

Grzegorz WIELGOSIŃSKI¹*, Dorota WASIAK¹ and Alicja ZAWADZKA¹

THE USE OF SEQUENTIAL EXTRACTION FOR ASSESSING ENVIRONMENTAL RISKS OF WASTE INCINERATION BOTTOM ASH

WYKORZYSTANIE EKSTRAKCJI SEKWENCYJNEJ DO OCENY ZAGROŻEŃ DLA ŚRODOWISKA POWODOWANYCH PRZEZ ŻUŻLE I POPIOŁY Z PROCESU TERMICZNEGO PRZEKSZTAŁCANIA ODPADÓW

Abstract: Thermal treatment of waste is one of the ways of their processing. It is commonly used in most developed countries of the European Union. Major by-products of the combustion processes are slag and bottom ash. In the majority of EU countries bottom ash and slag are used as a priming for road construction. In Poland slag and bottom ash from incineration process are stabilized with the addition of cement and some polymers and are landfilled as wastes. In accordance to Polish law, depending on the leaching of heavy metals from fly ash and slag after thermal treatment of waste can be regarded as both hazardous and non-hazardous wastes. At present work sequential extraction methods described in the literature: Tessier's method, van Herck's method and BCR method were compared experimentally with the results of using Swiss standard TVA.SA.1991 and European standard EN 12457 and total concentration of metals in sample analyzed after complete digestion of sample. The study sample was bottom ash from the medical waste incineration plant.

Keywords: waste incineration, slag and bottom ash, environmental impact, heavy metal leaching, sequential extraction

Introduction

The municipal waste management system in Poland differs in a fundamental way from the system generally functioning in the most developed countries of the European Union and is not compatible with the EU strategy for waste management. This strategy assumes that the primary emphasis should be placed on the avoidance of the generation of waste, in the second place on the processes of recovery and recycling (recycling of raw materials and energy) while waste disposal, including storage, should be considered as a last resort. Unfortunately, we still have a long way to reach this model. At present the dominant method of dealing with waste management in Poland is disposal - but the amount of landfilled waste is steadily decreasing, while the volume of recycled and recovered waste is growing.

¹ Lodz University of Technology, ul. Wolczanska 175, 90-924 Lodz, Poland, phone +48 42 631 37 95, fax +48 42 636 81 33, email: grzegorz.wielgosinski@p.lodz.pl, 800033@edu.p.lodz.pl

* Corresponding author: grzegorz.wielgosinski@p.lodz.pl

Incineration is one of the methods of waste processing. It is used widely in the most developed countries of the European Union, in Poland we have at present only one small municipal waste incineration plant (in Warsaw) and actually we have just started the implementation of the incineration plants construction program. Originally it was assumed that by 2013 twelve thermal waste treatment plants would be built in Poland, within the framework of the Operational Programme for Infrastructure and Environment, today we already know that there will be maximum 6 plants started up till the end of 2015 with a total capacity of about 1 million Mg/year. The plans for the years 2015-20 indicate the need to build about 20-30 plants (according to the regional waste management plans) where realistically speaking there will be constructed about 10 plants with a total capacity of about 1.5-2.0 million Mg/year. Moreover, at present in Poland there are about 30-35 incineration plants for hazardous, including medical waste and 10 incineration plants for sewage sludge. All of these are the source of secondary waste from the incineration process which requires treatment and disposal.

Incineration causes a significant reduction of the amount of waste deposited in landfills and allows the recovery of energy. The main by-products of the incineration process are slag and bottom ash. The technologies of waste incineration that are used today allow the reduction up to approx. 20% of the original volume of waste without processing of slag and approx. 5% with slag processing. The reduction of mass amounts respectively 70 and 90-95%. At the same time the secondary waste from the incineration process contains considerable amounts of heavy metals and therefore it is regarded by many as hazardous for the environment. These make usually about 0.1-0.3% of the total mass of incineration waste. In most EU countries slag and ashes are used economically for example as ballast for the construction of roads. In some countries *eg* in Austria such waste is considered hazardous and is deposited in special landfills. Recently, however, other use of slag and ashes is often mentioned - they really contain significant amounts of metals which can be recovered. For example, it is estimated that in all the ashes and slag from nearly 500 operating waste incineration plants in Europe there is about 200 000 Mg of aluminum and the concentration of zinc (0.8-1.2%) is comparable to the concentration of this element in the zinc ore. In Poland, slag and ashes from thermal processing are stabilized with the addition of cement and polymers and landfilled as waste.

In Poland, in accordance with the applicable law, depending on the elution of heavy metals from slag and ash, slag and ashes from thermal waste processing can be considered as hazardous and other than hazardous waste. For example, slag and ash from the only Polish municipal waste incineration plant in Warsaw are subject to a solidification process on site (by Swiss technology Geodur®) with the use of cement and polymers.

Methods for the assessment of environmental hazards caused by metals

The applied in Poland procedure (according to the Regulation of the Minister of Economy on the requirements for the process of thermal treatment of waste [1]) of metals elution tests involves waste elution with distilled water (a ratio of 10 dm³ of water per 1 kg of waste). It complies with the standard PN-EN 12457.

According to the above-mentioned methodology, the analytical sample of mass corresponding to approx. 0.090 kg of dry matter is placed in a bottle (from PP), a suitable amount of distilled water is added to ensure that the ratio of the liquid to the solid phase

(L/S) is equal to 10 dm³/kg, is mixed for 24 hours, and then the content is filtered and the resulting eluate is tested for the concentration of certain components.

In the United States two elution tests are used: EP toxicity test or TCLP (Toxicity Characteristic Leaching Procedure) [2]. According to EP toxicity test the sample is ground to grain size about 9.5 mm and is subjected to elution with deionized water of pH 5.0±0.2 adjusted with 0.5 M solution of CH₃COOH and agitated for 24 hours. In TLCP method the sample of 5 g is flooded with 96.5 cm³ of water and the pH is adjusted to 5.0 with 1 M of HCl solution. The sample is shaken on a rotary shaker for about 18±2 hours at room temperature. The suspension is then filtered through a borosilicate fiber filter and the eluate is analyzed.

In Switzerland a leaching test developed by the local Federal Office for the Environment Protection (BAFU) is used - this is the TVA.AS.1991 [3-6] standard, according to which the waste is mixed with carbonated water at a mass ratio of water to waste (L/S) 10:1. Through the water CO₂ (pH = 4.0-4.5) is passed continuously. Two extracts are obtained: the first one after 24 hours extraction with continuous water carbonation, the second one after next 24 hours extraction under the same conditions [3, 6]. The assessment of the toxicity of waste according to TVA.AS.1991 will be made as follows: the mean calculated concentration of each leaching stage for individual hazardous substances must be within the allowable concentration range to be discharged to a sewerage system (according to standards), the maximum amount of leached substance after 24 hours should not be greater than 0.05%, the concentration of hazardous substances in the eluate samples after 24 and 48 hours should be decreasing (in the second eluate the concentration of hazardous substances can not exceed the concentration values measured in the first eluate) [3, 6]. The leaching test is performed in such a way that the test sample is put into the distilled water saturated with carbon dioxide so that it does not touch the walls of the vessel and the water is still saturated with carbon dioxide, while ensuring that the sample is rinsed uniformly. This procedure is repeated twice always with a fresh portion of water [3, 6].

Other methods to assess the environmental hazards are used in other countries - such as Germany, Sweden and the Netherlands. General principles of the extraction methods are presented in Table 1.

Table 1

Comparison of elution methods used in different countries

Test according to	EN 12457-3	EN 12457-2/ DIN EN 12457-4 [7]	TVA.AS.1991 [3]	NEN 7340 [8]
Country	EU	Germany	Switzerland	Holland
Granulation [mm]	10	Without sieve analysis	Without sieve analysis	4
Eluent	Distilled water	Distilled water	Distilled water saturated with CO ₂	solution HNO ₃ concentration 1 mol/dm ³
Amount of fraction	2	1	2	7
L/S [kg/kg]	1-2 2-8	10	10	0.1-10
Elution time	1-6 h 2-18 h	24 h	2 x 24 h	16 days
Elution	mixing	mixing	saturation CO ₂	mixing

Sequential extraction

The research shows that such procedure is not sufficient. The total content of metals defines by the degree of contamination only and it does not tell us anything about their bioavailability, and thus we do not know anything about the hazards to the ecosystem [9-12]. Methods based on sequential analysis allow for a wider assessment of heavy metals impact on the environment. Fractionation enables the separation of metal forms from solid samples, it is based on the classification of an analyte or a group of analytes from a given sample by physical and chemical properties [13]. This principle is used in the sequential extraction, which allows the separation of the trace metal into chemical forms, which can be released into a solution in different conditions of increasing activity [14]. The general principle of sequential extraction involves the treatment of the same sample with different solutions of increasing aggressiveness [15, 16]. The extracts are separated by centrifugation and the solid part is subjected to the next extraction stage using an increasingly stronger extractants. In the next fractions there are used such mechanisms as: physical and chemical solubility in water, ion exchange, oxidation and reduction as well as complexation. The following fractions can be distinguished:

- water-soluble fraction,
- exchange fraction,
- hydroxide fraction,
- fraction bound to the organic substance,
- residual fraction.

Water-soluble fraction is the least often isolated fraction due to lack of buffer capacity and high solubility of organic compounds, which results in a small extraction effect. In the exchange fraction a process of adsorption and desorption are used, for the extraction there are used neutral salts such as acetates. In the hydroxide fraction, basing on the co-precipitation of metals in Mn and Fe oxides, there are used reductive properties of compounds. In the fraction bound to the organic substance there are used oxidation reagents and chelating agents which cause strong complexation of metals. Sulfide fraction is based on the dissolution of carbonate minerals. The residual fraction determined after complete mineralization is *eg aqua regia*.

The most mobile metal fractions separated in the process of sequential extraction include those that were leached in the first two stages. However, the greatest hazards to the environment are the metals of an ion exchange fraction, because their elution takes place as a result of contact with water. The carbonate fraction is also relatively easy to elute, but only under conditions of low pH which can be caused by acid rain precipitation. Hydroxyl fraction is moderately mobile and possible only under adverse environmental conditions, *eg* caused by oxygen deficiency. Virtually immobile organic fraction may be started in the intensified aerobic conditions. The residual fraction is not dangerous for the ecosystem because it is virtually immobile [14, 17-20].

Many methods of sequential extraction were described. In practice, the most commonly used extraction technique is a five-step scheme proposed by Tessier and co-workers in 1979 [19] who distinguished and defined five chemical fractions: ion exchange fraction in which metals being adsorbed on the surface of a solid, due to the changes in ionic composition of water, pass to the solution easily; carbonate fraction where metals are bound with carbonates; oxygen fraction contains metals co-precipitated with the carbonates and those

which are in the form of carbonates, these metals are soluble in weakly acidic environment ($\text{pH} \approx 5$) and are released from the soil due to reducing pH of the solution; hydroxide fraction comprises metals bound with hydrated iron and manganese oxides, this fraction is very sensitive to changes in redox potential, sludge can be dissolved and metals can migrate from the soil to the solution and the organic fraction containing metals bound with organic matter which were adsorbed on the surface of organic matter and metals embedded in this matter. These metals are not available for neutral solutions. However, with the ongoing natural process of aerobic or anaerobic decomposition, mineralization of sludge, these metals easily pass to solution or to other fractions. The last fifth fraction is the residual fraction (that is metals are permanently bound with minerals), in this fraction metals are incorporated into the crystalline structure of primary and secondary minerals which are part of the soil. This fraction comprises immobilized metals under natural conditions. Compounds of these metals are passive and biologically unavailable so they are not a real threat to the environment [1, 16, 21].

The second commonly used method is the van Herck [22] method. It provides the division of heavy metals leaching into 7 individual fractions I - soluble in water which include easily soluble metal salts; II - calcium-ion-exchange, includes metals reacting with calcium ions in exchange reactions; III - acid-soluble metals from easily soluble acid salts; IV - oxidizing, includes metals included in organic and oxidizing compounds; V - organic, includes mainly metals bound in iron and manganese oxides, soluble under reducing conditions; VI - medium complexing, includes metals contained in crystalline oxides; VII - residual, metals that were not leached in the previous fractions [22].

Within the Standard Measurement and Testing Programme (SM&T, Community Bureau of Reference - BCR [23-26]), a new three-step sequential extraction method was developed for the purpose of testing the soil and sediment. In the first carbonate and ion exchange fraction the extraction is performed with a solution of 0.11 M AcOH (acetic acid), the oxygen fraction - extraction is performed with 0.1 M $\text{NH}_2\text{OH HCl}$, when $\text{pH} = 2$, the organic fraction - is performed with a solution of 30% H_2O_2 , when $\text{pH} = 2$ and 1 M NH_4OAc (ammonium acetate) [25]. It was used for the fractionation of metals in dust and ashes. BCR standard procedure allows to extract metals bound with three fractions: acid soluble metals bound with carbonates, reducible metals bound with iron and manganese hydroxides, oxidative metals bound with the organic material. In this procedure it is possible to introduce additionally the fourth fraction - residual, obtained during the extraction by means of aqua regia [27-29]. The comparison of Tessier, van Herck and BCR procedures are summarized in Table 2.

Comparison of sequential extraction methods with the methodology according to EN 12457

The purpose of the research presented in this paper is to investigate the extent to which ashes and slags, subject to sequential extraction and leaching according to PN-EN 12457, are a source of emissions of heavy metals to the environment. All of the studies, the results of which are shown below, were carried out using the same ash from incineration plant. The ash was brought to air-dry state, sieved through a screen, dried to solid mass at 105°C then it was stored in PP containers and used for the test.

Table 2

Comparison of sequential extraction procedures

Tessier procedure	Van Herck procedure	BCR procedure
F-0 - fraction soluble in water and containing metals in the form of compounds which may be dissolved in the rain water	F-I - extraction with demineralized water for 3 h at room temperature with continuous stirring	-
F-I - soluble fraction, extraction with 1 M MgCl_2 solution at pH = 7.0 for 1 h, at room temperature with constant stirring	F-II - soluble fraction. extraction in a solution of 0.5 M $\text{Ca}(\text{NO}_3)_2$ at pH = 7.0 for 1 h with continuous stirring at room temperature	F-I - ion exchange and carbonate fraction, extraction with 0.11 mol/dm ³ of acetic acid for 16 h at 22±5°C with constant stirring
F-II - exchange fraction, extraction with 1 M sodium acetate solution acidified with acetic acid to pH = 5.0 for 5 h at room temperature with constant stirring	F-III - exchange fraction, extraction with 0.5 M CH_3COOH , with correction of pH to 2.5 with 12 M HCl, extraction time 3 h with continuous stirring at a temperature of 95±3°C F-III - exchange fraction, extraction with 1.9 M NaOCl, pH correction to 2.5 with 12 M HCl, extraction time 3 h, continuous stirring at 95±3°C	
F-III - hydroxide fraction, extraction with a solution of 0.04 M Na_2OH HCl for 6 h, at room temperature with continuous stirring	F-IV - soluble metals fraction, dissolution in 0.175 M ammonium oxalate + 0.1 M oxalic acid, acidified with 2 M HCl to pH = 2.5, extraction time of 3 h, with continuous stirring	F-II - Hydroxide fraction, extraction with 0.5 mol/dm ³ $\text{Na}_2\text{OH} \cdot \text{HCl}$, during 16 h, with continuous stirring at pH = 2 (with supplied HNO_3)
F-IV - fraction bound to the organic substance, subject to dispersion in 0.02 M of HNO_3 solution, 30% H_2O_2 solution (at pH corrected to 2.0 with HNO_3) and adding $\text{CH}_3\text{COOHN}_4$, extraction time - successively 2 h, 3 h and 0.5 h	F-V - extracted metals fraction, extraction with a 0.1 M of disodium edetate solution Na_2EDTA + 0.3 M hydroxylamine hydrochloride solution $\text{NH}_2\text{OH} \cdot \text{HCl}$, extraction time 5 h in a water bath 96±3°C, stirring from time to time	F-III - organic fraction 1) 2 h in water bath at temp. 85±2°C dispersion H_2O_2 at pH = 2 2) 16 h in waterbath at temp. 22±2°C, continuously stirring, dispersion 1.0 mol/dm ³ $\text{NH}_4\text{OAc}(\text{CH}_3\text{COOHNH}_4)$, at pH = 2 (with supplied HNO_3)
F-V - residual faction, including permanent forms of metal which are not subject to dissolution or dispersion, mineralization with mixture $\text{HCl} + \text{HNO}_3$ (1:3)	F-VI - residual fraction, including metals dispersed in hot acids - mixture of HF, HCl and HClO_4	F-IV - residual fraction includes dispersed metals mixture of concentrated hot acids HNO_3 and HCl

The following sequential extractions and leaching were performed according to the following methods:

- 1 - sequential extraction carried out in accordance with Tessier procedure [19],
- 2 - sequential extraction carried out according to van Herck procedure [23],
- 3 - sequential extraction carried out in accordance with the BCR procedure [25],
- 4 - extraction carried out in accordance with TVA.AS.1991 [3],
- 5 - leaching carried out in accordance with PN-EN 12457 [30].

Each experiment was performed in three parallel samples using 10-gram initial ash samples and a reagent blank sample. After extraction, the suspension

was settling for 15 minutes. Then the eluate was filtered through a membrane filter of 0.45 μm with a filtering device. The obtained eluates were stored in accordance with the requirements of DIN EN ISO 5667-3. The composition and concentrations of extraction solutions are shown in Table 3. Reagents pure for analysis class and reference standard solutions for AAS were used.

The study of the content of heavy metals in the environment complex matrix requires its mineralization leading to the decomposition of a complex to simple inorganic compounds [31-33]. In the study wet mineralization was applied and the following chemical oxidants were used: hydrogen peroxide, inorganic acids and their mixtures. This process was carried out in an open system. Wet mineralization enabled to avoid losses caused by volatilization of specific components of the sample, which takes place during dry mineralization [34]. The applied analytical technique FAAS (flame technique atomic absorption spectrometry - Flame Atomic Absorption Spectrometry) enables precise determination of concentrations of heavy metals that can migrate in the eluate to the environment. This is extremely important from the point of view of the assessment of the risk of contamination [35].

Concentrations of heavy metals in post-extraction and post-mineralization solutions were determined by FAAS, the assay results were corrected for a reagent blank sample and converted to dry weight of the ash.

On the basis of the results of analytical determinations of heavy metals content in filtrates and the volumes of filtrates, the content of metals extracted in the individual fractions was determined and then the percentage of metal content in the individual fractions was calculated. The results are shown in Table 3.

Table 3

Summary of sequential extraction test results

Fraction	Elution of individual elements in a given fraction [in %]								
	Pb	Cr	Co	Cu	Mn	Ni	V	Zn	As
Van Herck procedure									
Fraction 1	2.39	1.33	0.96	1.92	0.83	2.26	1.85	4.32	2.68
Fraction 2	5.53	2.96	1.08	4.47	0.92	6.64	2.07	6.12	3.00
Fraction 3	19.31	6.80	5.16	9.07	2.40	14.34	5.39	3.15	13.10
Fraction 4	21.39	7.09	13.10	34.83	10.33	8.80	21.04	10.04	36.58
Fraction 5	2.23	3.46	20.31	5.52	22.60	7.58	6.67	14.96	13.70
Fraction 6	49.15	78.36	59.40	44.19	62.93	60.38	62.97	61.41	30.93
Tessier procedure									
Fraction 1	2.69	1.08	0.78	2.37	0.88	1.68	0.29	2.96	4.46
Fraction 2	4.12	2.05	9.21	4.19	1.04	4.40	0.34	3.83	5.26
Fraction 3	31.40	7.19	2.31	18.49	2.60	21.28	87.84	3.05	13.17
Fraction 4	61.06	88.98	86.28	71.82	93.88	72.15	11.01	83.37	68.99
Fraction 5	0.73	0.70	1.42	3.13	1.60	0.50	0.52	6.79	8.12
BCR procedure									
Fraction 1	0.80	0.29	0.18	0.38	0.29	0.51	0.56	0.33	6.88
Fraction 2	1.29	0.29	0.70	1.25	0.40	1.56	0.78	0.20	9.61
Fraction 3	5.83	0.38	2.03	2.48	0.53	16.25	1.03	0.34	12.66
Fraction 4	92.08	99.05	97.09	95.89	98.77	81.68	97.62	99.14	70.85

The variability within the laboratory is set at 18%, for a confidence level of 95% and $k = 2$ as recommended by the Guide to the Expression of Uncertainty in Measurement

(GUM) [36]. The uncertainty of the results of leaching tests include: the origin of the material or its variation during the incineration process, the differences in the representativeness of the sample, the initial preparation of the sample, study of leaching and extraction, variability of experimental conditions and the analysis of chemical compounds in the eluate that is, the uncertainty of the determination of elements. Then the amount of total extracted metal from the sample for each sequential extraction procedure were compared; the procedures were compared with each other and with the results of the extraction of metals from ash samples according to PN-EN 12457 and TVA.AS.1991. The results of these comparisons are summarized in Table 4.

Table 4

Comparison the amount [mg/kg d.s.] of the determined metal in samples using sequential extraction in comparison with the determined amount using the methodology described in standard PN-EN 12457 and TVA.AS.1991

Method	Pb	Cr	Co	Cu	Mn	Ni	V	Zn	As	Total
Van Herck procedure	1 069.9	1 799.3	265.4	2 004.7	308.7	559.4	137.7	2 394.9	95.1	8 635.1
Tessier procedure	877.7	1 873.6	190.1	1 391.1	168.5	540.4	516.5	2 609.3	33.3	8 200.4
BCR procedure	686.4	2 147.1	181.2	1 349.1	114.9	458.2	59.2	2 733.8	4.8	7 734.7
Standard PN-EN 12457	96.4	99.5	9.3	189.7	9.3	43.2	9.3	373.6	9.3	839.7
Standard TVA.AS	136.2	246.9	16.6	213.5	16.6	176.2	16.6	614.9	16.6	1 454.2
Full mineralization	852.9	2 306.8	257.5	1 453.1	313.9	556.5	140.5	2 414.0	47.2	8 342.4

Summary and conclusions

The assessment of the risks to the environment caused by slag and ashes from waste incineration involves among others determination of the degree of release of heavy metals to the environment. The results of sequential extraction make it possible to make such an assessment. In Tessier procedure, metals determined in fraction IV and V are considered as practically non-releasable to the environment, in the procedure of van Herck - metals identified in fraction V, and the procedure of BCR - metals in the last IV fraction.

The analysis of the results leads to the conclusion that there are significant differences in release between the individual metals. Lead and arsenic are most easily released to the environment (the smallest share in non-releasable fractions). Of course on the one hand it depends on the properties of an element and on the other hand - on the form (salt, oxide, etc.) in which it appears. For example, high releasability of lead to the environment is probably due to the frequent presence of lead in the slag and ash from waste incineration process in the form of chlorides.

There are also considerable differences between the results obtained using different sequential extraction procedures. In general, the results using the procedures of van Herck and Tessier give quite similar results, but the results of the BCR procedure are significantly different from other results. It seems, therefore, that this procedure gives too optimistic results and should not be used.

Significant differences in the amount of determined metals using various procedures indicate that the applied methods are not ideal and each of them is burdened with a certain error, resulting from the application of different solutions as well as different extraction times and conditions.

Analyzing the obtained results it can be concluded that in the studied ash from incineration of medical waste the share of non-releasable fraction to the environment ranges from 40 to 80%. This result is quite good, but far from the possibility of recognizing the ash as safe for the environment. This means that the tested ash should be subjected to stabilization processes before sending it to the landfill in order to reduce significantly heavy metals leaching.

The results shown in Table 4 also indicate clearly that the applicable method in Poland (as described in Regulation of the Minister of Economy [1]) in accordance with PN-EN 12457 standard should not be used, because it does not present a real ability to release metals to the environment. Swiss standard TVA.AS.1991 is not very useful to assess the hazards to ecosystems by ashes and slags either.

The comparison of the results allows to recommend the method of Tessier, as on the one hand the simplest and on the other giving good and reproducible results. However, this recommendation applies to the study the leaching of heavy metals from slag and ash by sequential extraction only. For other matrices (*eg* sewage sludge, soil samples, etc.) the application of another method of assessment of leaching, such as the use of sequential extraction, may give better results.

References

- [1] Rozporządzenie Ministra Gospodarki z dnia 21 marca 2002 roku w sprawie wymagań dotyczących prowadzenia procesu termicznego przekształcania odpadów (DzU 2002, Nr 37, poz. 339 z późn. zm.).
- [2] US EPA 1311 Leaching Test TCLP (toxicity characteristic leaching procedure).
- [3] Technische Verordnung über Abfälle - TVA AS 1991 vom 10 Dezember 1990. Der Schweizerische Bundesrat.
- [4] Yang R, Liao WP, Wu PH. Basic characteristics of leachate produced by various washing processes for MSWI ashes in Taiwan. *J Environ Manage.* 2012;104:67-76. DOI 10.1016/j.jenvman.2013.03.0008.
- [5] Kim YJ. Comparative Study of Leaching Characteristics of Industrial Sludge and Fly Ash using KSLP and TLPC Techniques. PhD. Department of Environmental Engineering, Kyungpook National University.
- [6] Dąbrowska L. Fractions of heavy metals in residue after incineration of sewage sludge. *Environ Protect Eng.* 2013;39:105-113. DOI 10.5277/EPE130210.
- [7] DIN EN 12457-4. Januar 2003. Charakterisierung von Abfällen - Auslaugung; Übereinstimmungsuntersuchung für die Auslaugung von körnigen Abfällen und Schlämmen - Teil 4: Einstufiges Schüttelverfahren mit einem Flüssigkeits-/Feststoffverhältnis von 10 l/kg für Materialien mit einer Korngröße unter 10 mm (ohne oder mit Korngrößenreduzierung); Deutsche Fassung EN 12457-4:2002.
- [8] NEN 7340:2000 Uitloogkarakteristieken van vaste grond- en steenachtige bouwmaterialen en afvalstoffen - Karakteriseringsproeven - Algemene aanwijzingen.
- [9] Ahnstrom ZS, Parker DR. Development and assessment of a sequential extraction procedure for the fractionation of soil cadmium. *Soil Sci Society of America J.* 1999;63:1650-1658.
- [10] Dahl O, Nurmesniemi H, Pöykiö R. Sequential extraction partitioning of metals, sulfur, and phosphorus in bottom ash from a coal-fired power plant. *Inter J Environ Anal Chem.* 2008;88:61-73. DOI: 10.1080/03067310701461615.
- [11] Pöykiöet R, Rönkkömäki H, Nurmesniemic H, Tennod T, Paamad L. Extractability of heavy metals in cyclone ash. *Proc of the Estonian Academy of Sci.* 2008;57:100-106. DOI: 10.3176/proc.2008.2.04.
- [12] Kennedy VH, Sanchez AL, Qughton DH, Rowland AP. Use of single and sequential chemical extractants to assess radionuclide and heavy metal availability from soils for root uptake. *Analyst.* 1997;122:89-100.

- [13] Świątlik R, Trojanowska M, Siwiec J. Formy występowania metali w popiołach lotnych. Ochrona powietrza w teorii i praktyce. Koniecznyński J, editor. Zabrze: Instytut Podstaw Inżynierii Środowiska Polskiej Akademii Nauk w Zabrzu; 2008.
- [14] Szumska M, Gworek B. Metody oznaczania frakcji metali ciężkich w osadach ściekowych. *Ochr. Środow. i Zasob. Natural.* 2009;41:42-58.
- [15] Kalemekiewicz J, Socho E. Ekstrakcja sekwencyjna metali z próbek środowiskowych. *Wiadomości Chem.* 2005;40:601-607.
- [16] Pérez-Cid B, Lavilla I, Bendicho C. Analytical assessment of two sequential extraction schemes for metal partitioning in sewage sludge. *Analyst.* 1996;121:1474-1884.
- [17] Okoro HK, Fatoki OS, Adekola FA, Ximba BJ, Snyman RG. A review of sequential extraction procedures for heavy metals speciation in soil and sediments. *Open Scientific Reports.* 2012;1:181. DOI: 10.4172/scientificreports.181
- [18] Rauret G, Rubio R, Lopez-Sanchez JK. Optimization of Tessier procedure for metal solid speciation in river sediments. *Intern J Environ Anal Chem.* 1989;36:69-83.
- [19] Tessier A, Campbell P, Bisson M. Sequential extraction procedure for the speciation of particulate trace metal. *Anal Chem Acta.* 1979;286:423-42.
- [20] Williams PT. Pollutants from Incineration: An Overview. In: Waste Incineration and the Environment. Hester RE, Harrison RM, editors. Cambridge: Royal Society of Chemistry; 1994.
- [21] Świątlik R, Trojanowska M. Metody frakcjonowania chemicznego stosowane w badaniach środowiskowych. *Monit Środow Przyrod.* 2008;9:29-36.
- [22] van Herck P, Vandecasteele C. Evaluation of the use of a sequential extraction procedure for the characterization and treatment of metal containing solid waste. *Waste Manage.* 2001;21:685-694. DOI: 10.1016/S0956-053X(01)00011-3
- [23] Fernández E, Jiménez R, Lalena AM, Aguilar J. Evaluation of the BCR sequential extraction procedure applied for two unpolluted Spanish soils. *Environmental Pollution.* 2004;131:355-364. DOI: 10.1016/j.envpol.2004.03.013
- [24] Sahuquillo A, Lopez-Sanchez JF, Rubio R, Rauret G, Thomas RP, Davidson CM, et al. Use of a certified reference for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. *Analytica Chimica Acta.* 1999;382:317-327.
- [25] Sutherland RA. BCR®-701: a review of 10-years of sequential extraction analyses. *Analytica Chimica Acta.* 2010;680:10-20. DOI: 10.1016/j.aca.2010.09.016
- [26] Ure AM, Quevauviller Ph, Muntau H, Gripink B. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under auspices of the BCR of the Commission of the European Communities. *Inter J Environ Anal Chem.* 1993;51:135-151.
- [27] Petit MD, Rucondio MI. Sequential extractions for determination of cadmium distribution in coal fly ash, soil and sediment samples. *Anal Chim Acta.* 1999;401:283-291.
- [28] Rauret G, López-Sánchez JF, Lück D, Yli-Halla M, Muntau H, Quevauviller Ph. BCR information reference materials BCR-701.
- [29] Wang CH, Hu X, Chen ML, Wu YH. Total concentrations as fractions of Cd, Cr, Pb, Cu, Ni and Zn in sewage sludge from municipal and industrial wastewater treatment plants. *J Hazard Mater.* 2005;119:245-249. DOI: 10.1016/j.jhazmat.2004.11.023.
- [30] PN-EN 12457-2:2006. Charakteryzowanie odpadów - Wymywanie - Badanie zgodności w odniesieniu do wymywania ziarnistych materiałów odpadowych i osadów - Część 2: Jednostopniowe badanie porcjowe przy stosunku cieczy do fazy stałej 10 l/kg w przypadku materiałów o wielkości cząstek poniżej 4 mm (bez redukcji lub z redukcją wielkości).
- [31] PN-EN 13346:2002. Charakterystyka osadów ściekowych. Oznaczanie pierwiastków śladowych i fosforu. Metody ekstrakcji wodą królewską.
- [32] PN-ISO 8288:2002. Jakość wody. Oznaczanie kobaltu, niklu, miedzi, cynku, kadmu i ołowiu. Metody atomowej spektrometrii absorpcyjnej z atomizacją w płomieniu.
- [33] Ciszewski D. Heavy metal in vertical profiles of the Middle Odra River ower bank sediments. Evidence for pollution changes. *Water Air and Soil Pollut.* 2003;143:81-98.
- [34] Dahlin CL, Williamson CA, Collins WK, Dahlin DC. Sequential extraction versus comprehensive characterization of heavy metal species in brownfield soils. *Environ Forensics.* 2002;2:191-201. DOI: 10.1006/enfo.2002.0090.
- [35] Patrick WH, Verloo M. Distribution of soluble heavy metals between ionic and complexed forms in a saturated sediments as affected by pH and redox conditions. *Water Science & Technol.* 1998;37:165-172.

- [36] GUM - Guide to the Expression of Uncertainty in Measurements. BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML. International Organization for Standardization. Switzerland; 1995.

WYKORZYSTANIE EKSTRAKCJI SEKWENCYJNEJ DO OCENY ZAGROŻEŃ DLA ŚRODOWISKA POWODOWANYCH PRZEZ ŻUŻLE I POPIOŁY Z PROCESU TERMICZNEGO PRZEKSZTAŁCANIA ODPADÓW

Wydział Inżynierii Procesowej i Ochrony Środowiska, Politechnika Łódzka

Abstrakt: Termiczne przekształcanie odpadów jest jednym ze sposobów ich przetwarzania. Głównymi produktami ubocznymi procesu spalania są żużel i popiół paleniskowy. W większości krajów UE są one wykorzystywane gospodarczo. W Polsce żużle i popioły po termicznym przekształcaniu stabilizuje się z dodatkiem cementu i polimerów i składa jako odpad. Zgodnie z obowiązującym prawem, w zależności od wymywalności metali ciężkich, żużel i popioły po termicznym przekształcaniu odpadów mogą być uznawane zarówno za odpady niebezpieczne, jak i inne niż niebezpieczne. W pracy porównano doświadczalnie metody ekstrakcji sekwencyjnej opisane w literaturze: metodę Tessiera, metodę van Hercka oraz metodę BRC. Badaniu poddano próbkę popiołu pochodzącą ze spalarni odpadów medycznych.

Słowa kluczowe: spalanie odpadów, żużle i popioły, oddziaływanie na środowisko, wymywanie metali ciężkich, ekstrakcja sekwencyjna