

INVESTIGATION OF THE DISTRIBUTION OF CHEMICAL COMPONENTS IN SELECTED LANDFILL LAYERS AND FLY ASH FRACTIONS

Aleksandra Sambor^{*}, Arkadiusz Szymanek

Czestochowa University of Technology, Department of Engineering and Environmental Protection, Institute of Advanced Energy Technologies, ul. Dąbrowskiego 73, 42 –200 Częstochowa, Poland

The article concerns fly ashes generated from the combustion of hard coal and deposited on landfills. Investigation results describing fly ash taken from a combustion waste landfill are presented in the article. The investigation results indicate a possibility for combusting the coal reclaimed by separation from the fly ash and utilizing the remaining fly ash fractions.

Keywords: combustion by-products, fly ash, combustible matter, separation, fly ash utilization

1. INTRODUCTION

The production of electric energy in Poland is based on the combustion of fossil fuels in as much as 96%. The share of coal fuels in fuel balances is forecast to remain at the unchanged level, with an increasing coal share trend after 2030. At the same time, an increase in the amount and types of combustion by-products (CBP) will follow, with the CBP including: fly ash, slag, ash – cinder mixtures, microspheres and fluidized-bed boiler ashes. The annual amount of CBP generated from coal combustion amounts to over 100 million tons in the European Union area, approx. 15 million tons in Poland, and more than 700 million tons in the world. Among these CBP, fly ash has the largest share of as much as 68.30%, followed by FGD gypsum with 17.70%, bottom ash – 9.40%, boiler slag – 2.40%, and fluidized-bed ash – a mere of 1.50%. Due to its chemical, fraction and phase compositions, fly ash constitutes an attractive raw material for various branches of industry (Bech and Feuerborn, 2008; Hycnar and Szczygielski, 2008). Unfortunately, fly ashes generated in Polish power plants and thermal-electric power stations are not fully utilized; their major part is disposed of on waste landfills, where they pose an economic and an ecologic problems. The most important factor influencing the water – soil environment is the elution of chemicals from the landfills in the form of salts, or trace elements, and their penetration to surface waters, as well as waste erosion processes that may lead to the leaching of dissolved components. The leaching of those components may be caused by rain water on dry landfills and through the contact with process water on wet landfills. The literature lacks information on the effect of climatic conditions and erosion processes on the stability of the fly ash grain structure which is undoubtedly associated with their influence on the susceptibility of chemical compounds to being leached to surface water and soil (Woźniak and Żygadło, 2002).

In order to depart totally from the current negative tendency to regarding fly ashes as hazardous wastes and depositing them on landfills, attention should be drawn to their very valuable chemical components that might directly form a full-value economic product. Such an approach is favoured by the Regulation

^{*}Corresponding author, e-mail: asambor@fluid.is.pcz.pl

of the European Parliament and of the EU Council called REACH, which entered into force on 1 June, 2007, and covers the registration, evaluation and authorization of chemicals. Therefore, today's generators of CBPs, before introducing them into the European market, will have to meet the conditions set out in the Regulation to assure the safety of their application in various branches of industry. Aside from the conditions of the REACH Regulation, in order to manufacture finished, valuable economic products, CBP generators must adjust their products to comply with specific requirements of standards and other technical specifications related to the utilization of CBPs in specific economic areas. Hence, the extent of the economic use of fly ashes in the EU territory is systematically increasing, with the building and road construction sectors being the areas of their most common utilization (Fig.1) (Feuerborn, 2008).

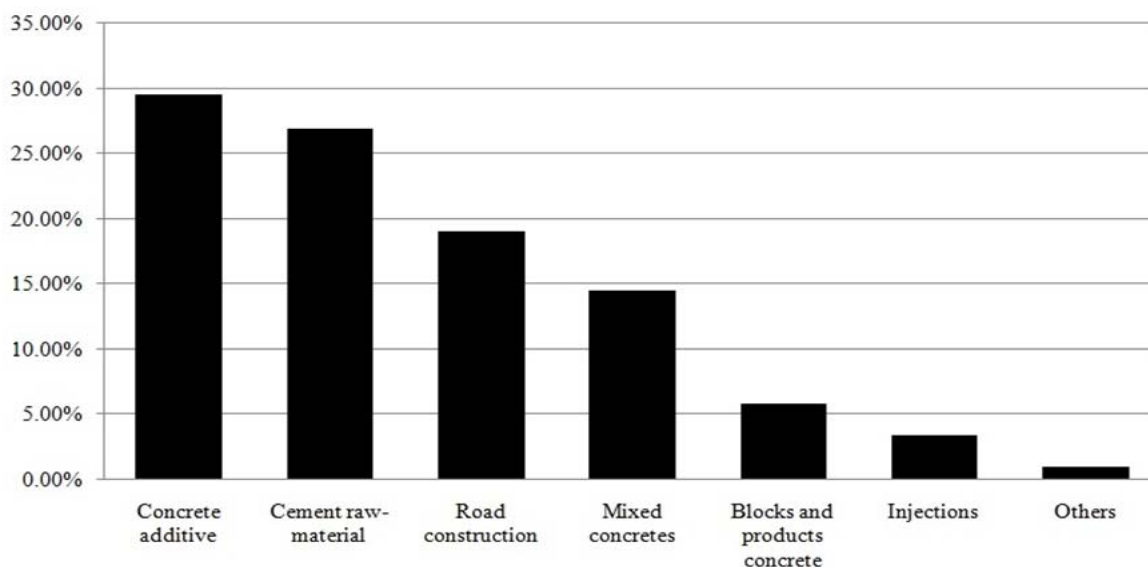


Fig. 1. Utilization of combustion by-products in 2007 (Feuerborn, 2008)

Studies on the properties of coal combustion fly ashes and the experience of their generators indicate that, in addition to the above-mentioned application examples, their valuable chemical components could be used in other sectors of the economy, such as:

- the manufacture of set ash grouts in the technology of hardening (stabilizing) of grounds, banks, dumping grounds, etc.;
- use in agriculture and horticulture;
- stabilization of levees;
- manufacture of ceramic products;
- use in the plastic and paint industry;
- synthesis of zeolites;
- for the synthesis of sialons (the oxy-nitrogen silicon and aluminium compounds occurring in the Si-Al-O-N arrangement) (Galos and Uliasz – Bocheńczyk, 2005; Ściubidło et al., 2008; Szymanek, 2008, Sambor and Szymanek, 2011).

The possibility of such multidirectional utilization of fly ashes is determined by their specific physical and chemical parameters. In terms of its mineralogy, fly ash is regarded as silica – aluminium glass with some crystalline components present. A predominant part of the mineral substance in coal (10-60 wt%) occurs in several groups of minerals:

- silty materials: aluminosilicates (chiefly kaolinite and illite);
- carbonates: calcite, CaCO_3 ; siderite, FeCO_3 ; and dolomite, $\text{CaCO}_3 \cdot \text{MgCO}_3$;
- oxides: quartz, SiO_2 ; as well as hematite, Fe_2O_3 ;

- sulphides: pyrite and markasite (FeS_2);
- sulphates: gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; and anhydrite, CaSO_4 ;
- salt minerals: halite, NaCl (Szymanek, 2008).

However, due to the different coal grades combusted and energy boiler types used, fly ashes have diverse properties that determine their usability in a particular sector. The BN-79/6722-09 standard distinguishes the following fly ash types derived from the combustion of coals:

Table 1. Fly ash types (BN – 79/6722 – 09)

Ash type	Symbol	Contents, wt%			
		SiO_2	Al_2O_3	CaO	SO_3
Silicate	k	> 40	< 30	< 10	< 4
Aluminium	g	> 40	> 30	< 10	< 3
Calcium	w	>30	< 30	> 10	> 3

The parameters determining the suitability of fly ash for commercial purposes according to PN-EN 450 standard: 2007 "Fly ash – Specifications and compliance criteria", are provided in Table 2.

Table 2. Parameters determining the suitability of fly ash for commercial purposes (PN EN 450)

Component	Allowable content	
	Ash generated exclusively by burning coal dust	Ash generated exclusively by co-combustion
Sintering losses Category A Category B Category C	$\leq 5.0\%$ 2.0% - 7.0% 4.0% - 9.0%	
Chlorides	$\leq 0.10\%$	
SO_3	$\leq 3\%$	
Free CaO	$\leq 2.5\%^{1)}$	
Reactive CaO	$\leq 10.0\%$	
Reactive SiO_2	No content determination is necessary; the requirement should be assumed to be met.	$\geq 25,0\%$
Total contents of the oxides: SiO_2 , Al_2O_3 , Fe_2O_3		$\geq 70,0\%$
MgO content		$\leq 4.0\%$
Total contents of alkalis, as converted to $\text{Na}_2\text{O}_{\text{eq}}$		$\leq 5.0\%$
Total contents of soluble phosphorus compounds, as converted to P_2O_5		$\leq 100 \text{ mg/kg}$

1) Fly ash in which the free CaO content is greater than 1.0 wt%, but not exceeds 2.5 wt%, can be acceptable, on condition of retaining the constancy of volume; Le Chatelier test $\leq 10\text{mm}$

The current knowledge, experience gained and favourable regulations enable CBP generators to manufacture new full-value, safe products that find wide application in industry. However, the problem

of fly ashes that have already been disposed of to landfills still remains unresolved. In Poland alone, combustion waste landfills take up an area of approx. 2883.77 ha and, most often, are in the final phase of their use, storing millions of tons of fly ashes (Galos and Uliasz – Bocheńczyk, 2005).

2. PURPOSE OF THE INVESTIGATION

The purpose of the investigation undertaken was to identify the chemical components contained in fly ashes deriving from the combustion of hard coal in stoker-fired and pulverized-fuel boilers and having been stored on a landfill for 50 years. As the parameter determining the utilization of fly ash in the construction industry is the combustible matter contents that may not exceed 5%, the recovery of the valuable carbon and its reburning, with the simultaneous use of the carbon-free fraction in other economic sectors, is promoted. Hence, in order to accurately identify the distribution of chemical components within the whole body of a landfill, it is important to determine the effect of climatic conditions and deposition time on their distribution in selected layers of the body, as well as in specific fly ash fractions. It is also essential to determine the pH and different fly ash moisture content types, and to indicate the fraction of the highest percentage and mass carbon fraction, which could make an energy fuel. A specific fraction containing separated pure ash, being desirable by the road construction or the building industry, will also be singled out.

3. EXPERIMENTAL

Test material was taken from a combustion waste landfill with a container of an area of 67000 m², a total cubage of 283500 m³, and a usable cubage of 216500 m³. Fly ash coming from a power plant was deposited on that combustion waste landfill starting from the early 70s. On the landfill, 50 representative measurement points were set, from which, using a handheld geotechnical survey set, 6 samples were taken from a varying depth of 0m, 0.5m, 1m, 1.5m, 2m, and 2.5m. A total of 297 samples were taken from each depth. 1-2 kg of the test material was taken. The landfill is characterized by an inhomogeneous body, being partially gritty, and partially waterlogged and clayey, which made the sampling considerably difficult. During sampling of the material, the geographical coordinates of all the 50 measurement points were recorded with the aim of future processing of the results using a GIS (Geographical Information System), specifically the ArcView program. This program enables the collection of testing results and their visualization, depending on the spatial position, the landfill layer, or the specific fly ash fraction. Using the GIS, extension of the database will be possible by adding further test results, such as those of the analysis of the remaining chemical compounds contained in the fly ash. There is also a possibility of looking at the effect of climatic conditions on the landfill body structure through the determination of chemical component distribution at particular landfill body depths.

3.1. Moisture content determination

Moisture content determination was made according to the applicable standard, PN-75-Z-04002/13. Each of the 5 g samples taken from all depths was dried for 48 hrs under dry air conditions to determine the evaporative moisture content, and then for 1 hr of in a drier at a temperature of 105°C to determine the hygroscopic moisture content. The mean values for different moisture content types varied with depth. For evaporative moisture content, the lowest value was at a depth of 0 m and amounted to 21.50%, then it increased steadily to reach the highest level of 37.15% at a depth of 2.5 m (Fig. 2).

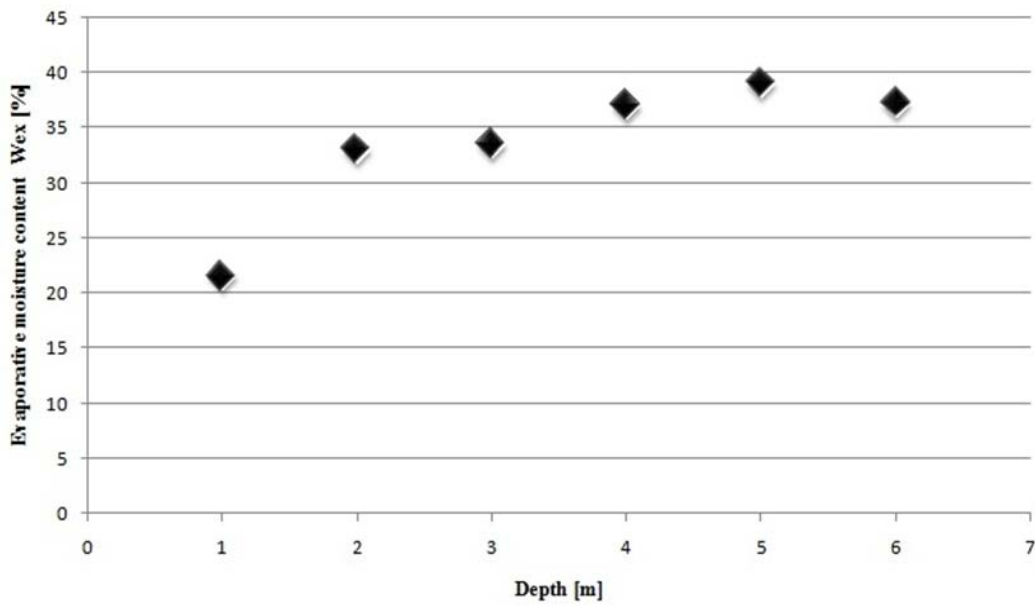


Fig. 2. Dependence of evaporative moisture content on the depth

Similarly for hygroscopic moisture content, the lowest value occurred at a depth of 0 m, after that it increased, then slightly decreased at a depth of 1 and 1.5 m, and finally reached a maximum of 2.74% at a depth of 2.5 m (Fig. 3).

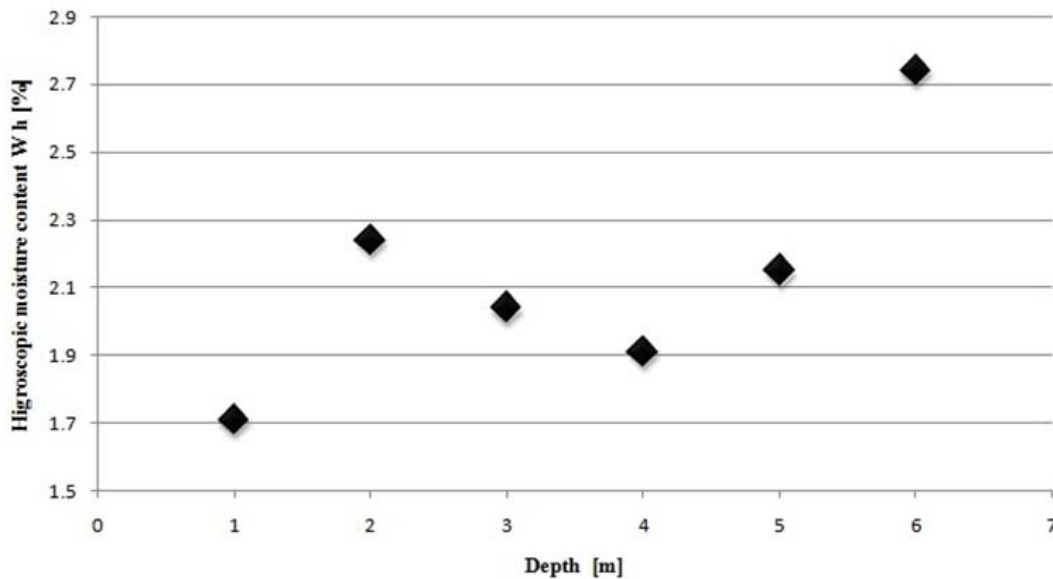


Fig. 3. Dependence of hygroscopic moisture content on the depth

Similarly to the evaporative and hygroscopic moisture content values described above behave the mean values as received state moisture content (W'_t) and analytical state moisture content (W^a).

3.2. pH determination

The determination of pH was made according to the applicable standard, PN-ISO 10390. From a representative 5 g ash sample (from all depths), ash suspension was prepared, which was then shaken

for 5-10 min. in a mechanical shaker, and then left for 2 hrs and 4 hrs. After these times had elapsed, the readings of pH and T were taken. The ash suspensions exhibited a basic reaction in all tests. The mean pH values varied with depth. The lowest pH was shown by all samples taken from the depth 0 m, whereas the highest pH values of 8.57 – 8.59 were achieved for the depths 2 and 2.5 m, which is indicative of the effect of climatic factors on the leaching of chemical compounds and passing of $[\text{OH}^-]$ ions deep into the landfill body (Fig. 4).

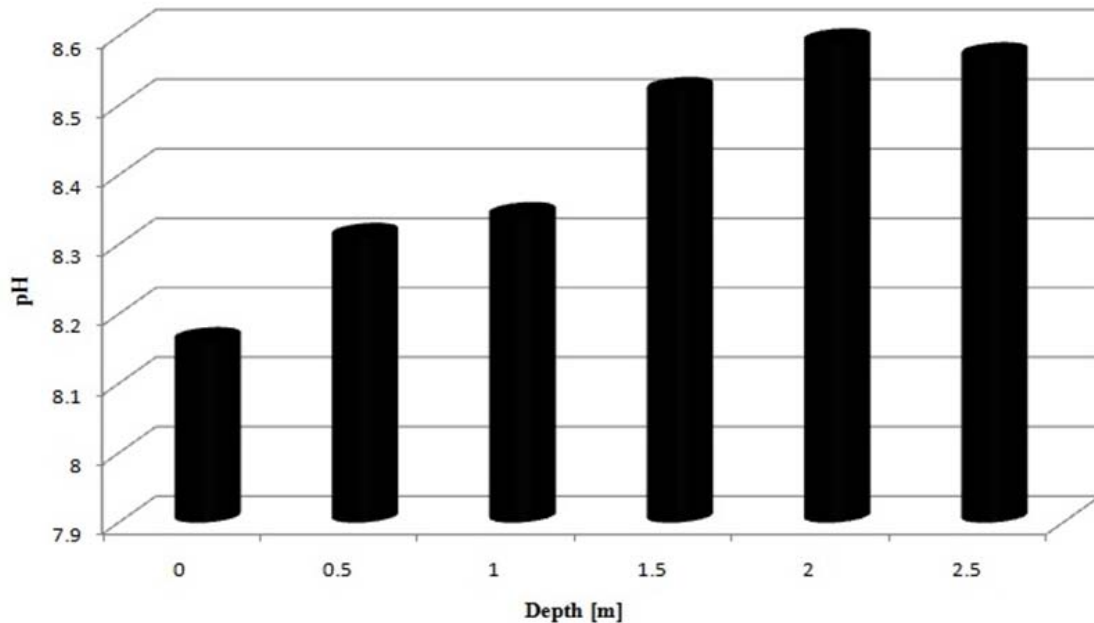


Fig. 4. Dependence of the value of pH on the depth

3.3. Division into fractions

In order to identify the fraction of the highest percentage carbon share, the fly ash taken was separated out into three fractions. A 200 g ash subsample was prepared from each of the 298 ash samples. So prepared subsamples were separated out on a screen into 0-80, 80-125 and 125-200 μm fractions. For the 0-80 μm fraction, the average mass was 92.5 g; for the 80-125 μm fraction, 42.8g; and for the 125-200 μm fraction, 28.2g. The test results discussed above are provided in Table 3.

3.4. Determination of carbon and sulphur

The most important stage of the tests included the determination of the combustible matter in the fly ash samples tested. All samples taken, which had previously been separated into 3 fractions, were subjected to testing. Using a LECO SC-144DR analyzer, which operates based on IR detection, 1900 measurements were taken. The measurements showed that the lowest percentage carbon content from all depths was in the 0-80 μm fraction, ranging from 4.21 to 5.09%. For the 80 - 125 μm fraction, from all depths, it ranged from 6.91 to 9.23%. It was clearly established that the fraction of the highest percentage C content was the 125-200 μm fraction, as its % C content ranged from 10.78 to 12.58% C. An inverse relationship occurred for sulphur, where the highest sulphur content of 0.39 to 0.83% was found for 0-80 μm the fraction; a medium sulphur content of 0.38 – 0.65% for the 80-125 μm fraction; and the lowest sulphur content of 0.33 to 0.42% for the 125-200 μm fraction. The discussed results are summarized in Table 4.

Table 3. Mean fly ash mass share as dependent on the fraction

Depth [m]	Fraction [μm]	Mean mass [g]
0	0-80	81.81
	80-125	38.21
	125-200	30.08
0.5	0-80	90.03
	80-125	47.61
	125-200	29.69
1	0-80	89.07
	80-125	44.79
	125-200	29.65
1.5	0-80	97.25
	80-125	44.07
	125-200	27.47
2	0-80	102.75
	80-125	43.04
	125-200	25.43
2.5	0-80	93.87
	80-125	38.74
	125-200	26.81

Table 4. Mean percentage shares of carbon and sulphur

Depth [m]	Fraction [μm]	$\bar{x}C \pm s_{\bar{x}}C$ [%]	$\bar{x}S \pm s_{\bar{x}}S$ [%]
0	0-80	4.03 \pm 1.58	0.45 \pm 0.68
	80-125	7.61 \pm 4.12	0.38 \pm 0.44
	125-200	10.87 \pm 5.9	0.33 \pm 0.30
0.5	0-80	4.11 \pm 1.50	0.65 \pm 0.91
	80-125	6.95 \pm 3.06	0.49 \pm 0.62
	125-200	12.15 \pm 6.07	0.41 \pm 0.35
1	0-80	4.30 \pm 1.72	0.64 \pm 1.63
	80-125	6.91 \pm 2.56	0.43 \pm 1.08
	125-200	10.78 \pm 4.6	0.35 \pm 0.48
1.5	0-80	4.50 \pm 1.69	0.39 \pm 0.81
	80-125	7.55 \pm 2.52	0.41 \pm 0.62
	125-200	11.67 \pm 4.99	0.37 \pm 0.31
2	0-80	5.01 \pm 2.35	0.58 \pm 0.68
	80-125	9.23 \pm 3.79	0.48 \pm 0.51
	125-200	12.09 \pm 5.67	0.42 \pm 0.34
2.5	0-80	5.09 \pm 2.01	0.83 \pm 1.22
	80-125	9.20 \pm 3.65	0.65 \pm 0.74
	125-200	12.58 \pm 5.49	0.41 \pm 0.31

From the performed tests, the inference about a significant effect of climatic factors on the distribution of chemical elements and compounds within the landfill body can be drawn. At the depth 0m, the mean values of different moisture content types and *pH* showed the lowest levels: 8.16 for *pH*; 21.50% for evaporative moisture content; and 1.71 for hygroscopic moisture content. They varied with depth, reaching, at the greatest depth of 2.5 m, their respective maxima: 8.57 for *pH*; 37.15% for evaporative moisture content; and 2.74 for hygroscopic moisture content.

The variations in these parameters indicate that the chemical elements were leached into the landfill body under the influence of climatic factors. However, the effect of climatic factors was found to be the most significant for the distribution of combustible matter within the landfill body, as the carbon had been leached down to the lowest landfill body layer of 2.5 m deep. At the depth 0m, the percentage carbon content turned out to be the smallest, being 5.09 %, and increasing with depth up to a value of 12.58% C. The test results are represented as arithmetical means, though, depending on the ash sampling point location, they were as large as 27% C at the depth 2.5 m, and as small as 1.5% C at some points at the level 0m. Nevertheless, a fraction of the largest percentage carbon content was invariably the 125-200 μm fraction, with the inverse relationship occurring for sulphur, where the highest sulphur percentage content of 0.39 to 0.83% was found for the 0-80 μm fraction.

4. CONCLUSIONS

In summary, it can be stated that the huge amounts of chemical compounds contained in fly ashes available domestically, which are generated in different coal combustion technologies, create possibilities for using them as alternative fuels for various economic sectors. The test results showed that the mean values of different moisture content types, as well as *pH*, varied with depth, which is undoubtedly associated with the effect of climatic conditions, as the highest values occurred at the lowest depth, and were found to be as follows: the evaporative moisture content value, 37.15%; the hygroscopic moisture content value, 2.74%; and the *pH* value, 8.59. A fraction of the largest mass share of all samples taken and depths is the 0-80 μm fraction with a mean value of 92.46 g, and it constitutes, at the same time, a fraction with the lowest carbon content, which creates the possibility for it to be directly utilized in the building industry. A fraction of the largest percentage carbon share, which can make a valuable energy fuel, is the 125-200 μm fraction, because its mean carbon content ranges from 10.78 to 12.58% C. An inverse relationship occurred for sulphur, where the highest sulphur share from 0.39 to 0.83% was found in the 0-80 μm fraction. The implementation of solutions involving reburning of unburned coal and utilization of pure ashes in economic sectors is not only correct from the technical point of view, but also constitutes an important element in the implementation of the sustainable development strategy by allowing the reclamation of wastes, saving of natural raw-material resources, reduction of energy consumption, limiting of landfill areas, and lowering of CO₂ emissions.

This work was supported by the European Community from the European Social Fund within the RFSD2 project

SYMBOLS

ECOBA	European Coal Combustion Products Association,
CBP	Combustion By-Products,
FGD	Flue Gas Desulphurization,
UE	European Union,
GIS	Geographic Information System,
REACH	Registration, Evaluation, Authorisation of Chemicals,

W_{ex}	evaporative moisture content, %
W_h	hygroscopic moisture content, %
W^*_t	mean as received state moisture content, %
W^{α}	mean analytical state moisture content, %

REFERENCES

- Bech N., Feuerborn H.J., 2008. Utilization of coal ash in Europe. *Int. Conf. Eurocoalash*, Warsaw, Poland, 6-8 October 2008, 9–27.
- BN – 79/6722 – 09. *Ash and slag from hard and brown coal-fired boilers. Classification, terms and designations* (in Polish).
- Hycnar J.J., Szczygielski T., 2008. Outlook for the coal combustion-based power industry. *Int. Conf. Eurocoalash*, Warsaw, Poland, 6-8 October 2008, 87- 101.
- Woźniak M., Żygadło M., 2002. Monitoring of combustion waste landfills. *Regionalny Monitoring Środowiska Przyrodniczego*, 3, 117–122 (in Polish).
- Feuerborn H.J., 2008. Coal combustion products and REACH. *Int. Conf. Eurocoalash*, Warsaw, Poland, 6-8 October 2008, 221–237.
- Galos K., Uliasz – Bocheńczyk A., 2005. Sources and utilization of fly ashes originating from the combustion of coals in Poland. *Mineral Resources Management*, 21, 23–42 (in Polish).
- PN EN 450. *Fly ash intended for concrete – Part 1: Definitions, specifications and compliance criteria* (in Polish).
- Ściubidło A., Nowak W., Majchrzak-Kucęba I., 2008. Utilization of fly ashes from Polish power plants and thermal-electric power stations through the modification of the ashes into mesoporous materials. *Int. Conf. EuroCoalAsh 2008*, Warsaw, Poland, 6-8 October 2008, 181-197.
- Szymanek A., 2008. The recovery of calcium oxide from fly ash. *Chem. Process Eng.*, 29, 895–908.
- Sambor A., Szymanek A., 2011. Fly ash utilization possibilities in the light of legal conditions. *Rozwój badań w ochronie i kształtowaniu środowiska – teoria i praktyka*. Kraków, Poland 28 May 2011 (in Polish).

Received 21 December 2011

Received in revised form 21 March 2012

Accepted 26 March 2012