

PACS 89.60.-k; 82.80.-d

FUNCTIONAL SPECIATION OF Pb AND Cd IN INDUSTRIAL ASH FROM CO-COMBUSTION OF COAL AND BIOMASS

J. Kalembkiewicz, U. Chmielarz

*Rzeszów University of Technology,
Powstańców Warszawy Ave. 6, 35-959 Rzeszów, Poland
e-mail: kalembic@prz.edu.pl*

A functional speciation and mobility of Pb and Cd in fly ash from co-combustion of coal and biomass (50 % coal : 50% mixture of sunflower pellets, wood chips and straw briquette) were determined by sequential extraction and FAAS methods. Fractions of metals: soluble in water and exchangeable, soluble in acid (pH 5), oxide, pseudosulfide and residue were characterized. Total contents of metals in ash amount 2.2 (Pb) and 0.3 (Cd) mg·kg⁻¹. The mobile fractions of metals possible to leaching in environmental conditions amount 27 % (Pb) and 6.7 % (Cd) of them total content in ash.

Key words: industrial ash from co-combustion of coal and biomass, lead, cadmium, sequential extraction, functional speciation, mobility.

The perspective of exhaustion the natural resources at fossil fuels character (coals, peat, petroleum, natural gas) as well as damages produce in environment through using them cause, that the alternative to fossil fuels which are the renewable sources of energy is researching. In Poland for the most promising source of renewable energy became the biomass. Biomass can be combustion directly, or for the sake of minimum content of mineral part and the sulphur (properly to 1 % and 0.01 %) it can enrich the coal, which has considerably worse parameters with point of view of the environmental protection [1].

Considerable quantities of solid waste which are fly ashes arise during co-combustion of coal with biomass. It is new group of the industrial waste at unstable composition and properties, difficult to forecast and dependent on the kind and the amount of added biomass. Heavy and toxic metals among others Pb, Cd, Ni, Zn, Hg and Cr contained in ashes during the transport, disposal, using or processing can be released and penetrate to the environment Physicochemical properties and chemical composition of ashes from co-combustion are directly connected with individual properties of combusted component of blend and conditions of combustion. From this reason ashes from co-combustion differ from coal ashes with proprieties and composition. However main differences concern the composition of ash and in consequence his application [2].

The production of waste in Poland reaches 111.1 mln Mg annually, in amongst which the waste from thermal processes (ashes) constitute 0.323 mln Mg [3]. Much quantities of disposal and directly use of ashes constitute the potential source of mobile metals. An evaluation of contents of heavy metals in ashes coming from co-combustion of coal and biomass and their chemical factions capable to migration is subject to a special control.

The ability of metal to the migration from ash to waters and the soil in environmental conditions is determined as mobility, and the quantitative evaluation of migration state the degree of mobility of metal. Five steps Tessier's method is the

sequential extraction procedure which giving the wide range about fractions of metal in environmental samples [4], this method was modified for investigation metals in industrial ashes [5]. Functional speciation and mobility of Pb and Cd in fly ash from co-combustion of coal and biomass (50 % coal : 50 % mixture of sunflower pellets, wood chips and straw briquette) were determined by sequential extraction and FAAS methods. Fractions of metals: soluble in water and exchangeable, soluble in acid (pH 5), oxide, pseudosulfide and residue were characterized. Results of analyses of the chemical fractions of metals were verified with the total content of metals in ash.

The fly ash from co-combustion of coal and biomass (composition: 50 % coal and 50 % mixture of sunflower pellets, wood chips and straw briquette) from the power station "Stalowa Wola S.A." (Poland) was investigated. The samples were collected according to norm BN-81/0623-01. Researches were carried on three parallel samples. The sample of fly ash which was used in experiments was first brought to air-dried condition (in laboratory the ash was air-dried at ambient temperature for two weeks), then ground to a grain diameter of $\phi_{\text{ash}} \leq 0.25$ mm.

Fractionation of samples was conducted by 5 steps Tessier's sequential extraction in conditions optimized for the Cr extraction from ash [4, 5]. Parallel an one-stage mineralization of ash was carried out for determined the "close to total" content of Pb and Cd [6]. Conditions of investigation were shown in Table 1.

Concentrations of Pb and Cd in eluates after extraction and mineralization were determined by FAAS method, $\lambda = 217.0$ nm (Pb) i $\lambda = 228.8$ nm (Cd). Results were corrected for the blank tests and converting into a dry mass of ash. An atomic absorption spectrometer PERKIN ELMER, model 3100 and analytically pure reagents were used in investigation. For obtained analytical results ($n = 3$) the confidence interval was calculated from the t -distribution ($p = 95$ %).

Table 1

Conditions of the sequential extraction

Fraction	Extractant
F1 Soluble in water and exchangeable	(0.5 M) MgCl ₂ , pH 7, $T = 25^{\circ}\text{C}$
F2 Soluble in acid	CH ₃ COOH/ CH ₃ COONa, pH 7, $T = 25^{\circ}\text{C}$
F3 Oxide	(0,04 M) NH ₂ OH·HCl w (25 %) CH ₃ COOH, pH 1.8, $T = 96^{\circ}\text{C}$
F4 Pseudosulfide	a) (30 %) H ₂ O ₂ , pH 2, $T = 85^{\circ}\text{C}$ b) (3.2 M) CH ₃ COONH ₄ w (20 %) HNO ₃ , $T = 25^{\circ}\text{C}$
F5 Residue	HClO ₄ : HNO ₃ (1:2), pH $\ll 1$, $T = 90^{\circ}\text{C}$
Mineralization	HClO ₄ : HNO ₃ (1:2), pH $\ll 1$, $T = 90^{\circ}\text{C}$

Total content and "close to total" content of Pb and Cd. Total contents of Pb and Cd in ash were determined as the sum of metal content in individual stage of chemical fractions. Total contents of Pb and Cd for ash from co-combustion coal and biomass amount 2.2 ± 0.11 mg·kg⁻¹ (Pb) and 0.3 ± 0.02 mg·kg⁻¹ (Cd) (Table 2).

Content "close to total" (metal release to solution without his forms content mainly in silicates) was determined by one step mineralization of ash by extractant NHO₃/HClO₄. Content "close to total" of Pb and Cd for ash from co-combustion coal and biomass amount 1.9 ± 0.10 mg·kg⁻¹ (Pb) and 0.2 ± 0.01 mg·kg⁻¹ (Cd) (Table 2). Quantity of release metal Pb and Cd as contents "close to total" are comparable with their total contents in investigated ash.

Table 2

Contents of Pb and Cd in ash from co-combustion of coal and biomass

FRACTION	ash from co-combustion of coal and biomass	
	Pb, [mg·kg ⁻¹]	Cd, [mg·kg ⁻¹]
F1	d. l.	d. l.
F2	0.6 ± 0.03	0.2 ± 0.01
F3	0.2 ± 0.01	d. l.
F4	d. l.	d. l.
F5	1.4 ± 0.07	0.1 ± 0.01
$\sum_{i=1}^5$	2.2 ± 0.11	0.3 ± 0.02
Mineralization	1.9 ± 0.10	0.2 ± 0.01

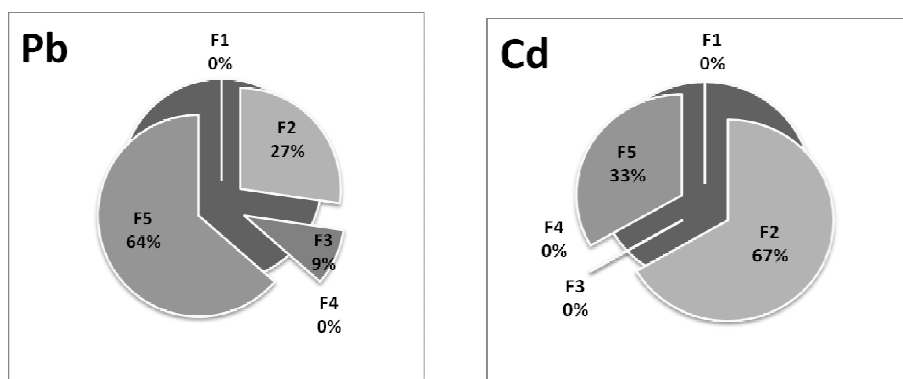
d. l. – detection limit

Obtained results shown on considerably higher content of Pb than the Cd in ash from co-combustion coal with biomass.

Functional speciation of Pb and Cd. Chemical fractions of Pb and Cd in ash by 5 step sequential extraction were determined. The following orders of Pb and Cd in studied fractions were found; (i) Pb: residue (1.4 mg·kg⁻¹) < soluble in acid (0.6 mg·kg⁻¹) < oxide (0.2 mg·kg⁻¹) << soluble in water and exchangeable, pseudosulfide (d.l.); (ii) Cd: soluble in acid (0.2 mg·kg⁻¹) < residue (0.1 mg·kg⁻¹) << soluble in water and exchangeable, oxide, pseudosulfide (d. l.).

Obtained results shown on considerably higher content of Pb in soluble in acid, oxide and residue fractions of ash in relation to content of Cd in appropriate chemical fractions.

Mobility of metals. The mobile fractions (soluble in water and exchangeable, soluble in acid) of Pb and Cd in investigated ash and their ability to migration were determined (see Figure). The mobile fractions of metals possible to leaching in environmental conditions amount 27 % (Pb) and 6.7 % (Cd) of them total content in ash.



The percentage contents of Pb and Cd in individual fractions of industrial ash from co-combustion of coal (50 %) and biomasses (50 %). Types of the fraction: F1 – soluble in water and exchangeable, F2 – soluble in acid (pH 5), F3 – oxide, F4 – pseudosulfide, F5 – residue

So, the next conclusions can be made:

1. Total contents of Pb and Cd for ash from co-combustion coal (50 %) and biomass (50 %) amount $2.2 \pm 0.11 \text{ mg}\cdot\text{kg}^{-1}$ (Pb) and $0.3 \pm 0.02 \text{ mg}\cdot\text{kg}^{-1}$ (Cd) while contents "close to total" of Pb and Cd for ash from co-combustion coal and biomass amount $1.9 \pm 0.10 \text{ mg}\cdot\text{kg}^{-1}$ (Pb) and $0.2 \pm 0.01 \text{ mg}\cdot\text{kg}^{-1}$ (Cd) (Table 2).
2. Chemical fractions of Pb and Cd in ash by 5 step sequential extraction were determined. The following orders of Pb and Cd in studied fractions were found; (i) Pb: residue ($1.4 \text{ mg}\cdot\text{kg}^{-1}$) < soluble in acid ($0.6 \text{ mg}\cdot\text{kg}^{-1}$) < oxide ($0.2 \text{ mg}\cdot\text{kg}^{-1}$) << soluble in water and exchangeable, pseudosulfide (d. l.); (ii) Cd: soluble in acid ($0.2 \text{ mg}\cdot\text{kg}^{-1}$) < residue ($0.1 \text{ mg}\cdot\text{kg}^{-1}$) << soluble in water and exchangeable, oxide, pseudosulfide (d. l.).
3. The mobile fractions of metals possible to leaching in environmental conditions amount 27 % (Pb) and 6.7 % (Cd) of them total content in ash.

-
1. *Lewandowski W.* The ecological and renewable sources of energy // Publication Sciences-Technical. Warsaw, Poland. 2007. P. 322-341.
 2. *Grammelis P., Skodras G., Kakaras E.* Effects of biomass co-firing with coal on ash properties. Part I: Characterisation and PSD // Fuel. 2006. Vol. 85. P. 2310–2315.
 3. Statistical Yearbook (Poland), Environmental protection. Central Statistical Office of Poland, Warsaw, 2010.
 4. *Tessier A., Campbell P.G.C., Bisson M.* Sequential extraction procedure for particulate trace metals // Anal. Chem. 1979. Vol. 51. P. 844–850.
 5. *Sočo E., Kalembkiewicz J.* Investigations of Cr mobility from coal fly ash // Fuel. 2009. Vol. 88. P. 1513–1519.
 6. *Ostrowska A., Gawliński S., Szczubiałka Z.* The methods of analysis and properties evaluation of soils and plants. Warsaw: Catalogue of Institute of Environmental Protection, 1991. P. 109.

ФУНКЦІОНАЛЬНІ ВИДОЗМІНИ РЬ І СД У ПРОМИСЛОВІЙ ЗОЛІ ВІД СУМІСНОГО СПАЛЮВАННЯ ВУГІЛЛЯ ТА БІОМАСИ

Й. Калембкевич, У. Хмеляж

*Жешувський технологічний університет,
вул. Повстанців Варшави, 6, 35-959 Жешув, Польща,
e-mail: kalembic@prz.edu.pl*

Функціональні видозміни і мобільність свинцю та кадмію у золі від сумісного спалювання вугілля і біомаси (50 % вугілля : 50 % суміші соняшнику, трісок та соломи у брикетах) досліджено методами послідовного вилучення та ААС. Схарактеризовано такі фракції, що містили метали: розчинна у воді, розчинна у кислоті (рН 5), оксид, псевдосульфід та залишок. Загальний вміст металів у золі становив 2,2 (Pb) та 0,3 (Cd) мг·кг⁻¹. Рухливі фракції металів, здатні до вилуговування в умовах доквілля, – 27 % (Pb) та 6,7 % (Cd) від їхнього сумарного вмісту в золі.

Ключові слова: промислова зола від сумісного спалювання вугілля та біомаси, свинець, кадмій, послідовне вилучення, функціональні видоутворення, мобільність.

**ФУНКЦИОНАЛЬНЫЕ ВИДОИЗМЕНЕНИЯ Pb И Cd В ПРОМЫШЛЕННОЙ
ЗОЛЕ ОТ СОВМЕСТНОГО СЖИГАНИЯ УГЛЯ И БИОМАССЫ****Й. Калембкевич, У. Хмеляж**

*Жешувский технологический университет,
ул. Повстанцев Варшавы, 6, 35-959 Жешув, Польша,
e-mail: kalembic@prz.edu.pl*

Функциональные видоизменения и мобильность свинца и кадмия в золе от совместного сжигания угля и биомассы (50 % угля : 50 % смеси подсолнуха, щепок и соломы в брикетах) исследовано методами последовательного извлечения и ААС. Охарактеризовано такие фракции, содержащие металлы: растворимая в воде, растворимая в кислоте (pH 5), оксид, псевдосульфид и остаток. Общее содержание металлов в золе равно 2,2 (Pb) и 0,3 (Cd) мг·кг⁻¹. Подвижные фракции металлов, способные к выщелачиванию в условиях окружающей среды, составляют 27 % (Pb) и 6,7 % (Cd) от их суммарного содержания в золе.

Ключевые слова: промышленная зола от совместного сжигания угля и биомассы, свинец, кадмий, последовательное извлечение, функциональные видоизменения, мобильность.

Стаття надійшла до редколегії 01.06.2011

Прийнята до друку 21.12.2011