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ASSESSMENT OF CHEMICAL COMPOSITION OF WASTE MATERIALS FROM HARD COAL BURNING IN VIEW OF THEIR AGRICULTURAL AND ENVIRONMENTAL APPLICATIONS

Abstract. Production of electric power in Poland bases on burning brown and hard coal. Currently over 90 % of electricity originates from this source. Generating electric power, like many other human activities, inevitably involves production of wastes. Considering the previous trends of these waste materials utilisation, one should analyse also potential use of biogenic components which they contain as fertilizers. The main objective of conducted investigations was an assessment of potential application of selected waste materials, i.e. fly ashes from production, fly ashes from the landfill site and slag sand from “KRAKÓW S.A.” heat and power plant for agricultural and environmental purposes. The assessment was made on the basis of analyses of the following physical and chemical properties of studied materials: pH, granulometric composition determined by Bouyoucose-Casagrande method in Prószyński’s modification, total alkalinity, total nitrogen content assessed by means of Kjeldahl’s method, organic carbon by Tiurin’s method, total contents of trace elements and the content of available forms of trace elements soluble in $1 \text{ mol} \cdot \text{dm}^{-3}$ HCl solution. On the basis of conducted laboratory analyses it should be stated that the amounts of heavy metals determined in the studied materials did not exceed the content allowable for waste materials designed for soil liming. The analysed materials reveal physical and chemical properties which do not exclude their potential application for soil liming. In this respect, fly ash from production seems the best. However, it contains about twice lower amounts of CaO in comparison with other calcium fertilizers available on the market.

Keywords: fly ashes from production, fly ashes from landfill, slag sand, heavy metals, retardation of natural resources transformation

INTRODUCTION

Over 90% of electric power is generated by burning brown and hard coal [Olkuski 2011]. On a global scale about 40% of electric power comes from coal burning and its share as a source of electricity in the world revealed a 3% growth over the last decade [International Energy Agency 2010, International Energy Agency 2010a]. Growth tendency of this source in energy generation for the next few decades has been confirmed by Energy Policy of Poland [Polityka Energetyczna Polski 2010] and world forecasts which inform about a crucial role of hard coal in electricity production in Poland and worldwide. Electric power production, like any other human activity, is inevitably linked with side effects, i.e. production of waste.

Electricity production generates various waste, including among others: fly ashes, slags, ash-and-slag mixtures, microspheres, ashes from fluidized-bed boilers, gypsum from wet flue

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gas desulphurization, waste from semi-dry and dry flue gas desulphurization, etc. [Galos, Uliasz-Bocheńczyk 2005]. Waste produced during coal burning were deposited on landfill sites for many decades. With growing volume of produced energy and therefore growing amount of generated waste, experts started to consider various potential applications of stored and produced waste, which can afford to slow down the negative processes of transformation the ecosystem and can cause retardation of use environmental resources.

Taking into consideration previous tendencies of utilisation of these materials, which are the secondary effect of coal burning in power stations [Iwanek et al. 2008] one may consider their possible applications under conditions in Poland as a fertilizer product used for soil de-acidification, as has been confirmed by numerous studies [Arivazhagan et al. 2011; Jasiewicz, Antonkiewicz 2009; Jahir et al. 2006; Eliot, Zhang Dong 2005; Wearing et al. 2004; Stout et al. 1997].

Economic and technical considerations cause the search for new materials, the properties of which will correspond with their particular application in various fields of industry. On the other hand, they are looking for beneficial solutions to rationalize waste management. Therefore, new solutions utilize waste or spare materials from various fields of industry, limiting significantly an impoverishment of natural habitats, including those rich in limestones, which, after appropriate preparation, are used as calcium fertilizer. This process can reduce the use of natural substrates for the production of lime fertilizers that is it can cause retardation of natural habitats.

In Poland, 568 thousand tons of calcium fertilizers have been used annually and these are amounts greatly insufficient to cover the needs in this respect [GUS 2010]. Utilisation of alkaline waste materials for soil de-acidification may considerably affect limiting the use of natural resources which are the substrate for calcium fertilizers manufacturing.

In compliance with the Act on fertilizers and fertilization [Dz. U. 2007, nr 147], the analyzed waste materials may be classified to the means which improve soil properties and are added for this purpose or to improve its chemical, physical and physicochemical or biological parameters [Dz. U. 2007, nr 147].

All premises mentioned above point to a necessity to conduct basic analyses of physical and chemical properties of the studied materials from "KRAKÓW S.A." heat and power station in view of their potential application to the soil. The main goal of conducted investigations was an assessment of possible use of selected waste materials, i.e. fly ashes from production, fly ashes from landfill site and slag sand from hard coal burning for agricultural and environmental purposes.

MATERIALS AND METHODS

Analyses of physical and chemical properties were conducted on fly ashes from production, fly ashes from dumping site and on slag sand from "KRAKÓW S.A." heat and power station. Collected materials were taken to the laboratory and air-dried till constant weight. The materials were assessed on the basis of essential analyses of the following properties:

- pH in water suspension,
- granulometric composition by means of Bouyoucose-Casagrande method in Prószyński's modification,
- total alkalinity,
- total nitrogen content using Kjeldahl's method,
- total organic carbon content using Tiurin's method [Ostrowska et al. 1991].

Apart from determining basic properties, total contents of trace elements were assessed in all samples. Analyzed materials were digested in concentrated nitric acid (65% Suprapure), perchloric acid (30% a.p.) and hydrochloric acid (30% Suprapure). The samples were digested using Multiwave 3000 mineralizer made by Anton Parr, following the recommended mineralization programme (tab. 1).

Table 1. Programme of microwave digesting of analyzed samples

Stage No.	Power [W]	Recovery time [min]	Stabilization time [min]	Ventilating hood [gear]
1	1400	5:00	15	1
2	0	-	5	3

After mineralization the samples were removed to measuring flasks using 1% solution of Suprapure nitric acid.

Content of available heavy metal were also assessed in the samples of analysed materials using 1 mol·dm⁻³ HCl solution [Karczewska, Kabała 2008] following previous extraction.

In the solutions prepared in these ways metal content was assessed by means of atomic emission spectrometer Optima 7300 Dual-View made by Perkin Elmer. All samples were analyzed in two replications. If the results of two replications differed by more than 5%, two additional assessments of a given sample were made.

Statistical analysis and presentation of obtained results were conducted using Microsoft Excel 2007 calculation sheet and Statistica 9.0. Programme.

RESULTS AND DISCUSSION

In compliance with the Act on fertilizers and fertilization [Dz. U. 2007, nr 147], fertilizers are described as products destined to supply nutrients to plants, improve soil fertility or increase fertility of fish ponds, and these are mineral fertilizers, natural fertilizers, organic fertilizers and mineral-organic fertilizers. In compliance with the above mentioned act, analyzed furnace ashes and slag sand may be classified to the materials which improve soil properties and they are added to the soil in order to improve its properties or its chemical, physical and physicochemical or biological properties [Dz. U. 2007, nr 147].

A big group of fertilizers listed among calcium and magnesium fertilizers are waste materials. It is recommended that application of this type of materials for acid soil liming should be preceded by analyses, which characterize basic parameters of this material including:

- content of de-acidifying components; it is assumed that content of these components should be as high as possible, whereas its fertilizer value verified in vegetation experiments on plants,
- amount of this material components harmful for people, animals and plants, which in case of their regular application would lead to their excessive accumulation in soil; therefore the quantity of these components should be as low as possible,
- physical form of the waste, which makes possible its direct use, or leading to necessary form [Gorlach, Mazur 2002].

All above mentioned reasons pointed to a necessity to conduct basic physical and chemical analyses of fly ashes and slag sand to assess their potential agricultural and environmental applications, which may reduce the use of natural substrates for

manufacturing calcium fertilizers and matches the main objectives of retardation.

Analyzed materials were characterized by alkaline reaction, as evidenced by the assessed pH values, ranging from pH = 8.5 for slag sand to pH =12.5 for fly ashes from production (tab. 2).

Strongly alkaline character of fly ash originating directly from production was confirmed by assessed calcium oxide content. The above mentioned ash contained over 20% of CaO, whereas the two other materials had much less, i.e. 11.9 and 12.8% fly ash from the landfill site and slag sand, respectively. Observed dependence indicates a considerable influence of atmospheric conditions on CaO amount in fly ash kept on the landfill site.

Table 2. Basic chemical properties of ashes and slag sand from “KRAKÓW S.A.” heat and power station (mean ± standard deviation)

Material	pH	CaO content [%]	N content [g · kg ⁻¹ d.m.]	C content [g · kg ⁻¹ d.m.]
Fly ashes from production	12.5	20.1 ± 2.2	0.50 ± 0.01	84.2 ± 3.6
Fly ashes from landfill	8.6	11.9 ± 0.6	0.53 ± 0.01	40.8 ± 1.1
Slag sand	8.5	12.8 ± 0.3	0.66 ± 0.01	45.1 ± 3.1

Another element assessed in waste materials was total nitrogen content. Analyzed materials revealed approximate quantities of total nitrogen (tab. 2), however the highest content was registered in slag sand and the lowest in fly ash originating directly from production. The content was in the lower limit of the most frequently noted range of total nitrogen content in mineral soils in Poland, i.e. from 0.5 to 3.0 g N · kg⁻¹ [Gorlach, Mazur 2002].

Organic matter content in the topsoil in Poland ranges from 15 to 40 g · kg⁻¹ d.m. [Kabata-Pendias, Pendias 1999]. In conversion to organic carbon in soil organic matter, the range would be from 8.5-22.8 g · kg⁻¹ d.m. In the analysed alkaline materials the content of carbon oxidized by potassium dichromate was 2-3.5- fold bigger than the upper limit of its content in the soils of Poland (tab. 2). However, it should be remembered that these are unburnt remnants of mineral carbon with diametrically different properties than the soil organic substance.

Table 3. Percentage of mechanical soil fractions in the analysed materials

Material	Sand	Coarse silt	Fine silt	Coarse silt clay	Fine silt clay	Colloidal clay	Mechanical group
	% of fractions with diameters [mm]						
	1.0-0.1	0.1-0.05	0.05-0.02	0.02-0.006	0.006-0.002	<0.002	
Fly ash from production	25	17	38	19	0	1	Silt deposit
Fly ash from landfill site	49	22	12	14	2	1	Loamy sand
Slag sand	74	21	1	1	1	2	Loose sand

On the basis of analysis of granulometric composition the investigated samples were classified to mechanical soil groups. Fly ash originating directly from production revealed the finest graining. It contained 20% of particles with diameter less than 0.02 mm and 75% of particles with diameter <0.1 mm (tab. 3). Ash which was for some time deposited on the landfill contained slightly more of coarser particles. On the other hand, slag sand contained 74% of particles classified to sands and only 4% of clay particles. Considering possible applications of these materials for soil de-acidification, bigger fineness of the applied materials is more advantageous because of their better solubility in soil.

Apart from determining fertilizer (biogenic) components in waste materials meant for soil liming, their contents of harmful elements, including heavy metals, must be also assessed [Antonkiewicz 2009]. However, their availability from the analyzed materials to plants is determined mainly by the chemical form in which they occur in the materials and properties of the substratum to which they are applied. For that reason not only total contents of heavy metals were assessed in the analysed materials (tab. 4), but also their content extracted with diluted hydrochloric acid, used for assessment of bioavailable microelements in soil (tab. 5).

Table 4. Total content of heavy metals in analysed waste materials [$\text{mg} \cdot \text{kg}^{-1}$ d.m. – mean \pm standard deviation]

Material	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Fly ash from production	1.63 ± 0.16	78.9 ± 1.8	97.5 ± 1.4	35641 ± 691	747 ± 19	62.5 ± 0.8	62.0 ± 2.8	160.3 ± 5.9
Fly ash from landfill site	1.77 ± 0.14	32.3 ± 1.1	31.3 ± 3.5	15254 ± 408	217 ± 2	33.1 ± 1.5	19.1 ± 2.1	65.6 ± 2.8
Slag sand	0.36 ± 0.26	35.9 ± 1.1	48.2 ± 2.7	21320 ± 531	376 ± 9	29.6 ± 1.3	4.2 ± 1.1	24.9 ± 0.7

Table 5. Contents of heavy metal forms soluble in $1 \text{ mol} \cdot \text{dm}^{-3}$ HCl in analysed materials [$\text{mg} \cdot \text{kg}^{-1}$ d.m. – mean \pm standard deviation]

Material	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Fly ash from production	1.26 ± 0.14	37.5 ± 0.6	60.0 ± 0.8	10833 ± 115	551 ± 4	19.82 ± 0.23	30.1 ± 0.1	65.1 ± 0.8
Fly ash from landfill site	1.05 ± 0.01	12.6 ± 0.2	14.2 ± 0.8	3778 ± 58	186 ± 2	8.88 ± 0.07	10.0 ± 0.5	35.1 ± 1.2
Slag sand	0.13 ± 0.02	4.3 ± 0.1	17.0 ± 1.4	6775 ± 54	272 ± 3	5.35 ± 0.10	4.7 ± 1.1	11.2 ± 0.8

On the basis of the results of analyses of various recyclables meant for liming Gorlach and Mazur [2002] determined the range of heavy metal content in waste materials used for fertilization (tab. 6).

Table 6. Heavy metal contents in secondary waste materials used for soil liming [$\text{mg} \cdot \text{kg}^{-1}$ d.m.]

Material	Cd	Cu	Ni	Pb	Zn
Calcium fertilizers	0.1-15	1-800	<200	5-600	16-4000

Considering results of conducted analyses (tab. 4), it should be said that the content of all analysed metals fall within the lower ranges stated by Gorlach and Mazur [2002] for waste materials used for soil liming.

Results of extraction of analyzed materials using $1 \text{ mol} \cdot \text{dm}^{-3}$ HCl (tab. 5) indicate that quantities of Cd, Cr, Cu, Mn, Ni, Pb and Zn soluble in this acid were about twice lower in comparison with total contents of these metals in all investigated materials. Iron formed the forms relatively the least soluble in the analysed materials. Diluted hydrochloric acid dissolved only about $\frac{1}{4}$ of total content of this material in analysed materials. Therefore, conducted laboratory analyses revealed that the studied materials are characterized by physical and chemical properties which allow to use them for soil liming.

In view of fertilizer applications of the analyzed materials, fly ash from direct production reveals the best physical and chemical properties. However, because of its about

twice lower content of CaO in comparison with other calcium fertilizers (manufactured of natural lime rocks) available on the market, the profitability of its application should be considered. Fly ash stored for some time on a landfill site shows slightly worse properties considering its fertilizer application, mainly due to its low CaO content. On the other hand the lowest fertilizer usability characterizes slag sand. The use of these waste materials for soil liming may lead to a reduced use of natural substrates for manufacturing calcium fertilizers and therefore it matches the main objectives of retardation.

CONCLUSIONS

1. Analyzed materials revealed alkaline reaction, at pH from 8.5 in slag sand to 12.5 for fly ash from production.
2. CaO contents in individual materials were 20.1, 12.8 and 11.9%, in fly ash from production, slag sand and fly ash from landfill site, respectively.
3. Heavy metal contents in the analyzed waste materials fall within lower ranges stated for waste materials used for soil liming. These metals dissolve in about 50% in diluted hydrochloric acid.
4. Fly ash originating directly from production reveals the best physical and chemical properties in view of its application for soil liming.
5. The use of these waste materials for soil liming may lead to a reduction of natural substrates use for manufacturing calcium fertilizers and therefore it matches the main objectives of retardation.

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OCENA SKŁADU CHEMICZNEGO MATERIAŁÓW ODPADOWYCH ZE SPALANIA WĘGLA KAMIENNEGO W ASPEKcie MOŻLIWOŚCI ICH ROLNICZEGO I ŚRODOWISKOWEGO WYKORZYSTANIA

Streszczenie. Produkcja energii elektrycznej w Polsce oparta jest na spalaniu węgla brunatnego i kamiennego. Obecnie ponad 90% energii elektrycznej pochodzi z tego źródła. Z wytwarzaniem energii elektrycznej, tak jak z wieloma innymi aktywnościami człowieka, wiąże się nieodłącznie wytwarzanie odpadów. Biorąc pod uwagę dotychczasowe kierunki wykorzystania tych materiałów odpadowych należy przeanalizować możliwości nawozowego wykorzystania zawartych w nich składników biogennych. Głównym celem prowadzonych badań było ocena możliwości wykorzystania wybranych materiałów odpadowych, tj. popiołu lotnego z produkcji, popiołu lotnego ze składowiska oraz piasku żużlowego z Elektrociepłowni „KRAKÓW” S.A. do celów rolniczych i środowiskowych. Oceny dokonano na podstawie wyników wykonanych analiz, obejmujących następujące właściwości fizyczne i chemiczne badanych materiałów: pH, skład granulometryczny (metodą areometryczną Bouyoucosa-Casagrande’a w modyfikacji Prószyńskiego), ogólną alkaliczność, zawartość azotu ogólnego (metodą Kjeldahla), zawartość węgla organicznego (metodą Tiurina), całkowitą zawartość pierwiastków śladowych oraz zawartość ich form przyswajalnych rozpuszczalnych w roztworze $1 \text{ mol} \cdot \text{dm}^{-3}$ HCl.

Na podstawie przeprowadzonych analiz należy stwierdzić, że badane materiały zawierały metale ciężkie w ilościach nie przekraczających zakresów ich zawartości dopuszczalnych w materiałach odpadowych przeznaczonych do wapnowania gleb. Badane materiały charakteryzują się właściwościami fizycznymi i chemicznymi, które nie wykluczają możliwości ich wykorzystania do wapnowania. Najlepszym pod tym względem wydaje się być popiół lotny z produkcji. Zawiera on jednak około dwukrotnie mniejsze ilości CaO w porównaniu z innymi nawozami wapniowymi dostępnymi na rynku.

Słowa kluczowe: popiół lotny z produkcji, popiół lotny ze składowiska, piasek żużlowy, metale ciężkie, retardacja przekształcania zasobów naturalnych