

## EFFICIENCY OF LEACHING TESTS IN THE CONTEXT OF THE INFLUENCE OF THE FLY ASH ON THE ENVIRONMENT

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### ABSTRACT

The leachability of heavy metals (Cu, Pb and Zn) from the coal fly ash samples was studied. The investigations executed using three leachability tests (USEPA, TCLP, ASTM). The effect of different parameters was determined (the diameter of ash grains, the kind of leaching solutions, pH of leaching solutions, the volume ratio of leaching solutions to the mass of ash samples, and the leaching time) on the leachability of the heavy metals from fly ash samples. Moreover, the influence of pH and changes in the redox potential of the leaching solutions as well as the presence of organic compounds that could potentially form complexes with metals and solubility changes of metals. The concentration of the metals studied (Cu, Pb and Zn) in all obtained solutions was determined by FAAS method. On the basis of the research investigations, optimal leachability conditions for Cu, Pb and Zn from fly ash in this study have been determined. We have also found that pH of the leaching solution, and the presence of organic compounds which have a potential capacity of complexation the metals are the important factors in determining the solubility of Cu, Pb and Zn.

**Keywords:** heavy metals, fly ash, leaching test.

### INTRODUCTION

Depositing waste at landfills and taking place in these uncontrolled processes physical, chemical, and biological properties pose a serious threat to the environment. For this reason, the waste from storage must be evaluated together with organic designation degree of toxicity [Witkowska-Kit 2000]. The degree of impact on the environment of waste containing contaminants in a form of toxic substances or harmful, depending on is not only the type and concentrations of these substances, but mainly their mobility. The mobility of pollutants contained in the waste, expressed as susceptibility to leaching them in water (also called leaching test), is the most important ecological sights indicator release for depositing waste at landfills. In Poland there is a lack of uniform standards and regulations relating to the preparation of aqueous extract and evaluate the

reliability of the results obtained in the leaching test. Currently, two procedures are used to draw up the waste water. The first procedure is the result of the regulation of the Council of Ministers, 1997. The second procedure was established by Polish Standards [PN-Z-15009/1997]. The results obtained after the application of the above procedures do not indicate a total of the contents of the component in the waste, which can be subject to physicochemical change in the environment, give only an approximate indication in terms of assessing potential risks posed to the environment at the time referred to the waste.

Leaching tests can be divided into two main categories: 1. static tests and group and 2. dynamic tests and core barrels. In the static tests and group a quantity of the sample solution is specified and joined by a fixed period of time. The product of this connection is the leach substance. The main goal of the tests is a group that,

at the end of the entire period of the process will be given a stable state of molecules. In the dynamic tests and column, the substance resulting in leaching constantly flows through the sample. Summary and comparison of group recruitment tests and column charts are contained in the following works [Zandi et al. 2007, Fällman, Aurell 1996, Egemen, Yurteri 1996, Lewin 1996, Wahlström 1996, Quevauviller et al. 1996].

Most waste in the field of employment is due to the structure of coal-fired power generation. As a result of burning coal solid waste (furnace waste) is produced: fly ash, slag, mixture of ash and slag, microspheres, boiler ash, flue gas desulfurization gypsum fluidized beds using limestone (wet method), wastes from flue gas desulfurization methods (dry and semi-dry methods), etc. [Galas et al. 2005]. Fly ash according to [Bilitewski et al. 2003] its the residues from the combustion of ground coal in amber furnaces, which are lifted of emissions and are captured by dust device. Ashes are contained in the mixture of dust-gas created from coal (hard coal and lignite).

Ash properties primarily depend on the chemical composition of non-flammable substances contained in different grades of coal burned [Pachowski 2002]. Fly ash, formed as a result of burning coal, may contain trace amounts of substances which during liquidation or disposal may be washed out, what poses a potential threat to the environment. Environmental conditions have a huge impact on the mobility of ash as well as on the physical and chemical properties. In order to simulate the behavior of the leached fly ashes in different environmental conditions and to reduce the discrepancies between the measurements made on the ground, and these have been developed in the laboratory, standard leaching tests. The most common tests used by eluting extraction procedures, i.e. the "Extraction" Procedure (EP) [Esakku et al 2008, Sophia, Swaminathan 2005], the "Toxicity by Characteristic Leaching Procedure" (TCLP) [Gitari et al. 2009, Lu et al. 2009, Jing et al 2006, Janus et al. 1998] and standardized extraction procedure developed by the American Society Of Testing And Materials (ASTM) [Dermata et al. 2004, Mangialardi 2003]. The leaching tests are widely used mainly as indicators to estimate the potential release of trace metals from the ash, in order to assess their impact on the environment in the process of rendering or deposition of fly ash under laboratory conditions [Sarode et al., 2010]. In addition, they allow the

classification of trace elements of ash on the basis of their behavior during the leaching under different conditions and to identify the mechanisms of leaching [Fytiano, Tsaniklidi 1998, Hardaway et al. 1999, Janus et al. 1998, Praharaj et al. 2002, Sitarz-Palczak, Kalembkiewicz 2012].

Existing standard leaching schemes are insufficient because they do not depict any scenarios of waste liquidation or disposal, including ash. To reduce the surface storage of the ashes, new marketing options for their re-use are still searched for, which requires comprehensive and preceded by studies of their composition, physicochemical properties and susceptibility to further processing by various technologies and behavior in contact with various external factors.

The tests carried out in the framework of this work were to assess the impact on the environment from coal ash as they deposit in landfills and the certification of fitness for non-industrial utilization. To this end, studies were carried out regarding changes to the solubility of selected heavy metals (Cu, Pb and Zn) in the fly coal ash in anaerobic conditions.

## MATERIALS AND METHODS

### Apparatus

The flame atomic absorption spectrometer Perkin-Elmer 3100 Model (Shelton Instruments, CT USA) was used for Cu, Mn and Zn determination in the solutions. Measurements were performed at wavelength 324.8 nm (Cu), 217 nm (Pb) and 213.9 nm (Zn) using a yellow fuel-rich air-acetylene flame (acetylene flow velocity 2.0 dm<sup>3</sup>·min<sup>-1</sup>; air flow velocity 8.0 dm<sup>3</sup>·min<sup>-1</sup>) and burner height of 3 mm. The analytical lines were selected using a slit width 0.7 mm and followed by [Perkin-Elmer 1982]. Hollow cathode lamp at 10 mA (Cu and Zn), 20 mA (Pb) was used. The centrifuge tube-test Model WE 1 (Precision Engineering, Poland) – was used for the centrifugation of the soil extracts at the at appropriate rotary speed of 3000 rpm. The universal laboratory shaker Vibramax 100 Model (Heidolph Instruments, Germany) and a hot plate HP 88720-26 Model (Barnstead/Thermolyne, USA) were used for the extraction. The pH of the extraction solutions was determined with a pH meter CPI-551 Model (Elmetron, Poland) supplied with a glass combination electrode (Eurosensor, Poland).

## Reagents and solutions

All chemicals and reagents were of analytical grade or higher purity and were obtained from POCH, Gliwice, Poland. The solutions were prepared by dissolving appropriate compounds in double-distilled water from the Water Purification System (SolPure 7 POLL LAB, Poland). The reagents were prepared and stored in clean polyethylene bottles. Glassware and plastic ware (PE) used throughout the experimental work were previously soaked in 10% nitric acid bath overnight and washed thoroughly in double distilled water. Standard solutions were prepared from standard solutions for atomic absorption (Sigma-Aldrich Chemie GmbH, Switzerland) – the concentration of all metals in standard solutions were the same and equals  $1.000 \mu\text{g}\cdot\text{cm}^{-3}$  in 1% of  $\text{HNO}_3$ . Working standard solutions containing Cu, Pb and Zn were prepared by serial dilution of the appropriately of standard solution for atomic absorption.

## Sample collection and preparation

Coal fly ash samples used for the experiments were collected from the electric filter from Rzeszów S.A power-plant (Rzeszów, Poland). The 0.5 kg sample was prepared from overall air-dried 10 kg sample by a “quarterning” method – according to Polish Branch Standard [BN-81/0623–01] procedure. After that, the air-dried ash was sieved, initially through a laboratory sieve of 1 mm diameter, and then milled in an agate mortar to fine powder ( $\varphi \leq 100 \mu\text{m}$ ) – according to Polish Standard [PN-77/G-04528/00].

## Fly ash

Physicochemical characteristics of ash samples included determination of pH using potentiometric method [PN-ISO-10390]; determination of organic carbon content - Tiurin method [PN-95-Z-15005] and composition of granulometric by using the sieve methods [PN-R-04032]. The total content of metals is obtained after mineralization in a mixture of concentrated  $\text{HNO}_3$  acid, HF and HCl under conditions described in the work [Sitarz-Palczak, Kalembkiewicz 2008].

## Standard leaching tests

Three standard leaching tests (USEPA, TCLP, ASTM) were selected for this study to determine stability of trace elements (Cu, Pb and Zn) in fly

ash samples under three different conditions (Table 1). Leaching tests were carried out based on the principles laid in standard procedures. To obtain USEPA, TCLP and ASTM extracts 5 g of fly ash was agitated in polyethylene bottle containing  $100 \text{ cm}^3$  of extracting medium for the specified time periods of 24 and 18 h, respectively. After the required period of agitation, all extracts were stirred with a glass rod and filtered through  $0.45 \mu\text{m}$  filter paper. The filtrates were acidified with a concentrated  $\text{HNO}_3$  addition and transferred to a polyethylene bottle and stored in a cool dry place for further analysis by atomic absorption spectrophotometry (FAAS). All extractions were carried out as triplicate runs.

## Effect of parameters of ash and leaching process

The effect of selected parameters on the output samples of ash (particle diameter ash) and leaching process (a type of leaching solution, the pH of the solution, the ratio of volume of leaching solution to mass of the sample and the influence of the ash leaching time) on the leaching of heavy metals from the ash samples was studied. In order to determine the effect of particle diameter ash and the type of leaching solution has three standard tests of leaching: USEPA TCLP, and ASTM (Table 1), with respect to the fraction of the ashes received after the sieve analysis. The proceedings were the same as in the case of a standard leaching procedures described above. In order to determine the effect of pH leaching solution (2.5%  $\text{CH}_3\text{COOH}$ ) on the leachability of metals from the ash particle diameter  $\varphi = 1.5 \text{ mm}$  done series of 2.5%  $\text{CH}_3\text{COOH}$  that pH values: 2; 3; 4; 7 and 12. Adjust the pH was carried out using  $0.1 \text{ mol}\cdot\text{dm}^{-3}$  HCl and  $0.1 \text{ mol}\cdot\text{dm}^{-3}$  NaOH. Then use the so prepared solutions 2.5%  $\text{CH}_3\text{COOH}$  fixed pH values were leaching of metals (Cu, Pb and Zn) under the conditions given in Table 1 – in relation to a standard TCLP procedure. To determine the influence of relative elution volume [ $\text{cm}^3$ ] to mass [g] on the leaching Cu, Pb and Zn with samples of ash made a series of leaching tests according to the standard TCLP procedure, in which the ratio of L:S [ $\text{cm}^3$ :g] was, respectively: 1: 1; 2: 1; 5: 1; 10: 1, 20: 1 and 50: 1. In order to determine the influence of time on the leachability Cu, Pb and Zn from ash fractions with a diameter of  $\varphi = 1.5 \text{ mm}$  using standard leaching test, the following conditions were established as optimal i.e. leach-

**Table 1.** Conditions of leaching tests

Tests conditions	USEPA [USEPA 1987]	TCLP [TCLP 1311 1990]	ASTM [ASTM D 3987-85 2001]
Leaching solution	0,5 mol/dm <sup>3</sup> nitric acid	2,5% acetic acid	Distilled water
Liquid to solid ratio [cm <sup>3</sup> /g]	20:1	20:1	20:1
Leaching time [h]	24	24	24
pH of leachig solutions	0.6 ± 0.1	4.0 ± 0,1	6.3 ± 0.1
Temperature [°C]	19 – 25	19 – 25	19 – 25
Number extraction	1	1	1

ing solutions 2.5% CH<sub>3</sub>COOH (TCLP); pH = 2.5; the ratio of the volume of leaching solution to the mass of the sample L:S = 50:1 [cm<sup>3</sup>:g]. Assuming the following leaching times: 0,5; 2; 4; 6; 8, 12 and 24 h. subsequent procedure was the same as in the case of leaching procedures described above.

Effects of selected organic compounds with a potential capacity of complexation the metals on the solubility of Cu, Pb and Zn in anaerobic conditions

In order to determine the effect of complexation substances on the contents of selected metals in the soluble forms contained in the ashes two series of complete extractions by shaking samples of ash were performed, with the complexation addition substances: citric acid or tartaric acid with the following concentrations: 10, 20, 40, 100 mg·dm<sup>-3</sup> corresponding 6.25; 12.50; 25.00; 62,50 mg·kg<sup>-1</sup> ash. The solubility change of Cu, Pb and Zn in anaerobic conditions was studied in a series of incubation of samples of ash with the addition of organic substances constituting a potential source of easily accessible coal they were glucose and tartaric acid with a concentration of 200 mg·dm<sup>-3</sup>. Incubations are performed at in confinement without access of oxygen for a period of 7 days, stirring the sample for 10 minutes from time to time to ensure the balance between the permanent and the solution. After the incubation was carried out through the extraction conditions of shaking in leaching tests (USEPA and TCLP), which is given in Table 1.

## RESULTS AND DISCUSSION

Basic physicochemical properties of ash were presented in Table 2. On the basis of the obtained results, it was concluded that coal ash shows slightly alkaline pH. Working with [Łączny 2002] it is known that the energy (fly ashes) compounds of heavy metals present in the waste are

in slightly alkaline environment, because the ions of these metals in this environment are generally less mobile complex compounds. If intended for the storage of fly ash, or other energy waste will have basic character, the main threat to the environment will be releasing such compounds as sodium, potassium and calcium sulphate. So in the case of investigational ash (wood and coal) there is no risk of wash of heavy metal ions with alkaline base nature of these wastes. Organic carbon content in the ash residue of unburned carbon [Su, Wong 2003]. Based on the results of the analysis, the granulometric composition it was found that the greatest part is the fraction of particulate matter, which is consistent with the results obtained by [Antonkiewicz 2014]. The total content of trace metals in the ash is varied. Since they all occur at concentrations above 50 mg·kg<sup>-1</sup> can they have a large impact on the environment (Table 2). In a view of the fact that ash is a heterogeneous material, elements contained therein are not evenly distributed. The content of organic carbon assessed in fly ash reveal the presence of unburned coal residues. The surface layer is enriched in

**Table 2.** Physicochemical properties of fly ash (the results presented reflect values of data taken from 10 samples)

Parameter	Value of parameter
pH:	
H <sub>2</sub> O	9.1
1 mol·dm <sup>-3</sup> KCl	8.9
Content of organic carbon [g·kg <sup>-1</sup> ]	53.9
Texture [%]:	
Clay (0 – 2 µm)	0.9
Silt (2 – 50 µm)	75.7
Sand (> 50 µm)	23.4
Total content [mg·kg <sup>-1</sup> ] of metal	
Cu	63.7 (± 3.9)
Pb	101.2 (± 4.6)
Zn	200.0 (± 4.1)

copper and zinc, while lead is distributed evenly between the sensor and the surface of the grains [Izquierdo, Quero 2012].

### Standard leaching tests

In natural conditions (under the influence of atmospheric conditions and the presence of microorganisms – in landfills there are numerous physical, chemical and biological processes, not subject to the control. These processes give rise to, first and foremost, the aging of the deposited material, its weathered and leaching. Aging is generally to reduce the solubility, and weathered to the creation of partially soluble products. The leachability applies to an easily soluble metal form, present in the waste, i.e. first of all, salt, in which the composition has sulfates of calcium, potassium, sodium and magnesium. The immediate effect of leaching is an increase in permeability of the deposits, increased salinity of groundwater and surface water. The leachability of Cu, Pb and Zn in fly ash obtained after the application of three standard leaching tests (USEPA TCLP and ASTM) was presented in Table 3. The highest degree of leaching for Pb of 56.8% in relation to the total content of Pb in the fly ash, were obtained using the USEPA test; respectively 22.3% was obtained by means of TCLP procedure. While the ASTM test using distilled water was obtained the lowest value of leaching equal to 2.5% in relation to the total contents of Pb in the fly ash. The degree of leaching for copper was 62.7% using the USEPA test and only 19.6% in the case of the TCLP test in relation to the total content of Cu in the fly ash. The leachability of copper in the case of ASTM test was below the limit of detection for this metal, as determined by FAAS method. Zinc showed the greatest percent-

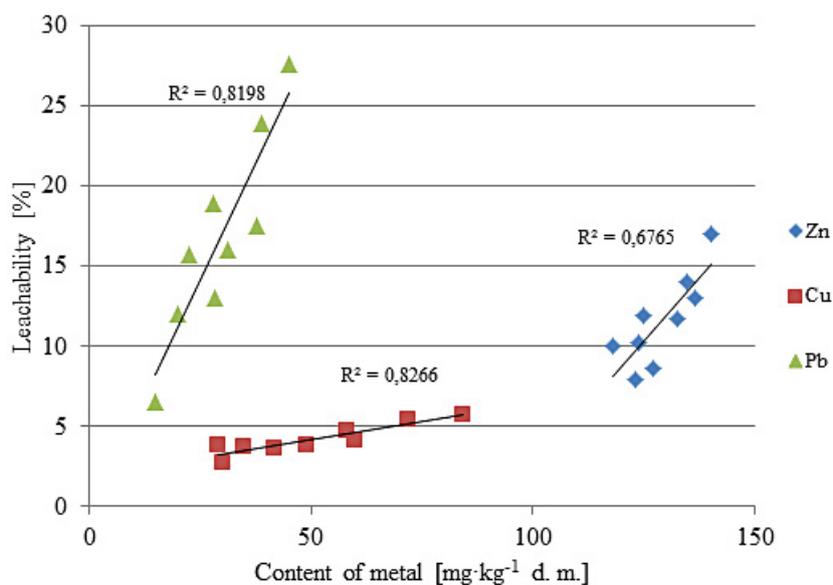
age of leachability using the USEPA procedures and it was 35% in relation to the total content of the metal in the ashes. and 14.6% after applying the TCLP test. The leachability of Zn in ASTM test does not exceed the limit of detection for the determination of this metal by the FAAS method. In summary, containing a test in which the largest were the concentration of soluble forms in respect of all designated metals in coal ash is the USEPA. In the light of the above, it can be concluded that this test shows the highest efficiency in relation to the determined metals Cu, Pb and Zn. The USEPA procedure is more effective due to aggressive conditions during the leaching of metals. Taking into account the value of the degree of leaching of individual elements, it can be concluded that the degree of leaching of Cu, Pb and Zn is decreasing in the following series: Cu > Pb > Zn. In spite of all processes taking place in the environment it is suggested that the most appropriate and best simulating natural conditions is ASTM procedure, in which the eluting solution is distilled water. However, research carried out for the TCLP test may be helpful in the diagnosis of possible risks which might occur in the event of “acid rain”.

Statistical analysis of the results obtained on the concentrations of metals in the soluble forms, and their total content in the ash was carried out using a linear regression. Figure 1 shows the obtained relationship between leachability of Cu, Pb and Zn in relation of the total content of these metals in studied the ashes after application of the TCLP test. On the basis of the obtained result, it was found that an important relationship between the soluble forms of metals and their total content in fly ash prove the obtained correlation values of the coefficients, which are : Zn – 0.68, Cu – 0.83, Pb – 0.82. The results of the studies on the content of the soluble forms Cu, Pb and Zn in fly ash al-

**Table 3.** Summary of the concentrations of Cu, Pb and Zn in the soluble forms and relative leaching of these metals by USEPA TCLP and ASTM procedures (concentration of metal in the fly ash and the confidence interval were given for n = 10 at p = 95%)

Procedure	Concentration of metals [mg·kg <sup>-1</sup> ]	Cu	Pb	Zn
USEPA	Leachability	40.0 (± 2.6)	57.5 (± 2.9)	70 (± 3.5)
	Relative leaching [%]	62.7	56.8	35.0
TCLP	Leachability	12.5 (± 0.7)	22.6 (± 1.1)	29.1 (± 1.6)
	Relative leaching [%]	19.6	22.3	14.6
ASTM	Leachability	< l. d.	2.5 (± 0.2)	< l. d.
	Relative leaching [%]	-	2.5	< l. d.
Leachability limit [Rozporządzenie...2006]		0.05	0.5	2.0

l. d. - limit of detection by FAAS method.



**Figure 1.** Relation between leachability of Zn, Cu and Pb and total concentration this metals in fly ash after the TCLP test used

low an approximate assessment of the risks posed to the water – soil environment at the time by a specified waste. For this purpose, the concentrations of trace investigated metals received in the soluble forms in the ash were compared with the limit values for wastewater entering into waters or into the ground, assembled in a Table 3. On the basis of the obtained results, it was found that the concentration of Zn obtained after leaching at the USEPA, TCLP and ASTM tests exceed acceptable concentrations for this metal for wastewater entering into waters or into the ground. The same situation occurs in the case of Cu and Pb after leaching with USEPA TCLP, tests from the fly ash. The obtained results, due to the heterogeneity of the test material, should be verified on the basis of the follow-up testing of leachability of metals from the ashes.

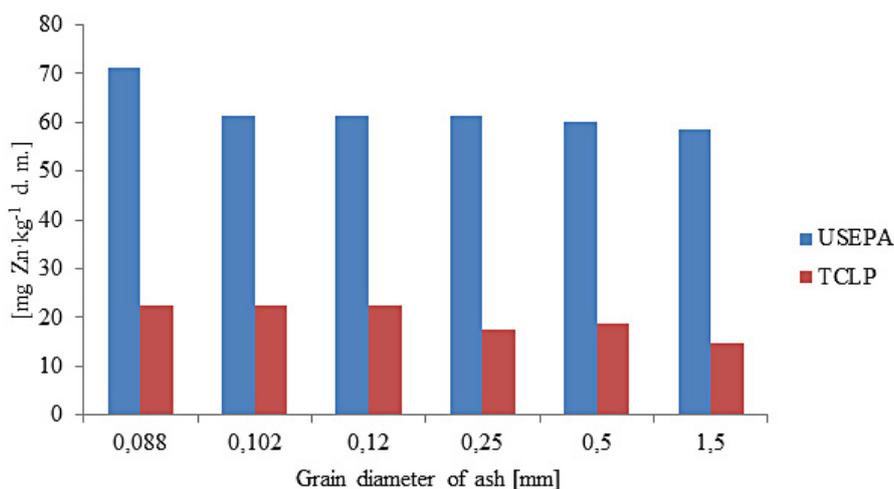
In assessing the dangers of fly ash containing pollution in a form of heavy metals, in addition to the degree of leaching, one should take into account the additional effect of the aging of waste. It can be both beneficial and detrimental. This is a very important ecological factor for the future in relation to the waste deposited in landfills. It may actually happen that the waste with low leaching today become more washed out after a few years, or waste with high leaching become harmless after a few years of storage. Linked to this need for constant monitoring of ash storage facilities, which, in the light of the obtained results pose a risk of contamination of the environment water near the landfill.

### Effect of parameters of ash and leaching process

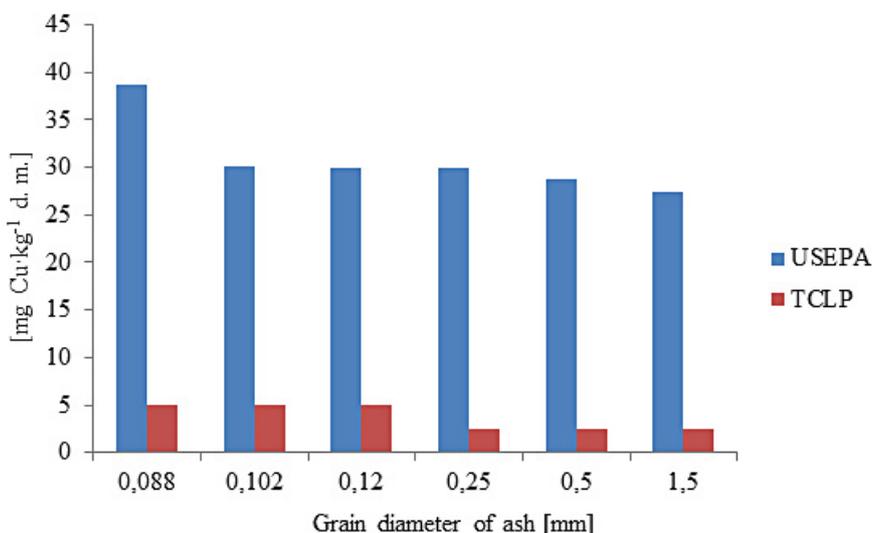
There is a number of factors that may affect the leach of each constituent elements in fly ash leaching tests. Some of these factors are related to the properties and composition of fly ash, others depend on conditions of leaching [Zandi et al., 2007]. Test conditions (LS ratio, leachant pH and leaching time) have a great impact on these results. The conditions for measuring potential leachability have not been clearly addressed in literature; there are a few contradictory studies on the principles of leaching and effects of control factors such as pH and LS ratio on fly ash leaching behavior [Fällman 1997].

### Particle size of fly ash

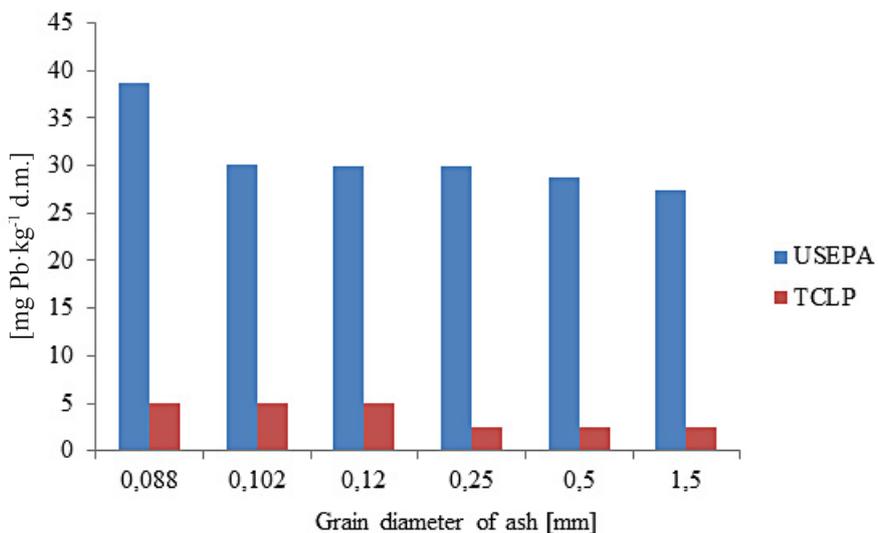
Fly ash have poorly developed a pore structure. The degree of development of the structure of the surface of the grains and the size of the specific surface area to a large extent determine the susceptibility of the ashes on the leaching of soluble parts from them. Therefore, it can be seen, that both the grain diameter as well as their appropriate size will determine indirectly the leaching solutions on the tested metals. Figures 2 - 4 illustrate the effect of particle diameter on the leachability of soluble forms of Cu, Pb and Zn from the fly ash using the USEPA TCLP tests. On the basis of the results presented in Figures 2 - 4, it was concluded that particle diameter of fly ash has a significant effect on the leachability



**Figure 2.** Content of Zn in the soluble forms in the fly ash with different grain diameter of ash obtained by the use of the leaching test (USEPA, TCLP) and determined by FAAS method



**Figure 3.** Content of Cu in the soluble forms in the fly ash with different grain diameter of ash obtained by the use of the leaching test (USEPA, TCLP) and determined by FAAS method



**Figure 4.** Content of Pb in the soluble forms in the fly ash with different grain diameter of ash obtained by the use of the leaching test (USEPA, TCLP) and determined by FAAS method

of soluble forms of Zn and Cu, as well as in the application of the tests USEPA and TCLP. With regard to both the highest of leaching metals were received by the ash of 0.088 mm diameter and solution of  $\text{HNO}_3$  (USEPA) respectively, for was equal to  $72 \text{ mg}\cdot\text{kg}^{-1}$ , while for Cu  $38 \text{ mg}\cdot\text{kg}^{-1}$  in respect of the dry mass of the ash. The effect of particle of diameter of ash on leachability of Pb shows an inverse relationship, as in the case of other metals by applying USEPA and TCLP tests, namely the leachability of Pb increases with ash particle diameter. The leachability of lead using the USEPA test shows the highest concentration of soluble forms of metal particle diameter ash equal: 0.088 and 1.5 mm. The lowest Pb content in the soluble forms was received for grain diameter of ash equals 0.102 mm.

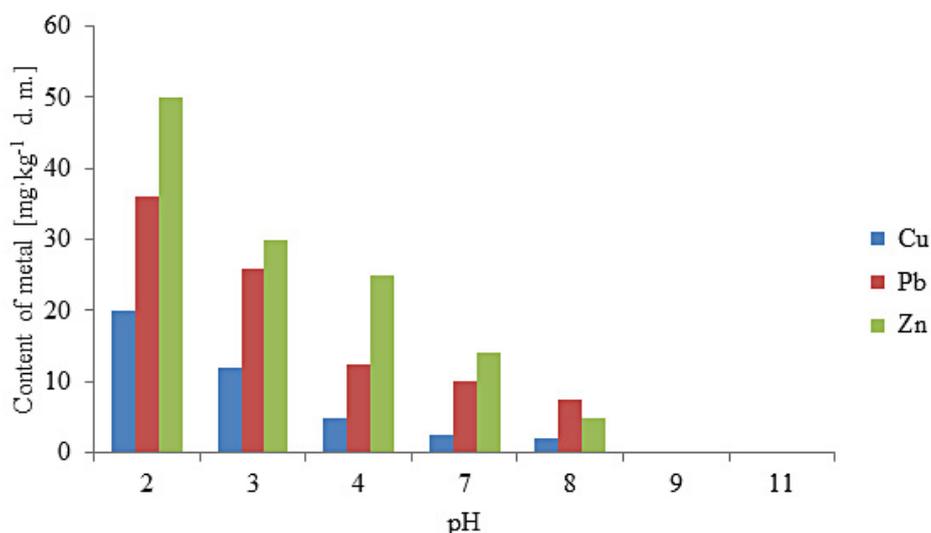
### Leachability as a function of pH

The pH of the solution is very important as it determines the surface charge of the fly ash, and the degree of ionization and speciation of the elements in solution. The interactions between the charged ions in solution and the surface of fly ash particles contribute to release or adsorption of species. The results shown in Figure 5 indicate the trend of pH release of Cu, Pb and Zn. The concentration of soluble forms of all studied metals in fly ash decreases with increasing alkalinity of the leaching solution. pH in the range of 2 to 3 found the largest leachability for all heavy metals tested; respectively for Zn 25–15%, copper 31–19% and lead 36–26% in relation to the total contents of the metals in the fly ash. Low concentrations of these

metals were observed in leachate solution (2.5%  $\text{CH}_3\text{OOH}$ ) at high pH ( $> 9$ ) but increased at pH  $< 9$ . The leaching trend for these metals indicates the dependence of the release of some metals on the dissolution of hydrous oxides of iron and manganese. Mn and Fe-oxides present in fly ash are formed during combustion of coal, and on hydrolysis form Mn and Fe hydroxides. Trace metals, such as Cu and Pb are associated with these hydroxides and on dissolution of these hydroxides, the trace metals are bound to be released into solution. Adsorption/desorption also plays a role in controlling the concentrations of heavy metals.

Fly ash material generates an alkaline pH within a few minutes of contact with water in most cases, due to higher quantities of soluble basic oxides than the soluble acid phases [Choi et al 2002, Reardon et al. 1995]. Several studies [Cho et al. 2005, Lee, Saunders 2003, Steenari et al. 1999] have shown that at higher pH, the surfaces of the fly ash particles are negatively charged. This would lead to increase in the adsorption of most heavy metals from the solution. The increase in adsorption of heavy metals ions in fly ash solutions at higher pH ( $> 10$ ) may also be attributed to calcium content which provides alkalinity in the system raising the pH to strongly alkaline values, thereby facilitating the uptake of metal ions by the fly ash.

The pH of the environment has a great impact an chemical speciation of leachate elements from fly ash in the aqueous environment except for highly soluble elements which are mobile under both acidic and basic conditions. The difference



**Figure 5.** Change of content of Cu, Pb, Zn in the soluble forms in the fly ash under the influence of changes to the influence pH of leaching solution obtained after the TCLP procedure

between total quantity of element in the fly ash and the potentially leachable constituent is due to structure and mineralogy of the fly ash and associations of the element major insoluble phases present in the fly ash.

Solubility of metal compounds is an important property that allows metals to penetration into the structure of the porous adsorbent. The concentration of such speciation forms of metals as:  $\text{MOH}^+$ ,  $\text{M(OH)}_2$ ,  $\text{M(OH)}_3^-$ ,  $\text{M(OH)}_4^{2-}$  at pH  $6 <$  are too small to affect the sorption process the dominant forms of metal  $\text{M}^{2+}$  ( $\text{M} = \text{Cu}, \text{Zn}, \text{Pb}$ ) [Ho, et al., 2002]. This is confirmed by the data presented in Figure 6 the speciation graph of metal ions, whose curves are compatible with the data from literature [Zirino, Yamamoto, 1972, Cuppett et al. 2006, Cárdenas López et al. 2007, Deliyanni et al., 2007]. They have been generated on the basis of the program Medusa [<http://www.kemi.kth.se/medusa/>]. The speciation curves for the different ions of heavy metals indicate that different forms dominate in the solution within a certain range of pH; for example  $\text{Zn}^{2+}$  is a dominant form in solution at pH  $< 6$ . Above this pH in solution increases the concentration of  $\text{ZnOH}^+$  and  $\text{ZnO}$ . With regard to the adsorption of Cu and Pb it should be kept in mind that these speciation forms of metals, or simple ions  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  have mainly to pH about 6, above which exponentially increases the concentration of  $\text{CuO}$  and  $\text{Pb(OH)}_2$ . In general, there are different mechanisms that may control the release of a particular constituent from a particular fly ash in an aqueous environment. Highly soluble elements available on the surface of the fly ash often fall into the category of available controlled leaching if the concentration released into the leachant is limited only by the amount of the element in the fly ash. These element are expected to become mobile soon after contact with

aqueous environment and leach at high concentrations. Leachability of some other constituents may be solubility controlled where leachability of elements in the fly ash can be described by dissolution and precipitation processes.

### Leachability as a function of redox potential

The leaching of some metals e.g., Fe, Cr, As can depend significantly on the redox conditions. The redox conditions can change due to the access of air to the sample during the storage or in performing the leaching test [Wahlström1996]. The results concerning the effect of the potential redox on the contents of metals in the soluble form in the fly ash are shown in Table 4. At high values of the potential ( $\approx 170$  mV), the concentration of Cu, Pb and Zn in the soluble forms are highest and are respectively equal to: Cu - 37.5; Pb - 50 and Zn - 80  $\text{mg}\cdot\text{kg}^{-1}$ . At the same time, as the high value of the potential suggests, these metals are present in the oxidized forms by taking the highest oxidation:  $\text{Cu}^{\text{II}}$ ,  $\text{Pb}^{\text{IV}}$  and  $\text{Zn}^{\text{II}}$ . Along with the decline in the potential decrease the content of Cu, Pb and Zn in the soluble forms, which testifies to their presence in the reduced forms.

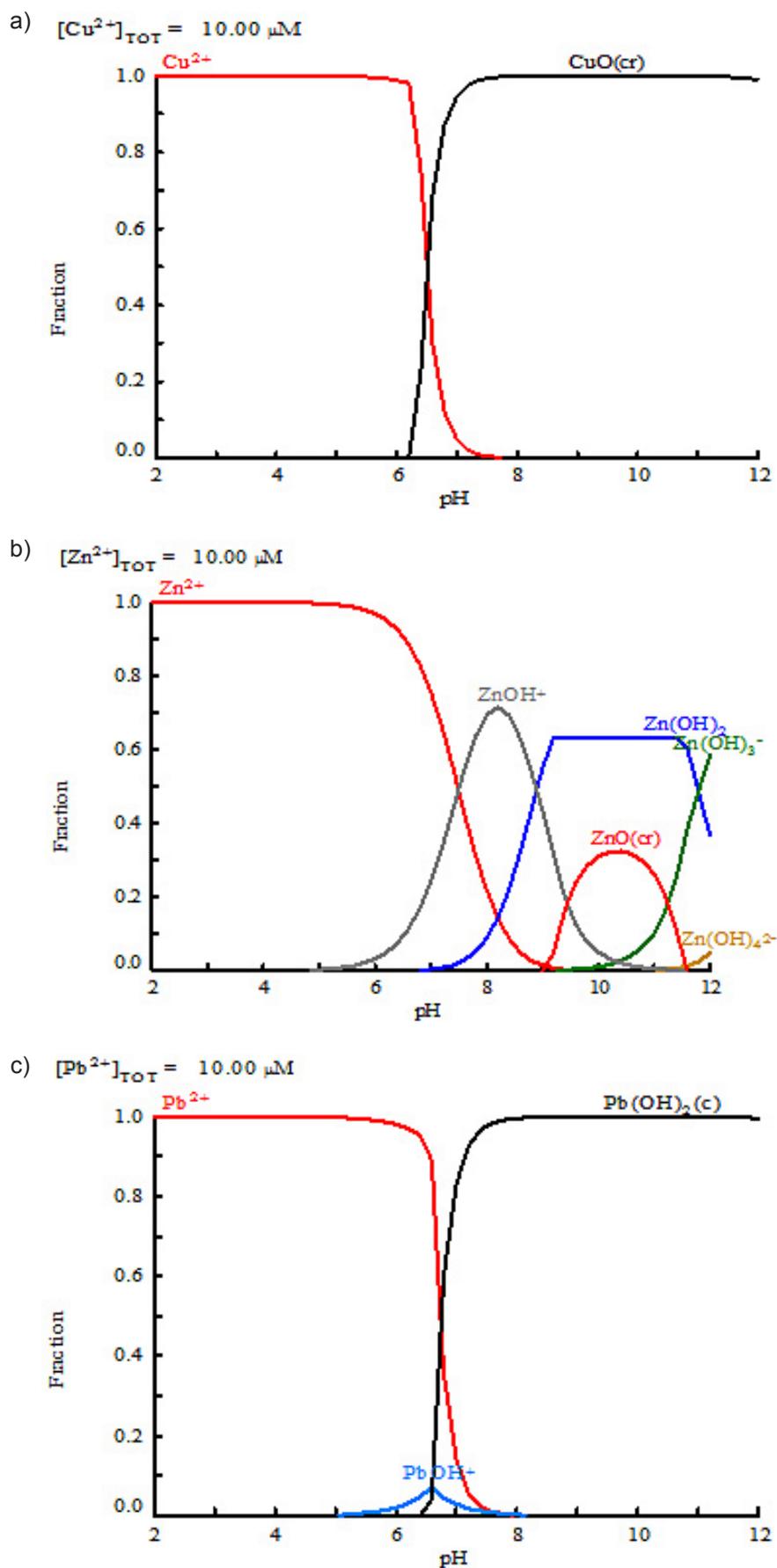
### Leachability as a function of L:S ratio

The ratio of the volume of leaching solution to the mass of sample fly ash (L:S) is one of the more important factors affecting the leaching of trace elements from the ashes samples. The most commonly used ratio of the liquid phase to the solid phase (L:S) is located in the range (10–20): 1, but with a higher ratio, for example 50:1, the leaching substance is more easily mixed with fly ash, and trace components are increasingly leached away from the seeds of the ash. The results shown in Table 5 fully confirmed the correlation.

**Table 4.** Effect of the redox potential of leaching solutions on the content of Cu, Pb and Zn in the soluble form in the fly ash obtained after the TCLP procedure (concentration of metal in the fly ash and the confidence interval were given for  $n = 6$  at  $p = 95\%$ )

Value of SEM [mV] of leaching solutions	Value of SEM [mV] before leaching	Value of SEM [mV] after leaching	Concentration of soluble forms of metal [ $\text{mg}\cdot\text{kg}^{-1}$ ]		
			Cu	Pb	Zn
189	178	170	37.5 ( $\pm 5.5$ )	50.0 ( $\pm 7.2$ )	70.0 ( $\pm 9.5$ )
162	159	140	20.5 ( $\pm 2.8$ )	26.0 ( $\pm 3.3$ )	55.0 ( $\pm 5.8$ )
100	95	89	5.0 ( $\pm$ )	12.5 ( $\pm 1.5$ )	25.0 ( $\pm 6.5$ )
-25	-20	-10	2.5 ( $\pm 1.1$ )	12.5 ( $\pm 3.1$ )	7.5 ( $\pm 1.8$ )
-96	-96	-88	< l. d.	5.0 ( $\pm 1.9$ )	5.0 ( $\pm 1.7$ )
-161	-167	-158	< l. d.	< l. d.	< l. d.

l. d. – limit of detection by FAAS method.



**Figure 6.** Speciation curves of a) Cu, b) Zn, c) Pb  
 Comments: (c) – solid substance , (cr) – crystalline form

**Table 5.** The content of Cu, Pb and Zn in the soluble forms in fly ash ( $\varphi = 1,5$  mm) obtained by a variety relations of volume of 2.5% acetic acid ( $\text{pH} = 2.5$ ) to the mass of the sample – L:S (concentration of metal in the fly ash and the confidence interval were given for  $n = 6$  at  $p = 95\%$ )

Ratio L:S [cm <sup>3</sup> :g]	Concentration of soluble forms of metal [mg·kg <sup>-1</sup> ]		
	Zn	Cu	Pb
2:1	2.5 ( $\pm 0.2$ )	2.5 ( $\pm 0.2$ )	< l.d.
5:1	2.5 ( $\pm 0.1$ )	2.4 ( $\pm 0.1$ )	< l.d.
10:1	14.9 ( $\pm 0.7$ )	2.4 ( $\pm 0.5$ )	12.4 ( $\pm 0.9$ )
20:1	30.0 ( $\pm 1.6$ )	8.9 ( $\pm 0.6$ )	24.9 ( $\pm 1.3$ )
50:1	29.4 ( $\pm 1.6$ )	8.7 ( $\pm 0.7$ )	24.0 ( $\pm 1.6$ )

l. d. – limit of detection by FAAS method.

### Leachability as a function of time

The execution time of the leaching test is an important parameter affecting the mobility and speciation of trace elements in fly ashes. The study of the effect of execution time of leaching of trace metals (Cu, Pb and Zn) from ash are essential from the perspective of the protection of the environment. The main objective of the research is to estimate the leaching time quantity of heavy metals in the soluble forms that are subject to migration, with the ash landfills in the wild in real life conditions. The results of these studies are necessary to assess the potential of the possible time of the release of the components of fly ash in the context of its liquidation in rendering specific conditions [Zandi et al., 2007]. The results obtained for this aspect of the study are shown in Figure 7. Time of leaching showed a significant impact on the concentration of Cu, Pb and Zn in soluble forms. Copper concentrations were relatively constant for the execution time of the leaching test from 0.5 to 12 h. For the leaching time equal to 24 h, the contents of this metal increases. Lead showed a tendency to increase the concentration over the execution time of leaching test from 15 to 25 mg·kg<sup>-1</sup>. Zinc, like lead, showed an increase to the highest concentration with increasing execution time of the leaching test. It achieved the highest concentration after 24 hours of leaching test duration.

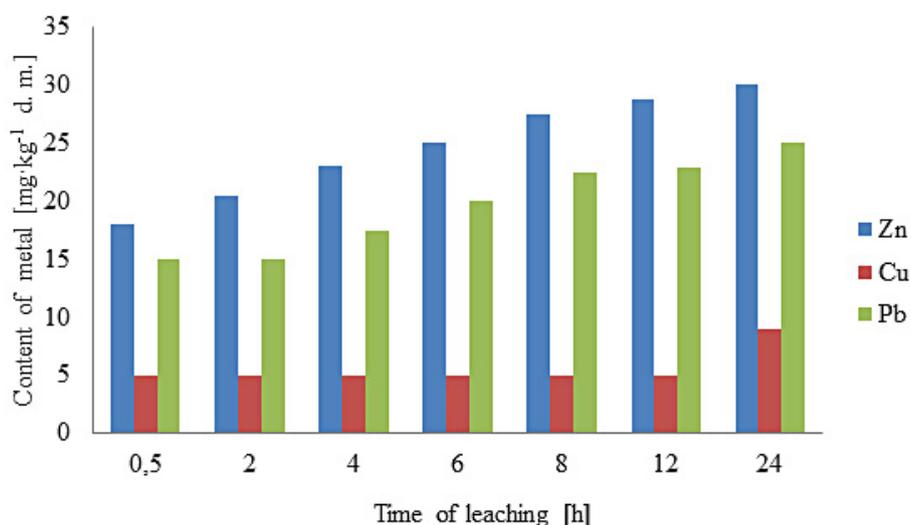
Effects of selected organic compounds with a potential capacity of complexation the metals on the solubility of Cu, Pb and Zn in anaerobic conditions

One of the effective ways of reducing the solubility of heavy metals is the use of probing

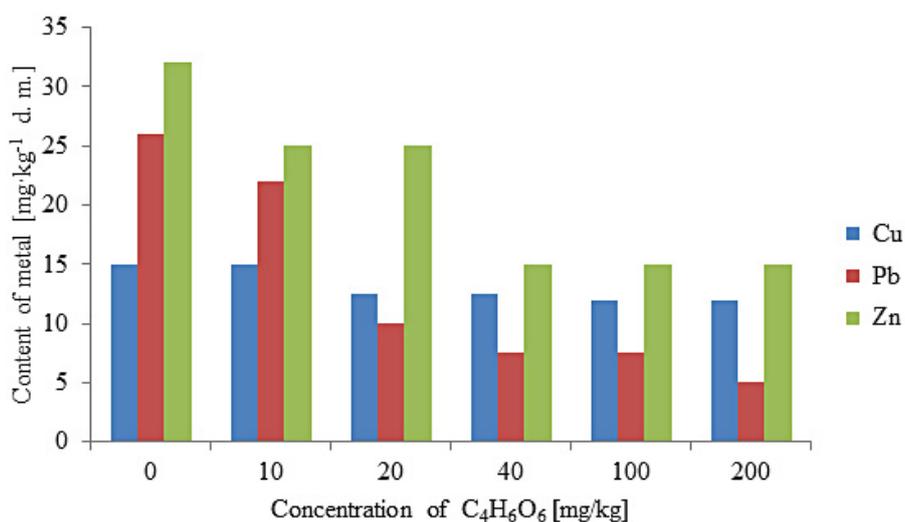
by using specific groups of organic compounds, obtained by chemical synthesis or isolated from natural substances. For complexation compounds tartaric acid, citric acid, glucose were used. For complexation compounds of natural origin may be classified as humic substances. In order to determine the effect of selected organic compounds with a potential capacity of complexation of metals on the solubility of Cu, Pb and Zn in anaerobic conditions, the fly ash made with the addition of complexation reagents i.e. tartaric acid, citric acid and glucose. The results of the concentrations of studied metals in the soluble forms in fly ash containing tartaric acid in the concentration range 10–200 mg dm<sup>-3</sup>, the obtained after applying the TCLP test are shown in Figure 8. The presence of tartaric acid affects the concentration of the form soluble forms of Pb. Namely, for Zn there was an increase in the concentration of metal in relation to the concentration of the metal in the soluble forms in the ash without tartaric acid, whereas for Pb it was reduced. The concentration of the soluble forms of Cu in the fly ash throughout the range of concentrations C<sub>4</sub>H<sub>6</sub>O<sub>6</sub> is the same.

Figure 9 illustrates the changes in concentrations of metals in the soluble forms contained in the ashes under the influence of different concentrations of citric acid in the range of 10-100 mg·dm<sup>-3</sup> introduced into the fly ash. The addition of citric acid to the fly ash caused an increase in the concentration of soluble forms of Zn in the ash as compared with to the fly ash no the complexation substances addition. This is different in the case of the other elements; for Cu concentration in the soluble forms decreased by half the value of the concentration of copper in the soluble forms in the fly ash with no citric acid addition, whereas for Pb it was equal to zero. Regardless of the value of the concentrations C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, the quantity of soluble forms of metal in the ash remains the same. Generally, the presence of citric acid is beneficial for leaching of Zn, as compared to other elements.

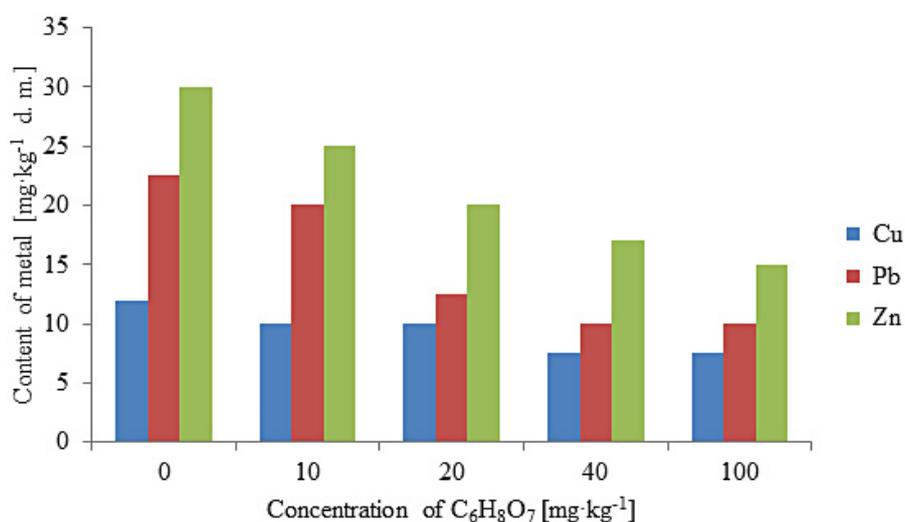
The concentrations of the investigated metals in solutions obtained after leaching containing fly ash with addition of 200 mg·dm<sup>-3</sup> of glucose by TCLP procedure revealed no significant results. Comparing the results obtained with the concentrations of metals in the soluble form of fly ash with no glucose addition, an increased concentration of Zn can be seen. The contents of Cu and Pb in soluble forms has not changed significantly.



**Figure 7.** Relation between a time of leaching and the concentration of Zn, Cu and Pb in the soluble forms in the fly ash having a grain diameter  $\phi = 1.5$  mm, obtained by leaching with 2.5%  $\text{CH}_3\text{COOH}$ , pH 2.5



**Figure 8.** Changes of concentrations of soluble forms of Zn, Cu and Pb in the fly ash with the addition of tartaric acid, obtained by the use the TCLP test



**Figure 9.** Changes of concentrations of soluble forms of Zn, Cu and Pb in the fly ash with the addition of citric acid, obtained by the use the TCLP test

## CONCLUSIONS

1. The contents of metals in the soluble forms received after leaching the fly ash using the standard leaching testing exceeds the permissible concentrations of Cu, Pb and Zn in relation to the standards for waste entering into waters or into the ground.
2. Considering, the solubility and mobility of heavy metals the fly ash can pose a threat to water and soils in the area of storage and storage creates the risk of inorganic contamination of the environment.
3. With regard to the ageing of inorganic waste, such as fly ash, it should be pointed out that monitoring both the composition and mobility of heavy metals present in the fly ashes is important.
4. Depending on the chemical composition of the leaching solutions and the diameter of the grains examined fly ash, exhibits a different level of mobility of Cu, Pb and Zn in the soluble forms depending on the conditions of the leaching process.
5. On the basis of the conducted research it can be concluded that the optimal method for assessment of the impact of surface ash storage on the environment is the TCLP test made under the following conditions: particle diameter ash  $\phi = 1.5$  mm; pH 2.5% CH<sub>3</sub>COOH = 2.5; L:S ratio = (20) 50: 1; leaching time = 24 h.
6. In addition, it was found that the presence of organic compounds with a potential complexation of metals has a significant impact on the concentration of Cu, Pb and Zn in soluble forms. Generally, the addition of tartaric or citric acid in the fly ash causes a decrease in the concentrations of metals in the soluble forms, with regard to ash without the above mentioned acids added after being applied of the TCLP test in optimal conditions.
7. Presence of glucose in fly ash caused an increase in the concentration of the soluble forms of Zn received by TCLP procedure compared to the concentrations of the metal in the soluble forms in fly ash with no glucose addition. The contents of Cu and Pb in the soluble forms has not been a significant change.

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