0.97	0.64-1.22	0.60-1.21	0.45-1.22	
SI	0	0	0	28	44	16	18	
	0-0	0-0	0-0	0-82	2-81	0-46	0-82	
	0	0	0	8.2	4.5	1.5	3.1	
Vt (vol.%)	0-0	0-0	0-0	0-81	0-9	0-21	0-81	
	72.0	63.9	62.8	69.5	62.9	53.7	64.4	
L (vol.%)	64-80	48-85	52-74	49-86	40-84	23-77	23-86	
	7.5	7.6	7.9	5.7	5.0	8.0	6.6	
I (vol.%)	1-11	3-10	3-14	3-10	0-11	3-14	0-14	
	16.3	22.1	20.8	18.4	26.7	34.0	23.2	
MM (vol.%)	13-21	8-40	9-33	5-36	10-48	10-67	5-67	
	4.2	6.4	8.5	6.4	5.4	4.3	5.8	
Mi (vol.%)	3-6	1-19	1-14	1-17	1-13	0-10	0-19	
	0.0	0.6	3.5	1.5	1.7	0.6	1.3	
Mw (vol.%)	0-0	0-1	0-8	0-5	0-5	0-3	0-8	
	0.0	1.8	2.7	2.7	1.7	0.8	1.7	
Q (vol.%)	0-0	0-15	0-5	0-14	0-5	0-4	0-15	
	0.0	0.2	0.8	0.5	0.1	0.1	0.3	
Su (vol.%)	0-1	0-1	0-2	0-5	0-1	0-2	0-5	
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Sm (vol.%)	0-0	0-1	0-1	0-0	0-0	0-0	0-1	
	4.0	3.8	1.5	1.7	1.9	3.0	2.5	
	3-6	1-8	0-3	0-8	0-6	0-6	0-8	
A ₈₁₅ ^a (wt.%)	9.58	12.95	15.95	11.71	11.83	8.19	11.37	
	6.37-12.29	3.19-28.57	9.38-21.44	5.28-21.54	3.26-22.41	3.00-18.40	3.19-22.41	

I	2	3	4	5	6	7	8
V ^{daf} (wt.%)	40.85	39.88	38.24	33.78	29.10	30.61	33.95
C ^{daf} (wt.%)	37.67-43.44	37.36-42.04	36.15-42.21	26.61-37.64	20.77-36.36	20.52-39.08	20.52-43.44
	71.88	71.91	74.21	81.46	83.87	83.42	79.82
H ^{daf} (wt.%)	55.43-69.38	42.97-77.30	49.48-66.40	50.03-83.78	62.31-84.57	62.12-86.52	42.97-86.52
	4.35	4.07	4.36	4.63	4.64	4.59	4.45
	3.35-4.14	2.40-4.77	3.00-3.85	0.70-5.46	3.38-4.71	3.21-4.80	0.70-5.46
N ^{daf} (wt.%)	1.19	0.99	1.22	1.37	1.22	1.30	1.27
	0.79-1.20	0.59-1.37	0.61-1.37	0.81-1.60	0.88-1.54	0.78-1.59	0.59-1.60
O ^a (wt.%)	19.46	19.61	18.18	11.51	9.46	9.60	13.09
	15.36-17.28	12.05-18.53	13.38-15.88	3.26-25.89	3.47-14.48	4.06-14.30	3.26-25.89
S _{SO4} ^a (wt.%)	0.69	1.15	0.45	0.11	0.06	0.16	0.28
	0.25-0.91	0.03-4.23	0.05-1.02	0.03-0.21	0.02-0.14	0.03-0.30	0.02-4.23
S _p ^a (wt.%)	1.66	1.51	0.83	0.36	0.20	0.62	0.59
	1.08-1.83	0.19-3.94	0.23-1.44	0.09-0.60	0.01-0.61	0.03-1.17	0.01-3.94
S _o ^a (wt.%)	0.77	0.76	0.75	0.56	0.47	0.31	0.51
	0.44-0.90	0.30-1.72	0.29-1.02	0.13-1.05	0.11-0.60	0.08-0.58	0.10-1.72
S _t ^a (wt.%)	3.12	3.42	2.03	1.03	0.70	1.09	1.38
	1.82-3.18	0.77-8.84	0.74-3.37	0.50-1.74	0.29-1.22	0.27-1.61	0.26-8.84
Q _s ^{daf} (MJ/kg)	23.18	23.03	23.17	28.91	29.54	30.24	27.74
	21.76-25.20	15.90-27.49	19.57-26.46	22.57-34.38	26.48-34.45	26.14-35.47	15.90-35.47

* V_t – vitrinite, I – inertinite, MM – mineral matter, Mi – clay minerals (kaolinite, illite, montmorillonite, chlorite), Mw – carbonate minerals (ankerite, siderite, dolomite), Q – quartz, Su – sulphate minerals (gypsum, szomolnokite), Sm – sulfide minerals (pyrite, marcasite), R₀ – vitrinite reflectance, A₈₁₅^a – ash content, V^{daf} – volatile matter, Q_s^{daf} – heat combustion, C^{daf} – carbon, H^{daf} – hydrogen, N^{daf} – nitrogen, O^{daf} – oxygen, S_S^a – sulphate sulphur, S_p^a – pyritic sulphur, S_o^a – organic sulphur, S_t^a – total sulphur, RI – (Roga Index) coking strength, SI – swelling index;

** Coal from: Li – Libiąż Beds, La – Łaziska Beds, Or – Orzesze Beds, Za – Zateże Beds, Ru – Ruda Beds, Si – Saddle Beds, Total – Limmic Series (the petrographic composition of coal, based on coal without mineral matter is: Vt = 68.4%, L = 7.0%, I = 24.6%)

usually contributes to an increase in the coal ash melting temperature (Collot, 2006; Porada et al., 2014; Róg, 2003).

The content of Cd, Co, Cr, Cu, and Ni in coal is comparable with or lower than their average content in hard coal deposits around the world (Tab. 3). This feature of coal is favourable with regards to environmental protection and the solid waste

products of thermal coal processing, especially coal combustion waste. Only the content of Pb and Zn in the tested coal is greater than average. In comparison with coal from the LCB, the LSCB and the USCB, the content of Cd, Co, Cr, Cu, Ni, Pb and Zn in the tested coal is usually low. In the Limnic Series the highest content of: Cd and Cr was measured in the Załęże Beds, of cobalt – in the Libiąż Beds, copper – in the Ruda Beds, Ni and Zn – in the Saddle Beds, and lead – in the Łaziska Beds.

Few correlation dependences between the petrographic composition of coal and the content of oxides in some of the major elements in coal ash (Table 4) were observed. As the vitrinite content decreases and the liptinite and inertinite content in coal increases, the content of CaO, MgO and SO₃ in coal ash usually increases. This dependence indicates that porous macerals of the inertinite group and liptinite group could be saturated with non-crystallic mineraloids or crystallic submicroscopic Ca and Mg carbonates and sulphates. Non-mineral compounds of Ca and Mg are a significant component of mineral matter in coal, especially in low-rank coal (Dai et al. 2020a, 2020b; Finkelman et al., 2019; Ward, 2016). In turn, the amount of these elements in vitrinite is probably low, which dilutes the total content of Ca and Mg in the organic matter of coal. The following dependences are a consequence of the major elements occurring in the composition of the minerals which form the mineral matter of the tested coal: between the content of clay minerals and the content of SiO₂, Al₂O₃, K₂O and TiO₂ in coal ash, between the content of carbonate minerals and the content of CaO in coal ash, and between the content of sulphide minerals and the content of Fe₂O₃ in coal ash. In turn, the dependence between the content of carbonate minerals in coal and the content of SiO₂ and Al₂O₃ in coal ash, indicates the possible occurrence of clay mineral inclusions in the epigenetic veins of ankerite with inclusions of disulphides, which was observed in the coal of the Limnic Series (Parzentny & Róg, 2018).

Based on the content of trace elements in the organic matter, carbominerites, clay minerals, quartz, carbonate minerals and sulphide minerals (Fig. 3A), and the influence (wt.%) of each of the groups of coal components on the content of trace elements in the entire body of coal (Fig. 3B), the probable mode of occurrence of the elements in the tested coal of the USCB Limnic Series was determined. The following was observed: the highest content of Cd and Co and the increased content of Pb and Zn in carbonate minerals; the highest content of Cr and Zn and the increased content of Cd in clay minerals; and the highest content of Cu, Ni and Pb, as well as the increased content of Co in sulphide minerals. Few correlation dependences between the content of certain trace elements in the tested coal and its petrographic composition (Tab. 4) were observed. The dependences indicate an affinity of Cr to organic matter and of Pb to sulphide minerals in coal.

In bituminous coal seams from different deposits around the world, elements such as Cd, Co, Cu, Ni, Pb and Zn most often occur in native sulphides and in the form of substitutions for iron and/or sulphur in pyrite (Dai et al., 2020a; Finkelman et al., 2018, 2019; Jiang et al., 2016; Kolker, 2012; Kucha & Lipiarski, 1998; Ward, 2016; Yudovich & Ketris, 2005). Nanoparticles of sulphides and sulphosalts containing, for example Co, Cu, Ni, Pb and Zn (5nm – 100 nm) in hydrothermal pyrite (Deditius et al., 2011) can also be observed. The content of elements in pyrite often differs depending on its mode of occurrence in coal. In USCB coal it was observed that the content of Ni, Zn, Cr, Pb and Mn in pyrite framboids is either very low or the elements

TABLE 2

Content of major elements in the researched coal ash

Element	Arithmetic mean / Range (wt.%)									
	Li*	La*	Or*	Za*	Ru*	Si*	Total*			
SiO ₂	23.63	25.34	42.44	38.15	39.44	27.84	33.61			
Al ₂ O ₃	13.05-30.81	6.49-42.55	32.78-52.59	12.66-52.78	9.89-48.93	11.68-46.18	6.49-52.78			
Fe ₂ O ₃	15.39	18.36	26.56	26.04	26.97	15.59	22.15			
	10.87-19.76	6.02-30.09	19.28-30.03	11.37-32.94	8.95-33.71	8.10-32.64	6.02-33.71			
	33.05	24.76	12.76	12.79	9.24	18.30	17.03			
	20.33-41.21	7.09-46.89	4.16-17.86	4.39-27.14	4.58-22.66	5.65-28.18	4.16-46.89			
CaO	7.39	8.50	5.42	6.16	6.24	12.28	7.65			
	5.56-9.63	3.78-23.90	0.59-12.12	1.66-19.25	1.82-20.81	2.79-21.31	0.59-23.90			
MgO	2.94	3.46	2.39	3.47	3.21	5.85	3.69			
	2.07-4.13	0.88-12.75	1.32-3.80	1.51-8.06	1.22-10.68	1.23-11.08	0.88-12.75			
Na ₂ O	1.13	1.56	0.53	1.18	1.70	1.05	1.23			
	0.12-3.56	0.02-4.83	0.06-1.23	0.40-3.02	0.47-4.06	0.26-3.27	0.02-4.83			
K ₂ O	0.72	0.52	1.68	1.93	2.29	0.95	1.48			
	0.50-1.04	0.04-1.07	0.36-3.30	0.38-3.41	0.25-3.00	0.32-2.98	0.04-3.41			
SO ₃	15.12	16.39	6.28	8.16	8.74	17.12	11.55			
	4.64-25.06	4.98-28.96	1.69-12.61	1.67-24.29	2.08-21.89	4.19-31.55	1.67-31.55			
TiO ₂	0.59	0.73	1.05	0.98	1.12	0.85	0.91			
	0.46-0.70	0.22-1.23	0.74-1.21	0.37-1.59	0.23-1.46	0.22-1.98	0.22-1.98			
P ₂ O ₅	0.05	0.37	0.90	1.15	1.05	0.15	0.70			
	0.03-0.06	0.04-1.62	0.11-2.39	0.13-2.40	0.09-4.79	0.05-0.55	0.03-4.79			

* Explanations as in Table 1

TABLE 3

Trace elements in coal from the study area and other Polish and global bituminous coals

Element	Study area (g/Mg)										Other Polish coals (g/Mg)				HCCV*** (g/Mg)
	Lj*	La*	Or*	Za*	Ru*	Si*	Total*	LCB**	LSCB**	USCB**	LCB**	LSCB**	USCB**		
Cd	<0.00	<0.00	<0.00	0.02	<0.00	0.00	0.01	1.19 ²	0.2 ⁵	no data	0.20±0.04 ³				
Co	<0.06	3.8	4.0	6.1	5.6	7.4	6.2	31.53 ²	8.7-10.6 ¹	15	6.0±0.2 ³				
Cr	2.2-18.3	1.1-8.0	0.3-6.9	0.4-12.3	0.2-9.7	0.1-16.7	0.1-18.3	13.3 ²	26.6-30.8 ¹	37	17±1 ³				
Cu	4.2-22.1	0.3-16.2	1.8-14.2	0.2-34.8	1.8-17.3	0.2-20.8	0.2-34.8	25.33 ²	31.9-39.9 ¹	42	16±1 ³				
	3.8	1.6	2.0	6.4	23.7	9.1	8.7								
	0.1-4.5	0.1-10.6	0.1-5.8	0.2-21.9	4.4-52.9	0.1-43.0	0.1-43.0								
Ni	12.7	3.5	4.0	13.9	13.5	13.9	11.5	49.9 ²	16.0-26.6 ¹	31	17±1 ³				
	0.1-25.7	0.1-13.0	0.1-8.7	0.2-26.5	1.5-21.3	0.4-40.7	0.1-40.7								
Pb	22.3	39.2	27.6	19.5	22.0	20.5	23.6	17.7 ²	55.2-98.0 ¹	35	9.0±0.7 ³				
	16.7-32.6	10.5-93.3	6.0-63.3	5.5-66.3	1.1-55.6	3.1-54.6	1.1-93.3								
Zn	77.9	32.7	32.7	49.5	33.0	132.6	61.5	32.6 ²	57.1-125.4 ¹	94	28±2 ³				
	30.3-176.7	6.5-121.1	8.4-54.2	5.0-138.2	7.7-132.0	4.5-1171.4	4.5-1171.4								

* Explanations as in Table 1;

** Lublin Coal Basin (LCB), Lower Silesian Coal Basin (LSCB);

*** hard coal Clarke values; Citation of results after: 1 – Cebulak (1983), 2 – Ketrnis and Yudovich (2009), 3 – Parzentny (2007), 4 – Ptak and Rózkowska (1995).

TABLE 4

Pearson coefficient values from the petrographic, technological quality index of bituminous coal and major elements in coal ash and trace elements content in coal

Vt	L	I	Mi	Mw	Sm	Ro	C ^{daf}	Q _s ^{daf}	V ^{daf}	RI
CaO (-0.50)	CaO (0.41)	CaO (0.55)	SiO ₂ (0.68)	SiO ₂ (0.61)	Al ₂ O ₃ (-0.36)	L (-0.55)	Cu (0.43)	Cu (0.47)	Fe ₂ O ₃ (0.51)	SiO ₂ (0.50)
MgO (-0.45)	SO ₃ (0.45)	MgO (0.54)	Al ₂ O ₃ (0.65)	Al ₂ O ₃ (0.61)	Fe ₂ O ₃ (0.56)	I (0.44)	Pb (-0.38)	Ni (0.37)	Cu (-0.65)	Al ₂ O ₃ (0.51)
SO ₃ (-0.43)	V ^{daf} (0.50)	SO ₃ (0.48)	Fe ₂ O ₃ (-0.55)	CaO (0.38)	Pb (0.41)	Cu (0.65)	V ^{daf} (-0.76)	V ^{daf} (-0.79)	Ni (-0.35)	Fe ₂ O ₃ (-0.49)
Cr (0.44)	O ^{daf} (0.44)	V ^{daf} (-0.51)	CaO (-0.52)	SO ₃ (-0.54)	A ^a (0.48)	Ni (0.37)	Q _s ^{daf} (0.64)	RI (0.57)	RI (-0.66)	CaO (-0.39)
		Q _s ^{daf} (0.44)	K ₂ O (0.62)	A ^a (0.59)	S _s ^a (0.46)	V ^{daf} (-0.96)	RI (0.50)	SI (0.35)	O ^{daf} (0.83)	K ₂ O (0.58)
		C ^{daf} (0.51)	SO ₃ (-0.60)		S _p ^a (0.65)	Q _s ^{daf} (0.81)	A ^a (-0.67)	C ^{daf} (0.97)	S _s ^a (0.50)	TiO ₂ (0.59)
		S ₀ ^a (-0.37)	TiO ₂ (0.41)			RI (0.77)	S _s ^a (-0.57)	O ^{daf} (-0.85)	S _p ^a (0.60)	Cu (0.62)
			A ^a (0.68)			SI (0.35)	S _p ^a (-0.52)	S _s ^a (-0.58)	S ₀ ^a (0.54)	O ^{daf} (-0.80)
						C ^{daf} (0.75)	S ₀ ^a (-0.42)	S _p ^a (-0.56)		S _s ^a (-0.37)
						S _s ^a (-0.47)		S ₀ ^a (-0.38)		S _p ^a (-0.45)
						S _p ^a (-0.54)		A ^a (-0.58)		
						S ₀ ^a (-0.45)				

* Explanations as in Table 1

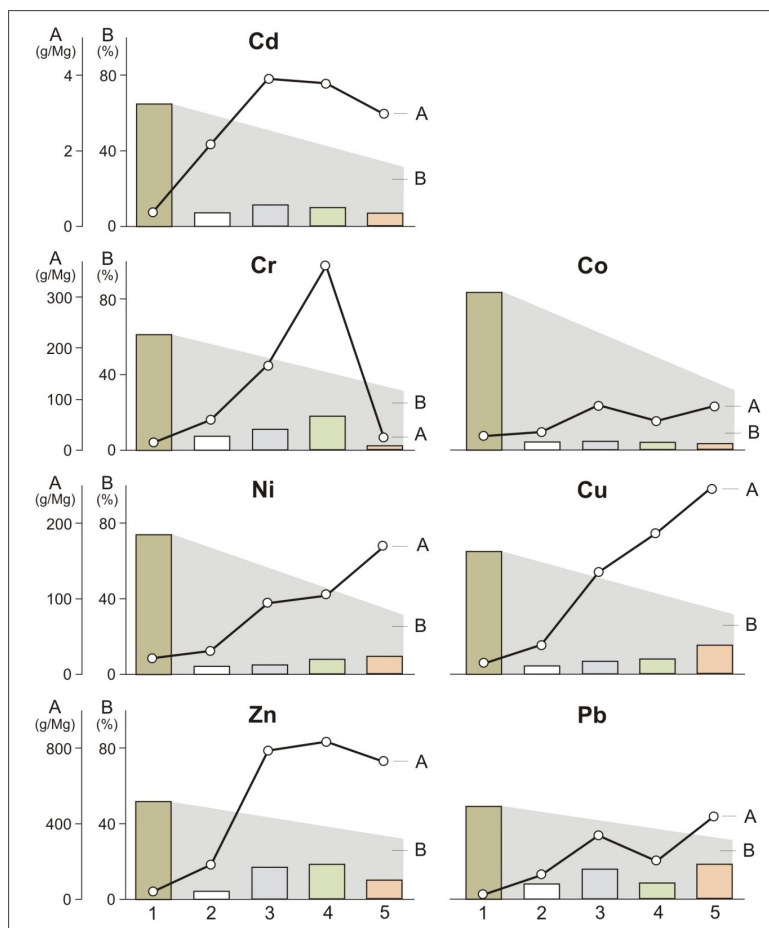


Fig. 3. The distribution of the content of elements in the petrographic groups of USCB coal components (A) and their proportion (in wt%) in determining the average element concentration (Cd, Co, Cr, Cu, Ni, Pb, and Zn) in coal (B)

1 – Organic matter (91.8%)*, 2 – Carbominerite (3.6%)*, 3 – Carbonate minerals (1.8%)*,

4 – Clay minerals + Quartz (1.7%)*, 5 – Sulfide minerals (1.1%)*

* percentage share of coal component groups separated from the coal

do not occur there at all. In the epigenetic fractures of exogenic cleavage, in massive grains with few inclusions of other minerals of diagenetic origin and in massive grains with numerous inclusions of other minerals of epigenetic origin, the content of elements increases in regard to framboids (Ni has the highest content). The content of these elements is the highest in epigenetic associations of disulphides with other minerals (Parzentny & Róg, 2018). In coal deposits from around the world, carbonates most often host Zn (Dai et al., 2020a; Finkelman et al., 2018, 2019). The observed occurrence of the increased content of Cd, Co and Pb in carbonate minerals is probably characteristic for the USCB. The occurrence of these elements in separate grains, in spheroids, and, most often, in veins within coal seams, probably results from the crystallisation

of hydrothermal solutions (Kucha & Lipiarski, 1998; Parzentny & Róg, 2018). The solutions probably have similar origins as Triassic Silesian-Cracow Zinc-Lead Ore Deposits, which are in direct contact with the roof of the USCB Limnic Series (Górecka et al., 1996; Rózkowski et al., 1979). In turn, clay minerals in the coal most often host Cr and Ni (Dai et al., 2020a; Finkelman et al., 2018, 2019). Minerals, most often illite, occur not only as thin layers and streaks between macerals but also as local inclusions in carbonate minerals and pyrite. Such forms were described, for example, in Pennsylvanian Coal in the Adaohai Mine and the Daqingshan Coalfield, China (Dai et al., 2003; Huggins et al., 2000).

The a for mentioned high content of elements in carbonate minerals (Cd, Co, Pb and Zn), clay minerals (Cd, Cr and Zn) and sulphide minerals (Co, Cu, Ni and Pb), and, simultaneously, the low content of mineral groups in the tested USCB coal results in a situation where these are not the mineral groups which have dominant influence on the average content of the discussed elements in coal, but it is organic matter of coal whose share in coal is the greatest (Fig. 3). These observations are significant for predicting the efficiency of producing coal which is free of potentially environmentally harmful mineral matter and ecotoxic elements. The high content of these elements in minerals loosely associated with macerals of coal (e.g. terygenic quartz, epigenetic concentrations of sulphide minerals and carbonate minerals) is a favourable feature of coal. These elements, generally, can be removed from coal sufficiently (up to 80%), through applying gravity separation and/or flotation (Liu et al., 2019; Makowska et al., 2014; Mohanty et al., 1998; Parzentny, 1995). However, quite often the content of the elements in processed coal is still higher than the average content of the elements in hard coals from around the world (Chen et al., 2017; Duan et al., 2018a, 2018b; Dai et al., 2020b; Liu et al., 2019; Makowska et al., 2018; Strugała et al., 2014). Removing these elements from macerals and submicroscopic minerals of the elements from coal, through gravity separation and flotation, is considered to be ineffective and improbable.

The significant influence of organic matter on the content of the elements in coal (see Fig. 3), even when there is low content of these elements in the matter, is always an unfavourable feature of coal for combustion. It is assumed that the elements mainly associated with organic matter and sulphide minerals in coal are first to evaporate in the combustion chamber. When flue gases cool down, the elements are easily absorbed by fine dust particles. The situation is different for elements associated with other minerals, as they probably remain within the ash matrix or evaporate slowly (Duan et al., 2017; Hower et al., 2016; Huang et al., 2004; Linak & Wendt, 1993; Querol et al., 1995; Sekine et al., 2008; Xu et al., 2003; Zhao et al., 2018). Fine particles released into the atmosphere may increase the magnetic susceptibility of the top layer of soil even at great distances from power plants (Blaha et al., 2008; Çayır et al., 2012; Huggins & Goodarzi, 2009; Kisku et al., 2012; Magiera et al., 2015; Veneva et al., 2004). They can also increase the content of ecotoxic elements in soil, water and plants (Parzentny, 2019; Sanei et al., 2010; Turhan, 2019).

4.2. Technological indicators of coal quality

Based on the data in Table 1, it was determined that the tested bituminous coal is according to Polish standards (following PN-82/G-97002): mainly flame coal (type 31.1) in the Libiąż Beds, Łaziska Beds and Orzesze Beds; gas-flame coal (type 32.1) in the Saddle Beds and (type 32.2) in the Załęże Beds; and mostly gas-coal (type 33) in the Ruda Beds. The coal from the Libiąż Beds has the highest content of V^{daf} , Sp^{a} and S_{o}^{a} ; from the Łaziska Beds – the highest content of O^{daf} , $S^{\text{a}}_{\text{SO}_4}$ and S_{t}^{a} ; from the Orzesze Beds – the highest content of A_{815}^{a} ; from the Załęże Beds – the highest content of N^{daf} and the highest value of SI; and from the coal of Ruda Beds – the highest

values of Q_s^{daf} , C^{daf} , H^{daf} and RI. The observations indicate that the coal from the Ruda Beds may be suitable for coking and unsuitable (due to its high sinterability) for combustion. The coal from other beds in the USCB, especially the Libiąż Beds, Łaziska Beds and Orzesze Beds, can still be used for combustion, but it is unsuitable for coking. The aforementioned observations confirm hitherto described regularities in the distribution of coal types in the USCB (Gabzdyl, 1987; Jureczka & Kotas, 1995). Generally, the coals of the Libiąż Beds, Łaziska Beds and Orzesze Beds are of a low rank, and the coals of the Ruda Beds and Saddle Beds, especially in the USCB zones of tectonic and volcanic activity, are of a higher rank.

It was observed that an increase in the degree of carbonization (expressed by an increase in the value of R_0 , Q_s^{daf} and the content of C^{daf} in coal as well as a decrease in the content of V^{daf} in coal), is often accompanied by an increase in the content of Cu and Ni in coal and a decrease in the content of Pb and sulphur (S_s^a , S_p^a , S_o^a) in coal, and in the Fe_2O_3 content in coal ash. A decrease in the content of sulphur and lead in coal and in the content of Fe_2O_3 in coal ash is probably a result of the destruction of metal-organic compounds and/or separation of functional groups from condensed atoms of carbon during the carbonization of organic matter. This regularity is observed in many coal deposits around the world (Dai et al., 2020a; Finkelman et al., 2018; Zubovic et al., 1964; Teichmüller & Teichmüller, 1979) and, most often, it is considered to be a favourable feature of high-rank coal for thermal processing. The high content of elements in low-rank coal, which is most often combusted, is an unfavourable feature. An increase in the content of Cu and Ni in coal, following an increase in the carbonization of organic matter, is probably a result of epigenetic mineralization of coal seams with sulphate and sulphide compounds. Such mineralization has already been observed in the USCB coal (e.g. Nieć & Łabuś, 1966; Kucha & Lipiarski, 1998; Kuhl & Dąbek, 1961; 1980, Parzentny, 2008). Moreover, correlation dependences were also observed. According to these dependences, the higher the content of liptinite and the lower the content of inertinite, the higher the content of volatiles in coal. Additionally, the higher the content of inertinite, the higher the heating value and the content of fixed carbon in coal. These correlations result from the aforementioned (e.g. Gabzdyl, 1987) technological properties of macerals. Liptinite has the highest and inertinite the lowest content of volatiles, and, additionally, the content of fixed carbon in liptinite is usually lower than in inertinite.

It was also observed that an increase in the value of the RI, is accompanied by an increase in the content of SiO_2 , Al_2O_3 , K_2O and TiO_2 in coal ash and the content of Cu in coal, as well as a decrease in the content of Fe_2O_3 and CaO in coal ash and the content of O^{daf} and sulphur (S_s^a , S_p^a) in coal. The increase in the value of the RI in coal generally results from an increase in the value of the indicators of the carbonization of organic matter (R_p , C^{daf} , Q_s^{daf} , V^{daf}). It is a result of a previously observed regularity, i.e. the value of the RI increases, from gas-flame coal to ortho-coking coal, together with the depth of the coal deposit (Gabzdyl, 1987; Probiez et al., 2012). Diagenesis and metamorphism of organic matter leads to an increase in the degree of carbonization, as well as the initiation of the process of the destruction of metal-organic and sulphur-organic compounds in the coal-forming matter and the redistribution of trace elements in a coal seam (e.g. Bouška, 1981; Chou et al., 2012; Dai et al., 2020a, 2020b; Teichmüller & Teichmüller, 1979). Metal-organic compounds and chelates of sulphur, Fe, Ca, as well as trace elements and major elements are common in low-carbonized organic matter of peats and lignites, and in bituminous coal the content of the aforementioned organic compounds significantly decreases. The observed increase in the content of Si, Al, K and Ti in coal ash and in the content of Cu in coal which follows the increase in the value of the RI, is probably not significantly associated with the aforementioned carbonization of organic matter. This tendency probably results from

the course of coal formation and/or sorption of compounds from solutions migrating into a coal deposit, which is specific for the USCB Limnic Series. To date, this supposition has only been confirmed by the measurements of the differences in the content of silicon in the coal ash of the USCB coal. It was observed that the content of Si in coal ash increases from the rocks and coal seams of the Limnic Series towards the Paralic Series (Parzentny and Marczak 1990).

5. Conclusions

1. The tested coal of the Limnic Series of the USCB has a low content of mineral matter (5.8%) and the medium-high content of total sulphur (1.09%) in coal increased the content of Al_2O_3 (22.15%), Fe_2O_3 (17.03%) and P_2O_5 (0.70%) in coal ash, low content of Cd, Co, Cr, Cu and Ni in coal and quite high content of Pb and Zn in coal. The highest share of the composition of mineral matter was observed for sulphide minerals, which constitute 2.5%, and carbonate minerals which constitute 1.7%. High content of the following was observed: in carbonate minerals – Cd and Co, in clay minerals – Cr and Zn, and in sulphide minerals – Cu, Ni and Pb.
2. Organic matter has the greatest influence on the content of Cd, Co, Cr, Cu, Ni, Pb, and Zn in coal, and this is an unfavourable feature of coal for thermal processing. In coal, the following have a secondary influence: carbonate minerals on the content of Cd and Co; clay minerals on the content of Cr and Zn; and sulphide minerals on the content of Cu, Ni and Pb.
3. The differences in the values of certain petrographic, technological and geochemical indicators of coal quality in the vertical profile of the Limnic Series, which were previously observed by other authors, were confirmed. The coal from the Libiąż Beds has the highest content of Vt, Sm, V^{daf} , Sp^{a} and S_0^{a} , Fe_2O_3 and Co. The coal from the Łaziska Beds has the highest content of O^{daf} , $\text{S}_{\text{SO}_4}^{\text{a}}$, S_t^{a} , SO_3 , and Pb. The coal from the Orzesze Beds has the highest content of Mi, Mw, SiO_2 , Al_2O_3 and value of ash yield. The coal from the Załęże Beds has the highest content of N^{daf} , P_2O_5 , Cd, Cr, Ni and value of SI. The coal from the Ruda Beds has the highest content of R_r , Q_s^{daf} , C^{daf} , H^{daf} , Al_2O_3 , Na_2O , K_2O , TiO_2 , Cu and value of RI. And the coal from the Saddle Beds has the highest content of I, C^{daf} , Q_s^{daf} , CaO, MgO, Ni and Zn. These observations indicate that the coal from the Ruda Beds may be suitable for coking, but that it is unsuitable for combustion. Coals from other USCB beds, especially the Libiąż Beds, Łaziska Beds and Orzesze Beds, can still be combusted, but they are unsuitable for coking.
4. Mutual dependences between petrographic, geochemical and technological indicators of coal quality were observed.
 - 4.1. As the content of vitrinite in coal decreases and the content of liptinite and inertinite in coal increases, the content of CaO, MgO and SO_3 in coal ash usually increases.
 - 4.2. An increase in the degree of the carbonization of organic matter is often accompanied by an increase in the content of Cu and Ni in coal, as well as a decrease in the content of Pb and sulphur in coal and the content of Fe_2O_3 in coal ash.
 - 4.3. An increase in the value of RI is accompanied by an increase in the content of SiO_2 , Al_2O_3 , K_2O and TiO_2 in coal ash and the content of Cu in coal, as well as a decrease in the content of Fe_2O_3 and CaO in coal ash and in the content of O^{daf} and sulphur in coal.

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