Determination of forms of heavy metals in bottom ash from households using sequential extraction

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Abstract. The paper presents the results of heavy metals mobility obtained by sequential extraction method and leaching test. Heavy metals in solid waste material occur in different forms and phases that differ in terms of the toxicity, mobility and bioavailability. The sequential extraction analysis is widely used in order to predict the behaviour of heavy metals in a solid material. The sequential extraction methods involve a gradual separation of metals in various forms by means of specific extractants. The material used in the research applied bottom ash derived from households. The results of heavy metals concentrations (Cd, Pb, Ni, Cr, Cu, Zn) in extractable forms and total content in waste were presented. The five forms of heavy metals were determined. The concentrations of heavy metals were analyzed by FAAS. The lowest concentrations of analyzed heavy metals were determined in the exchangeable form. The author observed that the particular elements occurred mainly in forms: zinc and cadmium associated with carbonates, lead and copper in the organic and residual form, chromium and nickel in the residual form. Heavy metals in the residual fraction do not pose a possible environment hazard. The application of speciation analysis of heavy metals in bottom ash provide the means to assess the content of dissoluble forms of metals in water relative to their total content. This information is useful in assessing the migration capabilities of heavy metal ions from waste to the ground-water environment. The potential for the reuse of bottom ash was also discussed in the paper.

1 Introduction

Combustion of fuels in households is accompanied by the production of bottom ashes. They form the by-product of the combustion of hard coal, coke, eco-pea coal or wood in boilers in household heating systems. Bottom ash is also the powder residue left after the combustion of wood, and is gained in a process involving burning wood in a fireplace [1]. Until recently, low-quality fuels and even waste were applied for heat production in households. The most common way of utilizing household ash was based on depositing it in landfills. This formed an additional burden on the environment due to the risk of

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potential leaching of pollutants into the aquatic environment as a result of both atmospheric precipitation and its storage [2]. However, the implementation of EU legal regulations regarding waste management imposed the need to find new approaches to manage bottom ash. In accordance with the guidelines included in the Act on Waste [3], the waste that is generated should be re-used in the greatest possible extent, and ultimately it needs to be disposed of taking into account environmental protection regulations. Waste recycling should be implemented as much as possible in various branches industry and in agriculture. Bottom ash could be applied for the purposes of land rehabilitation and levelling, and for sealing the bottom of a landfill. In addition, this type of waste can be applied in agriculture, horticulture, mining and construction [1]. In case when ashes are re-used, experiments need be carried out to test the composition and leaching of pollutants, in particular heavy metals. In order to identify possible contamination of waste with heavy metals most accurately, their soluble, bioavailable and biologically active forms, also called bioavailable have to be determined. Speciation analysis methods are employed for this purpose (single-stage or sequential extraction). As a result of applying sequential analysis tools, it is possible to determine the concentrations of given elements in a sludge – soil – plant – human food chain [4]. This is very important aspects for the case when waste is designed for use in agriculture.

An important aspect in environmental research is concerned with the forecasting of hazards resulting from the occurrence of heavy metals in various elements of the environment. Heavy metals in solid samples derived from the environment are present in many forms and phases that vary in terms of their mobility, bioavailability and toxicity. The assessment of the impact of heavy metals on the environment needs to involve the identification of the forms of metallic elements in the material, in addition to their total content. A variety of speciation analysis methods, including sequential extraction (SE), are commonly used to predict the behavior of metals present in solid samples. This process involves taking subsequent extractions with solutions of an increasing leaching strength. Gradually, various forms of metals are extracted under the effect of extraction agents. SE provides a manner in which the simulation of environmental conditions can be performed, both with regard to natural and anthropogenic factors. Until recently, SE was only applied in the analysis of soils and sludges. Quite recently, it was applied in the investigations concerned with the composition of solid waste. The use of SE also contributes to the improvement of waste re-use and reduction of its negative impact on the environment [5, 6].

The phenomenon associated with the occurrence of various chemical and physical monatomic forms or molecular configurations of an element in the environment is defined by the notion of speciation. The mobility of metals and their circulation in the environment are determined by bonding forms. Plants and animal organisms are capable of taking up only bioavailable forms of heavy metals. In turn, these could be embedded in tissues and partially excreted along with metabolic products and organic substances [7]. Fractioning forms a concept that is directly related to the speciation analysis. SE forms a process through which a sample is fractionated in accordance with its solubility and reactivity. In this sense, fractionation can be defined as the process of classifying an analyte or a group of analytes from a particular sample according to its physical properties (particle size, solubility) or chemical properties (ability to form bonds, reactivity) [6, 8].

The SE method has been in use since 1979 for the analysis of sediments [9–11] and since then it has also been used for soils [12–14] and waste materials [15, 16]. Currently, the studies reported in the literature apply a variety of extraction techniques. The scheme developed by Tessier et al. [9] can be applied to identify ion-exchangeable, carbonate, oxide (associated with to iron and manganese oxides), organic and residual element and fraction forms. The exchangeable form demonstrates the high mobility of

metals and their availability for plants. The availability of remaining forms to plants and animals is known to be smaller. However, in some conditions (i.e. in the conditions accompanied by low pH, fluctuations in the oxidation and reduction potential), carbonates and oxides can complement the soluble and exchangeable forms. The metals associated with the organic matter can also be available to plants in the conditions when their oxidization is promoted [7, 17]. Another common method of speciation analysis applies *Community Bureau of Reference* (BCR) technique [18, 19]. In this technique, four stages are identified, whose goal is to identify and measure the content of mobile metals as well as the ones bound in carbonate forms (mobile), identification and measurement of metals associated with amorphic iron and manganese oxides (prone to reduction), identification and measurement of the organometallic and sulphide fraction (prone to oxidation) as well as mineralization of the residual fraction by subjecting it to action of concentrated acids with the purpose of identifying and measuring of metals associated with silicates (immobile).

2 Material and methods

The research material applied bottom ash derived from households in one of the communes in the Opole Province in Poland. Quartering of waste derived from a landfill site was applied to provide the material use in the tests. In a laboratory, a representative sample with a weight of 2 kg was prepared from the material, from which test batches were subsequently taken. With the purpose of determining the total content of heavy metal, ash mineralization was performed by use of concentrated HNO_3 and HCl acids in the ratio of 1:3. The samples were digested in a microwave oven in accordance with the guidelines provided by the manufacturer of the microwave mineralizer. The determination of the forms of the heavy metals in the waste applied a sequential extraction based on the method developed by Tessier et al. [9]. The diagram of the sequential extraction applied for metal fractioning of the examined ashes is presented in Table 1. It contains the types of the extractants applied in the particular stages of the procedure, along with the duration of sample agitation and details of the temperature.

The particular stages of the sequential extraction were performed in centrifuge tubes and the samples were shaken on a horizontal shaker. After each stage of the experiment, the samples were subjected to centrifuging over the period of 30 minutes at the rotational speed of 10000 revs/min. The clear supernatant was carried in a pipette to a beaker and used for further analyses. The residue left in the tube was rinsed with demineralized water and subjected to another round of centrifuging. Subsequently, the solution was separated from the supernatant and combined with the first batch of the extract.

The concentrations of heavy metals (Cd, Pb, Ni, Cr, Cu, and Zn) were determined in the resulting extracts and mineralizers by application of the Flame Atomic Absorption Spectrometry method (FAAS).

The comparison of the concentrations of individual heavy metal forms with their total content determined independently formed the way in which the reliability of results could be evaluated [20, 21]. The conformity of the total metal content (T) in the waste with the cumulative metal concentrations in the individual fractions (from F1 to F5) was also verified. The level of the conformity was calculated according to equation 1:

$$Conformity = (F1+F2+F3+F4+F5/T) \cdot 100 \quad [\%] \tag{1}$$

Table 1. Sequential extraction procedures [9].

Form/fraction	Condition of extraction and extractant
F1-exchangeable	Stage 1
	8 ml 1M NaOAc, pH 8.2
	continuous shaking 1h
	temperature 25°C
F2-carbonate	Stage 2
	8 ml 1M NaOAc, pH 5
	continuous shaking 5h
	temperature 25°C
F3-oxide	Stage 3
	20 ml 0.04M $NH_2OH \cdot HCl$ in 25%NOAc
	periodic shaking 5h
	temperature 96 ± 2°C
F4-organic	Stage 4
	1) 3 ml 0.2M HNO_3 + 5 ml 30% H_2O_2, pH 2
	periodic shaking 2h
	temperature 85 ± 2°C
	2) 3 ml H_2O 30%, pH 2
	periodic shaking 3h
	temperature 85 ± 2°C
	3) 5 ml 3.2M NH_4OAc in 20% HNO_3
	0.5h continuous shaking after cooling
	temperature 25°C
F5-residual	Stage 5
	10 ml HF + 2 ml $HClO_4$
	evaporating to white fumes
	dissolution of a residue in HNO_3

In addition, the testing of the heavy metal leaching was performed by use of the standard leaching test in accordance with the procedure specified in PN-EN 12457-2 standard [22].

3 Results and discussion

The range of the characteristics of bottom ash derived from households is summarized in Table 2 in terms of the heavy metal content. The data contained in this table provide the concentrations of elements determined following mineralization of ash by a mixture of concentrated acids: HNO_3 and HCl, calculated per dry mass of the waste.

Table 2. Total content of heavy metal obtained after acid mineralization.

Total content of heavy metal [mg/kg]					
Cd	Pb	Ni	Cr	Cu	Zn
1.35	58.0	63.0	82.5	183	941

Among the analyzed metals, zinc was the element with the highest concentration (941 mg/kg), whereas cadmium was the lowest (1.35 mg/kg). However, the analysis of the total heavy metal content in the waste does not offer measurable results applicable for the assessment of the hazard posed by the waste to the environment in terms of the toxicological aspect. The provided measure offers only insight into the level of contamination present in the waste and it does not offer information regarding the potential

leaching of pollutants into the ground and water environment. Hence, it is necessary to find out the details regarding the particular forms and assess the mobility of these elements in the environment. The testing of the sequential extraction of the bottom ash was performed for this purpose.

Sequential extraction offers the identification of the following heavy metal forms in the investigated materials: exchangeable (fraction I), carbonate (fraction II), oxide (fraction III), organic (fraction IV), and residual (fraction V). Table 3 contains the results of the concentrations of the particular metals in the bottom ash and their ratios in relation to the cumulative content in the five fractions expressed in percent. The per cent ratio of the heavy metals in the identified fractions are presented in the following series in order of the decreasing values:

- for Cd: F2 > F3 > F5 > F4 > F1,
- for Pb: F5 > F4 > F3 > F2 > F1,
- for Ni: F5 > F3 > F2 > F4 > F1,
- for Cr: F5 > F3 > F4 > F2 > F1,
- for Cu: F4 > F5 > F3 > F2 > F1,
- for Zn: F2 > F3 > F5 > F4 > F1.

Table 3. Heavy metal content of particular fractions obtained by sequential extraction.

Fraction of heavy metal	Content of heavy metal											
	Cd		Pb		Ni		Cr		Cu		Zn	
	[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]
F1	0.009	0.73	0.009	0.01	0.19	0.28	0.14	0.13	0.41	0.28	0.00	0.00
F2	0.64	52.1	3.40	5.55	3.55	5.14	1.21	1.15	4.71	3.24	386	46.5
F3	0.39	31.7	15.3	25.0	6.12	8.86	24.2	23.0	6.78	4.66	247	29.7
F4	0.07	5.70	20.0	32.7	1.93	2.80	8.56	8.14	69.9	48.1	36.4	4.38
F5	0.12	9.76	22.5	36.7	57.3	82.9	71.1	67.6	63.6	43.7	161	19.4
∑	1.23	100	61.2	100	69.0	100	105	100	145	100	830	100

Fraction: F1-exchangeable, F2-carbonate, F3-oxide, F4-organic, F5-residual

The results of the testing involving the ash demonstrated that among all analyzed metals, zinc was the element with the highest concentration (830 mg/kg). Zinc occurred in the greatest concentration in the form of the carbonate fraction F2 (386 mg/kg). This result demonstrates the mobility of zinc in the environment. The subsequent step involved the determination of the copper content, which was equal to 145 mg/kg. The level of 69.9 mg/kg was determined in the organic fraction F4 (conditionally immobile) and 63.6 mg/kg in the residual fraction F5 (immobile). The content of chromium was equal to 105 mg/kg, for nickel it was – 69.0 mg/kg, and for lead – 61.2 mg/kg. For the case of these elements, residual form was the dominant one (F5) and it does not pose any significant toxicological hazard. The lowest concentration was recorded for cadmium (1.23 mg/kg). It was primarily cadmium associated with carbonates (F2) in the volume of 0.64 mg/kg. The lowest values of the analyzed metals were recorded in the exchangeable fraction (F1), i.e. the group representing water-soluble metals. The levels of heavy metals in these formed were at a level just under 0.73%.

Table 4 contains the results regarding the total content of heavy metals determined following mineralization of the ash with a mixture of concentrated acids: HNO_3 and HCl as well as the cumulative content calculated on the basis of the amounts in the five chemical fractions.

Table 4. Total content of heavy metals in communal bottom ash.

Heavy metal	Content obtained after acid mineralization [mg/kg]	Sum of content obtained in sequential extraction method [mg/kg]	Conformity [%]
Cd	1.35	1.23	91.1
Pb	58.0	61.2	106
Ni	63.0	69.0	110
Cr	82.5	105	127
Cu	183	145	79.2
Zn	941	830	88.2

The cumulative contents of cadmium, lead, copper and nickel recorded in the testing applying sequential extractions did not differ considerably from the results that were obtained following the direct mineralization using the mixture of concentrated acids. The cumulative content of these elements in the analyzed fractions was in the range from 91.1–110% in relation to the concentration gained during mineralization. In contrast, for chromium, copper and zinc, the results differed more substantially. The comparison offered a level of conformity in the range from 79.2–127%. Nevertheless, these differences are due to the application of different approaches to determine the heavy metal concentrations. These approaches are performed in a different manner and have various duration of the procedure as well as apply different reagents. Higher levels of copper and zinc were gained using mineralization applying a mixture of concentrated acids, whereas the higher levels of chromium were determined by use of sequential extraction.

Beside sequential extraction, the determination of heavy metal mobility also applied the basic leaching test conducted in accordance with the procedure detailed in PN-EN 12457-2 [22] (Table 5). The concentrations of heavy metals were measured following a 24-hour shaking test involving waste sample immersed in water. This procedure resulted in leaching of the following levels of pollutants in relation to their total content recorded after mineralization with a mixture of concentrated acids (Table 2): Cd: 2.22%, Pb: 0.003%, Ni: 0.22%, Cr: 0.07%, Cu: 0.51%, Zn: 0.009%. This result also demonstrates the low mobility of heavy metals into the water environment. We can note here that the testing of heavy metals applying the basic procedure presented above does not provide comprehensive information regarding the hazard that is posed by the waste to the environment. In reality, depending on a variety of environmental factors and waste properties, the levels of heavy metals released into the environment can vary.

Table 5. Leaching of heavy metals from communal bottom ash.

Content in water extract [mg/kg]					
Cd	Pb	Ni	Cr	Cu	Zn
0.03	0.002	0.14	0.06	0.94	0.09

If we seek for a manner in which bottom ash from households can be utilized, it is first necessary to follow the procedures described in the Act on Waste [3]. On the basis of the guidelines presented in this law, the waste needs to be subjected to recycling to the greatest potential extent, and finally have to be utilized with due regard for the requirements of environmental protection. One way to re-use the bottom ashes derived from fuel combustion involves a process termed R10 – "Land treatment resulting in benefit to agriculture or ecological improvement" [3]. The results of the concentrations of the

particular heavy metals determined in this study were subsequently compared with the data in guidelines stipulated in the Regulation of the Minister of Agriculture and Rural Development implementing some of the provisions of the Fertilizer Act [23]. This was done with the purpose of analyzing the potential for the application of bottom ash as a mineral fertilizer or growth stimulation agent. This regulation only details the admissible level of lead and cadmium, i.e. 140 mg/kg d.m. and 50 mg/kg d.m. in the fertilizer, respectively. In accordance with this regulation, it is not necessary to test the levels of remaining heavy metals. In connection with the above, we can assume that the cadmium and lead contents determined during mineralization and sequential analysis are at admissible levels (Table 4). This means that the waste can be applied for use in agriculture. Another measure, which gains considerable popularity and is applied to utilize bottom ashes involves its application for rehabilitation of post-industrial areas and landfill sites. The material applied for such rehabilitation is generated on the basis of bottom ash mixed with stabilized sewage sludge. In this process, wastewater sludge is combined with ash collected in a selective manner in a mass ratio 1:1 [24]. The introduction of this material into the surface layer of the landfill site can lead to an increase of the organic matter content in soil and increase in the content of soil nutrients. In turn, the greater mass of organic substance contributes to initiate topsoil processes and can consequently increase the levels of absorbable forms of nutrients in soil. These processes create more favorable conditions to sustain vegetation on post-industrial and degraded lands.

4 Conclusions

In terms of the content, the following heavy metals were determined in the analyzed bottom ash Zn > Cu > Cr > Ni > Pb > Cd in order from the highest to lowest. The sequential analysis demonstrated the occurrence of heavy metals in all fractions. Zinc was the only exception, as it was not found in the exchangeable fraction (F1). Immobile associations were the dominant fractions for lead, nickel and chromium, and they were mainly found to be bound to aluminosilicates forming residual fraction (F5). The presence of these metals in the waste does not pose a hazard to the environment. The greatest content of copper was determined in the organic (F4) as well as residual fractions (F5). Cadmium and zinc occurred primarily in the carbonate associations. Copper forms were associated with inorganic forms (F4). The content of heavy metals in the mobile fraction (F1) was negligible and was found to be in the range 0.00–0.73% in relation to the cumulative content recorded in all five fractions. Heavy metals were also characterized by low mobility in the eluates derived from ashes in accordance with PN-EN 12457-2 standard. The multi-stage procedure of sequential analysis forms the preferred tool applied in the analysis of the potential hazard that is formed by the ashes. This approach offers means to forecast the hazards resulting from the occurrence of heavy metals in waste as well as in soils and sludges. The analysis of the total content of heavy metals in the waste only demonstrates the degree of its contamination and should not be applied as a sole tool to assess environmental hazard. It does not offer a measurable tool in the assessment of the hazard that is posed by heavy metals to the environment in terms of the toxicological aspects. It is necessary to get to know the particular forms and fractions forming the cumulative content of a given metal and assess the potential for its leaching into the environment.

Due to the very small ratio of heavy metal forms that are water soluble, the waste was considered to be safe to the soil and water environment. The analyzed ash also meets the requirements specified to enable its utilization as a mineral fertilizer and plant growth stimulant. Hence, this type of waste can be applied in agricultural lands. Another potential

application for reusing such waste involves its application for land rehabilitation in the form of mineral-organic composite formed by combining ashes with stabilized sewage sludge.

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