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ORIGINAL PAPER

PHYSICAL AND CHEMICAL PROPERTIES OF ASH FROM THERMAL POWER STATION COMBUSTING LIGNITE. A CASE STUDY FROM CENTRAL POLAND*

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ABSTRACT

Hard coal and lignite are the main sources of electricity and heat in many countries. Waste generated during lignite combustion is deposited primarily on disposal sites. In the development of its reclamation technologies, it is crucial to precisely specify the physical and chemical properties of coal ash. The aim of this study was to determine selected physical and chemical parameters of an unreclaimed fragment of the disposal site established for the disused Adamów power plant. These properties were analysed in terms of the potential to support vegetation cover growth and development. It was also undertaken to determine the effect of the distance from the coal ash discharge outlet on these properties. Particle density of that rock was 2.23-2.56 Mg m⁻³, bulk density ranged from 0.99 to 1.18 Mg m⁻³. Its reaction was alkaline (pH in 1 M KCl 9.68-12.19). Hydrogen carbonate content amounted to 40.50-76.00 g kg⁻¹. The organic substance found in the rock was identified as residues of unburned coal. Analyses showed no nitrogen and phosphorus content, at excessive amounts of Ca and Na. Cation exchange capacity (CEC) ranged from 57.2 to 128.4 cmol₍₊₎ kg⁻¹. It is the so-called "apparent capacity" resulting from the reaction of ammonium acetate with calcium compounds, mainly hydrogen carbonates. The study showed that properties of coal ash deposited in wet surface impoundments (storage lagoons) depended on the distance from the discharge outlet. Greater particles, less abundant in alkali metals, are deposited closer to the discharge outlet. With an increase in the distance from the ash discharge outlet we observe an increase in the share of smallest particles, a more alkaline reaction and greater amounts of calcium, sodium, potassium and magnesium.

Keywords: ash storage lagoons, ash, physical properties, chemical properties.

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INTRODUCTION

Hard coal and lignite are the primary sources of electricity and heat in many countries. Combustion of these fossil fuels generates waste, whose annual production worldwide amounts to 750 mln t (YAO et al. 2014), while in Poland alone it is as much as approx. 13.7 mln t (ANTONKIEWICZ 2010). As it was reported by HAYNES (2009), almost 70-75% of this waste is bottom ash and fly ash. UZAROWICZ and ZAGÓRSKI (2015) indicated that fly ash is composed of spherical grains, while bottom ash consists of angular ones. Bottom ash is partly used in other branches of economy. Its most frequent applications include production of construction materials, addition to road base and structural fill materials in road and railway construction. Nevertheless, the share of unmanaged coal ash ranges from 85% in Germany to 27% in India (JALA, GOYAL 2006). Unmanaged coal ash is deposited on disposal sites. In Poland, only as little as approx. 50% bottom ash is recycled. This is mainly ash generated from the combustion of hard coal. In contrast, waste produced from the combustion of lignite is primarily deposited on disposal sites. According to ANTONKIEWICZ (2010), approx. 280 mln t of ash are deposited on such sites in Poland. In the Konin-Turek coal basin alone, the area of active disposal sites exceeds 800 ha. In most cases, coal ash is delivered to disposal sites by hydraulic transport. Due to such processes as leaching, hydrolysis or hydration, physical and the resulting chemical and physico-chemical properties of coal ash vary considerably. Strongly cemented ash rock is formed, in which silicon and calcium compounds predominate. AHMARUZZAMAN (2010), UKWATTAGE et al. (2013) and MOCEK-PLÓCINIĄK (2018) reported that lignite coal ash may contain as much as 12 up to 25% calcium. A significant effect on the properties of coal ash is exerted by the adopted transport system, as well as the quality of coal itself and the applied combustion technology GILEWSKA (2004). For this reason, detailed and accurate information on the physical and chemical properties of coal ash deposited on disposal sites is crucial for the development of appropriate reclamation technologies (WOŹNIAK, ŻYGADŁO 2016).

Studies conducted to date have typically focused on the chemical and mineral composition of coal ash and their changes in time (KUMAR et al. 2017, STEFANIAK et al. 2014, WIRTH et al. 2018). Current literature on the subject also includes publications concerning properties of soils developing from the ash rock (UZAROWICZ et al. 2017, 2018, WEBER et al. 2015,) and the development of various plant species introduced in the course of the reclamation process (ŻOŁNIERZ et al. 2015, PIETRZYKOWSKI et al. 2018).

The aim of this study was to determine selected physical and chemical properties of an unreclaimed fragment of the ash storage lagoons at the Adamów power plant. The analyses of these properties focused on the potential for growth and development of the vegetation cover. It was also undertaken to determine the effect of the distance from the coal ash discharge outlet on these properties.

MATERIAL AND METHODS

Study area and sampling

Analyses were conducted within the wet surface impoundment of the Adamów power plant, located 2.3 km west of the city limits of Turek (Figure 1),

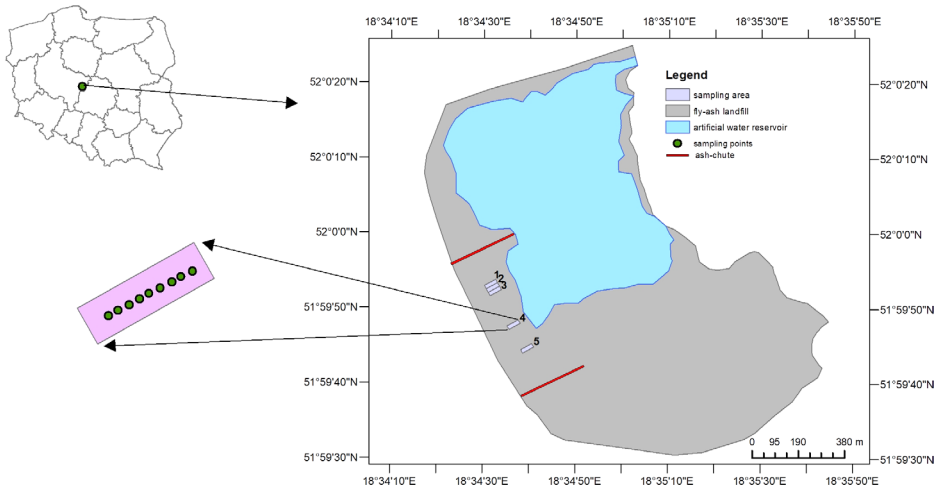


Fig.1. Location of the study area and sampling scheme

in the south-western part of the Koło Basin. Fly ash produced in the Adamów Power Plant is transported from the power plant as sludge and deposited in the former open cast working of a lignite mine. The entire disposal site is 184 ha in area, of which unreclaimed ash is deposited over approx. 88 ha. The accumulated waste deposit ranged from 40 to 45 m in thickness. From 10 selected sampling areas of 36 m² (6x6 m) each the surface samples were collected from fresh deposits of 0-30 cm in depth with the disturbed and undisturbed structure. In each sampling point, samples were collected in 9 replications according to the scheme presented in Figure 1. A total of 90 ash samples were obtained.

Laboratory analyses

From each area, monolith samples were collected for laboratory analyses and undisturbed ash samples were taken to determine bulk density (ρ_b), porosity (f_c), drainable porosity (f_D) and microporosity (f_M). Bulk density was determined by the core method in a cylindrical metal sampler of 100 cm³, porosity ρ_b and particle density ρ_p were assessed from the equation ($f_c = 1 - \rho_b/\rho_p$), drainable porosity was determined as the difference between f_c and ρ_{fc} (field capacity) and the f_M was the difference between f_c and f_D . The volumetric water content at field capacity (θ_{fc}) was determined at the water potential of -10 kPa using Richards extraction chambers (KLUTE 1986).

The disturbed samples were air-dried and ground to pass through a 2-mm mesh size sieve prior to analysis. In laboratory analyses, the silt and clay fractions were determined by the areometric method, while sand particles were isolated using the sieve method with wet fractioning. The divisions into textural classes were made according to the USDA classification systems (SCHOENEGER et al. 2012) and PTG (2009). Particle density (ρ_p) was determined by the pycnometric method, the reaction (pH) was measured potentiometrically in an ash:water ($\text{pH}_{\text{H}_2\text{O}}$) and ash:1M KCl (pH_{KCl}) 1:5 suspension (v/v) according to the Polish Standard PN-EN ISO 10390. Carbonates (CaCO_3) were estimated by a gas-volumetric Scheibler method, the content of active carbonates (HCO_3^-) was assayed according to the Drouineau-Gallet method by dissolving carbonates in 0.2 N $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and titrating the filtrate with a 0.1 N KMnO_4 solution. Organic carbon (C) was determined based on wet dichromate oxidation by the Tiurin method, the content of nitrogen (N) was assayed according to Kjeldahl (PN-EN ISO 11261), whereas contents of available forms of phosphorus (P_2O_5) and potassium (K_2O) were determined according to Egner-Riehm. Contents of calcium, magnesium, sodium and potassium were determined using the ASS method in extracts of HF and HCl 1:4 and H_2O (Ca_{HF} , Na_{HF} , Mg_{HF} , K_{HF} , Ca_{HCl} , Na_{HCl} , Mg_{HCl} , K_{HCl} , $\text{Ca}_{\text{H}_2\text{O}}$, $\text{Na}_{\text{H}_2\text{O}}$, $\text{Mg}_{\text{H}_2\text{O}}$, $\text{K}_{\text{H}_2\text{O}}$), while the content of exchangeable cations was identified in 1 M dm^{-3} ammonium acetate at pH 8.2. Due to the high pH and lack of acidity, the CEC was calculated as the sum of cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) determined in an extract of ammonium acetate.

Statistical analyses

Statistical analyses were performed using Statistica software (version 13) (StatSoft, Inc., USA). Each of the variables was tested for normality using the Kolmogorov-Smirnov test. Relationships between fly ash properties were analysed using the Pearson correlation coefficient. Additionally, the Kruskal-Wallis test was used to determine significant differences between properties of the sampling areas. This nonparametric test was applied because the analysed properties did not show a normal distribution within the established sampling areas. Cluster analysis (CA) was conducted applying Ward's method, and the Euclidean distance was used as a distance measure after data standardisation. The CA analysis was carried out separately for all physical properties and for all chemical properties. The principal component analysis (PCA) was conducted in order to verify the relations between sampling area location, physical and chemical properties of coal ash. The correlation between principal components and analysed data was classified according to the values >0.75 , $0.75-0.50$, and $0.50-0.30$, proposed by LIU et al. (2003) as strong, moderate and weak, respectively.

RESULTS

The texture of the tested rock in individual sampling sites varied and according to the USDA classification it was Sand for site 1, Sandy Loam for sampling sites 2, 3 and 4 and Loamy Sand for site 5 (Table 1). The mean content of the sand fraction ranged from 63 % in sampling site 3 up to 90% in site 1, and it was negatively correlated with the distance of the sampling site from the coal ash discharge outlet (Table 2). The mean amount of silt ranged from 10% to 33%. The lowest share was recorded for particles with diameters below 0.002 mm (1-4%). The contents of ash particles with diameters corresponding to the silt and clay fractions were positively significantly correlated with the distance from the discharge outlet.

The particle density (ρ_p) in the ash rock was within the range of 2.23-2.56 Mg m⁻³ (Table 1). These values are lower compared to most soils formed

Table 1

Average values of basic physical properties of ash samples

No. areas	Distance from chute	Percentage of soil fraction at diameter (mm)			Texture class		ρ_p	ρ_b	f_c	f_M	f_D
		2-0.05	0.05-0.002	< 0.002	PTG* 2008	USDA	(Mg m ⁻³)		(m ⁻³ m ⁻³)		
1	130	89	10	1	ps	S	2.42	1.03	0.574	0.528	0.046
2	146	69	27	4	gp	SL	2.44	1.08	0.558	0.495	0.062
3	152	69	27	4	gp	SL	2.34	0.99	0.576	0.514	0.063
4	300	60	33	7	gp	SL	2.23	1.06	0.525	0.473	0.052
5	170	78	19	3	pg	LS	2.56	1.18	0.538	0.463	0.075

* Soil Science Society of Poland

Table 2

Correlation matrix of the physical properties of ash

Specification	Distance	2-0.05	0.05-0.002	< 0.002	ρ_p	ρ_b	f_c	f_M	f_D
Distance	1.000								
2-0.05	-0.978*	1.000							
0.05-0.002	0.976*	-0.941*	1.000						
< 0.002	0.825*	-0.737*	0.871*	1.000					
ρ_p	-0.574*	0.603*	-0.445*	-0.268	1.000				
ρ_b	-0.127	0.162	-0.016	0.216	0.766*	1.000			
f_c	-0.430*	0.507*	-0.351	-0.255	0.370	-0.195	1.000		
f_M	-0.396	0.481*	-0.331	-0.175	0.168	-0.312	0.939*	1.000	
f_D	0.124	-0.075	0.228	0.294	0.701*	0.770*	0.059	-0.205	1.000

* Statistically significant at level of 0.05

from postglacial deposits. This density was positively correlated with the content of ash particles corresponding to the sand fraction, while it was negatively correlated with the distance from the coal ash discharge outlet and contents of particles with diameters corresponding to the silt fraction (Table 2). In comparison to cultivated mineral soils the determined bulk density (ρ_b) was also much lower. The numerical values ranged from 0.99 Mg m^{-3} to 1.18 Mg m^{-3} . This density showed a statistically significant positive relationship only with ρ_p . The porosity (f_c) of analysed ash was high and ranged from 0.525 to $0.576 \text{ cm}^3 \text{ cm}^{-3}$. Its values decreased with an increase in the distance from the ash discharge outlet. Nevertheless, small pores predominated, hindering free movement of water and air. Microporosity (f_M) ranged from 0.463 to $0.528 \text{ m}^3 \text{ m}^{-3}$. The share of macropores and mesopores, in which water and air may freely penetrate, ranged from 0.046 to $0.075 \text{ cm}^3 \text{ cm}^{-3}$.

In view of the statistically significant differences in physical properties of ash (Table 3), it needs to be stated that sampling site 1 differed from sites

Table 3

Matrix result of the Kruskal-Wallis test of the significant differences of the physical properties of ash

No. area	1	2	3	4	5
1					
2	<i>b</i>				
3					
4	<i>a, b, c, f, g</i>		<i>f</i>		
5	<i>e, g, h</i>		<i>e</i>	<i>a, b, d, h</i>	

Explanation: *a* – $2-0.05$, *b* – $0.05-0.002$, *c* – <0.002 , *d* – ρ_p , *e* – ρ_b , *f* – f_c , *g* – f_M , *h* – f_D

4 and 5. Significant differences were also found between sites 4 and 5. Sampling sites 1 and 2 differed in terms of the content of particles with diameters of $0.05-0.002 \text{ mm}$, while site 3 differed from sites 4 and 5 in terms of f_c and ρ_b values, respectively. The cluster analysis showed the greatest similarity in terms of physical properties between sites 2 and 3, which formed a single cluster, to which physical properties of ash from sites 4 and 5 were next added (Figure 2). Physical properties of site 1 were the least similar to those from the other sites.

In the case of plant reclamation, the value of pH is considered as a fundamental indicator for nutrient bioavailability. In the analysed fly ash, the pH is very strong alkaline. The pH value in H_2O ranged from 9.9 for sampling site 4 to 12.3 for site 3, while the reaction measured using 1 M KCl ranged from 9.7 pH to 12.1 pH, respectively (Table 4). The high ash reaction results mainly from the presence of metals, mainly calcium, sodium and magnesium, as evidenced by the recorded values of correlation coefficients (Table 5) between contents of these components extracted using different

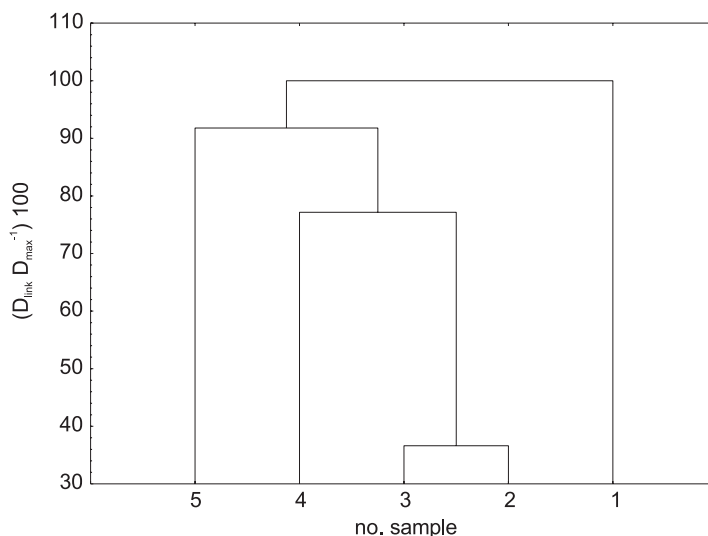


Fig. 2. Dendrogram of the hierarchical cluster analysis of ash's physical properties

solutions and pH values. Among the analysed sampling sites, it was only the reaction of sites 3 and 4 that differed statistically significantly (Table 6).

Contents of active carbonates (HCO_3^-) ranged from 40.5 g kg^{-1} for sampling site 1 to 76.0 g kg^{-1} for site 4 (Table 4), and they were statistically significantly correlated with the distance of a given site from the ash discharge outlet, as well as the contents of calcium, sodium and magnesium (Table 5). The Kruskal-Wallis analysis showed that the amount of HCO_3^- in the ash material from site 1 differed from that in sites 4 and 5 (Table 6). In comparison to HCO_3^- , the amounts of CaCO_3 were slightly greater and ranged from 43.2 g kg^{-1} to 91.7 g kg^{-1} . These contents were also statistically significantly correlated with the distance of the site from the ash discharge outlet, and with the amounts of calcium, sodium and magnesium (Table 5). Compared to HCO_3^- , only sites 1 and 4 contained significantly different amounts of carbonates (Table 6).

Data presented in Table 4 indicate that contents of individual metals varied. Metals were found mainly in sparingly soluble and slightly soluble forms. Calcium was the dominant metal. Its total content amounted to 71.5 – 120.5 g kg^{-1} , and it was positively correlated with the distance of the site from the ash discharge outlet, reaction, contents of organic carbon, total nitrogen and the other cations (Table 5). Statistically significant differences in the amount of sparingly soluble calcium (Ca_{HF}) were observed between sites 1 and 3 as well as sites 3 and 5 (Table 6). Water soluble forms accounted for a small percentage of the total amount of this element. Their content ranged from 0.97 g kg^{-1} to 1.48 g kg^{-1} (Table 4). However, it was excessive in relation to the requirements of plants. Also, the sodium content was high, ranging from 5.09 g kg^{-1} to 7.04 g kg^{-1} in the case of sparingly soluble forms (Table 4).

Table 4

Average values of chemical properties of ash samples

No. areas	HCO ₃ ⁻	CaCO ₃	Ca			Na			Mg			K		
			HF	HCl	H ₂ O	HF	HCl	H ₂ O	HF	HCl	H ₂ O	HF	HCl	H ₂ O
1	40.5	43.2	71.520	56.55	0.970	5.090	1.270	0.120	0.200	0.200	0.040	1.650	0.210	0.040
2	65.3	75.5	107.97	100.25	1.020	4.700	2.340	0.250	0.340	0.330	0.020	1.430	0.420	0.150
3	69.0	76.2	120.52	118.80	1.020	7.040	1.990	0.560	0.390	0.280	0.050	1.090	0.210	0.050
4	76.0	91.7	96.370	69.35	1.450	6.660	2.220	0.580	0.390	0.300	0.040	2.000	0.380	0.240
5	73.1	76.2	79.650	42.58	1.480	5.750	1.130	0.190	0.200	0.200	0.020	1.550	0.130	0.030
No. areas	pH _{H₂O}	pH _{KCl}	N	C	C/N	P			K ₂ O	Ca ⁺²	Mg ⁺²	K ⁺	Na ⁺	CEC
						HF	HCl	P ₂ O ₅						
		pH		(g kg ⁻¹)	-	(g kg ⁻¹)			(cmol ₍₊₎ kg ⁻¹)					
1	10.17	10.05	0.25	24.3	87:1	7.9	5.3	32	155	54.3	1.3	0.2	1.4	57.2
2	10.56	10.43	0.31	24.9	80:1	14.1	3.5	20	140	82.8	0.8	0.6	3.3	87.4
3	12.29	12.19	0.18	18.4	107:1	3.5	3.4	18	205	125.0	0.9	0.2	2.4	128.4
4	9.94	9.68	0.13	10.5	80:1	2.9	2.1	6	175	63.2	1.3	1.1	4.3	69.9
5	10.27	10.1	0.06	4.7	78:1	2.9	1.8	22	185	62.3	0.9	0.2	2.0	65.3

Table 5

Correlation matrix of the chemical properties of ash

Specification	Distance	pH _{H2O}	pH _{JCI}	HCO ₃ ⁻	CaCO ₃	N	C	P _{JHF}	P _{-HCl}	P ₂ O ₅	K ₂ O	Ca _{JHF}	Na _{JHF}	Mg _{JHF}	K _{JHF}	Ca _{JCI}	Na _{JCI}	Mg _{JCI}	K _{JCI}	Ca _{JH2O}	Na _{JH2O}	Mg _{JH2O}	K _{JH2O}		
	1.00																								
pH _{H2O}	0.18	1.00																							
pH _{JCI}	0.11	0.99*	1.00																						
HCO ₃ ⁻	0.70*	0.35	0.36	1.00																					
CaCO ₃	0.79*	0.31	0.29	0.98*	1.00																				
N	-0.15	0.38	0.32	-0.16	-0.06	1.00																			
C	-0.23	0.47*	0.41*	-0.24	-0.15	0.98*	1.00																		
P _{JHF}	-0.17	0.20	0.17	-0.04	0.03	0.92*	0.84*	1.00																	
P _{-HCl}	-0.54*	0.38	0.35	-0.42*	-0.37	0.82*	0.90*	0.64	1.00																
P ₂ O ₅	-0.82*	0.26	0.31	-0.35	-0.42*	0.53*	0.60*	0.53	0.80*	1.00															
K ₂ O	0.24	0.68*	0.71*	0.61*	0.52*	-0.25	-0.15	-0.36	-0.05	0.04	1.00														
Ca _{JHF}	0.62*	0.83*	0.78*	0.64*	0.67*	0.43*	0.42*	0.34	0.13	-0.11	0.49*	1.00													
Na _{JHF}	0.50*	0.63*	0.60*	0.67*	0.66*	-0.17	-0.09	-0.34	-0.06	-0.19	0.92*	0.60*	1.00												
Mg _{JHF}	0.77*	0.63*	0.54*	0.67*	0.77*	0.37	0.34	0.24	0.08	-0.31	0.44*	0.91*	0.68*	1.00											
K _{JHF}	0.10	-0.37	-0.41*	0.29	0.38	0.09	0.03	0.15	0.10	0.02	0.01	-0.15	0.20	0.18	1.00										
Ca _{JCI}	0.42*	0.88*	0.82*	0.40	0.45*	0.63*	0.64*	0.48	0.39	0.08	0.38	0.96*	0.48*	0.84*	-0.22	1.00									
Na _{JCI}	0.70*	0.47*	0.38	0.57*	0.70*	0.58*	0.50*	0.52	0.16	-0.23	0.14	0.85*	0.40*	0.94*	0.25	0.80*	1.00								
Mg _{JCI}	0.69*	0.46*	0.38	0.60*	0.72*	0.58*	0.49*	0.56	0.13	-0.21	0.12	0.85*	0.35	0.91*	0.21	0.80*	0.99*	1.00							
K _{JCI}	0.52*	0.14	0.05	0.41*	0.56*	0.67*	0.55*	0.68	0.25	-0.12	-0.16	0.57*	0.12	0.73*	0.50*	0.56*	0.91*	0.91*	1.00						
Ca _{JH2O}	0.31	0.11	0.07	0.77*	0.73*	-0.36	-0.43*	-0.19	-0.38	-0.15	0.50*	0.07	0.51*	0.22	0.69*	-0.16	0.15	0.16	0.18	1.00					
Na _{JH2O}	0.75*	0.61*	0.54*	0.73*	0.80*	0.08	0.10	-0.08	-0.04	-0.35	0.69*	0.79*	0.90*	0.92*	0.25	0.67*	0.74*	0.70*	0.50*	0.42*	1.00				
Mg _{JH2O}	0.14	0.66*	0.60*	0.14	0.19	0.26	0.40*	-0.06	0.51*	0.16	0.65*	0.48*	0.77*	0.58*	0.17	0.55*	0.37	0.28	0.18	0.04	0.71*	1.00			
K _{JH2O}	0.66*	0.01	-0.07	0.59*	0.74*	0.33	0.22	0.34	0.00	-0.33	0.05	0.46*	0.36	0.74*	0.72*	0.36	0.82*	0.80*	0.90*	0.50*	0.65*	0.25	1.00		

* Statistically significant at level of 0.05

Table 6

Matrix result of the Kruskal-Wallis test of the significant differences of the chemical properties of ash

No. area	1	2	3	4	5
1					
2					
3	<i>f, g, h, l</i>	<i>g, j, l</i>			
4	<i>b, c, h, k</i>	<i>d, g, j</i>	<i>a, i</i>		
5	<i>b, d, e</i>	<i>d, e, j</i>	<i>f, h</i>	<i>h</i>	

Explanation: *a* – pH_{KCl} , *b* – HCO_3^- , *c* – CaCO_3 , *d* – N, *e* – C, *f* – Ca_{HF} , *g* – Na_{HF} , *h* – Mg_{HF} , *i* – K_{HF} , *j* – P_{HF} , *k* – P_2O_5 , *l* – K_2O

In turn, the content of sparingly soluble forms of potassium (K_{HF}), which are important for plant growth, ranged from 1.09 g kg^{-1} to 2.00 g kg^{-1} , whereas the concentrations of water soluble forms ($\text{K}_{\text{H}_2\text{O}}$) were from 0.03 g kg^{-1} to 0.24 g kg^{-1} . The content of magnesium forms, both soluble in HCl, HF and in H_2O , was the lowest among the analysed cations and comparable to the levels observed in mineral soils. The amounts of sodium and magnesium cations, similarly as those of calcium, assayed using HCl, HF and H_2O were mostly positively correlated with the distance of the sampling site from the ash discharge outlet, as well as with the pH value (Table 5). Concerning the spatial distribution of concentrations of sodium extracted with HF, the amounts of this cation in site 1 were statistically significantly different from those in site 3. Similarly, the sodium content in ash from site 2 differed from the levels recorded in sites 3 and 4. In the case of magnesium, significant differences in its content were found between site 1 and sites 3 and 4, and between site 5 versus sites 3 and 4. Potassium was a metal whose content significantly differed only between sites 3 and 4 (Table 6).

Nitrogen and phosphorus are essential macronutrients, whose deficit in soil limits plant growth and development. The nitrogen content in the ash rock ranged from 0.06 g kg^{-1} in site 5 to 0.31 g kg^{-1} in site 2 (Table 4). Its content was significantly correlated with concentrations of carbon and phosphorus as well as metals extracted with HCl (Table 5). Regarding site 5, the recorded content was statistically significantly different from the results achieved at sites 1 and 2. Considerable spatial diversification was observed in terms of the content of organic carbon ($4.7\text{-}24.9 \text{ g kg}^{-1}$), which differed significantly between site 5 and sites 1 and 2 (Tables 4, 5). The results were positively correlated with pH as well as the levels of nitrogen, phosphorus, calcium or magnesium. The wide range of the C/N ratio values at 78-107:1 indicated conditions hindering decomposition of organic substances contained in ash, as residues of unburned coal. The total phosphorus content (P_{HF}) was high when compared to concentrations observed in arable soils. It ranged from 2.0 g kg^{-1} for site 4 up to 14.1 g kg^{-1} for site 2 (Table 4), and it was positively correlated with the content of nitrogen and carbon (Table 5). The ob-

served high content of P_{HF} at site 2 significantly differed from the concentrations recorded at sites 3, 4 and 5 (Table 6). However, the total phosphorus content does not translate to amounts available to plants. The data given in Table 4 suggest that the amount of available phosphorus forms (P_2O_5) was very low, within the range of 6-32 mg kg^{-1} , with significant differences in the P_2O_5 content detected only between sites 1 and 4 (Table 6). The content of P_2O_5 was negatively correlated with the distance of a given site from the ash discharge outlet and with the CaCO_3 content, while being positively correlated with the amounts of carbon and nitrogen. The ash contained much greater amounts of available potassium forms (K_2O), ranging from 155 for site 1 up to 205 mg kg^{-1} for site 3 (Table 4), and they were positively correlated with the pH as well as amounts of HCO_3^- , CaCO_3 , Ca, Na and Mg (Table 5). Significant differences were verified only for the content of K_2O at site 3 versus sites 1 and 2 (Table 6).

Attention needs to be paid to the data concerning the content of exchangeable cations, presented in Table 4. Ca^{+2} ions prevailed among cations, as their content was very high and ranged from 54.3 for site 1 to 125.0 $\text{cmol}_{(+) } \text{kg}^{-1}$ for site 3. Such high values are not uncommon in mineral soils. Sorption capacity in relation to Na^+ ions was also high (1.4-4.3 $\text{cmol}_{(+) } \text{kg}^{-1}$). Mg^{2+} cations reached 7.7-13.11 $\text{cmol}_{(+) } \text{kg}^{-1}$, while potassium ones varied from 1.7 to 10.7 $\text{cmol}_{(+) } \text{kg}^{-1}$. No hydrogen ions were detected. The cation exchange capacity ranged from 57.1 to 128.4 $\text{cmol}_{(+) } \text{kg}^{-1}$. These values are very high.

The cluster analysis shows the greatest similarity in terms of chemical properties between sites 3 and 4 as well as 1 and 2, which form single clusters (Figure 3). The former cluster includes also chemical properties of ash from site 5.

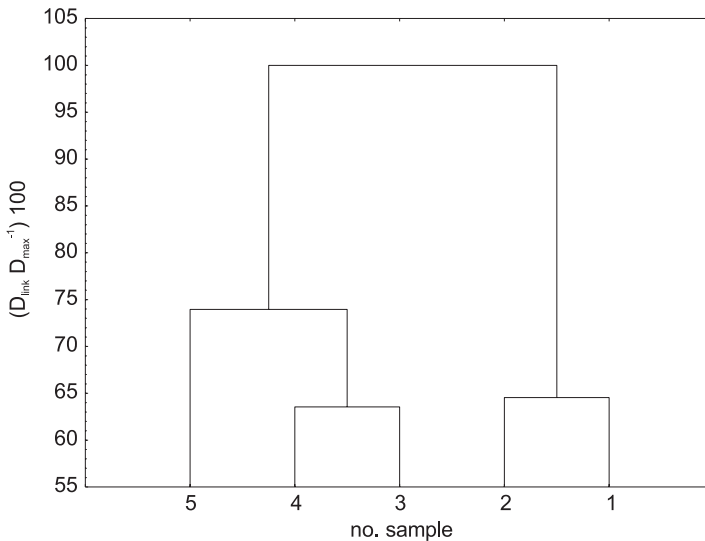


Fig. 3. Dendrogram of the hierarchical cluster analysis of ash's chemical properties

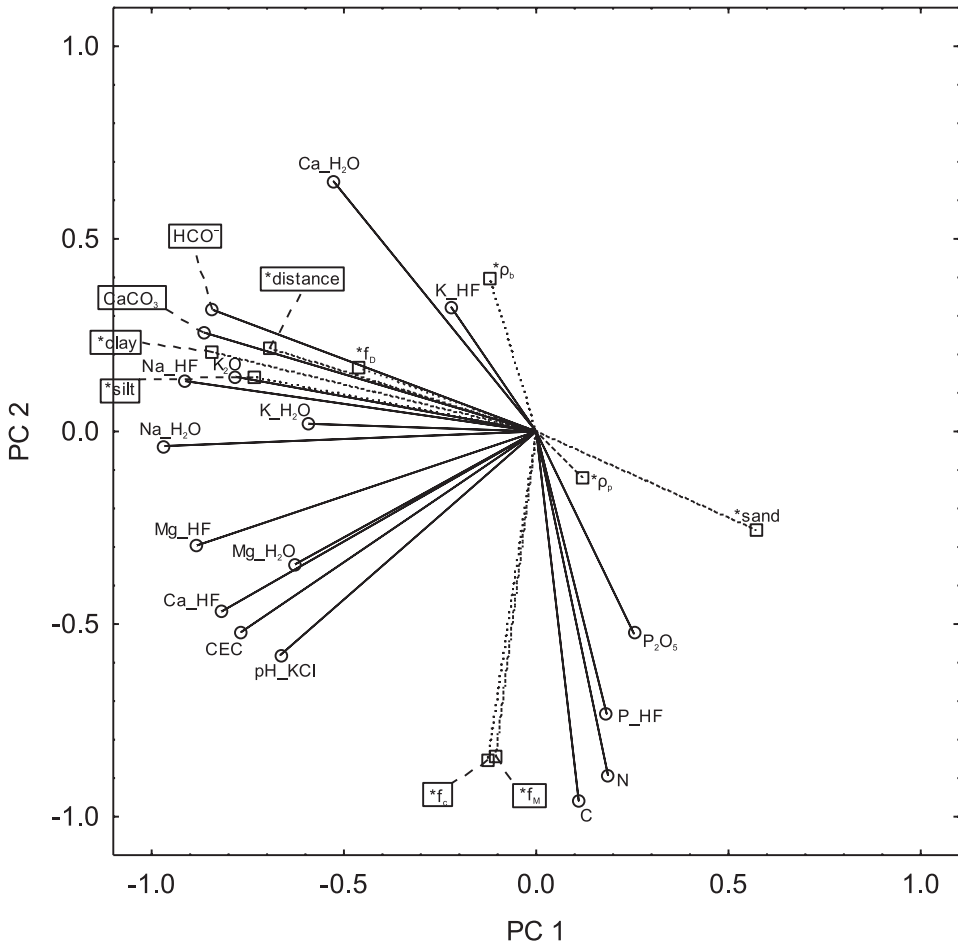


Fig. 4. Results of the principal component analysis (PCA) between chemical and physical properties of fly ash

Relationships between the sampling site location, physical and chemical properties of ash were explained by means of a PCA analysis (Figure 4). Among chemical properties of ash, the first principal component PC1 was strongly negatively correlated with HCO_3^- , CaCO_3 , K_2O , CEC, Ca_{HF} , Na_{HF} , Mg_{HF} and $\text{Mg}_{\text{H}_2\text{O}}$, whereas the correlation with pH_{Cl} , $\text{Ca}_{\text{H}_2\text{O}}$, $\text{Mg}_{\text{H}_2\text{O}}$ and $\text{K}_{\text{H}_2\text{O}}$ was moderate. None of the analysed chemical properties was positively correlated with PC1 at a level greater than 0.3. The second principal component PC2 was strongly negatively correlated with N and C, and the correlation with pH_{KCl} , P_{HF} , P_2O_5 and CEC was moderate. The PC1 was positively correlated only with $\text{Ca}_{\text{H}_2\text{O}}$ (moderately) and with HCO_3^- and K_{HF} (weakly). Also, most physical properties of ash and the distance from the ash discharge outlet were negatively correlated with PC1 – either strongly (clay), moderately

(distance, silt) and weakly (f_D). Only the sand variable was moderately positively correlated with PC1. PC2 was strongly negatively correlated with f_M and f_p , while it was moderately positively correlated only with ρ_b .

DISCUSSION

The texture of analysed waste ranged from Sand to Sandy Loam and it was similar to that relatively often found in ash (ZIKELI et al. 2002, WEBER et al. 2015, KOSTIĆ et al. 2018, UZAROWICZ et al. 2018). In the tested deposits, this property depended on the distance from the ash discharge outlet. Ash deposited closer to the discharge outlet contained larger amounts of particles with diameters corresponding to the sand fraction at lower contents of the silt and clay fractions in comparison to ash deposited at greater distances from the discharge outlet (Figure 4). The small amount of the fraction with a diameter of <0.002 mm needs to be considered as a drawback to using the ash rock. Sedimentation processes of ash particles in storage lagoons, in addition to the particle size distribution, depend on the concentration of solid particles in coal ash slurry (CHANDEL et al. 2009). Research carried by KOSTIĆ et al. (2018) showed that the content of clay and silt fractions increases as ash ages due to weathering processes. Density of the solid phase (ρ_p) of the analysed ash was lower (2.23 - 2.56 Mg m⁻³) than observed in mineral soils formed from postglacial parent materials. Similar ρ_p values in ash were reported by GILEWSKA and OTREMBA (2010), WEBER et al. (2015), UZAROWICZ et al. (2017, 2018), while those presented by MOCEK-PLÓCINIĄK (2018) were even lower. Low ρ_p values are determined by the presence of porous glass grains with hollow pores, cenospheres, as well as residues of unburned lignite (UZAROWICZ, ZAGÓRSKI 2015, UZAROWICZ et al. 2017). The PCA showed that its value is positively correlated with the content of ash particles which in terms of their size correspond to the sand fraction, and negatively correlated with the distance from the ash discharge outlet and the content of particles corresponding to the silt fraction (Figure 4). In comparison to mineral soils, the bulk density was also much lower, and the values determined in this study are consistent with the results obtained by ZIKELI et al. (2002), WEBER et al. (2015) and ŻOŁNIERZ et al. (2016). This density of the analysed ash was negatively correlated with its content of organic carbon (Figure 4). The low ρ_b values resulted in high porosity of the analysed ash (0.52 - 0.576 m³ m⁻³), which in mineral soils is generally lower (KOZŁOWSKI, KOMISAREK 2017). According to KUMAR et al. (2016), this is a characteristic property of deposits formed from ash. Despite high f_c values, drained porosity (f_D) is very low (0.046 - 0.075 m³ m⁻³) and comparable to that observed in mineral soils with a high content of the clay fraction (KOZŁOWSKI, KOMISAREK 2017). The f_D is the pore volume of water that is removed when the water table is lowered in response to gravity and

in the absence of evaporation, or the pore volume of soil air that provides active soil aeration (“oxygation”). According to BEN-NOAH and FRIEDMAN (2018), the lower volumetric air content required to properly conduct oxygen in soil is $0.075 \text{ m}^3 \text{ m}^{-3}$. Research conducted by WEBER et al. (2015) 11 years after revegetation of reclaimed fly ash showed that f_D values are much higher than those obtained in fresh ash in this study. Also MOCEK-PŁÓCINIĄK (2018) recorded higher f_D values in reclaimed ash. Thus, it may be assumed that as a result of reclamation measures and weathering processes the f_D value will increase. The analysed samples from the ash disposal site were characterised by high pH. Such values are not found in mineral soils. Under these conditions ion exchange and thus uptake of nutrients by plants are considerably hindered. STEFANIAK et al. (2015) reported that the reaction of ash generated in the course of hard coal combustion (type F containing up to 10% CaO) within a period of 40 years changed from alkaline to acidic, which was related with the initiation of soil formation processes (ZIKELI et al. 2002, MITROVIĆ et al. 2008, PANDEY 2012).

The content of total, sparingly soluble and water soluble calcium was very high. Even water soluble forms exceeded total calcium in soils and, according to PAKUŁA and KALEMBASA (2012), the total calcium content ranges from 0.839 g kg^{-1} in the A horizons of lessivé soils up to 32.4 g kg^{-1} in the parent material. Similar relationships were found in the case of sodium compounds. Results recorded for both calcium and sodium confirm the high content of these elements in the ash rock. Identical dependencies were indicated by GILEWSKA (2004) and WEBER et al. (2015). In turn, STEFANIAK et al. (2015) pointed to the fact that with time these metals are progressively leached. The content of both magnesium and potassium compounds in the ash rock, irrespective of their form, was not drastically different from the amounts of these macronutrients in mineral soils (PAKUŁA KALEMBASA 2012). The levels of both elements need to be considered high.

The very low content of nitrogen and available phosphorus forms are other drawbacks of lignite ashes from the reclamation point of view. This was also confirmed by GILEWSKA (2004), GILEWSKA and OTREMBIA (2010), WEBER et al. (2015) and MOCEK-PŁÓCINIĄK (2018). In turn, HAYNES (2009), TÉCHER et al. (2012) and ZHAO et al. (2013) stated that the absence of nitrogen is the main factor limiting the potential vegetation growth on the ash rock. The amount of phosphorus available to plants is very low, while the content measured in HCl is high. The total phosphorus content (P_{HF}) in analysed ashes ranged from 2.0 g kg^{-1} up to 14.1 g kg^{-1} , whereas according to SAPEK (2014), the content of phosphorus in soils in Poland ranges from 0.304 g kg^{-1} in Leptosols to 2.40 g kg^{-1} in Histosols. This indicates the presence of mainly water insoluble forms of phosphorus. As it was reported by GILEWSKA (2004), ZIKELI et al. (2002, 2004), WEBER et al. (2015) and KOSTIĆ et al. (2018), this characteristic feature of the ash rock is connected with the presence of coal residue, which was also confirmed in this study. The recorded content of carbon varied, ranging from 4.7 to 24.9 g kg^{-1} .

We need to focus particularly on the content of exchangeable cations and the determined total sorption capacity of the analysed material. The results (57.2-128.4 $\text{cmol}_{(+)}\text{kg}^{-1}$) indicate that the ash rock exhibits high sorption capacity in relation to cations. MOCEK-PŁÓCINIĄK (2018) reported CEC values ranging from 21.34 to 89.97 $\text{cmol}_{(+)}\text{kg}^{-1}$ in a dry ash disposal site of the Adamów power plant. The cited author expressed the opinion that such CEC values were too high considering the texture of ash. She suggested that the numerical values obtained in her study resulted from the applied method, which may have caused partial dissolution of readily soluble salts, i.e. gypsum and hydrogen carbonates. The same regularity was also indicated by ZIKELI et al. (2004). Solubility of hydrogen carbonates is rather obvious; in contrast, gypsum is not a readily soluble compound. Nevertheless, we may not exclude possible presence of sulphates of other metals (K, Mg, Na), which are readily soluble, as well as other calcium compounds, which enter into reactions with ammonium acetate.

CONCLUSIONS

1. Basic properties of material in the wet ash disposal site are dependent on the distance from the ash discharge outlet. Greater particles, less abundant in alkali metals, are deposited closer to the discharge outlet. With an increase in the distance from the ash discharge outlet we observe an increase in the share of smallest particles, a more alkaline reaction and greater amounts of calcium, sodium, potassium and magnesium.

2. The ash rock is a mineral material which is not found in nature. It is characterised by high alkaline reaction, excessive amounts of calcium and sodium, at the absence of phosphorus and nitrogen available to plants. Therefore, during biological reclamation, it is necessary to apply treatments to improve these properties.

3. The very high cation exchange capacity of ash is “apparent capacity” resulting from solubility of calcium compounds. The alkaline reaction, presence of hydrogen carbonates, as well as considerable dispersion of ash particles may cause an increase in the negative charge of the particles and an increase in the absorption capacity.

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