Original Research

Effects of Biomass Co-Combustion with Coal on Functional Speciation and Mobility of Heavy Metals in Industrial Ash

Jan Kalembkiewicz*, Urszula Chmielarz

Department of Inorganic and Analytical Chemistry, Faculty of Chemistry, Rzeszów University of Technology, Powstancow Warszawy Ave. 6, 35-959 Rzeszów, Poland

Received: 20 July 2012 Accepted: 13 February 2013

Abstract

Comparative studies of industrial fly ash from coal and biomass co-combustion (50%: mixture of sunflower pellets, wood chips, and straw briquettes) and coal ash were conducted. The functional speciation of metals (Pb, Cd, Zn, Cu) and mobility of chemical fractions of ash (soluble in water, exchangeable, soluble in acids pH5, oxide, pseudosulfide, residual) were carried out with a 6-stage sequential extraction and single-stage mineralization methods. It was found that the addition of biomass to coal results in ash containing more Zn, a decrease in the content of Cd, and no major changes in total content of Pb and Cu. A mixture of sunflower pellets, wood chips, and straw briquettes added to coal as biomass results in an increase of the ash fractions: exchangeable (Pb), pseudosulfide (Pb, Cu), oxide and residual (Zn), reduction in ash fractions: soluble in acid pH5 (Pb, Cd, Zn), oxide (Cu), pseudosulfide (Zn), residual (Cd). Biomass co-combusted with coal (50/50 m/m) improves the ash by reduction of the environmental mobility of Pb, Cd and Zn, but does not cause major changes in the mobility of Cu in relation to coal ash.

Keywords: heavy metals, ash from co-combustion, coal ash, functional speciation, mobility

Introduction

The prospect of the exhaustion of natural fossil resources used as fuel (coal, peat, petroleum, natural gas) as well as damage to the natural environment caused by the process of their utilization the resulted in the necessity to seek an alternative to fossil fuels. Renewable energy sources are one of these alternatives. Biomass is the most promising source of renewable energy in Poland. Biomass as fuel co-combusted with coal has a beneficial effect on the process of combustion thanks to its high volatility and reactivity. Overall low sulphur content (0.15 wt.%) in biomass is another advantage of this fuel. On the other hand, lower carbon and higher oxygen contents compared to solid fossil fuels means that it has a low calorific value [1, 2].

*e-mail: kalembic@prz.edu.pl

Fly ash is one of the most important energy generation wastes from the combustion process, because of large-ton-nage production. The major countries producing coal combustion residues are the USA, China, and India, with production estimated to be 129, 125, and 105 million tons per annum [3], respectively. In Poland production of coal fly ashes constitutes about 4.0 million tons per annum [4]. There is no data about ash from co-combustion (even though they appear in increasing numbers).

Chemical composition of ash produced in the process of coal and biomass co-combustion are directly related to individual properties of the burned mixture [5]. For this reason, co-combustion ash differs from coal ash in terms of properties and composition. Consequently, these ashes may exhibit different characteristics in terms of functional speciation and mobility of metals, making it difficult to predict their impact on the environment [6, 7].

Physicoch	emical properties	CFA1	CFA2	CBFA	Chemical co	mposition	CFA1	CFA2	CBFA
Bulk density	[g/cm³]	0.806±0.05	0.804±0.04	0.836±0.05	С		21.540±0.7	8.216±0.4	5.015±0.2
Humidity [%	p]	2.959±0.04	2.977±0.04	1.969±0.08	N		d.1.	d.1.	d.l.
Loss on ignit	tion [%]	10.855±0.4	7.281±0.6	2.604±0.7	S		d.1.	d.1.	d.l.
	H ₂ O (pH 7)	9.74±0.2	11.73±0.2	12.31±0.1	Н		d.1.	d.1.	d.l.
рН	0.01M CaCl ₂	9.45± 0.3	11.82±0.1	12.38±0.2	SiO ₂	[%]	46.1±1.0	45.2±0.9	44.9±0.9
	1M KCl	9.85±0.3	11.92±0.2	12.63±0.2	CaO		2.55±0.02	2.32±0.02	2.88±0.02
Solubility in	water (pH 7) [%]	2.8±0.5	2.5±0.5	1.7±0.5	Fe ₂ O ₃		7.67±0.06	7.93±0.06	6.40±0.05
Grain diameter [mm]			content [%]		K2O		3.48±0.05	3.36±0.04	4.15±0.05
Distribution of grain	0.25 < x < 0.5	0.09±0.02	0.13±0.05	6.45±0.05	Na ₂ O		1.12±0.02	1.04±0.01	1.20±0.02
	0.12 < x < 0.25	0.82±0.2	1.29±0.1	15.31±0.2	MgO		2.85±0.02	2.85±0.02	3.25±0.03
	0.102 < x < 0.12	1.35±0.4	1.12±0.1	7.45±0.1	Ni	[mg·kg ⁻¹]	139.3±4.1	139.3±4.0	139.3±4.0
	0.088 < x < 0.102	1.29±0.5	1.44±0.2	4.42±0.05	Cr		109.5±2.0	105.5±1.9	91.5±1.7
	0.088 > x	96.45±0.9	96.02±0.9	66.37±0.6	Mn		179.0±2.2	189.1±2.2	208.9±2.2

Table 1. Physicochemical properties and chemical composition of coal fly ashes (CFA1, CFA2) and ash from co-combustion of coal with biomass (CBFA).

 $d.l.-detection\ limit \leq 0.05\ mg\cdot kg^{{\scriptscriptstyle -1}},$

The confidence intervals determined from the t-distribution (n = 3, p = 95%).

Industrial ashes are a source of heavy metals. Coal fly ash is characterized by metal contents in the range: Pb 56.8-75 mg·kg¹, Cd 3.4-22 mg·kg¹, Zn 130-148 mg·kg¹, and Cu 47-112 mg·kg¹ [8, 9]. In ash from coal and biomass co-combustion, the heavy metal content also is varied. Grammelis has found in ash from co-combustion of coal and biomass: 75 (Pb) and 10 (Cd) mg·kg¹ (biomass 20%: forest residue; olive kernels) [9]; Zn – 270 and 1,240 mg·kg¹, Cu – 370 and 480 mg·kg¹ (biomass 20%, appropriately olive kernels and forest residue) [9].

Different directions of ash application (reclamation, construction of embankments, building material production, flue gas desulphurization, the production of ceramic membrane and geopolymers [10-18]) causes, knowledge of the distribution of heavy metals in the ash as the mobile fraction is necessary before their use [19], especially for little known ash from coal and biomass co-combustion. The presence of Pb, Cd, Zn, and Cu in ash from co-combustion, biological activity, and biotoxicology of these metals, the ability to accumulate in plants, and especially their mobility were the main reasons for investigation and evaluation of the impact of biomass on the content of heavy metals in ash from co-combustion, functional speciation and the ability to migrate to the solutions from the ash in environmental conditions in relation to coal ash.

Experimental

Fly Ash Samples

The study used a Polish industrial ash (CBFA – fly ash) sample produced in the process of fluidized co-combustion

of coal (50%) and biomass (50%, mixture of sunflower pellets, wood chips, and straw briquettes) from the Stalowa Wola Power Plant, CFA1 – fly ash sample produced in the process of fluidized coal combustion (Rzeszów Heat and Power Plant), CFA2 – fly ash sample produced in the process of fluidized coal combustion (Stalowa Wola Power Plant). The samples of fly ash were collected on electrostatic precipitators. The ashes were conditioned to air-dried state (room temperature, 14 days) and were grounded in a mortar and sifted through a sieve ($\phi = 0.50$ mm). Research was carried out on three parallel samples (n = 3) for each ash. Composition and physicochemical characteristic are presented in Table 1.

Sequential Extraction Procedure

Fractionation of the samples was carried out with a 6-stage sequential extraction, including the method of Tessier [20], and the initial stage of leaching with distilled water. The examination was carried out on 10 ± 0.0001 g for each ash sample. The extract was separated from the solid phase by centrifugation, and the solid residue was subject to the next extraction stage. The examination conditions were presented in Table 2.

Single Stage Mineralization Procedure

Mineralization in HNO₃/HClO₄ Mixture

Experiments were carried out in the conditions of the sixth step of sequential extraction (mineralization of airdried ash 10 ± 0.0001 g in the mixture of conc. HNO₃ and

Table 2. Fractions of Pb, Cd, Zn, and Cu in industrial ash. Type of ash fraction: F0 - soluble in water, F1 - exchangeable, F2 - soluble in acids pH5, F3 - oxide, F4 - pseudosulfide, F5 - residual.

						X, [mg·kg ⁻¹]	g·kg ⁻¹]	ıg·kg ⁻¹]				
Thus of function and one distance of investorization		Pb			Cd			Zn			Cu	
type of fraction and conditions of investigation	CFA1	CFA2	CBFA	CFA1	CFA2	CBFA	CFA1	CFA2	CBFA	CFA1	CFA2	CBFA
F0 soluble in water H_2O , pH7, 25°C	d.1.	d.1.	d.1.	d.1.	d.1.	d.1.	d.1.	d.1.	d.1.	d.1.	d.1.	d.1.
F1 exchangeable 0.5 M MgCl ₂ , pH7, 25°C	1.0±0.2	1.0±0.2	2.0±0.3	d.1.	d.1.	d.1.	d.1.	d.I.	d.I.	d.l.	d.1.	d.l.
F2 soluble in acids pH5 CH ₃ COOH/CH ₃ COONa, 25°C	73.0±2.2	62.0±1.9	56.0±1.6	2.2±0.3	2.0±0.2	d.1.	31.0±1.9	21.0±1.0	20.0±0.9	5.0±0.2	2.8±0.2	5.1±0.2
F3 oxide 0.04 M NH ₂ OH.HCl in 25% CH ₃ COOH, 96°C	12.0±0.9	19.0±1.0	19.0±1.0	d.1.	d.l.	d.1.	25.0±0.5	72.0±2.1	76.0±2.2	6.0±0.7	7.0±0.8	d.l.
F4 pseudosulfide a) 30% H ₂ O ₂ , pH2, 85°C b) 3.2 M CH ₃ COONH ₄ in 20% HNO ₃ , 25°C	3.0±0.4	3.0±0.3	7.0±0.4	d.1.	d.1.	d.1.	17.0±0.5	18.0±0.5	13.0±0.5	1.3±0.2	2.0±0.2	9.0±1.2
F5 residual HNO ₃ / HCIO ₄ (2:1), 90°C	50.0±1.2	56.0±1.6	54.0±1.4	2.6±0.3	2.5±0.3	1.2±0.3	114.0±2.9	109.0±2.5	121.0±2.0	16.0±1.5	18.0±1.3	16.0±1.2
$\sum_{l=0}^{S} [X]$	139.0±4.9 141.0±5.0	141.0±5.0	138.0±4.7	4.8±0.6	4.5±0.5	1.2±0.3	187.0±5.8	187.0±5.8 220.0±6.1 230.0±5.6 28.3±2.6	230.0±5.6	28.3±2.6	29.8±2.5	30.1±2.6

d.l. – detection limit $\leq 0.05~mg\cdot kg^{-1}$ The confidence intervals determined from the t-distribution (n = 3, p = 95%).

 $\mathrm{HClO_4}$ (2:1) acids, the conditions of sequential extraction were presented in Table 2). In obtained eluates the content "close to total" of Pb, Cu, Zn, and Cd was determined [21]. The results are presented in Table 3.

Digestion with Na₂CO₃

To the platinum crucibles the samples of ash 0.5±0.0001 g (CFA1, CFA2, CBFA) were weighed. To the beakers with a capacity of 25 cm³, the 4.0 g of sodium carbonate (Na₂CO₃) and 0.1 g of nitrate (V) sodium (NaNO₃) were weighed. Next, to each crucible containing the ash the mixture of Na₂CO₃+NaNO₃ was added and mixed. The crucibles were heated on a burner (45 min) and then calcined for 30 min in a muffle furnace at 1070°C. Obtained yellowgreen alloy was leached with 50 cm³ of HCl (1:1). Solutions were filtered on a Buchner funnel and the filtrate was collected in volumetric flasks. Obtained eluates were analyzed for total metal content. The results were presented in Table 3.

Determination of Metals

Metals (Pb, Cu, Zn and Cd) were determined in the eluates obtained by sequential extraction, single-stage mineralization, and digestion with Na₂CO₃ of industrial ashes (CFA1, CFA2, CBFA) by atomic absorption spectrometry (FAAS; $\lambda = 217.0$ nm (Pb), $\lambda = 228.8$ nm (Cd), $\lambda = 213.9$ nm (Zn), $\lambda = 324.8$ nm (Cu)). The calibrant solutions containing 0.0, 9.0, 20.0 mg·kg⁻¹ Pb; 0.0, 1.0, 1.5, 2.0 mg·kg⁻¹ Cd; 0.0, 1.0, 3.0, 5.0, 6.0 mg·kg⁻¹ Zn; and 0.0, 2.5, 4.0, 5.0 mg·kg⁻¹ Cu were prepared. The results of metals determination were corrected for the blank reagent and converted to dry weight of the ash. The results are presented in Tables 2 and 3. For obtained analytical results (n = 3) the confidence interval was calculated from the t-distribution (p = 95%).

Instruments and Reagents

Atomic absorption spectrometer PERKIN-ELMER Model 3100, Radwag MAX 50/1, 50 Hz moisture analyzer, WIGO MS 11 HS magnetic stirrer, Elemetron CP-501 pH meter, SML Zalmet Warsaw laboratory drier, high-temperature (up to 1,150°C) muffle furnace FCF 12 SM Czylok – Jastrzębie Zdrój (Poland), AJL electronic MLL 547/WM/4 water bath with shaker were used. Analytically pure reagents, standard solution for AAS determinations (Pb, Cu, Zn and Cd; Fluka, 1000±4 mg/l in nitric acid), and distilled water were used in research.

Results and Discussion

The total and "close to total" contents of Pb, Cd, Zn, and Cu in ash from co-combustion of coal with biomass (CBFA, 50%, mixture of sunflower pellets, wood chips and straw briquettes) and coal ash (CFA1, CFA2) and their functional speciation were investigated.

Table 3. Total contents and "close to total" contents of Pb, Cd, Zn, and Cu in industrial ash.

,	D.I	DI CI 7 C					
	Pb	Cd	Zn	Cu			
		[mg	kg-1]				
Total contents							
CFA1	159.2±2.1	4.97±0.6	204.9±4.8	39.79±1.0			
CFA2	159.3±2.5	4.90±0.5	238.9±7.0	39.82±1.4			
CBFA	159.2±3.2	1.50±0.3	244.8±5.6	39.80±1.4			
"Close to total" contents							
CFA1	127.0±1.4	3.9±0.2	181.0±4.4	26.4±1.5			
CFA2	129.0±2.1	3.9±0.2	215.0±6.2	27.6±1.5			
CBFA	129.0±2.6	1.0±0.1	222.0±2.7	28.7±2.0			

The confidence intervals determined from the t-distribution (n = 3, p = 95%).

Total and "Close to Total" Contents of Metals

Lead

The total content of Pb in the ashes, determined through digestion with Na₂CO₃, was 159.2 (CBFA), 159.2 (CFA1), and 159.3 (CFA2) mg·kg⁻¹. Biomass co-combusted with coal (50%) and does not cause changes in total content of lead in examined ashes in relation to coal ash. However, the analysis of Pb by single-stage mineralization in a mixture HNO₃/HClO₄ [21] showed that the Pb content is lower than the total content of ashes (Table 3). This may be caused by incomplete digestion of the sample during the experiment. The "close to total" content of Pb amounts to 127.0 (CFA1), 129.0 (CFA2), and 129.0 (CBFA) mg·kg⁻¹.

Cadmium

The total content of Cd changes from 4.97 (CFA1) and 4.90 (CFA2) up to 1.50 mg·kg¹ (CBFA). The addition of biomass to coal results in a decrease in the content of Cd. A similar relationship was observed for "close to total" content of Cd, which varies from 3.9 (CFA1, CFA2) to 1.0 mg·kg¹ (CBFA).

Zinc

The total and "close to total" content of Zn in ashes changes from 204.9 and 181.0 mg·kg $^{-1}$ (CFA1), through 238.9 and 215.0 mg·kg $^{-1}$ (CFA2), up to 244.8 and 222.0 mg·kg $^{-1}$ (CBFA). The addition of biomass to coal in the combustion process results in ash containing more Zn.

Copper

The total and "close to total" content of Cu in ashes amount to 39.8 and 26.4 (CFA1), 39.8 and 27.6 (CFA2), and 39.8 and 28.7 (CBFA) mg·kg⁻¹. Biomass (50%, mixture

of sunflower pellets, wood chips, and straw briquettes) cocombusted with coal does not cause major changes in the contents of Cu in relation to coal ash.

Chemical Fractions of Metals

Chemical fractions of Pb, Cd, Zn, and Cu in ash from co-combustion of coal with biomass (CBFA) and coal ashes (CFA1, CFA2) were investigated with a 6-stage sequential extraction method. Fraction: F0 – soluble in water, F1 – exchangeable, F2 – soluble in acids pH5, F3 – oxide, F4 – pseudosulfide, and F5 – residual were investigated. Results are presented in Table 2.

Lead

The presence of Pb was stated in ashes (sum of fractions) in amounts 138.0 (CBFA), 139.0 (CFA1), and 141.0 (CFA2) mg·kg¹. The largest amount of Pb was present in the F2 fraction – soluble in acids pH5 (41-52%) and F5 – residual (36-40%) for all examined ashes. The following orders of Pb in studied fractions were found: CFA1 – soluble in water (d.l.) < exchangeable (1.0 mg·kg¹) < pseudo-sulfide (3.0 mg·kg¹) < oxide (12.0 mg·kg¹) < residual (50.0 mg·kg¹) < soluble in acids pH5 (73.0 mg·kg¹) < residual (50.0 mg·kg¹) < pseudo-sulfide (3.0 mg·kg¹) < oxide (19.0 mg·kg¹) < residual (56.0 mg·kg¹) < soluble in acids pH5 (62.0 mg·kg¹) < residual (56.0 mg·kg¹) < soluble in acids pH5 (62.0 mg·kg¹) < pseudo-sulfide (7.0 mg·kg¹) < oxide (19.0 mg·kg¹) < residual (54.0 mg·kg¹) < soluble in acids pH5 (56.0 mg·kg¹) < residual (54.0 mg·kg¹) < soluble in acids pH5 (56.0 mg·kg¹) < residual (54.0 mg·kg¹) < soluble in acids pH5 (56.0 mg·kg¹).

Cadmium

The presence of Cd was stated in ash (sum of fractions) at 4.8 (CFA1), 4.5 (CFA2), and 1.2 (CBFA) mg·kg⁻¹. The largest amount of Cd was present in the F2 fraction – soluble in acids pH5 and F5 – residual for all examined ashes. In the other fractions the cadmium was not detected. The following orders of Cd in studied fractions were found: CFA1 – soluble in water, exchangeable, oxide, pseudosulfide (d.l.) < soluble in acids pH5 (2.2 mg·kg⁻¹) < residual (2.6 mg·kg⁻¹); CFA2 – soluble in water, exchangeable, oxide, pseudosulfide (d.l.) < soluble in acids pH5 (2.0 mg·kg⁻¹) < residual (2.5 mg·kg⁻¹); CBFA – soluble in water, exchangeable, soluble in acids pH5, oxide, pseudosulfide (d.l.) < residual (1.2 mg·kg⁻¹).

Zinc

The presence of Zn was stated in ash (sum of fractions) in amounts 187.0 (CFA1), 220.0 (CFA2), and 230.0 (CBFA) mg kg¹. The largest amount of Zn was present in the fraction F5 – residual (50-61%) for all examined ashes. The following orders of Zn in studied fractions were found: CFA1 – soluble in water, exchangeable (d.l.) < pseudosulfide (17.0 mg kg¹) < oxide (25.0 mg kg¹) < soluble in acids pH5 (31.0 mg kg¹) < residual (114.0 mg kg¹); CFA2 – soluble in water, exchangeable (d.l.) < pseudosulfide (18.0 mg kg¹) < soluble in acids pH5 (21.0 mg kg¹) < oxide (72.0 mg kg¹) < residual (109.0 mg kg¹); CBFA – soluble in water, exchangeable (d.l.) < pseudosulfide (13.0 mg kg¹) < soluble in acids pH5 (20.0 mg kg¹) < oxide (76.0 mg kg¹) < residual (121.0 mg kg¹).

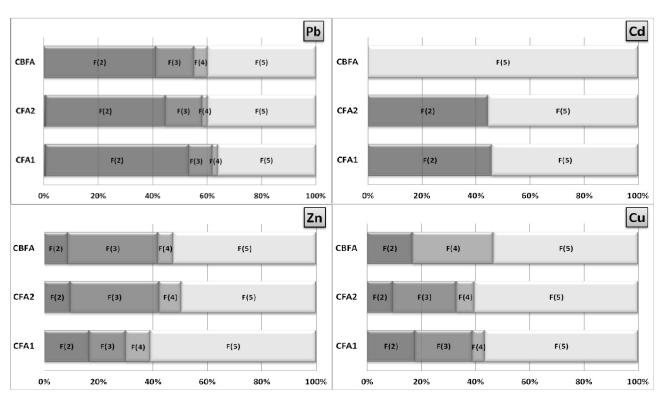


Fig. 1. The percentage contents of Pb, Cd, Zn, and Cu in individual fractions of industrial ashes (CFA1, CFA2, CBFA). Types of the faction: F0 – soluble in water (Pb Cd, Zn, Cu: not detected), F1 – exchangeable (Cd, Zn, Cu: not detected), F2 – soluble in acids pH5, F3 – oxide, F4 – pseudosulfide, and F5 – residual.

Copper

The sums of Cu fractions in ash are 28.3 (CFA1), 29.8 (CFA2), and 30.1 (CBFA) mg kg⁻¹. The largest amount of Cu was present in the fraction F5 – residual. The following orders of Cu in studied fractions were found: CFA1 – soluble in water, exchangeable (d.1.) < pseudosulfide (1.3 mg·kg⁻¹) < soluble in acids pH5 (5.0 mg·kg⁻¹) < oxide (6.0 mg·kg⁻¹) < residual (16.0 mg·kg⁻¹); CFA2 – soluble in water, exchangeable (d.1.) < pseudosulfide (2.0 mg·kg⁻¹) < soluble in acids pH5 (2.8 mg·kg⁻¹) < oxide (7.0 mg·kg⁻¹) < residual (18.0 mg·kg⁻¹); CBFA – soluble in water, exchangeable, oxide (d.1.) < soluble in acids pH5 (5.1 mg·kg⁻¹) < pseudosulfide (9.0 mg·kg⁻¹) < residual (16.0 mg·kg⁻¹).

Mobility of Metals

The mobility of Pb, Cd, Zn, and Cu in ash was characterized as the sum of fractions F0-F2 (soluble in water, exchangeable, soluble in acids pH5) able to migrate in environmental conditions. It was found (Fig. 1) that in environmental conditions the mobile fraction amounts: Pb – 53% (CFA1), 45% (CFA2), 41% (CBFA); Cd – 46% (CFA1), 44% (CFA2), 0% (CBFA); Zn – 17% (CFA1), 10% (CFA2), 9% (CBFA); and Cu – 18% (CFA1), 9% (CFA2), 17% (CBFA) of their total content in the ash.

Conclusions

- The addition of biomass to coal (50/50 m/m) results in composition of ash, a decrease in the content of Cd from 5 to 1.5 mg·kg⁻¹, and an increase of Zn contents from 205-239 to 245 mg·kg⁻¹: no major changes in total content of Pb (about 159 mg·kg⁻¹) and Cu (about 40 mg·kg⁻¹) occurred in relation to coal ash.
- 2. The impact of biomass addition to coal in combustion process on functional speciation of metals (fraction content) in the ash is observable. The result is an increase in metal fractions content: exchangeable (Pb), pseudosulfide (Pb, Cu), oxide and residual (Zn), and the decrease of the fraction: soluble in acid (pH5) (Pb, Cd, Zn), oxide (Cu), pseudosulfide (Zn), residual (Cd). Effect of biomass addition on the content of other metals fractions (soluble in water (Pb, Cd, Zn, Cu), exchangeable (Cd, Zn, Cu), oxide (Pb, Cd), pseudosulfide (Cd), residual (Pb)) in the ashes is low.
- 3. Mobile fractions of metals available for leaching from coal ash and ash from co-combustion with biomass in environmental conditions (soluble in water, exchangeable, soluble in acids pH5) amounts respectively: 42 and 53% (Pb), 0 and 46% (Cd), 9 and 17% (Zn), 17 and 18% (Cu) of their total content in the ash.
- 4. Biomass co-combusted with coal (50/50 m/m) improves ash by the reduction of the environmental mobility of Pb, Cd, and Zn, but does not cause major changes in the mobility of Cu in relation to coal ash.

Acknowledgements

This work is cofinanced with resources of the European Union within the framework of the European Social Fund, and the Podkarpacki Project Scholarship fund for doctoral students realized by Podkarpackie Province – Marshall office of the Podkarpacki Province in Rzeszow in frames of Operating Programme the Human Capital in 2007-13.

References

- KOUKOUZAS N., WARD C.R., PAPANIKOLAOU D., LI Z., KETIKIDIS C. Quantitative evaluation of minerals in fly ashes of biomass, coal and biomass-coal mixture derived from circulating fluidised bed combustion technology. J. Hazard. Mater. 169, 100, 2009.
- WIGLEY F., WILLIAMSON J., MALMGREN A., RILEY G. Ash deposition at higher levels of coal replacement by biomass. Fuel Process. Technol. 88, 1148, 2007.
- HAYNES R.J. Reclamation and revegetation of fly ash disposal sites Challenges and research Leeds. J. Environ. Manage. 90, 43, 2009.
- Statistical Yearbook (Poland), Environmental protection, Central Statistical Office of Poland, Warsaw 2009 [In Polish].
- GRAMMELIS P., SKODRAS G., KAKARAS E. Effects of biomass co-firing with coal on ash properties. Part I: Characterisation and PSD. Fuel 85, 2310, 2006.
- SHAHEEN S.M., TSADILAS C.D. Influence of Fly Ash and Sewage Sludge Application on Cadmium and Lead Sorption by an Acidic Alfisol. Pedosphere 20, (4), 436, 2010
- LIAO S.W., LIN C.I., WANG L.H. Kinetic study on lead(II) ion removal by adsorption onto peanut hull ash. J. Taiwan Inst. Chem. E. 42, 166, 2011.
- MEAWAD A.S., BOJINOVA D.Y., PELOVSKI Y.G. An overview of metals recovery from thermal power plant solid wastes. Waste Manage. 30, 2548, 2010.
- GRAMMELIS P., SKODRAS G., KAKARAS E., KARANGELOS D.J., PETROPOULOS N.P., ANAGNOS-TAKIS M.J., HINIS E.P., SIMOPOULOS S.E. Effects of biomass co-firing with coal on ash properties. Part II: Leaching, toxicity and radiological behavior. Fuel 85, 2316, 2006.
- RAM L.C., MASTO R.E. An appraisal of the potential use of fly ash for reclaiming coal mine spoil. J. Environ. Manage. 91, 603, 2010.
- PANDEY V.C., SINGH N. Impact of fly ash incorporation in soil systems. Agr. Ecosystems Environ. 136, 16, 2010.
- 12. JOHNSON A., CATALAN L.J.J., KINRADE S.D. Characterization and evaluation of fly-ash from co-combustion of lignite and wood pellets for use as cement admixture. Fuel **89**, 3042, **2010**.
- AHMARUZZAMAN M. A review on the utilization of fly ash. Prog. Energ Combust. 36, 327, 2010.
- PANDEY V.C., ABHILASH P.C, SINGH N. The Indian perspective of utilizing fly ash in phytoremediation, phytomanagement and biomass production. J. Environ. Manage. 90, 2943, 2009.
- REIJNDERS L. Cleaner phosphogypsum, coal combustion ashes and waste incineration ashes for application in building materials: A review. Build. Environ. 42, 1036, 2007.

- REIJNDERS L. Disposal, uses and treatments of combustion ashes: a review. Resour. Conserv. Recy. 43, 313, 2005.
- ONISEI S., PONTIKES Y., VAN GERVEN T., ANGELOPOULOS G.N., VELEA T., PREDICA V., MOLDOVAN P. Synthesis of inorganic polymers using fly ash and primary lead slag. J. Hazard. Mater. 205, 101, 2012.
- DONG Y., HAMPSHIRE S., ZHOU J., LIN B., JI Z., ZHANG X., MENG G. Recycling of fly ash for preparing porous mullite membrane supports with titania addition. J. Hazard. Mater. 180, 173, 2010.
- SYC M., POHORELY M., KAMENIKOVA P., HABART J., SVOBODA K., PUNCOCHAR M., Willow trees from heavy metals phytoextraction as energy crops, Biomass Bioenerg. 37, 106, 2012.
- TESSIER A., CAMPBELL P.G.C., BISSON M. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. Anal. Chem. 51, 844, 1979.
- OSTROWSKA A., GAWLIŃSKI S., SZCZUBIAŁKA Z. Methods of Analysis and evaluation of soil and plant properties. Catalogue of the Institute of Environment Protection, Warsaw, pp.109, 1991 [In Polish].