

Investigations of sequential leaching behaviour of Cu and Zn from coal fly ash and their mobility in environmental conditions

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Abstract

The quantitative evaluation of chemical fraction of Cu and Zn in the coal fly ash by methods of five-step sequential extraction was carried out in order to characterize metal mobility in environmental conditions. The research involved (i) water-soluble (pH 7), (ii) acid-soluble (pH 5), (iii) oxide, (iv) difficult reducible and (v) residual metal fractions. It was discovered, that the total extraction of the studied metals from coal fly ash to solutions take place in the following quantities Cu—39.0 mg kg⁻¹ and Zn—89.0 mg kg⁻¹. The investigations of chemical fractions proved that the subject metals occur mainly in coal fly ash as: oxide (Cu—12.0 mg kg⁻¹, Zn—37.0 mg kg⁻¹) and residual (Cu—9.5 mg kg⁻¹, Zn—27.0 mg kg⁻¹) as well as difficult reducible (Cu—16.5 mg kg⁻¹, Zn—22.0 mg kg⁻¹). Low concentrations of metals for water-soluble fraction (Cu < d.l., Zn—0.5 mg kg⁻¹) and acid-soluble fraction (Cu—1.0 mg kg⁻¹, Zn—2.5 mg kg⁻¹) were observed. The fractions of Cu and Zn leachable from the ash in environmental conditions contain: 2.6% (Cu) and 3.4% (Zn) of metal total amount in the coal fly ash. The obtained mobility parameter of Cu and Zn can be applied to estimate the concentration increase of mobile and hardly mobile forms of these metals in soil polluted with the ash.
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1. Introduction

Reemission of metals from the coal fly ash to the environment can be carried out by: (i) direct action of the coal fly ash on the environment in the place where they are stored and (ii) utilization of the coal fly ash or chemical processing. Coal fly ashes are applied, among others, in the production of building materials, manufacture of cement, concrete, ceramics, products, construction fill, road base, mineral filler in asphalt, embankments construction, desulphuration of combustion gases and land reclamation. The largest ash quantity is stored on slag heap (Poland—approximately 12 million Gg/year [1]). The production of increasing amounts of fly ash, resulting from coal combustion, is of major interest due to its environmental impact [2]. The physical and chemical properties of this industrial waste product, in general, are quite variable, as they are influenced by coal source, particle size, type of coal burning process and degree

of weathering. Composition and characteristic of coal fly ash are shown in Table 1.

Water extracts from fly ash are commonly alkaline and contain excessive amounts of dissolved solids [2]. Leachability of heavy metals presents a hazard for natural waters [3]. Since many trace elements existing in fly ash can leach out and groundwater resources, the study of them has been regarded in recent years as important in connection with protection of the environment. Trace metals, though present as a relatively small fraction in fly ash, are of special interest, due to their cumulative build up, long life and high toxicity to man, plants and animals through air, water, and soil intake [2]. Several studies [2–6], show the efficiency of fly ash in the removal of these heavy metals. The fly ash also is contaminated with polychlorinated dibenzodioxins and dibenzofurans (PCDD/PCDF) [2,5]. The discussion about test methods to assess the leaching behaviour of waste materials has entered a new phase as the urge to recycle and re-use waste materials has been increasing. The policy of recycling and re-use of waste materials requires a better control over the undesired release of contaminants into the environment [2].

Ash contamination poses a serious threat to inorganic environment. The confirmed presence of Cu and Zn in coal fly ashes

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Table 1
Composition and characteristic of coal fly ash

No.	Determination	Value
1	Size distribution (wt.%)	
	0.315–0.2 mm	2.7
	<0.2 mm	97.3
2	Bulk density (kg m^{-3})	540
3	Content of combustible part (wt.%)	10.1
4	Moisture content (wt.%)	0.47
5	Content of metals oxide (wt.%)	
	SiO ₂	47
	Al ₂ O ₃	24
	Fe ₂ O ₃	14
	CaO	2.5
	MgO	3
6	Content of heavy metals (mg kg^{-1})	
	Lead	137
	Cadmium	5
	Chromium	82
	Copper	66
	Nickel	78
	Zinc	133
	Manganese	939

(max. content about 300 and 700 mg kg^{-1}) [7,8] their bioactivity and biotoxicology [9,10], their ability to accumulate in plants [11,12] and, first of all, their mobility in the environment [13] were the main reasons for research into Cu and Zn chemical fractions in the coal fly ash and their ability to migrate from the ash to water solutions in environmental conditions.

Research into metal migration from environmental samples to solutions is most often carried out by sequential extraction methods (s.e.). For sequential environmental materials and waste (coal fly ash) in practice; various methods are applied. Review of these methods was put in the paper [14].

From the researchers point of view, essentially these methods give information about composition of material as well as mobility of metals in studied samples—a solution system in environmental conditions. In this case, the most important information is: (i) how many metal, (ii) chemical forms and (iii) condition of metal migration from studied material to environmental.

According to current research on s.e. of coal fly ash, five-step Tessier's method [15–17] and the simultaneous modification of the fifth step prove to be the most effective [18,19]. The replacement of HF/HClO₄ solutions with HNO₃/HClO₄ solutions allows: (i) the parallel application of these solutions to single-stage sample digestion the analysis of metal total concentration so-called “content close total” and (ii) the determination of metal mass balance and the verification of analytical results [20].

In analytical research, component content in material can be determined as: (i) content close total (when dose does not proceed total digestion silicate and aluminium silicate) or (ii) total content—after total digestion of sample and transition of components to solution.

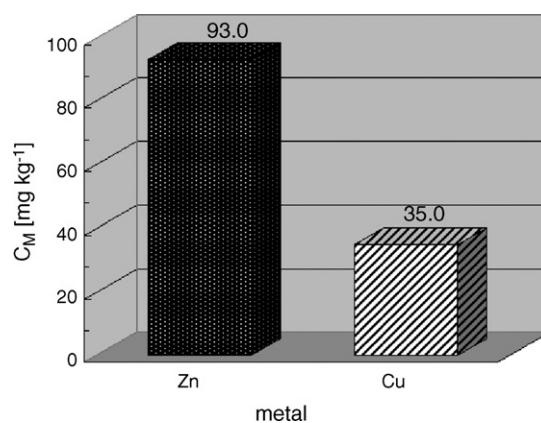


Fig. 1. The total contents of Cu and Zn in the coal fly ash obtained by single-stage coal fly ash digestion in the mixture of HNO₃/HClO₄ (2:1) and determination of metals in solution after leaching by FAAS method.

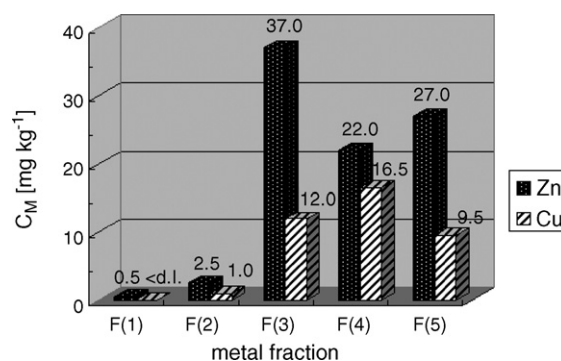


Fig. 2. Distribution of chemical fraction of Cu and Zn in the coal fly ash: F(1)—water-soluble, F(2)—acid-soluble, F(3)—oxide, F(4)—difficult reducible and F(5)—residual.

In coal fly ash mainly metal fractions are characterized: (i) soluble in water, (ii) soluble in acids, (iii) oxide, (iv) difficult reducible and (v) residual [2,3,5,21,22]. The reagents used in the various stages selectively leach certain fractions of the ash. For example, the reagents are designed to attack specific chemical forms, but a given reagent may in fact mobilize inorganic of other forms [2,3,5].

The five-step s.e. of coal fly ash was carried out and quantitative evaluations of Cu and Zn chemical fractions were made. The studies into Cu and Zn fractions leachable from the ash in environmental conditions as well as their mobility were of particular interest. The results are shown in Table 2 and Figs. 1–4.

2. Experimental

2.1. Sampling and sample pre-treatment

The coal fly ash obtained from coal combustion in the Heat and Power Plant (Rzeszow, Poland) was used in the experiment. Five samples were collected by multiple sampling according to the BN-81/0623-01 norm (by Polish Standards). All of them were collected at a depth of about 10 cm. The ash samples were put into polyethylene bags and transported to the laboratory. The wet weight of each sample was about 5 kg. Air-dry ash subsam-

Table 2
The compositions of extracting solution and conditions of s.e. and results of Cu and Zn analysis in coal fly ash by sequential extraction (fraction F(1)–F(5)) and by single-stage digestion of ash with HNO₃/HClO₄ ($[M]_{\text{total}}$)

Number of metal fraction	Kind of fraction	Conditions of sequential extraction				Method of metal determination in eluates	Concentration of Cu and Zn in ash (mg kg ⁻¹)	
		Extractant	Time (h)	Temperature (°C)	King of mixing		Separation of phases	Cu (mg kg ⁻¹)
F(1)	Water-soluble	1 M MgCl ₂ , pH 7	0.5	25	Continuous	Centrifugation	<d.l.	0.5 ± 0.1
F(2)	Acids-soluble	(CH ₃ COOH + CH ₃ COONa), pH 5	5	25	Continuous	Centrifugation	1.0 ± 0.4	2.5 ± 0.5
F(3)	Oxide	0.04 M NH ₂ OH·HCl in 25% CH ₃ COOH	6	96	Periodic	Centrifugation and filtration	12.0 ± 0.9	37.0 ± 1.1
F(4)	Difficult reducible	30% H ₂ O ₂ in HNO ₃ , pH 2	5	85	Periodic	Centrifugation and filtration	16.5 ± 1.4	22.0 ± 1.4
F(5)	Residual	Conc. HNO ₃ and HClO ₄ (2:1)	6	100	Periodic	Centrifugation and filtration	9.5 ± 1.2	27.0 ± 1.5
$\sum_{i=1}^n [M]_i$	Sum of metals content in appropriate ash fraction						39.0 ± 2.0	89.0 ± 2.2
$[M]_{\text{total}}$	Single-stage digestion of ash with mixture of HNO ₃ /HClO ₄ (2:1)						35.0 ± 1.8	93.0 ± 1.9

Student correlation coefficient were calculated, significance was set at $p = 95\%$ and $n = 4$.

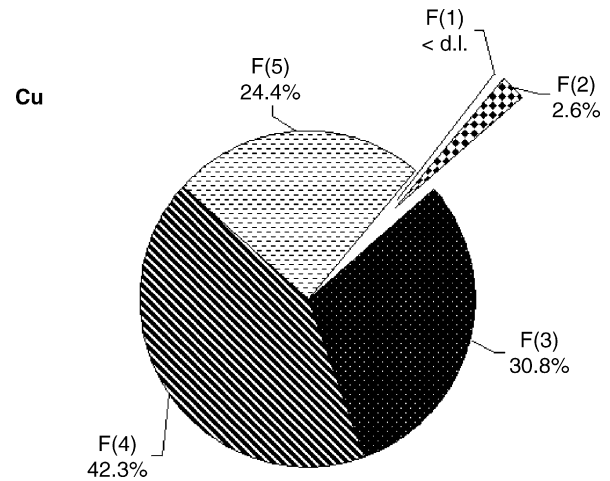


Fig. 3. Percentage share of mobility fractions of Cu in the coal fly ash: F(1)—water-soluble, F(2)—acid-soluble (pH 5) and hard mobility: F(3)—oxide, F(4)—difficult reducible, F(5)—residual.

ples weighing 0.5 kg were prepared from the 5 kg sample. In the laboratory the ashes were air-dried at ambient-temperature for 2 weeks. The dried material was sieved through a 0.25 mm sieve. The obtained material was homogenized by shaking and placed in the dark. Then, the ash samples were kept in polyethylene containers until extraction. The containers were rinsed with acetonitrile.

2.2. Analysis of chemical fraction and total concentration of metals

The five-step s.e. (2.1 item) and a single-stage ash leaching in the conditions of fifth stage s.e. (2.2 item) have been performed. The aim of s.e. and single-stage coal fly ash digestion was to determine: (i) the concentration of Cu and Zn chemical fractions, (ii) metal total concentration (content close total [23]), and (iii) the metal mass balance as well as to check the consistency of the analytical results.

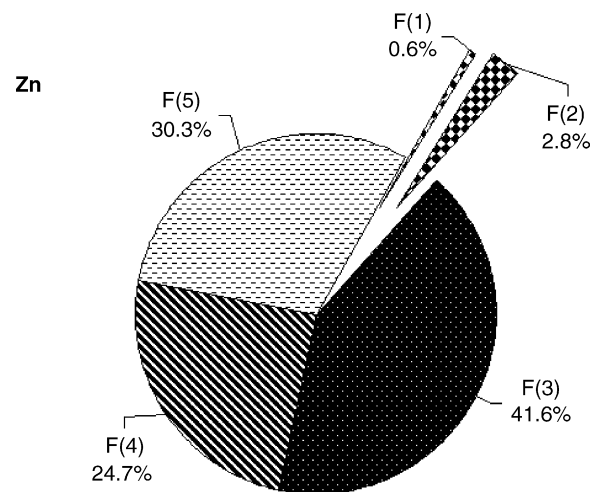


Fig. 4. Percentage share of mobility fractions of Zn in the coal fly ash: F(1)—water-soluble, F(2)—acid-soluble (pH 5) and hard mobility: F(3)—oxide, F(4)—difficult reducible and F(5)—residual.

The concentration of Cu and Zn in ash eluates after extraction by FAAS method was determined. Obtained results were calculated per ash dry weight.

2.3. Sequential extraction of ash

The experiment was carried out on four parallel samples (applying ash sample of 10.00 g prepared according to 1 item) and reagent blank. The compositions of extracting solutions and research conditions are shown in Table 2.

- Step one. The ash sample was transferred to an Erlenmeyer flask and 50 ml 0.5 mol l^{-1} MgCl_2 solution (pH 7) was added. The obtained mixture was shaken for 30 min at ambient-temperature in a horizontal rotary mechanical shaker at a speed of 200 rpm. The extract was separated from the solid residual by centrifugation at 3000 rpm for 5 min and decantation of the supernatant liquid into a polyethylene container. The metals were measured in the supernatant. The solid residual was retained for the next step.
- Step two. In the next step the residual was treated with 50 ml acetate buffer: $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ at pH 5, shaking for 1 h and centrifuging. The ash extract and the ash residual were obtained. The metals were measured in the supernatant. The solid residual was retained for the next step.
- Step three. In the next step, the residual was treated with 20 ml of 0.04 mol l^{-1} $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% CH_3COOH and digestion was performed for an hour on a heating plate at 96°C . A subsequent portion of the solution of 30 ml hydroxylamine hydrochloride of concentration 0.04 mol l^{-1} in 25% CH_3COOH was added, digestion was continued for the next hour and centrifuged for 5 min. The metals were measured in the supernatant. The solid residual was retained for step four.
- Step four. To the obtained residual small portions of 20 ml of 30% H_2O_2 (adjusted to pH 2 with HNO_3) were added and heated at 85°C . The flask was covered with watch glass and the content was digested for an hour. The glass was taken off and the flask content was evaporated to a small volume (1–2 ml). Later a successive portion of 30% H_2O_2 was added, heated for an hour in a temperature of 85°C and the flask content was evaporated again. To the cooled residual after vaporization of the solution, 20 ml of 3.2 mol l^{-1} $\text{CH}_3\text{COONH}_4$ in 20% HNO_3 was added and agitated continuously for 30 min. After centrifugation, the obtained supernatant was analyzed for Cu and Zn.
- Step five. The residual was treated with mixture of concentrated HNO_3 and HClO_4 acids (2:1). The flask was covered with a watch glass, put on a heating plate (temp. 90°C) and heated for an hour. After a lapse of 1 h the flask content was evaporated to dryness. To the dry cooled residual 15 ml of HCl solution (1:1) was added, it was put again on a heating plate and heated as before. The flask content was hot-filtered by a medium quantitative filter paper, decanting sediment traces with the help of the hot 1% HCl. Residual Cu and Zn were determined in the obtained solution.

Blank extractions were carried out for each set of analysis using the same reagent as described above.

2.4. Single-stage coal fly ash leaching

The research was carried out on four parallel samples ($n = 4$) in the conditions of fifth stage of s.e. (the conditions of s.e. are shown in Table 2).

The air-dried ash samples of 10.00 g and a diameter of ash grains $\phi = 0.25 \text{ mm}$ were wetted with deionized water. Ten milliliters of concentrated HNO_3 acid and 5 ml of concentrated HClO_4 acid was added to the samples. The flask was covered with a watch glass, put on a heating plate (temp. 90°C) and heated for an hour. After that the flask content was evaporated to dryness. Fifteen milliliters of HCl solution (1:1) was added to the cooled dry residual, which was then put on a heating plate and heated as before. The flask content was hot-filtered by a medium quantitative filter paper, decanting sediment traces with the help of the hot 1% HCl. The obtained supernatant was analyzed for Cu and Zn. The reagent blank was simultaneously run.

2.5. Determination of metals

Concentrations of Cu and Zn in ash eluates (after s.e. and single-stage ash leaching) was determined by FAAS method (conditions look 3 item). All analytical determinations were carried out in triplicate.

The calibrant solutions containing 0.0, 2.0, 4.0, and 5.0 mg kg^{-1} Cu and 0.0, 1.0, 3.0, 5.0, and 6.0 mg kg^{-1} Zn were prepared. The interferences of other metals were eliminated by adding 1 ml: 0.5 mol l^{-1} sulphuric acid—W(VI), 1% sodium fluoride—Fe(III), 1% sodium azide—Mn(VI), 0.5 mol l^{-1} ammonium tetrathiomolybdate and 0.5 mol l^{-1} sulphuric acid—As(III), Bi(III), Hg(II), Sb(III), Sn(II), Sn(IV) [24]. The results of Cu and Zn concentrations for reagent blank were corrected. The obtained results were calculated per dry weight of ash. The statistical analysis of the results was performed for the studied chemical fraction as well as for the total metal content in the ash.

The arithmetic mean of the obtained results, after each extraction step are presented in Table 2. The obtained results have the following value of standard deviation $s_R = 2.5\%$. The standard deviation (s_R) value was estimated according to the literature. The relative standard deviation (R.S.D.)% and Student correlation coefficient were calculated, significance was set at $p = 95\%$ and $n = 4$.

2.6. Reagents

The reagents used for the preparation of the extracting agents were: magnesium chloride, acetate buffer, hydroxylamine hydrochloride, 30% solution of H_2O_2 , nitric(V) acid, chloric(VII) acid, hydrofluoric acid, acetic acid and ammonium acetate. All reagents were Fluka or Aldrich analytical grade or suprapur grade. More diluted working solutions were prepared daily with the corresponding final medium for each of the steps of the sequential extraction procedure.

Stock solutions containing 1000 mg l^{-1} of the analyte were prepared in the laboratory. Solutions of Cu and Zn were prepared from nitrate salts.

One thousand milligram per liter stock solution of Cu: $1.0000 \pm 0.0002 \text{ g Cu}$ in the form of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Aldrich, pro-analysis) was dissolved in 0.2% HNO_3 (v/v) (Aldrich, supra-pur) and made up to 1000 ml. One milliliter of basic stock solution contains 1.00 mg Cu.

One thousand milligram per liter stock solution of Zn: $1.0000 \pm 0.0002 \text{ g Zn}$ in the form of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, pro-analysis) was dissolved in 0.2% HNO_3 (v/v) (Aldrich, supra-pur) and made up to 1000 ml. One milliliter of basic stock solution contains 1.00 mg Zn.

All calibrants and reagent solutions were prepared using double deionized water. If the analysis could be performed immediately, the extracts were stored in polyethylene flasks. All glassware and plastic ware were soaked in 5% (v/v) nitric(V) acid for at least 24 h and rinsed with deionized water before use.

2.7. Instrumentation

Metal determination in the extracts was carried out by means of a PERKIN-ELMER Model 3100 atomic absorption spectrometer. Hollow cathode lamp at 10 mA for Cu and Zn was used. The analytical lines were selected using a slit width of 0.7 nm [24]. Measurements were performed at 324.8 nm (Cu) and 213.9 nm (Zn) using a yellow fuel-rich air-acetylene flame (o/f ratio 1.5) and burner height of 3 mm.

The Elmetron Company (Poland), CP-I-551 model pH-meter was used for pH adjustment of the extracts. A universal shaker Model 358 A of the ELPIN-PLUS company (Poland) operating at 200 rpm in horizontal position and electric hotplate with temperature control and digital display to 1°C Model SD 300 of the STUART company (England) were used for the extraction. A centrifuge tube test Model WE-6 (Precision Engineering, Poland) was used for the centrifugation of the ash extracts at the speed of 2500 rpm for 5 min. The deionizer of the Cobrabid-AQUA Company (Poland) was used for the deionization of water.

3. Results and discussion

3.1. Total content of Cu and Zn

The total contents of Cu and Zn have been studied as “content close total” [23] in fly coal ash by means of single-stage coal fly ash digestion in the mixture of conc. acids HNO_3 and HClO_4 (2:1). It was found that the contents of Cu and Zn are: 35.0 ± 1.8 and $93.0 \pm 1.9 \text{ mg kg}^{-1}$, respectively (Fig. 1).

The total content of metals from coal fly ash (Cu— 66 mg kg^{-1} and Zn— 133 mg kg^{-1}) with hydrofluoric acid (after total digestion sample) was studied. Recovery of analyte by using references materials CTA-FFA-1 was obtained at the level 97% Cu and 95% Zn.

The obtained results prove a high concentration ratio of Cu and Zn in the process of coal combustion and ash for-

mation (about 10^3) as well as risk of soil contamination by Cu and Zn from ashes. Chemical fractions and mobility in environmental conditions were examined in order to assess the risk of soil contamination with Cu and Zn from ashes.

3.2. Chemical fraction of Cu and Zn

The five metal fractions in the coal fly ash have been researched: F(1)—soluble fraction including metals compounds soluble in water (pH 7), which can occur in natural conditions and cause migration of metal to underground water and be absorbed by plants, F(2)—fraction including soluble forms in slightly acid solutions (pH 5), F(3)—oxide fraction, F(4)—difficult reducible fraction susceptible to reduction in acid conditions and F(5)—so-called residual, digested in strongly acidic conditions ($\text{HNO}_3:\text{HClO}_4$, 2:1), fraction including the most chemically inert Cu and Zn forms. Metals included in this fraction are chemically inert and biologically inactive. Studies on distribution of Cu and Zn in ash indicate that their content in various fractions is different (Fig. 2).

Low concentrations of metals were found in water-soluble fractions (Cu < d.l.; Zn— 0.5 mg kg^{-1}) and acid-soluble (Cu— 1.0 mg kg^{-1} ; Zn— 2.5 mg kg^{-1}). It was found that the subject metals occur mainly in the residual (Cu— 9.5 mg kg^{-1} ; Zn— 27.0 mg kg^{-1}), oxide fractions (Cu— 12.0 mg kg^{-1} ; Zn— 37.0 mg kg^{-1}) and the difficult reducible fraction (Cu— 16.5 mg kg^{-1} ; Zn— 22.0 mg kg^{-1}).

The following orders of metal content in the studied fractions were found:

- Cu: soluble in water < soluble in acids < residual < oxide < difficult reducible.
- Zn: soluble in water < soluble in acids < difficult reducible < residual < oxide.

3.3. Mobility of Cu and Zn

Essential from a practical point of view is quantitative evaluation of Cu and Zn leachable from coal fly ash to surface waters in environmental conditions and metal contamination of the environment. Mobility of metals from coal fly ash in environmental conditions depends on the pH of rain water or ground water, whose values of pH do not exceed 7. Research is carried out for $\text{pH} \leq 7$. It is obvious; that reflux from coal fly ash in environmental conditions is an alkaline reaction, for the sake of ash composition.

Cooper and zinc, mobile in environmental conditions are bound to: (i) water-soluble (exchangeable fraction, pH 7) and (ii) acid-soluble fractions, pH 5. The other metal fractions present in ashes (oxide, difficult reducible, residual) are bound to highly mobile fractions and can migrate to the environment in specific conditions, i.e. aggressive environments (F(3) and F(4) fraction) and/or the presence of microorganisms (F(3)–F(5) fraction).

In order to characterize Cu and Zn mobility in coal fly ashes, the mobility parameter was calculated as

$$\alpha (\%) = \frac{\sum_{i=1}^2 [M]_i}{\sum_{i=1}^5 [M]_i} \times 100\%$$

α parameter presents the percentage share of metal mobile forms in relation to total contents in the ash. The calculations of the percentage contents of each fraction of Cu and Zn in the ash are shown in Figs. 3 and 4.

The results of the performed research indicate that the mobility of Cu and Zn fractions in environmental conditions is (%): 2.6 (Cu, Fig. 3) and 3.4 (Zn, Fig. 4), respectively.

3.4. Mass balance of Cu and Zn in coal fly ash and verification of results

The evaluation of trace elements in industrial and environmental materials requires special control of the analytical process and verification of the results. So-called analyte mass balance is, among others, an instrument used to verify the correctness of the obtained analytical results when the simultaneous one-step and multi-step procedures are performed. The mass balance of Cu and Zn in the ash was checked in the investigated system by comparing the total contents of metals, analyzed by single-stage ash digestion in the conditions of fifth step of s.e. with a sum of Cu and Zn contents in appropriate ash fractions obtained by means of s.e. The coincidence factor of mass balance of analyte was calculated as

$$\eta = \left(1 - \frac{\sum_{i=1}^5 [M]_i - [M]_{\text{total}}}{[M]_{\text{total}}} \right) \times 100\%$$

where $\sum_{i=1}^5 [M]_i$ is the sum of metal contents in appropriate chemical fractions of ash (fifth step of s.e.) and $[M]_{\text{total}}$ is the total content of metals in ash (“content close total” [23]) single-stage ash leaching. It was found that coincidence factor of mass balance of metal mass balance corresponded to: 88.6% Cu; 95.7% Zn.

4. Conclusions

1. The total contents of Cu and Zn in coal fly ash equal: 35.0 mg kg⁻¹ (Cu) and 93.0 mg kg⁻¹ (Zn).
2. Mobility fraction of Cu and Zn contain of 2.6% (Cu) and 3.4% (Zn) of their total concentration in the ash and can be leached from the ash in environmental conditions.
3. The following orders of Cu and Zn content in the studied fractions were found:
 - Cu: water-soluble (<d.l.) < acid-soluble (1.0) < residual (9.5) < oxide (12.0) < difficult reducible (16.5).
 - Zn: water-soluble (0.5) < acid-soluble (2.5) < difficult reducible (22.0) < residual (27.0) < oxide (37.0).
4. The coincidence of mass balance calculations for Cu and Zn in the ash together with single-stage digestion and multi-stage s.e. of ash equals: 88.6% for Cu and 95.7% for Zn.

References

- [1] Statistical yearbook 2004, Warsaw (Poland), Condition and environmental protection, 2004, pp. 316–317.
- [2] K. Fytianos, B. Tsaniklidi, Leachability of heavy metals in Greek fly ash from coal combustion, *Environ. Int.* 24 (4) (1998) 477–486.
- [3] P. Ricou, I. Lecuyer, P. Le Cloirec, Removal of Cu²⁺, Zn²⁺ and Pb²⁺ by adsorption onto fly ash and fly ash/lime mixing, *Wat. Sci. Technol.* 39 (10–11) (1999) 239–247.
- [4] S. Landsberger, J.F. Cerbus, S. Larson, Elemental characterization of coal ash its leachates using sequential extraction techniques, *J. Radioanal. Nucl. Chem.* 192 (1995) 265–274.
- [5] P. Van Herck, B. Van der Bruggen, G. Vogels, C. Vandecasteele, Application of computer modeling to predict the leaching behaviour of heavy metals from MSWI fly ash and comparison with a sequential extraction method, *Waste Manage.* 20 (2000) 203–210.
- [6] B. Bayat, Comparative study of adsorption properties of Turkish fly ashes, the case of nickel(II), copper(II) and zinc(II), *J. Hazard. Mater. B* 95 (2002) 251–273.
- [7] A. Kida, Y. Noma, T. Imada, Chemical speciation and leaching properties of elements in municipal incinerator ashes, *Waste Manage.* 16 (5–6) (1996) 527–536.
- [8] J.L. Wong, J. Qian, C.H. Chen, Nickel speciation of fly ash by phase extraction, *Anal. Chim. Acta* 349 (1997) 121–129.
- [9] S. Kawanishi, Y. Hiraku, M. Murata, S. Oikawa, The role of metals in site-specific DNA damage with reference to carcinogenesis, *Free Radical Biol. Med.* 32 (9) (2002) 822–832.
- [10] H.G. Seiler, A. Sigel, H. Sigel (Eds.), *Handbook on Metals in Clinical and Analytical Chemistry*, Marcel Dekker Inc., New York, 1994.
- [11] S.M. Ross, *Toxic Metals in Soil–Plant Systems*, J. Wiley and Sons, Chichester, 1994.
- [12] J.A.C. Broekaert, S. Gucer, F. Adams (Eds.), *Metal Speciation in the Environment*, Springer, Berlin, 1990.
- [13] T. Kowalkowski, B. Buszewski, Sorption and migration of selected heavy metals in different soil matrices, *Pol. J. Environ. Stud.* 11 (2) (2002) 135–139.
- [14] J. Kalemkiewicz, E. Sočo, Sequential extraction of metals from environmental samples, *Wiad. Chem. (Poland)* 59 (7–8) (2005) 697–721.
- [15] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.* 51 (7) (1979) 844–851.
- [16] A. Tessier, F. Rapin, R. Carigan, Trace metals in oxic lake sediments: possible adsorption onto iron oxyhydroxides, *Geochim. Cosmochim. Acta* 49 (1985) 183–194.
- [17] M.A. Armienta, R. Rodriguez, N. Cencieroz, F. Juarez, O. Cruz, Distribution, origin and fate of chromium in soils in Guanajuato, Mexico, *Environ. Pollut.* 91 (3) (1996) 391–397.
- [18] J. Kalemkiewicz, E. Sočo, Investigations of sequential extraction of Cr, Fe, Co and Ni from industrial ash, *Chem. Ing. Ecol.* 11 (4–5) (2004) 347–352.
- [19] J. Kalemkiewicz, E. Sočo, Investigation of sequential extraction of chromium from soil, *Pol. J. Environ. Stud.* 11 (3) (2002) 245–250.
- [20] W. Hyk, Z. Stojek, *Statistical Analysis in Analytical Laboratory*, Committee of Analytical Chemistry, Polish Academy of Sciences, Warsaw, 2000, p. 33.
- [21] H.K. Hansen, A.J. Pedersen, L.M. Ottosen, A. Villumsen, Speciation and mobility of cadmium and wood combustion fly ash, *Chemosphere* 45 (2001) 123–128.
- [22] J. Hwang, W.-J. Wang, Determination of hexavalent chromium in environmental fly ash samples by an inductively coupled plasma-atomic emission spectrometer with ammonium ion complexation, *Appl. Spectrosc.* 48 (9) (1994) 1111–1117.
- [23] A. Ostrowska, S. Gawliński, Z. Szczebiałka, *The Methods of Analysis and Properties Evaluation of Soils and Plants*, Catalogue of Institute of Environmental Protection, Warsaw, 1991, p. 109 (in Polish).
- [24] The Perkin-Elmer Corporation, *Analytical Methods for Atomic Absorption Spectrophotometry*, Norwalk Connecticut, USA, 1982.