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SELECTED PHYSICOCHEMICAL PROPERTIES OF TESTED WASTES FROM COMBINED HEAT AND POWER PLANTS WITH REGARDS TO THEIR POTENTIAL APPLICATIONS

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Summary. Presented investigations aimed at gaining knowledge about fly ashes and ash-slags from the thermal power plants in Skawina, Wrocław and Kraków in respect of their geotechnical parameters and content of some heavy metals in view of their potential utilization.

Investigated were fly ashes from the thermal power plants (EC) from Skawina and Kraków, and ash-slags from the thermal power plant in Wrocław. Ashes from the „Skawina" power plant were collected from the discharge from the electrofilters from two final discharge funnels, in Kraków – from the 1.5 m deep settlement tank in Nowa Huta, whereas ash-slags in Wrocław were collected from the depth of 0–0.3 m of the 10-year-old landfill located in Siechnica.

The furnace wastes were characterized on the basis of the Regulation of the Minister of the Natural Environment on soil quality standards and earth quality standards of 9 September 2002. The ashes were also assessed in the paper according to the criteria stated by the State Inspectorate for the Environmental Protection and the Institute of Soil Science and Plant Cultivation in Puławy.

In compliance with the Regulation of the Minister of Natural Environment (2002), furnace wastes, due to their concentrations of zinc and nickel, and lead in case of thermal power plant in Skawina, were classified to group B, i.e. arable lands with some restrictions. Values of the other heavy metal concentrations did not exceed the allowable level determined for the waste from group A, i.e. grounds in the protected areas.

On the basis of the criterion established by the State Inspectorate of the Environmental Protection and the Institute of Soil Science and Plant Cultivation in Puławy it was established that the studied wastes corresponded to I degree of pollution due to their content of zinc and nickel, so they may be used under all field crops for full agronomic use, except the crops for manufacturing food with exceptionally low content of elements and harmful substances. The other studied element concentrations did not exceed value permissible for 0 level determined for horticultural and agronomic crops, particularly for crops meant for children's and infants' consumption.

Key words: furnace waste, fly ashes, ash-slags

INTRODUCTION

Electricity generation in Poland is based mainly on coal burning (96%) and the side effect is a large amount of furnace wastes negatively affecting the environment. Their management was counted among the priorities of the state ecological policy [Rosik-Dulewska *et al*. 2009].

Coarser fractions (slag) and fly ashes (ash) form during the process of hard or brown coal burning. Such process is an important source of heavy metal emission to the environment. Burning one ton of the above mentioned raw material produces about 250 kg of ashes and slag, of which 40% is accumulated on landfills or managed for economic purposes. Composition of these wastes comprise pollutants, including heavy metals. Deposited in an unprotected environment they may pose a hazard to soils and waters and in result lead to their pollution. This factor determined utilization of furnace wastes for economic purposes. Unfortunately, it requires testing a given raw material to determine its physicochemical composition, properties and susceptibility to further processing, using various technologies, as well as the influence of external factors. The raw material utilization is determined by radioactivity tests and heavy metal content. These are necessary for protection of human health [Williams 1994, Kabata-Pendias and Pendias 1999, Zawisza 2002].

Ashes are used for manufacturing various types of concrete, including cellular concrete, light aggregates, construction ceramics, cements and pozzolanic binders or asphalt concrete. Ashes may be applied in earth structures to fill post-mining voids, to make ground injections and road bases, improve ground workability, for road stabilization or construction of road and railroad embankments [Galos and Uliasz-Bocheńczyk 2005, Zawisza 2012].

Application of fly ashes in the above mentioned areas allows to decrease costs of production and improve a number of technical features of manufactured materials, but also affects the environment protection through diminishing the amount of wastes deposited in a landfill site [Wileński and Wójcicki 1996].

Presented investigations aimed at analysing fly ashes and ash slag from Combined Heat and Power Plants in Skawina, Wrocław and Kraków to learn their geotechnical properties and content of some heavy metals with regards to their potential applications.

MATERIAL AND METHODS

The investigations were conducted on fly ashes from Combined Heat and Power Plants (EC) in Skawina and ash slag from Combined Heat and Power Plant in Wrocław (Fig. 1). Ashes originating from Skawina Power Plant were collected from the discharge from electro filters from two last chute funnels. Due to their chemical composition, the ashes were determined as silica and according to the norm BN-79/6722-09 classified to pozzolanic materials, like ashes from

Kraków, collected from the sedimentation basin in Nowa Huta, from the depth of 1.5 m, whereas ash slag was sampled from the depth of 0–0.3 m from a 10-year-old landfill site localized in Siechnica.

Fig. 1. Location of Combined Heat and Power Plants (EC) Skawina, Wrocław and Kraków

Taking into consideration environmental hazard, total content of cadmium, chromium, copper, nickel, lead and zinc were assessed in the investigated wastes. It is the more important, as elevated concentrations of the above mentioned metals may not only affect negatively the environment but also limit their use.

Assessments were made following samples digestion in a mixture of nitric (V) and chloric (VII) acids (3 : 2) in a laboratory of the Department of Land Reclamation and Environmental Development at the University of Agriculture in Kraków.

Granulometric composition was determined by means of grain-size sieve analysis. For smaller fractions, from 0.063 and 0.053 mm (ash slag from EC Wrocław) aerometric analysis was conducted and on this basis grain size distribution curves were drawn and the kind of ground was determined (Tab. 1, Fig. 2).

Specific density was determined using measuring flask method in distilled water in two samples for each material with grain size lower than 0.063 and 0.053 mm (for ash from EC Wrocław – for material with full granulation).

Compaction parameters, i.e. maximum dry density and optimal moisture content, as well as the other parameters were determined in two replications in Proctor apparatus in a cylinder of 2.2 dm^3, using compacting energy 0.59 $J \cdot cm^{-3}$.

Table 1. Basic physical properties of ashes

Parameter	Waste		
	Wrocław	Kraków	Skawina
Fraction content, %:			
– gravel 40–2 mm	20.00	-	-
– sand 2–0.05 mm	44.55	20.00	3.25
– silt 0.05–0.002 mm	33.63	73.00	89.95
– clay < 0.002 mm	1.82	7.00	6.80
Name acc. to PN-86/B-02480	Po		
Uniformity coefficient	23.08	10.39	6.00
Optimum moisture content, %	40.10	19.90	23.50
Specific density, $g \cdot cm^{-3}$	2.41	2.24	2.45
Maximum dry density, $g \cdot cm^{-3}$	1.098	1.350	1.445

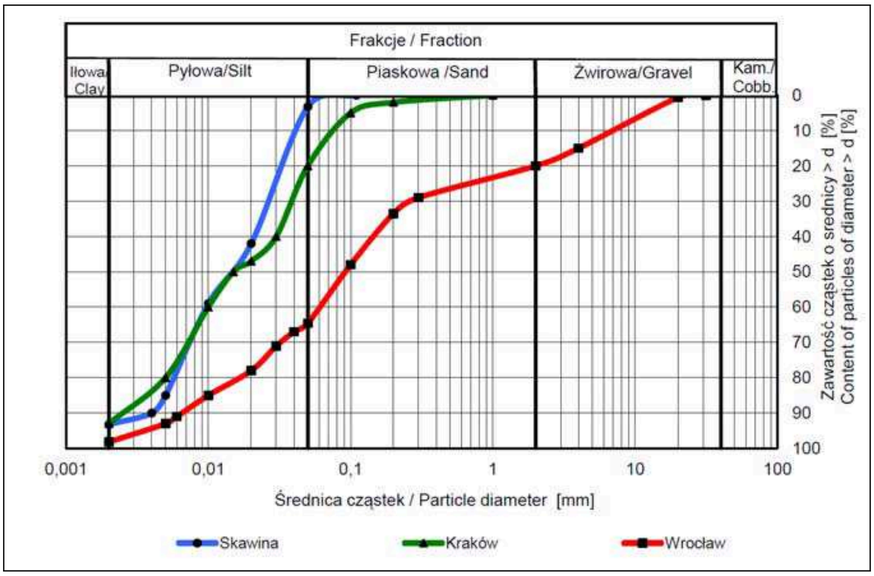

Fig. 2. Grain size distribution curves of the tested wastes

Characterization of furnace wastes was made on the basis of the Regulation of the Minister of Environment of 9 September 2002 on soil quality standards and ground/earth quality standards [Regulation… 2002]. The Regulation states the standards of soil quality with regards to the current and planned function of the ground, identifying three groups. Group A are protected areas. Because of potential consideration of the agronomic use of the analysed wastes, their pollutant concentrations should not exceed values determined for group B (grounds counted among farmlands, excluding the grounds under ponds and dykes, woodlands and bushlands, wastelands but also built up and urbanized areas, excluding industrial areas, mining grounds and communication areas). Group C comprises industrial areas, mining grounds and transportation areas. These areas have the lowest quality standards and may be subjected to recultivation activities using ashes and ash slag [Regulation… 2002].

Ashes were also assessed in the paper according to the criterion determined by the State Inspectorate for Environment Protection and the Institute of Soil Science and Plant Cultivation in Puławy [Tarnawski and Michalec 2006, Madeyski *et al*. 2008]. The guidelines determine the indices of pollution as maximum and permissible values of heavy metals in the topsoil. The criteria identify five degrees of soil pollution.

RESULTS

Physical properties of ashes depend on the kind of burned coal, technology of burning and method of their deposition. Table 1 shows granulometric composition of investigated wastes, as well as compaction parameters and specific density, which were determined in compliance with PN-88/B-04481 norm in the geotechnical laboratory at the Department of Water Engineering and Geotechnics at the University of Agriculture in Kraków.

According to the norm PN-86/B-02480, granulometric composition of ash slag from EC Wrocław corresponds to sand and gravel mix (Tab. 1, Fig. 2). Sand and silt fractions prevail and their joint share constitutes 78% with a considerable proportion of gravel fraction – 20%. Moreover, the value of uniformity coefficient allows to classify them to greatly non-uniformly grained materials, which affects good compaction when built in the embankments. On the other hand, in terms of granulation, fly ashes from Kraków and Skawina were classified to silts. Silt fraction dominated in the composition of ash granulation, constituting 73% in the ash from Kraków and almost 90% in Skawina. These ashes have proper uniformity coefficient, respectively 10.39 in Kraków and 6 in Ska wina, which causes that they may be used in geotechnical works.

Specific density of fly ashes ranged from 2.24 to 2.45 $g \cdot cm^{-3}$, whereas the maximum specific dry density ranged from 1.1 to 1.4 $g \cdot cm^{-3}$. Fly ash from EC Wrocław revealed the highest optimal moisture content – about 40%, whereas the lowest was noted in the ash from Kraków – about 20%.

Due to their chemical composition, fly ashes in Poland were divided into three groups silica, aluminium and calcium. The classification is based on the proportional content of dominant silica, aluminium and iron oxides in the ashes in a smaller amount of calcium, magnesium sodium and other oxides [Łączny *et al*. 1990]. Table 2 shows chemical composition of ashes from EC Skawina and Kraków. It may be seen that silica was the dominant component both in ashes from Kraków (about 61%) and Skawina (over 56%). The next, in terms of its quantity, was aluminium oxide -24% in ashes from Skawina and 19.1% in ash from EC Kraków. Other chemical compounds occurred in considerably smaller amounts: Fe_2O_3 – c.a. 5–7%, CaO and MgO – c.a. 3–2% and K_2O slightly over 2%.The other chemical compounds were present in small amounts, below 1%.

Table 2. Chemical composition of fly ashes from EC Kraków and Skawina

Determined index	Content, %	
	Skawina*	Kraków**
SiO_2	56.30	60.70
Al_2O_3	24.10	19.10
Fe_2O_3	7.10	5.45
CaO	3.17	3.15
MgO	2.31	3.57
Na_2O	0.88	1.25
K_2O	2.52	2.05
SO_3	0.61	0.60
TiO_2	1.02	0.36
P_2O_5	0.34	0.40
BaO	0.13	0.39
SrO	0.03	0.09
Mn_3O_4	0.13	-
H_2O^-	-	0.21
Calcination loss	0.92	2.50
Total	99.56	99.82

*Source: Zakłady Pomiarowo-Badawcze Energetyki „Energopomiar" w Gliwicach
**Source: Operat do wydania Pozwolenia wodno-prawnego na eksploatację składowiska popiołów i żużli, 2005.

Chromium content in ashes (Fig. 3) ranged from 0.77 to 7.31 mg · kg^{-1} and the highest amount was noted in a sample from Wrocław, whereas the lowest in Skawina. The results did not exceed the permissible value (50 mg · kg^{-1}) for group A, i.e. the areas under protection [Regulation… 2002]. Zinc content noted during the period of investigations ranged from 74.90 to 146.84 mg · kg^{-1}. In samples of ashes from Wrocław zinc concentrations did not exceed 100 mg · kg^{-1}, whereas in Skawina and Kraków it did exceed 100 mg mg · kg^{-1}, so the samples were classified to group B. Results showing cadmium content in collected ash samples did not exceed value of 1 mg mg · kg^{-1}, which is the value permissible by the Regulation [Regulation… 2002] for grounds in group A. The highest content of cadmium in ashes was 0.41 mg · kg^{-1}, while the lowest 0.01 mg · kg^{-1} in Wrocław. The highest concentration of copper (51.83 mg · kg^{-1}) was registered in ashes from Wrocław, whereas the lowest (49.21 mg · kg^{-1}) in Skawina. These concentrations fell within the standard which is below 30 mg · kg^{-1} for grounds in group A. The highest concentration of nickel (64.63 mg · kg^{-1}) in ashes was found in Skawina, whereas the lowest (62.30 mg · kg^{-1}) in Kraków. Unfortunately, all obtained results exceeded the permissible value of 35 mg · kg^{-1} for the grounds in group A. The biggest lead content – 53.78 mg · kg^{-1} was noted in Skawina and the smallest (30.49 mg · kg^{-1}) in Wrocław. Only the results obtained in Skawina were higher than 50 mg · kg^{-1}, i.e. the value permissible for grounds in group A [Regulation… 2002].

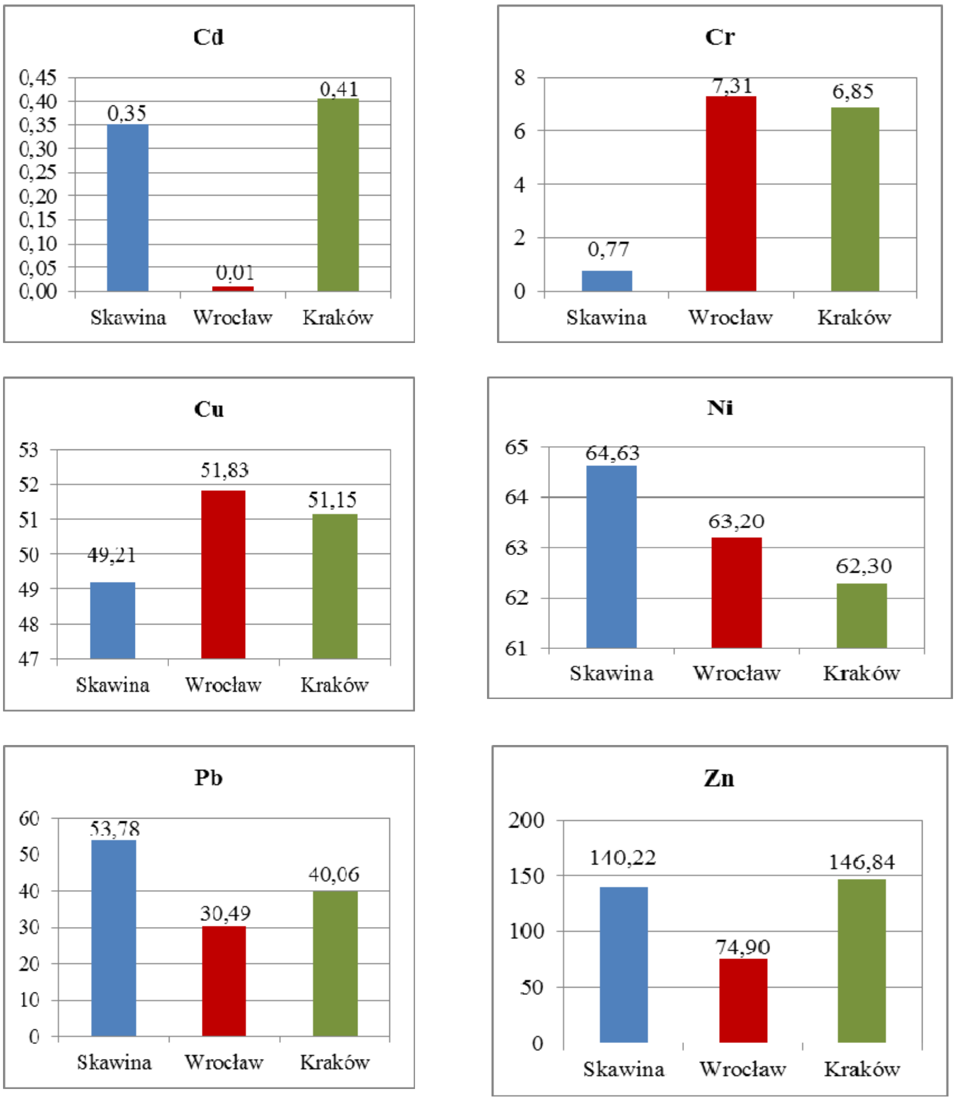

Fig. 3. Total contents of selected heavy metals in mg · kg^{-1} in ashes from Combined Heat and Power Plants Skawina and Kraków and in ash slags from EC Wrocław

On the basis of criterion of soil pollution assessment determined by the State Inspectorate of the Environment Protection and Institute of Soil Science and Plant Cultivation in Puławy [Madeyski *et al*. 2008], maximum chromium concentrations measured in samples from Wrocław was 7.31 mg · kg^{-1} and was much lower than the permissible value 50 mg · kg^{-1}. The investigations of ashes revealed that zinc concentrations registered in the ash samples from Skawina and Kraków, respectively 140.22 and 146.84 mg · kg^{-1}, exceeded the limit value 100 mg · kg^{-1} for 0 level of soil pollution. Therefore the ashes may be used for all field crops for full agronomic use, excluding the crops destined for production of food with especially low content of harmful elements and substances. Cadmium concentration fluctuated from 0.01 to 0.41 mg· kg^{-1}. None of presented results exceeded the limit value of 1 mg · kg^{-1}, which is stated for 0 level of soil pollution. Maximum copper concentration in ashes reached the value of 51.83 mg · kg^{-1} in samples from Wrocław. The limit value for 0 pollution level is 25 mg · kg^{-1}, which means that all results exceeded the permissible value. Therefore, they may be used on soils intended for all horticultural and agronomic crops excluding plantations of crops for manufacturing food with especially low content of harmful elements and substances. Maximum concentration of nickel assessed during the investigations was 64.63 mg · kg^{-1}. This value is slightly higher than 50 mg · kg^{-1}, i.e. the value admissible by the criteria of soil pollution assessment. Ashes from Skawina containing such amount of nickel corresponded to1st degree of soil pollution, like the ashes in Kraków (62.30 mg · kg^{-1}) and Wrocław (63.20 mg · kg^{-1}). The highest value of lead (53.78 mg · kg^{-1}) was assessed in ashes from Skawina. All results obtained during the period of investigations were below the threshold value, admissible for 0 level of soil pollution, so the ashes may be used under all agronomic and horticultural crops, particularly under crops for human consumption [Madeyski *et al*. 2008].

CONCLUSION

Proportional content of the finest particles, i.e. silt and clay fractions determines filter and dust properties of fly ashes. They affect the ashes use for recultivation and environmental management of devastated areas.

Total content of heavy metals in the studied ashes fluctuated from 0.01 to 0.41 mg · kg^{-1} d.m. cadmium, 0.77–7.31 mg · kg^{-1} d.m. chromium, from 49.21 to 51.83 mg · kg^{-1} d.m. copper, 62.30–64.63 mg · kg^{-1} d.m. nickel, 30.49–53.78 mg · kg^{-1} d.m., lead and from 74.90 to 146.84 mg·kg^{-1} d.m. zinc (Tab. 1, Fig. 3). Considering the analyzed ashes, the highest concentration of chromium and copper were assessed in ashes from Wrocław, nickel and lead were the highest in ashes from Skawina, whereas the ashes from Kraków revealed the highest content of cadmium and zinc (Tab. 1, Fig. 3). Mean contents of heavy metals in the soils of Poland are as follows: 0.22 mg Cd, 24.0 mg Cr, 13.7 mg Cu, 6.3 mg Ni and 32.5 mg Zn · kg^{-1} d.m. [Kabata-Pendias and Pendias 1999, Terelak *et al*. 2001].

In compliance with the Regulation of the Minister of Environment [2002], due to their contents of zinc and nickel, furnace wastes from EC Skawina were classified to group B, i.e. grounds used as agricultural lands with some limitations. Values of the other heavy metal concentrations did not exceed the permissible levels determined for the wastes in group A, i.e. the grounds in the protected areas.

On the basis of the criterion of the State Inspectorate of the Environmental Protection and Institute of Soil Science and Plant Cultivation in Puławy [Rosik-Dulewska *et al*. 2009] it was stated that the analyzed wastes corresponded to I level of pollution due to their contents of zinc and nickel and may be destined for all field crops, excluding the crops for manufacturing food with exceptionally low content of harmful elements and substances. The other analyzed elements did not exceed their values permissible for 0 level determined for horticultural and agronomic crops, in the first place for crops destined for consumption by children and infants.

Moreover, it was found that the finest fraction (below 10 μm) of fly ashes accumulated the biggest quantities of heavy metals, which is a factor enhancing their leaching into the soil profile.

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WYBRANE WŁAŚCIWOŚCI FIZYKOCHEMICZNE BADANYCH ODPADÓW Z ELEKTROCIEPŁOWNI W ASPEKCIE MOŻLIWOŚCI ICH WYKORZYSTANIA

Streszczenie. Celem prezentowanych badań było scharakteryzowanie popiołów lotnych i popioło-żużli z Elektrociepłowni ze Skawiny, Wrocławia i Krakowa ze względu na właściwości geotechniczne oraz zawartość niektórych metali ciężkich w aspekcie możliwości ich wykorzystania.

Ocenę odpadów paleniskowych dokonano na podstawie Rozporządzenia Ministra Środowiska z dnia 9 września 2001 roku w sprawie standardów jakości gleby oraz standardów jakości ziemi. W pracy dokonano również oceny popiołów według kryterium określonego przez Państwową Inspekcję Ochrony Środowiska i Instytutu Uprawy, Nawożenia i Gleboznawstwa w Puławach.

Zgodnie z Rozporządzeniem Ministra Środowiska odpady paleniskowe ze względu na zawartości cynku i niklu oraz ołowiu w przypadku EC Skawina zostały zaliczone do grupy B, czyli gruntów wykorzystywanych jako użytki rolne z pewnymi ograniczeniami. Wartości pozostałych metali ciężkich nie przekraczały dopuszczalnego poziomu określonego dla osadów z grupy A, czyli gruntów na obszarach chronionych.

Na podstawie kryterium Państwowej Inspekcji Ochrony Środowiska i Instytutu Uprawy, Nawożenia i Gleboznawstwa w Puławach stwierdzono, że badane odpady odpowiadały I stopniowi zanieczyszczenia z powodu zawartości cynku, niklu oraz miedzi i mogą być przeznaczone pod wszystkie uprawy polowe do pełnego użytkowania rolniczego, z wyłączeniem upraw roślin do produkcji żywności o szczególnie małej zawartości pierwiastków i substancji szkodliwych. Wartości pozostałych pierwiastków nie przekroczyły dopuszczalnych dla 0 stopnia określonego dla upraw ogrodniczych i rolniczych, przede wszystkim pod uprawy roślin przeznaczonych do spożycia dla dzieci i niemowląt.

Słowa kluczowe: popioły lotne, popioło-żużle, zawartość metali ciężkich