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A comparative study of the oxide and elemental composition of ash from lignite burned at various temperatures – Konin Lignite Mine, Central Poland

Introduction

In Poland, lignite is mined at four mine-mouth power plants to provide one-third of the total domestic electric energy, approximately 50–55 TWh (Tajduś et al. 2014; Kasztelewicz et al. 2018). Lignite is currently exploited at five mines in eight opencasts, including those belonging to the Konin Lignite Mine (Chomiak 2020a). The total annual production of Polish lignite has decreased slightly in recent years, reaching 52.9 Mt in 2019, of which 5.8 Mt is extracted from the Konin Mine in the Józwin IIB, Drzewce and Tomisławice opencasts (Figure 1, Mazurek and Tymiński 2020).

Burning large amounts of lignite (and similar amounts of hard coal) produces large amounts of both fly ash and bottom ash. In general, ash chemistry is of great importance in many aspects of lignite (and hard coal) exploitation, combustion, and ash utilization, including environmental protection (e.g., Filippidis et al. 1996; Vassilev et al. 1997;

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Ratajczak et al. 1999; Ward 2002; Galos and Uliasz-Bocheńczyk 2005; Carmona and Ward 2008; Markič and Sachsenhofer 2010; Misiak 2015; Karayiğit et al. 2019; Oskay et al. 2019; Životić et al. 2019; and references therein). In Poland, fly ash is analyzed for critical elements content in lignite intended for the production of 'clean energy' (Bielowicz 2016; Wagner et al. 2019) and/or its utilization (Galos and Uliasz-Bocheńczyk 2005; Uliasz-Bocheńczyk 2011), while bottom ash obtained in the laboratory is studied for purposes of environmental protection, including human health (Goldsztejn 2007; Bielowicz 2013).

In general, ash is an undesirable by-product of lignite combustion; hence, the major aim of this study was to identify changes in the chemical composition of ashes obtained by burning lignite samples at various temperatures (i.e., 100, 850, 950°C). Secondary goals were threefold:

- present the oxide and elemental composition of the ashes,
- determine if any correlations exist between oxides,
- compare results to their corresponding Clarke values.

1. Geology of the study area

Lignite deposits currently mined in the vicinity of Konin cover fault-bounded and relatively shallow (up to a few tens of meters deep) graben-like structures. These tectonic

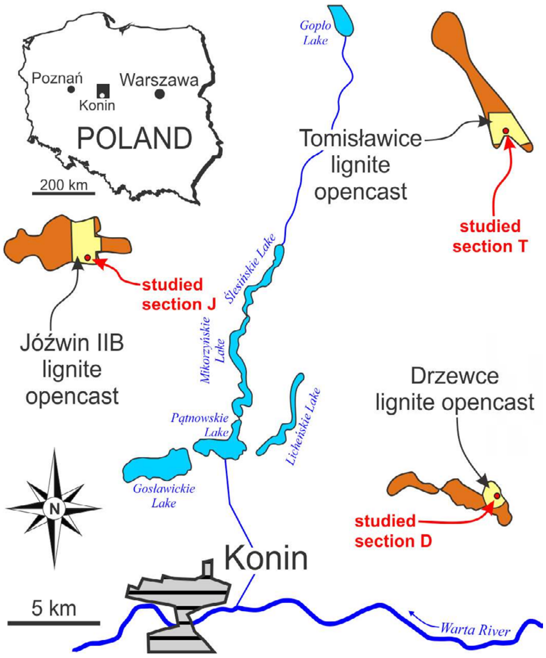

Fig. 1. An approximate location of the sampling sites (sections) in the area of the lignite opencasts belonging to the Konin Lignite Mine

Rys. 1. Przybliżona lokalizacja miejsc (profili) poboru próbek na obszarze odkrywek węgla brunatnego należących do Kopalni Węgla Brunatnego Konin depressions are filled with productive lignite deposits of the first Mid-Polish lignite seam (MPLS-1) greater than 3 m thick, while the flanks are covered by lignite beds thinner than 3 m; therefore, these lignite deposits represent both epeirogenic and tectonic types of genesis, with a graben subtype (Widera 2016a).

Sedimentary logs modified from Bechtel et al. (Bechtel et al. 2019, 2020); ash yield and its average values taken from Chomiak (Chomiak 2020a); lignite lithotype codification modified from Widera (Widera 2016c); for location of examined sections J, D and T see Figure 1.

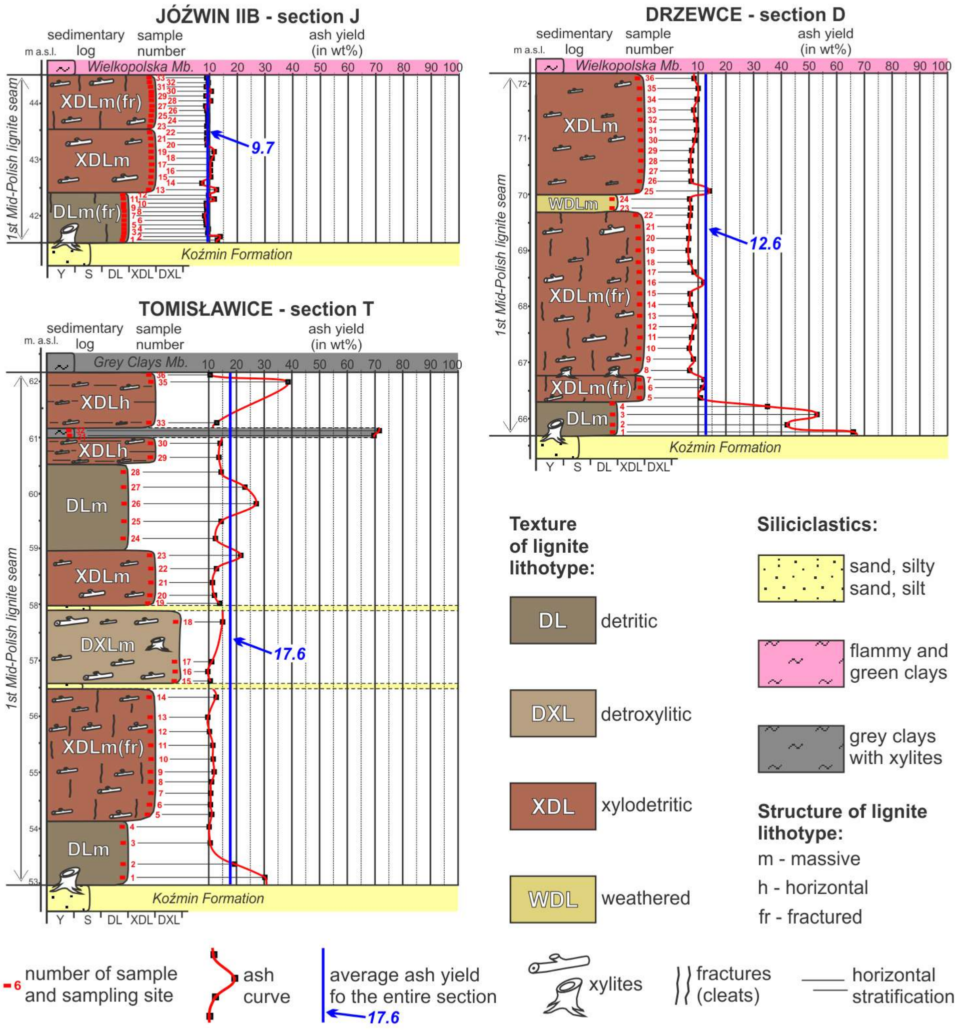

Fig. 2. Distribution of ash yield (obtained at 850°C) along the examined sections of the first Mid-Polish lignite seam (MPLS-1) in the Jóźwin IIB, Drzewce and Tomisławice opencasts

Rys. 2. Rozkład zawartości popiołu (uzyskanego w temp. 850°C) wzdłuż badanych profili pierwszego środkowopolskiego pokładu węgla brunatnego (MPLS-1) w odkrywkach Jóźwin IIB, Drzewce i Tomisławice

In general, the Mesozoic top contains marl and limy sandstone of the Late Cretaceous age (Dadlez et al. 2000). Paleogene strata of the Early Oligocene age, mostly glauconitic sand of marine origin, occur only locally, e.g., in Drzewce and Tomisławice lignite deposits (Chomiak et al. 2019, 2020a). The Grey Clays Member of the MPLS-1 is underlain by the sandy-coaly Koźmin Formation of Early to Mid-Miocene age and overlain by the muddy Wielkopolska Member of Late Mid-Miocene to Early Pliocene age (Figure 2). The Grey Clays Member (with MPLS-1) and the Wielkopolska Member together create the Poznań Formation (Piwocki and Ziembińska-Tworzydło 1997; Widera 2007). The Neogene succession is capped by a continuous layer of Quaternary glaciogenic deposits. Due to the destructive processes of the Scandinavian ice sheets and meltwaters during the Pleistocene, the uppermost beds, including the MPLS-1, were strongly deformed and/or zonally removed (Widera 2018; Maciaszek et al. 2020).

2. Materials and methods

2.1. Collection of lignite samples

The samples were collected in 2018–2019 on fresh exposures (exploitation fronts) at three operational opencasts belonging to the Konin Lignite Mine (Figure 1). Three vertical sections (referred to as sections J, D, and T) were sampled from the floor to the roof at an interval of 10–20 cm (Figure 2, Chomiak 2020a). A total of 105 lignite samples were collected from these sections for analysis to include ash content and chemistry.

2.2. Preparation of ash samples

In the laboratory, samples were divided into groups depending on the analysis for which they were intended. Ash yields were determined for all samples, while chemical analyses were performed on three representative groups of samples (assigned on the basis of an average mixture of 33–36 samples taken from each of the three sections J, D, and T, Figure 2). Each of these three groups were further subdivided into three groups for a total of nine lignite samples.

The first three samples (one from each section/opencast) were ashed using 30% hydrogen peroxide (H_2O_2) heated to 100°C. This procedure was time consuming because complete oxidation of the organic matter took several weeks. The second group of samples, analyzed in detail for the purpose of this study, was burnt at 850°C according to the ISO 1171:2010 standard and its Polish equivalent, the PN-ISO 1171:2002 standard. The third group of lignite samples was burnt at 950°C for at least 4 hours.

2.3. Analytical methods applied

Nine ash samples, obtained according to the procedure described in Section 2.2, were analyzed at the Central Measuring and Research Laboratory in Jastrzębie-Zdrój (Poland). The analytical procedure was carried out in accordance with the ASTM D6349-13 standard. The analyses were conducted using inductively-coupled plasma-optical emission spectrometers (ICP-OES), and the composition of the following oxides was determined: Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2, Mn_3O_4, Fe_2O_3, P_2O_5, and SO_3 (Table 1). For these oxides, Pearson's correlation coefficient (r) was calculated using Microsoft® Excel (Table 2). The concentrations of trace elements were measured for Ag, Zn, Ba, Cd, Co, Cr, Cu, St, Ni, Pb, V, Mo, Sn, Sb, As, Rb, Be, Tl, and Li (Table 3).

The concentrations of the trace elements were compared to the corresponding Clarke value for the world's lignite deposits, sedimentary rocks, and upper continental crust as summarized in Ketris and Yudovich (Ketris and Yudovich 2009), as well as Rudnick and Gao (Rudnick and Gao 2003) (Table 4, Figure 3). In sections 3 and 4, the results are briefly discussed to highlight the pros and cons of MPLS-1 combustion in the context of the chemical composition of its ashes.

3. Results

3.1. General characteristics of MPLS-1

Lignite exploited by the Konin Lignite Mine represents the MPLS-1 (first Lusatian). This is the only seam currently mined in opencasts in the vicinity of Konin. It can be up to several meters thick, 6–8 m on average. The MPLS-1 formed during the middle part of the Mid-Miocene (Piwocki and Ziembińska-Tworzydło 1997; Kasiński and Słodkowska 2016) as peat accumulated in a backswamp (low-lying mire) in the overbank zone of a Mid-Miocene fluvial system (Widera 2016b; Chomiak et al. 2019; Chomiak 2020b).

The MPLS-1 is described as a humic low-rank lignite B (ASTM D 388:2005) or ortho-lignite (ECE-UN 1998) characterized by an average reflectance coefficient (R^o) of eu-ulminite B below 0.3% and a carbon content (C^{daf}) in the range of 60–70 wt% (Kwiecińska and Wagner 2001). The MPLS-1 produces medium ash yield (A^d) according to the classification of Vassilev et al. (Vassilev et al. 1997), with A^d from 10–20 wt% on average (Chomiak 2020a; Chomiak et al. 2020a) and low average sulphur content (≤1.2 wt%, Bechtel et al. 2019, 2020). The lignite from the Konin Mine is mainly composed of detritic (42 vol.%) and detroxylitic (35 vol.%) lithotype associations (Widera 2016c). The association of xylodetritic lithotypes occupies ~35 vol.% (section J) to more than 80 vol.% (section D) of the MPLS-1 sections examined in this study (Figure 2).

3.2. Chemical analysis of ashes

3.2.1. Oxide composition

The composition of the oxides varied with temperature at which the lignite samples were ashing, especially if the oxidation/burning occurred at 100, 850, or 950°C. Silicon dioxide (SiO_2) and calcium oxide (CaO) were the most abundant oxides (exceeding 80 wt%) in all samples. Oxides such as aluminum oxide (Al_2O_3), sulphur trioxide (SO_3), iron (III) oxide (Fe_2O_3), and titanium dioxide (TiO_2) were present in much smaller but significant amounts, while other oxides were present in trace amounts (Table 1).

The results from lignite samples burned at 850°C are presented herein as to illustrate the overall results analyzed in accordance with ISO 1171:2010 and PN-ISO 1171:2002 standards. The composition of the oxides (expressed in wt%) were 47.6–54.8 (SiO_2), 30.9–33.5 (CaO), 1.92–2.35 (Al_2O_3), 0.43–2.11 (SO_3), 0.26–0.69 (Fe_2O_3), and 0.25–0.57 (TiO_2). The content of the other oxides (Na_2O, MgO, K_2O, P_2O_5) did not exceed 0.3 wt% (Table 1).

Table 1. Oxide composition of the studied ashes (wt%)

Tabela 1. Skład tlenkowy badanych popiołów (% wag.)

Oxides	100°C			850°C			950°C		
	J1	D1	T1	J2	D2	T2	J3	D3	T3
Na_2O	<0.14	<0.14	<0.14	<0.14	0.17	<0.14	<0.14	<0.14	<0.14
MgO	<0.08	<0.08	<0.08	0.17	0.15	0.13	0.19	0.14	0.19
Al_2O_3	0.62	1.03	0.79	2.13	2.35	1.92	2.44	2.55	2.10
SiO_2	14.6	25.8	23.4	54.8	48.9	47.6	48.3	42.4	48.2
K_2O	0.13	0.22	0.08	0.48	0.44	0.19	0.47	0.47	0.18
CaO	8.57	11.5	13.6	30.9	32.9	33.5	34.9	34.0	37.9
TiO_2	0.17	0.1	0.16	0.57	0.25	0.4	0.63	0.25	0.43
Mn_3O_4	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.01	0.02
Fe_2O_3	0.16	0.25	0.12	0.55	0.69	0.26	0.62	0.69	0.31
P_2O_5	0.05	0.1	0.07	0.17	0.29	0.11	0.2	0.27	0.17
SO_3	1.29	0.74	0.2	2.11	1.68	0.43	2.48	2.14	0.95
Loss on ignition	>74.18	>60.03	>61.35	>7.96	12.17	>15.3	>9.61	>16.94	>9.61
Total	100	100	100	100	100	100	100	100	100

J1–J3 – samples from the studied section J (Jóźwin IIB opencast); D1–D3 – samples from the studied section D (Drzewce opencast); T1–T3 – samples from the studied section T (Tomisławice opencast); for location of the studied sections see Figure 1.

3.2.2. Interpretation of oxide composition

Large quantitative differences in ash oxide compositions at low (100°C) and high (850 and 950°C) temperatures can be explained by the loss of ignition. Simply put, a temperature of 100°C was too low to initiate mineralogical transformations and the incomplete combustion of organic and mineral-organic particles occurred (e.g., Filippidis et al. 1996; Markič and Sachsenhofer 2010). Since the CaO content in ashes from lignite burned at different temperatures was relatively high (second only to SiO_2, Table 1), they can be called Ca-rich ashes (>10 wt%) according to the BN-79/6722-09 standard (e.g., Galos and Uliasz-Bocheńczyk 2005; Wagner et al. 2019).

According to Moore et al. (Moore et al. 2018), values of |r| larger than 0.7 indicate a strong linear (positive or negative) correlation. In this study, a perfect negative correlation (r = –1) between SiO_2 and CaO (Table 2) means that as the SiO_2 content increased, the CaO content decreased, and vice versa. Moreover, such a high negative correlation is indicative of a detrital origin for SiO_2 (quartz grains) and an authigenic origin for CaO in the form of $CaCO_3$ (calcium carbonate, Filippidis et al. 1996). A weak correlation (r = 0.16) between SiO_2 and Al_2O_3, and an Al_2O_3 content of ~2 wt% indicates a low content of kaolinite (Carmona and Ward 2008), the main clay mineral in Polish lignite. This observation was corroborated by depletion in Na_2O, MgO, and K_2O (but not kaolinite), which were widely present in minerals such as mica and illite (Ward 2002; Markič and Sachsenhofer 2010).

Table 2. Pearson's correlation coefficient (r) between oxides content of ashes for lignite samples burned at 850°C

Tabela 2. Współczynnik korelacji Pearsona (r) między zawartością tlenków w popiołach dla próbek węgla brunatnego spalonego w temp. 850°C

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Mn_3O_4	Fe_2O_3	P_2O_5	SO_3
Na_2O	1.00	0.00	**0.87**	–0.35	0.39	0.30	**–0.85**	**–1.00**	**0.75**	**0.94**	0.27
MgO		1.00	0.49	**0.94**	**0.92**	**–0.95**	0.53	0.00	0.66	**0.96**	**0.96**
Al_2O_3			1.00	0.16	**0.79**	–0.21	–0,48	**–0.89**	**0.98**	**0.98**	**0.71**
SiO_2				1.00	**0.73**	**–1.00**	**0.79**	0.35	0.36	–0.02	**0.81**
K_2O					1.00	**–0.77**	0.16	–0.39	**0.90**	0.67	**0.99**
CaO						1.00	**–0.79**	–0.30	–0.41	–0.03	**–0.84**
TiO_2							1.00	**0.85**	–0.28	–0.63	0.28
Mn_3O_4								1.00	**–0.75**	**–0.94**	–0.27
Fe_2O_3									1.00	**0.93**	**0.84**
P_2O_5										1.00	0.57
SO_3											1.00

In bold are marked strong and very strong correlations (|r| ≥ 0.7); for calculation data see Table 1.

The SO_3 content in the ashes showed a strong negative correlation ($r = -0.84$) with a CaO, but strong positive correlation ($r = 0.84$) with a Fe_2O_3 (Table 2). The first case is most likely related to the emission of sulphur (S) in the form of SO_2 in the process of high-temperature combustion because the ash generated was enriched in CaO and depleted in SO_3. In the second case, a small amount of S of inorganic origin (i.e., pyrite) was a typical authigenic mineral (e.g., Ward 2002; Životić et al. 2019) as demonstrated by the Fe_2O_3 content 3–4 times less than SO_3 (cf. Table 1). Obviously, SO_3 was classified as pyrite and gypsum/anhydrite in high-temperature ashes as in this case (cf. Filippidis et al. 1996).

Table 3. Selected trace elements content in the studied ashes (ppm)

Tabela 3. Skład wybranych pierwiastków śladowych w badanych popiołach (ppm)

Trace elements	100°C			850°C			950°C		
	J1	D1	T1	J2	D2	T2	J3	D3	T3
Ag	<4	<4	<4	<4	<4	<4	<4	<4	<4
Zn	32.1	60.3	40.1	47.9	118.1	63.7	7.45	14.5	60.2
Ba	588.8	337.3	308.0	2046	921.5	798.5	2470	985.0	794.0
Cd	<4	<4	<4	<4	<4	<4	<4	<4	<4
Co	<4	<4	<4	6.12	<4	4.15	6.81	<4	4.54
Cr	6.96	9.26	10.1	22.0	24.8	15.8	36.8	25.5	20.4
Cu	81.1	99.2	54.8	270.9	248.0	100.5	296.8	221.8	126.7
Sr	108.1	188.8	413.5	361.0	490.4	1102	415.2	512.1	1141
Ni	<4	7.69	7.23	10.6	13.5	10.4	7.57	11.9	7.73
Pb	23.7	32.9	36.7	61.0	67.3	84.6	52.6	45.7	65.9
V	4.19	4.81	5.67	17.8	12.9	14.6	20.8	13.5	15.7
Mo	<4	<4	<4	<4	<4	<4	<4	<4	<4
Sn	<4	<4	<4	<4	<4	<4	<4	<4	<4
Sb	5.11	< 4	5.77	6.31	6.97	9.88	7.55	8.17	8.62
As	<4	<4	<4	<4	<4	<4	<4	<4	<4
Rb	<50	<50	<50	<50	<50	<50	<50	<50	<50
Be	<4	<4	<4	<4	<4	<4	<4	<4	<4
Tl	<4	<4	<4	<4	<4	<4	<4	<4	<4
Li	4.33	5.35	4.11	17.9	14.1	10.1	16.8	14.3	12.1

Explanations as in Table 1.

3.2.3. Elemental composition

A total of 19 trace elements were identified and quantified in the ashes of lignite samples burned at 100, 850, and 950°C. The results obtained (and converted to 100%) show similar proportions between individual elements (Table 3). Among the trace elements, the average content of Ba, Sr, and Cu, each exceeded 100 ppm. The content of Zn, Pb, V, Rb, Cr, and Ni each ranged from 10–100 ppm. The remaining trace elements occurred in amounts below 10 ppm or below the detection limit of 4 ppm (cf. Tables 3 and 4). As an example, the elemental composition of ash from samples burned at 850°C (Table 4) is discussed below.

Table 4. Comparison of the study results obtained with various Clarke values (ppm)

Tabela 4. Porównanie uzyskanych wyników badań z różnymi wartościami klarków (ppm)

Trace elements	Average value for J2, D2 and T2 samples ashed at 850°C	Clarke value for world's lignite ashes*	Clarke value for sedimentary rocks*	Clarke value for upper continental crust**
Ag	<4	0.59	0.12	0.05
Zn	76.6	110	43	67
Ba	1255.3	900	410	628
Cd	<4	1.1	0.8	0.09
Co	<4.8	26	14	17.3
Cr	20.9	82	58	92
Cu	206.5	74	31	28
Sr	617.8	740	270	320
Ni	11.5	52	37	47
Pb	71.0	38	12	17
V	51.1	140	91	97
Mo	<4	15	1.5	1.1
Sn	<4	4.7	2.9	2.1
Sb	7.7	5.0	1.2	0.4
As	<4	48	7.6	4.8
Rb	<50	48	94	84
Be	<4	6.7	1.9	2.1
Tl	<4	5.1	0.89	0.9
Li	14.0	49	33	24

* – acc. to Ketris and Yudovich 2009; ** – acc. to Rudnick and Gao 2003.

3.2.4. Interpretation of trace elements

The trace elements listed in Tables 3 and 4 are recommended for further testing to assess the potentially toxic effects on the environment, including human health (e.g., Wagner 2001; Ma et al. 2020). The most harmful elements were Pb, Cd, Be, As, and Hg at any concentration; however, due to the high volatility of Hg, its content in bottom ash was negligible (beyond detection) and was not tested. Other analyzed trace elements (Ag, Zn, Co, Cr, Cu, Mo, Sn, Sb, Tl) are harmful only at elevated concentrations (Bielowicz 2013; Hycnar et al. 2015); therefore, the absolute content of these trace elements in relation to the corresponding Clarke values is important (Table 4, Figure 3).

Only four of the trace elements (Ba, Cu, Pb, Sb) were characterized by higher values as compared to Clarke values (Figure 3). In the case of Cu and Pb, the concentration was 3 and 2 times higher, respectively. On the other hand, the average results obtained for Co, Cr, Ni, As, and Rb were lower than the corresponding Clarkes. The content of Co, Cr, and Ni found in our samples were 3–5 times higher than the Clarke values but the curves are similar. The values of other trace elements fall between these curves and the curve of the Clarke values for the world's lignite ashes (Figure 3).

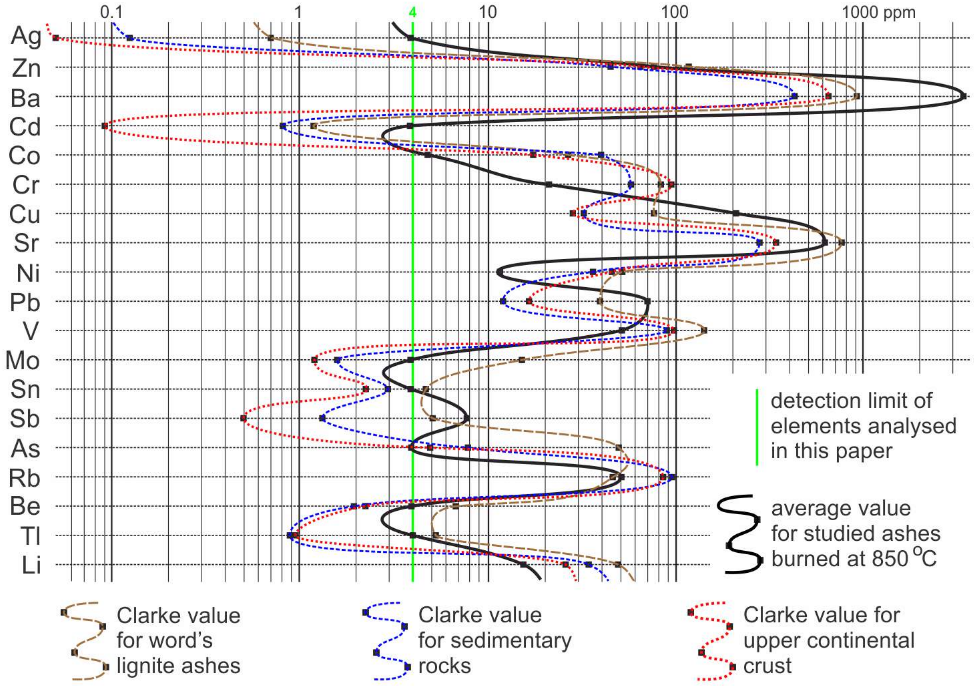

Fig. 3. Graphical presentation of the data contained in Table 4 on a logarithmic scale
For other explanations see captions to Table 4 and the text

Rys. 3. Graficzna prezentacja danych zawartych w tabeli 4 w skali logarytmicznej

4. Discussion

The oxide composition of ashes from MPLS-1 clearly indicates the dominance of SiO_2 and CaO with an average of 47.6–54.8 and 30.9–33.5 wt%, respectively (Table 1). Most of the SiO_2 occurs in the form of quartz grains in ashes and lignite seams. In the case of lignite seams, sandy, silty, and clayey interbeds (several dm to >1 m thick) are well documented in some parts of the lignite deposits exploited by the Konin Mine in central Poland (Figure 2; Widera 2016b; Chomiak 2020a, b; Chomiak et al. 2019; 2020a, b).

The situation with CaO is completely different from the one for SiO_2. No $CaCO_3$-rich layers (lacustrine chalk and/or gyttja) have been found macroscopically (in the field and borehole profiles) in any of the lignite deposits in the vicinity of Konin. Nevertheless, such carbonate interbeds (up to several dozen meters thick) are quite common in other Polish lignite deposits, such as Bełchatów, Szczerców, and Złoczew (Wagner and Matl 2007; Urbański and Widera 2020). Similar partings (referred to as chalk, marl, marly limestone, limestone, clayey limestone, etc.) also occur in some European lignite seams (e.g., Kolovos et al. 2002; Thomas and Frankland 2004; Akkiraz et al. 2012; Villalba-Breva et al. 2012; Oskay et al. 2019). Thus, the majority of CaO is dispersed within organic matter in the form of $CaCO_3$, while the remainder enters into other mineral phases.

Siliciclastics (sands and clays) and carbonates (predominantly calcite) increase the total ash content and decrease the calorific value of lignite. However, free CaO produced during combustion (mainly from decomposition of $CaCO_3$) has a positive impact on the environment because it holds SO_2 in the form of anhydrite ($CaSO_4$) and consequently limits SO_2 emissions (Filippidis et al. 1996; Galos et al. 2016). Simply put, the elevated $CaCO_3$ content in lignite (and free CaO in ash) promotes so-called natural desulphurization (Kolovos et al. 2002).

In general, bottom ashes, left as residue after the combustion process (e.g., Goldsztejn 2007; Chomiak 2020a), are less frequently investigated than fly ash which is relatively more harmful to the environment (e.g., Galos and Uliasz-Bocheńczyk 2005; Misiak 2015; Wagner et al. 2019). The rule is that as the temperature rises, the ash loses organic matter and gains mineral matter (e.g., Kolovos et al. 2002; Filippidis et al. 1996). In other words, low-temperature ash contains more unburned organic and mineral-organic particles than high-temperature ash as demonstrated herein (cf. Table 1). On the other hand, ashes obtained from lignite burned at different temperatures clearly show that the proportions between the oxides and the elements (after conversion to 100%) are similar (Table 1), hence, ash analysis for lignite samples burned at 850°C (i.e., acc. to the ISO 1171:2010 and PN-ISO 1171:2010 standards) appear to be sufficient in most (geo)chemical studies.

Conclusions

Based on the chemical analyses of ashes from the first Mid-Polish lignite seam (MPLS-1) the most important conclusions are:

- The ashes were enriched in silicon dioxide (SiO_2, ~50 wt% on average) and calcium oxide (CaO, exceeded 30 wt% on average); hence, these ashes have a calcium character.
- A perfect negative correlation ($|r| = -1$) between SiO_2 and CaO content indicates an exogenous origin for detrital quartz grains (SiO_2) and an authigenic origin for CaO in the form of calcium carbonate ($CaCO_3$).
- Among the trace elements identified, the greatest content belonged to Ba, Sr, Cu, and Pb characterized by values higher than their corresponding Clarke values.
- Based on the results obtained from this work, we conclude that combustion of lignite from MPLS-1 is no more harmful to the environment than coal from other countries burned in large amounts to generate electricity. In addition, a higher concentration of $CaCO_3$ facilitates flue gas desulphurization, which reduces SO_2 emission.

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REFERENCES

Akkiraz et al. 2012 – Akkiraz, M.S., Akgün, F., Utescher, T., Wilde, V., Bruch, A.A., Mosbrugger, V. and Üçbaş, S.D. 2012. Palaeofl ora and Climate of Lignite-bearing Lower−Middle Miocene Sediments in the Seyitömer and Tunçbilek Sub-basins, Kütahya Province, Northwest Turkey. *Turkish Journal of Earth Sciences* 21, pp. 213–235.

ASTM D 388:2005 – Standard Classification of Coals by Rank. American Society for Testing and Materials.

ASTM D6349-13 – Standard Test Method for Determination of Major and Minor Elements in Coal, Coke, and Solid Residues from Combustion of Coal and Coke by Inductively Coupled Plasma & mdash; Atomic Emission Spectrometry. American Society for Testing and Materials.

Bechtel et al. 2019 – Bechtel, A., Widera, M. and Woszczyk, M. 2019. Composition of lipids from the First Lusatian lignite seam of the Konin Basin (Poland): relationships with vegetation, climate and carbon cycling during the mid-Miocene Climatic Optimum. *Organic Geochemistry* 138, DOI: 10.1016/j.orggeochem.2019.103908.

Bechtel et al. 2020 – Bechtel, A., Widera, M., Lücke, A., Groß, D. and Woszczyk, M. 2020. Petrological and geochemical characteristics of xylites and associated lipids from the First Lusatian lignite seam (Konin Basin, Poland): implications for floral sources, decomposition and environmental conditions. *Organic Geochemistry* 146, DOI: 10.1016/j.orggeochem.2020.104052.

Bielowicz, B. 2013. Selected harmful elements in Polish lignite (*Występowanie wybranych pierwiastków szkodliwych w polskim węglu brunatnym*). *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 29(3), pp. 47–59 *(in Polish* with English abstract).

Bielowicz, B. 2016. Qualitative and chemical characteristics of mineral matter in the selected lignite deposits in light of their suitability for clean coal technologies. *E3S Web of Conferences 10*, 00002, DOI: 10.1051/e3sconf/20161000002.

BN-79/6722-09 – Fly ash and slag from coal and brown coal fired boilers.

Carmona, I. and Ward, C.R. 2008. Composition and mode of occurrence of mineral matter in some Colombian coals. *International Journal of Coal Geology* 73, pp. 3–8.

Chomiak, L. 2020a. Variation of lignite ash in vertical and horizontal sections of mining walls in the Konin Lignite Mine, central Poland. *Geology, Geophysics and Environment* 46(1), pp. 17–28.

Chomiak, L. 2020b. Crevasse splays within a lignite seam at the Tomisławice opencast mine near Konin, central Poland: architecture, sedimentology and depositional model. *Geologos* 26(1), pp. 25–37.

Chomiak et al. 2019 – Chomiak, L., Maciaszek, P., Wachocki, R., Widera, M. and Zieliński, T. 2019. Seismically-induced soft-sediment deformation in crevasse-splay microdelta deposits (Middle Miocene, central Poland). *Geological Quarterly* 63(1), pp. 162–177.

Chomiak et al. 2020a – Chomiak, L., Urbański, P. and Widera, M. 2020. Architecture and origin of clays within the upper part of lignites of the Poznań Formation (Middle Miocene) – the Tomisławice lignite opencast near Konin in central Poland (*Architektura i geneza iłów w górnym poziomie węgli brunatnych formacji poznańskiej (środkowy miocen) – odkrywka Tomisławice k. Konina w środkowej Polsce*). *Przegląd Geologiczny* 68(6), pp. 526–534 (*in Polish* with English abstract).

Chomiak et al. 2020b – Chomiak, L., Kaczmarek, P., Kubiak, M. and Widera, M. 2020. Chemical composition of ashes from selected sections of the lignite seam mined in the Konin Basin, Central Poland. *World Multidisciplinary Earth Sciences Symposium – WMESS 2020*, 7–11 September, 2020 – Prague (Czech Republic).

Dadlez et al. 2000 – Dadlez, R., Marek, S. and Pokorski, J. eds. 2000. Geological map of Poland without Cenozoic deposits, scale 1:1000000 (*Mapa geologiczna Polski bez osadów kenozoicznych w skali 1: 1 000 000*). Warszawa: Polish Geological Institute (*in Polish*).

ECE-UN 1998 – International classification of in-seam coals. ECE-UN Geneva, UN New York.

Filippidis et al. 1996 – Filippidis, A., Georgakopoulos, A. and Kassoli-Fournaraki, A. 1996. Mineralogical components of some thermally decomposed lignite and lignite ash from the Ptolemais basin, Greece. *International Journal of Coal Geology* 30, pp. 303–314.

Galos, K. and Uliasz-Bocheńczyk, A. 2005. Sources and utilization of fly ashes from coal combustion in Poland (*Źródła i użytkowanie popiołów lotnych ze spalania węgli w Polsce*). *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 21(1), pp. 23–42 (*in Polish* with English abstract).

Galos et al. 2016 – Galos, K., Szlugaj, J., Burkowicz, A. 2016. Sources of limestone sorbents for flue gas desulphurization in Poland in the context of the needs of domestic power industry (*Źródła sorbentów wapiennych do odsiarczania spalin w Polsce w kontekście potrzeb krajowej energetyki*). *Polityka Energetyczna – Energy Policy Journal* 19(2), pp. 149–170 (*in Polish*).

Goldsztejn, P. 2007. Abundances of selected elements in brown coal from Ościsłowo deposit in Konin area (Koncentracje wybranych pierwiastków w węglu brunatnym ze złoża Oscisłowo w rejonie Konina). *Prace Naukowe Instytutu Górnictwa Politechniki Wrocławskiej* 118(33), pp. 17–24 (*in Polish* with English abstract).

Hycnar et al. 2015 – Hycnar, E., Ratajczak, T., Jończyk, W. and Wagner, M. 2015. The ecological criteria for evaluation the quality lignite on the example of the Bełchatów deposit (*Ekologiczne kryteria oceny jakości węgla brunatnego na przykładzie złoża Bełchatów*). *Zeszyty Naukowe Instytutu Gospodarki Surowcami Mineralnymi i Energią Polskiej Akademii Nauk* 91, pp. 81–89 (*in Polish* with English abstract).

ISO 1171:2010 – Solid mineral fuels – Determination of ash.

Karayiğit et al. 2019 – Karayiğit, A.İ., Yğitler, Ö., İşerli, S., Querol, X., Mastalerz, M., Oskay, R.G. and Hower, J.C. 2019. Mineralogy and Geochemistry of Feed Coals and Combustion Residues from Tunçbilek and Seyitömer Coal-Fired Power Plants in Western Turkey. *Coal Combustion and Gasification Products* 11, pp. 18–31.

Kasiński, J.R. and Słodkowska, B. 2016. Factors controlling Cenozoic anthracogenesis in the Polish Lowlands. *Geological Quarterly* 60, pp. 959–974.

Kasztelewicz et al. 2018 – Kasztelewicz, Z., Ptak, M. and Sikora, M. 2018. Brown coal as an optimal energy raw material for Poland (*Węgiel brunatny optymalnym surowcem energetycznym dla Polski*). *Zeszyty Naukowe Instytutu Gospodarki Surowcami Mineralnymi i Energią Polskiej Akademii Nauk* 106, pp. 61–84 (*in Polish* with English abstract).

Ketris, M.P. and Yudovich, Y.E. 2009. Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals. *International Journal of Coal Geology* 78, pp. 135–148.

Kolovos et al. 2002 – Kolovos, N., Georgakopoulos, A., Filippidis, A. and Kavouridis, C. 2002. Environmental Effects of Lignite and Intermediate Steriles Coexcavation in the Southern Lignite Field Mine of Ptolemais, Northern Greece. *Energy Sources* 24, pp. 561–573.

Kwiecińska, B. and Wagner, M. 2001. Application of reflectance in natural and technological classification of brown coal (lignite) (*Zastosowanie współczynnika odbicia w naturalnej i technologicznej klasyfikacji węgla brunatnego (lignitu)*). Kraków: AGH, 35 pp. (*in Polish*).

Ma et al. 2020 – Ma, J., Liu, B., Zhang, K., Wang, Z., Li, J., Blokhin, M.G. and Zhao, C. 2020. Geochemical characteristics of No. 6 coal from Nanyangpo Mine, Datong coalfield, north China: Emphasis on the influence of hydrothermal solutions. *Energy Exploration & Exploitation*, pp. 1–20. DOI: 10.1177/0144598720922309.

Maciaszek et al. 2020 – Maciaszek, P., Chomiak, L., Urbański, P. and Widera, M. 2020. New insights into the genesis of the "Poznań Clays" – upper Neogene of Poland. *Civil and Environmental Engineering Reports* 30, pp. 18–32.

Markič, M. and Sachsenhofer, R.F. 2010. *The Velenje Lignite: Its Petrology and Genesis*. Ljubljana: Geološki Zavod Slovenije, 218 pp.

Mazurek, S. and Tymiński, M. 2020. *Lignites* (*Węgle brunatne*). [In:] Szuflicki, M., Malon, A. and Tymiński, M. (eds.) 2020. *The Balance of Mineral Resources Deposits in Poland as of 31.12.2018*. Warszawa: Polish Geological Institute, pp. 35–40 (*in Polish*).

Misiak, J. 2015. Coal particles in the fly ashes from Polish coal combustion (*Cząstki węglowe w popiołach lotnych ze spalania węgla z polskich złóż*). *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 31(3), pp. 111–120 (*in Polish* with English abstract).

Moore et al. 2018 – Moore, D.S., Notz, W.I. and Flinger, M.A. 2018. *The basic practice of statistics* (8th ed.). New York: Freeman and Company, 654 pp.

Oskay et al. 2019 – Oskay, R.G., Christanis, K. and Salman, M. 2019. Coal features and depositional environment of the Northern Karapınar–Ayrancı coal deposit (Konya, Central Turkey). *Turkish Journal of Earth Sciences* 28, pp. 260–274.

Piwocki, M. and Ziembińska-Tworzydło, M. 1997. Neogene of the Polish Lowlands – lithostratigraphy and pollen-spore zones. *Geological Quarterly* 41(1), pp. 21–40.

PN-ISO 1171:2002. Solid fuels. Ash determination (*in Polish*).

Ratajczak et al. 1999 – Ratajczak, T., Gaweł, A., Górniak, K., Muszyński, M., Szydłak, T. and Wyszomirski, P. 1999. Characteristics of fly ash from combustion of some hard and brown coals (*Charakterystyka popiołów lotnych ze spalania niektórych węgli kamiennych i brunatnych*). *Polskie Towarzystwo Mineralogiczne – Prace specjalne* 13, pp. 9–34 (*in Polish*).

Rudnick, R.L. and Gao, S. 2003. *The composition of the continental crust*. [In:] Rudnick, R.L. ed., *The Crust*. Elsevier-Pergamon, Oxford, 64 pp.

Tajduś et al. 2014 – Tajduś, A., Kaczorowski, J., Kasztelewicz, Z., Czaja, P., Cała, M., Bryja, Z. and Żuk, S. 2014. Brown coal – an offer for Polish power industry – development possibilities for brown coal mining functioning in Poland by the year 2050 (*Węgiel brunatny – oferta dla polskiej energetyki - możliwości rozwoju wydobycia węgla brunatnego funkcjonującego w Polsce do 2050 roku*). Kraków: Komitet Górnictwa PAN, 85 pp. (*in Polish*).

Thomas, L. and Frankland, S. 2004. Mining at Gacko opencast mine, Bosnia-Herzegovina a question of economics. *Geologica Belgica* 7(3–4), pp. 267–271.

Uliasz-Bocheńczyk, A. 2011. Mineral sequestration of CO_2 using water suspensions of selected fly ashes from the combustion of lignite coal (*Mineralna sekwestracja CO_2 przy zastosowaniu zawiesin wodnych wybranych popiołów lotnych ze spalania węgla brunatnego*). *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 27(1), pp. 145–153 (*in Polish* with English abstract).

Urbański, P. and Widera, M. 2020. Is the Złoczew lignite deposit geologically suitable for the first underground gasification installation in Poland? *Geologos* 26(2), pp. 113–125.

Vassilev et al. 1997 – Vassilev, S.V., Kitano, K. and Vassileva, C.G. 1997. Relations between ash yield and chemical and mineral composition of coals. *Fuel* 76, pp. 3–8.

Villalba-Breva et al. 2012 – Villalba-Breva, S., Martín-Closas, C., Marmi, J., Gomez, B. and Fernández-Marrón, M.T. 2012. Peat-forming plants in the Maastrichtian coals of the Eastern Pyrenees. *Geologica Acta* 10(2), pp. 189–207.

Wagner, M. 2001. Determination of toxic and harmful elements in coal and its ashes (*Oznaczanie pierwiastków toksycznych i szkodliwych w węglu i jego popiołach*). [In:] Stryszewski, M. Selective exploitation of lignite as a method of limiting the harmful environmental impact of elements present in coal and its combustion products (*Eksploatacja selektywna węgla brunatnego jako metoda ograniczenia szkodliwego oddziaływania na środowisko pierwiastków obecnych w węglu i produktach jego spalania*). Kraków: AGH (*in Polish*).

Wagner, M. and Matl, K. 2007. Stratigraphy of lacustrine chalk from the "Szczerców" lignite deposit (*Stratygrafia kredy jeziornej ze złoża węgla brunatnego „Szczerców"*). *Geologia* 33(3), pp. 289–315 (*in Polish* with English abstract).

Wagner et al. 2019 – Wagner, M., Bielowicz, B. and Misiak, J. 2019. Analysis of the occurrence of critical elements and raw materials in Polish lignite deposits with particular emphasis on coal ashes. [In:] *2nd International Conference on the Sustainable Energy and Environmental Development*. 14–17 November 2017, Kraków, Poland. IOP Conference Series: Earth and Environmental Science 214 (2019) 012026, DOI: 10.1088/1755-1315/214/1/012026.

Ward, C.R. 2002. Analysis and significance of mineral matter in coal seams. *International Journal of Coal Geology* 50, pp. 135–168.

Widera, M. 2007. Lithostratigraphy and palaeotectonics of the sub-Pleistocene Cenozoic of Wielkopolska (*Litostratygrafia i paleotektonika kenozoiku podplejstoceńskiego Wielkopolski*). Poznań: Adam Mickiewicz University Press, 224 pp. (*in Polish* with English abstract).

Widera, M. 2016a. Genetic classification of Polish lignite deposits: A review. *International Journal of Coal Geology* 158, pp. 107–118.

Widera, M. 2016b. Depositional environments of overbank sedimentation in the lignite-bearing Grey Clays Member: new evidence from Middle Miocene deposits of central Poland. *Sedimentary Geology* 335, pp. 150–165.

Widera, M. 2016c. An overview of lithotype associations forming the exploited lignite seams in Poland. *Geologos* 22(3), pp. 213–225.

Widera, M. 2018. Tectonic and glaciotectonic deformations in the areas of Polish lignite deposits. *Civil and Environmental Engineering Report*s 28, pp. 182–193.

Životić et al. 2019 – Životić, D., Cvetković, O., Vulić, P., Gržetić, I., Simić, V., Ilijević, K., Dojčinović, B., Erić, S., Radić, B., Stojadinović, S. and Trifunović, S. 2019. Distribution of major and trace elements in the Kovin lignite (Serbia). *Geologia Croatica* 72(1), pp. 51–79.

A COMPARATIVE STUDY OF THE OXIDE AND ELEMENTAL COMPOSITION OF ASH FROM LIGNITE BURNED AT VARIOUS TEMPERATURES – KONIN LIGNITE MINE, CENTRAL POLAND

Keywords

Ash yield, oxide composition, elemental composition, Pearson correlation, Clarke value

Abstract

Lignite still plays a key role in the production of electricity in Poland. About one-third of domestic electric energy comes from lignite burned in large power plants that produce megatons (Mt) of bottom ash and fly ash annually. Nearly 11 wt% of the total ash generated by the lignite-fired power industry in Poland comes from lignite extracted from the Konin Lignite Mine. Part of the ash escapes into the atmosphere, and the rest is utilized, which is expensive and often harmful to the environment; hence, geochemical studies of these ashes are fully justified and increasingly carried out. The lignite samples examined in this paper represent the entire vertical section of the first Mid-Polish lignite seam (MPLS-1) mined in opencasts at Jóźwin IIB, Drzewce, and Tomisławice. First, the samples were oxidized (burnt) at one of three temperatures: 100, 850, and 950°C; then the chemical composition of oxides and trace elements was determined according to the ASTM D6349-13 standard. The ashes were rich in SiO_2 and CaO; Ba, Sr, and Cu dominated the trace element content. Among the harmful elements found, Pb is of most concern. Only a few elements (Ba, Cu, Pb, Sb) reached values higher than their corresponding Clarke values. Based on the results obtained, it can be concluded that the examined ashes are approximately as harmful to the environment as ashes from other lignite used to generate electricity. Moreover, the increased amount of $CaCO_3$ in the MPLS-1 is beneficial in the process of natural desulphurization.

BADANIA PORÓWNAWCZE SKŁADU TLENKOWEGO I PIERWIASTKOWEGO POPIOŁÓW ZE SPALANIA WĘGLA BRUNATNEGO W RÓŻNYCH TEMPERATURACH – KOPALNIA WĘGLA BRUNATNEGO KONIN W CENTRALNEJ POLSCE

Słowa kluczowe

zawartość popiołu, skład tlenkowy, skład pierwiastkowy, korelacja Pearsona, wartość klarkowa

Streszczenie

W ostatnich latach około jednej trzeciej polskiej energii elektrycznej pochodzi z węgla brunatnego, który jest spalany w wielkich elektrowniach. Powoduje to produkcję popiołów (żużla paleniskowego i popiołu lotnego) w łącznej ilości wyrażonej w milionach ton (Mt). Blisko 11% wag. popiołu produkowanego przez polską energetykę opartą na węglu brunatnym pochodzi z węgla wydobywanego przez Kopalnię Węgla Brunatnego Konin. Oczywiście, popiół jest składnikiem niepożądanym w węglu z wielu względów. Część popiołu może przedostać się do atmosfery, a pozostałą część należy poddać utylizacji, co jest kosztowne i często szkodliwe dla środowiska naturalnego. Stąd badania geochemiczne tych popiołów wydają się celowe i dlatego są coraz częściej przeprowadzane. Badane w tej pracy uśrednione próbki węgla reprezentują cały profil pierwszego środkowopolskiego pokładu węglowego (MPLS-1) eksploatowanego w odkrywkach: Jóźwin IIB, Drzewce i Tomisławice. Te próbki zostały najpierw utlenione/spalone w temperaturze: 100, 850 i 950°C. Następnie został określony ich skład chemiczny (tlenki i pierwiastki śladowe) według normy ASTM D6349-13. Badane popioły cechują się dominacją SiO_2 i CaO, zaś w składzie pierwiastków śladowych przeważają: Ba, Sr i Cu. Natomiast wśród pierwiastków szkodliwych najważniejszy jest Pb. Wreszcie, tylko kilka z analizowanych pierwiastków (Ba, Cu, Pb, Sb) osiąga wartości wyższe niż wartości odpowiednich klarków. Na podstawie uzyskanych wyników można stwierdzić, że badane popioły są w przybliżeniu tak samo szkodliwe dla środowiska jak popioły z innych węgli brunatnych używanych do wytwarzania energii elektrycznej, a zwiększona ilość $CaCO_3$ jest też korzystna w procesie naturalnego odsiarczania.