



# Chemical Examination of Fly Ash and Bottom Ash Derived from Incineration of Hazardous Waste

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<http://doi.org/10.29227/IM-2018-01-35>

## Abstract

The content of heavy metals in solid residues from the incineration of hazardous waste affects the quality of the environment including soil and water and – most importantly – human health. The chemical composition is often decisive for the further management of the waste, which involves its direct use or conversion into an environmentally safe form. Therefore, the chemical and mineralogical composition of fly and bottom ash from the incineration of hazardous waste was examined. In addition, the results of leaching tests for heavy metals, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were performed. The obtained results indicate that the dominant components are SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub> and Cl<sup>-</sup>. Partitioning was observed for heavy metals such as Cr(III), Cu(II), Zn(II), Ni(II), Pb(II) and Cd(II) between fly ash and bottom ash. The leaching results showed a lower amount of heavy metals in eluates from bottom ash than fly ash as a result of their presence in the glassy phase.

Keywords: hazardous waste, incineration, fly ash, bottom ash, ecotoxicity

## Introduction

According to the European Union Directive [1] hazardous waste (HW) that is toxic, flammable, harmful, infectious, carcinogenic etc., may cause a health risk and lead to environmental pollution. A detailed register of toxic waste residues that defines their harmfulness, taking into consideration the chemical composition of toxic compounds and their origins, was mentioned in the Annex to the Directive.

The specific character of HW requires appropriate measures and continuous control during processing. One of the technical alternatives in the management of HW is the thermal treatment thereof in incinerators with air-pollution cleaning equipment.

Among a variety of proposed combustion technologies rotary kilns are generally used while less frequent use of multi-hearth furnaces and fluidized beds is observed [2–4].

The choice of technical operations such as discharge, storage and preparation of the HW, being performed prior to combustion, depends on its physical and chemical properties, i.e. the state of matter and chemical composition.

If possible, and if in accordance with the applicable rules and regulations, combustion wastes are homogenized by grinding and mixing. Afterwards, a material of suitable heating value is formed. The HW that is not permitted to mix with other wastes is discharged directly into combustors. Particular wastes requiring spe-

cial treatment, e.g. medical waste with infection risks, wastes differing in heating value, ethical standards to follow, or surgery remains, are directly delivered to the combustion installation in special containers that dump their contents directly into the incinerator.

As a result of the incineration process, different residues are generated, such as: bottom ash containing non-combustible materials and unburned organic matter, boiler ash carried over by the flue gases and collected in the heat recovery section. The finest particles (fly ash) are separated from exhaust gases by filters as well as air pollution control (APC) residues produced during the exhaust gas cleaning process [2, 5–7].

Bottom ash is usually collected at the outlet of the combustion chamber in a quenching/cooling tank. In turn, other wastes generated at each stage of thermal treatment are all collected in the silo.

As in the case of the thermal treatment of municipal solid waste (MSW), physical and chemical properties of solid residues generated during HW incineration depend on their chemical composition, grain size distribution, as well as on the type of combustor and installed flue gas cleaning technologies [8–10]. The cleaning method applied (wet scrubbers, semi-dry scrubbers and dry scrubbers) influences the physical and chemical properties of the solid residues [5, 11].

The HW, from the point of view of chemistry, can be organic, inorganic, metalorganic, or a mixture of all

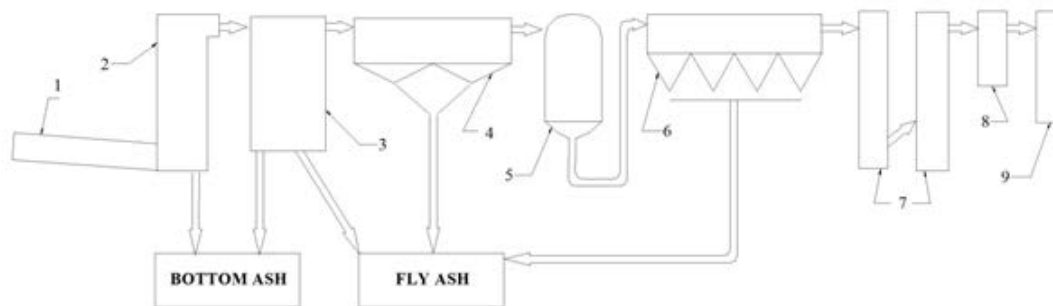


Fig. 1. Flowsheet of hazardous waste incinerator

Rys. 1. Schemat instalacji do termicznego przekształcania odpadów niebezpiecznych

these. Moreover, some HW are composites that consist of organic substances with properties improved by the addition of an inorganic compound. For example, heavy metals and their compounds are used as fillers, stabilizers, pigments and plasticizers in the manufacture of, for example: plastics, batteries, alloys, paper, pesticides, fertilizers, petrochemicals, metallurgy, textiles and ceramics [12–14].

Thus, the main elements present in the HW are: carbon, oxygen, nitrogen, sulfur and silicon, which are related to the chemical composition of fossil fuels. In contrast to fossil fuels, however, HW contain heavy metals in different chemical forms, and a significant amount of chlorine. The presence of chlorine leads to the formation of metal chlorides (e.g. Cd, Pb, Zn), which undergo evaporation and/or thermal dissociation followed by condensation in cooler parts of the furnace or surface deposition in the form of fine particles.

The type of combustor, combustion temperature, retention time, air flow and grain size distribution determines the behavior of heavy metals. The literature data [8–10, 14–16] indicate that metals such as Cd and Pb accumulate mostly in the fly ash while lithophile metals, such as Fe, Cu and Al, accumulate in bottom ash. In turn, metals of moderate volatility, such as Zn, Cr and Ni, are found in similar amounts in fly ash and bottom ash.

The thermal treatment of HW, as well as the management of resulting waste in such operations, are not often described in literature, in contrast to MSW processing. Taking into account the fact that in Poland such HW incinerator is in continuous use for a few years, there is a demand for the characterization of both bottom and fly ash. Therefore, the aim of this paper was to check if there is any correlation between selected heavy metal content in bottom and fly ashes, as well as their leachability from the HW. This will further enable the determining of the path followed by the metals found in solid residues following HW incineration.

## Materials and methods

For the presented research solid residues were collected from the HW incinerator shown in Fig. 1.

In this installation the HW (rubber, plastics, tarry sludge, detergent, car upholstery, medical waste, pesticides) is combusted in a rotary kiln (1). After passing the economizer, flue gases are cooled down in a heat recovery chamber (3) and, afterwards, separated from solid particles by an electrofilter (4). The flue gases from the electrofilter are mixed with Na<sub>2</sub>S<sub>4</sub> with the aim of retaining mercury vapors and directing them to the spray dryer (5) and bag filter (6). In the next step, the flue gases that are cleaned of acid pollutants such as SO<sub>2</sub> and HCl in the spray dryer (5) pass the wet scrubbers (7) and, in the final stage, the flue gases are cleaned using active carbon (8). The NO<sub>x</sub> are removed by selective catalytic reduction (SCR) – (9). Within the installation, bottom ash is collected from the rotary kiln and from the first part of the recuperator boiler, while the fly ash collected from the last section of the recuperator boiler, electrofilter and bag filter is directed into the same silo.

For the study, six solid residue samples were taken over two years:

- bottom ash – labeled from BA1 to BA6.
- fly ash mixture – labeled from FA1 to FA6.

The samples, prior to chemical composition analysis, were digested using a mixture of HNO<sub>3</sub>/HCl in a microwave oven. The obtained solution was analyzed after dilution by Inductively Coupled Plasma Spectrometry/Atomic Emission Spectroscopy (ICP-AES) and by Inductively Coupled Plasma Mass spectrometry (ICP-MS) with the use of the Perkin Elmer Elan 6100 apparatus.

Leachability tests were conducted according to the EN 12457-2 standard. The distilled water, with a liquid-to-solid ratio (L/S) of 10, was used as a leaching solution. The suspension was agitated in a plastic flask for 24 hours, then the mixture was filtered through a 0.45 μm membrane filter. The resulting leachate was

Tab. 1. Chemical composition of bottom ashes, (% wt.)

Tab. 1. Skład chemiczny badanych żużli, (% mas.)

Sample of bottom ash							Average
Elements	BA1	BA2	BA3	BA4	BA5	BA6	
SiO <sub>2</sub>	50.760	35.500	38.800	35.280	58.500	58.100	46.157
CaO	17.671	40.442	32.797	38.785	10.238	5.330	24.210
Al <sub>2</sub> O <sub>3</sub>	8.781	6.220	12.346	8.183	4.546	2.090	7.028
Fe <sub>2</sub> O <sub>3</sub>	5.217	4.382	4.081	5.008	7.787	3.460	4.989
MgO	2.239	1.667	2.755	2.040	1.375	0.304	1.730
P <sub>2</sub> O <sub>5</sub>	1.368	0.413	0.672	0.332	0.740	0.625	0.692
Na <sub>2</sub> O	0.941	0.303	2.232	2.874	1.296	0.656	1.384
Cl	0.938	1.187	0.799	0.237	0.233	2.300	0.949
SO <sub>3</sub>	0.501	0.228	0.107	0.306	6.868	1.160	1.528
BaO	0.483	9.041	3.826	4.871	0.143	2.368	3.455
K <sub>2</sub> O	0.247	0.100	0.136	0.364	1.691	0.215	0.459
Li <sub>2</sub> O	0.002	0.001	0.002	0.003	0.002	0.002	0.002

Tab. 1. Chemical composition of bottom ashes, (% wt.)

Tab. 1. Skład chemiczny badanych żużli, (% mas.)

Sample of fly ash							Average
Elements	FA1	FA2	FA3	FA4	FA5	FA6	
SiO <sub>2</sub>	30.715	30.400	13.200	29.100	9.200	22.300	22.486
CaO	26.916	32.297	37.600	9.492	67.474	25.110	33.148
SO <sub>3</sub>	10.159	9.474	23.025	25.099	9.184	7.210	14.025
Cl	6.641	4.950	9.134	3.775	9.894	3.880	6.379
Na <sub>2</sub> O	4.862	4.457	4.950	10.942	0.439	4.215	4.977
Al <sub>2</sub> O <sub>3</sub>	3.937	1.345	1.312	1.485	0.270	3.400	1.958
K <sub>2</sub> O	2.535	2.741	3.381	5.749	0.177	1.415	2.666
Fe <sub>2</sub> O <sub>3</sub>	2.515	1.461	1.313	1.063	0.682	3.370	1.734
MgO	1.418	0.762	1.488	0.554	1.198	0.749	1.028
BaO	0.582	0.266	0.595	0.009	0.026	0.213	0.282
P <sub>2</sub> O <sub>5</sub>	0.300	0.189	0.271	3.040	0.071	0.261	0.689
Li <sub>2</sub> O	0.007	0.003	0.005	0.008	0.000	0.004	0.004

analyzed for pH and trace elements using ICP-AES and ICP-MS methods. The amount of chlorides was analyzed using the Volhard titration method.

Phase composition was examined using the Philips APD PW 3020 X'Pert diffractometer. The scanning electron microscope JEOL 5500 LV equipped with the EDX system was used for the analysis.

## Results and discussion

### *Chemical and mineralogical composition*

The content of the principal elements in bottom ash (BA1-BA6) is shown in Table 1, while the data concerning fly ash (FA1-FA6) are presented in Table 2. SiO<sub>2</sub> was the dominant component of bottom ash samples (on average 46.2%), other components, such as CaO (24.2%), Al<sub>2</sub>O<sub>3</sub> (7.0%), Fe<sub>2</sub>O<sub>3</sub> (5.0%) and BaO (3.4%), were present in small amounts. In turn, fly ash samples contained large average amounts of CaO

(33.1%), SiO<sub>2</sub> (22.5%), SO<sub>3</sub> (14.0%), Cl (6.4%) and Na<sub>2</sub>O (5.0%). These observations are consistent with the literature data [4, 17–19].

Table 3 presents the amount of heavy metals in bottom ash. On average the highest content was observed for Cu(II), Cr(III), Zn(II) and Ni(II), while in the case of fly ash the amounts of Zn(II), Cd(II) and Pb(II) were the highest (Table 4). These observations are in agreement with the literature data [9, 10, 14, 16] concerning partitioning of metals as well as the volatility of some metals (e.g. Zn, Cd) during combustion and their subsequent conversion into oxides and chlorides. As a result, in fly ashes or in APC (air pollution control) residues, volatile metals are present in higher amounts than in bottom ashes, which mostly contain low volatile metals such as Cu, Cr, Fe and Al.

It is worth emphasizing that data regarding the amount of elements in fly ashes and bottom ashes pre-

Tab. 3. The content of trace elements in HW bottom ashes (mg kg<sup>-1</sup>) and occurrence of minerals and phases determined by XRD

Tab. 3. Zawartość składników śladowych w badanych żużlach (mg kg<sup>-1</sup>) wraz z obecnymi fazami mineralnymi

Elements	Metal concentrations in bottom ashes (mg/kg)						Average	Minerals and phases
	BA1	BA2	BA3	BA4	BA5	BA6		
Ni	8 670	125	263	98	202	189	1 591	
Cr	8 254	709	1 115	571	477	446	1 929	FeCr <sub>2</sub> O <sub>4</sub>
Cu	5 707	610	3 345	668	16 611	2 087	4 838	CuS
Zn	4 578	1 029	305	481	1 491	2 049	1 656	ZnSO <sub>4</sub> *2,5H <sub>2</sub> O, (MgMn) <sub>9</sub> Zn <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>22</sub>
Pb	727	227	180	38	3 668	66	818	
Cd	12	2	0.4	5	38	3	10	
Hg	0.150	6.500	0.185	0.065	126.938	2.309	22.691	

Tab. 4. The content of trace elements in HW fly ashes (mg kg<sup>-1</sup>) and occurrence of minerals and phases determined by XRD

Tab. 4. Zawartość pierwiastków śladowych w popiołach lotnych HW (mg kg<sup>-1</sup>) wraz z obecnymi fazami mineralnymi

Elements	Metal concentrations in fly ash (mg/kg)						Average	Minerals and phases
	FA1	FA2	FA3	FA4	FA5	FA6		
Zn	21 408	14 153	22 257	50 506	20 283	17 379	24 331	Zn <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> , ZnCO <sub>3</sub> , K <sub>2</sub> ZnCl <sub>4</sub> , ZnSO <sub>4</sub>
Pb	13 263	3 094	4 853	1 549	276	591	3 938	K <sub>2</sub> Pb(PO <sub>4</sub> ) <sub>3</sub>
Cu	3 632	2 422	2 428	3 660	1 089	1 686	2 486	
Cr	1 232	560	321	117	57	634	487	MgCrO <sub>4</sub>
Ni	1 130	118	149	88	10	130	271	
Cd	590	178	113	42 420	13	18	7 222	KCdCl <sub>3</sub> , CdCl <sub>2</sub>
Hg	15	127	80	2	249	83	93	

sented in Tables 1-4 show significant variability, which results from differences in the initial composition of incinerated materials. For example, the amount of CaO in the FA4 sample was equal to 9.5%, in turn this value was 7 times higher in the FA5 sample (67.5%). The amount of cadmium was in the range from 13 mg/kg (FA5 sample) to 42420 mg/kg (FA4 sample). Similar observations were noted for bottom ashes. In the example the amount of mercury for the BA4 sample was equal to 0.065 mg/kg, while for the BA5 sample it reached about 127 mg/kg. The above results clearly show that despite insignificant differences in the type and quantity of incinerated waste their chemical composition is very variable. Thus, the plant operators are required to possess extensive knowledge and experience regarding the waste dosing into the furnace, from the point of view of the type and quantity of waste incinerated on the properties of forming fly and bottom ashes. Waste generation with the lowest possible variability of their properties has important implications in terms of their impact on human health and the environment as well as it influences and facilitates the recovery or disposal of such waste. When considering the possibility of recovery of this type of waste they can serve as a source of rare metals found in nature or recognized as essential to the development of highly advanced technology.

The variability of chemical composition resulted in the appearance of different phases in examined bottom ashes and mixtures of fly ashes as is presented in Figures 2 and 3. It was possible to identify phases using XRD only in some cases, regardless of the heavy metal amounts present in the solid residues. It was noted that metals such as Zn, Pb and Cd appeared as chlorides, chlorates, sulfates and phosphates, in turn chromium was incorporated in the structure of chromates.

The XRD patterns of bottom ashes (Fig. 2) indicated that, apart from phases listed in Table 3, quartz, gehlenite, hematite, and magnetite were also present. Moreover, gypsum (BA5 and BA6) and ettringite (BA1) were also identified. Apart from gypsum and gehlenite, akermanite and covellite were also present in the BA3 sample. In turn, for the BA4 sample the above mentioned phases were not identified, however the dominant minerals were silicates such as wollastonite. The chlorine compounds identified in the bottom ash may be connected with chlorine present in the incinerated wastes. Amorphous glaze was the dominant phase in the bottom ashes subjected to examination.

In fly ashes (Fig. 3), apart from the phases listed in Table 3, significant amounts of halite, sylvite, CaCl<sub>2</sub> and anhydrite were noticed, whose presence could undoubtedly be related to the technology of gas cleaning (Fig. 1). Silicates and aluminosilicates were also present, as

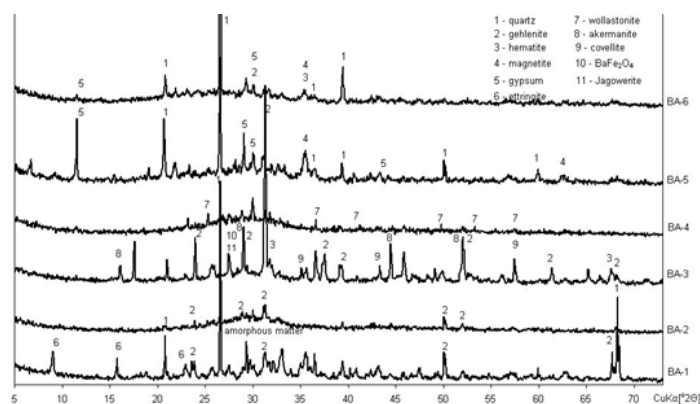


Fig. 2. X-ray diffraction pattern of bottom ashes

Rys. 2. Dyfraktogram badanych żużli

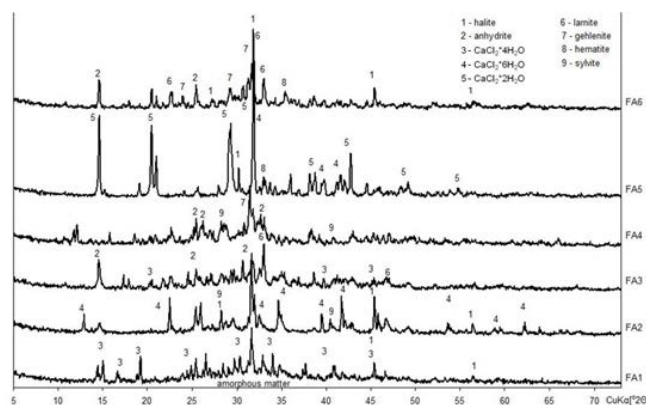


Fig. 3. X-ray diffraction pattern of fly ashes

Rys. 2. Dyfraktogram badanych popiołów lotnych

well as an amorphous phase. The difference in XRD patterns for samples of bottom ash and fly ash are the result of the changing composition of waste incineration. However, most of these mineralogical phases have been identified in fly ash and bottom ash from the incineration of medical waste [4, 17] and solid residues from the incineration of municipal solid waste [10, 20, 21].

SEM observations verified the presence of phases identified by XRD analyses in most cases, as well as allowing for the estimation of heavy metals in solid residues.

The main grain components of the examined bottom ashes were triangular, sharp-edged forms, while rounded forms were very rare. They were often covered with other phases, variable in size as shown in Fig. 4.

Glaze from bottom ash may be observed either as individual grains or as aggregates with crystalline phases (Fig. 5). Silica (Si) was the principal chemical component of the glaze, although present in lesser amounts than was observed for conventional bottom ash [21]. The following metals were also found: Ti, Hg, Fe, Pb, Cu and Zn.

The surface of glaze was rarely clean (Figs. 5a, 5b), more often the glaze was completely (Fig. 5c) or partially (Fig. 5d) covered with other phases. The covering phases were frequently composed of crystalline phases present as individual, well developed crystals (Syngen-

it – Fig. 5e) or poorly developed calcium plates forming aggregates (Fig. 5f).

As reported for the bottom ash that was formed during coal incineration, unburned carbon substance (Figs. 6a-6d) was noted, usually completely covered with other compounds. The covering phases formed small clusters of fine-grained structures, which were very difficult to identify. Their chemical composition contained Ba, Pb and Hg in the amount of more than a few percent. This was predominantly noted for the Ba present in all EDS analyses (Figs. 6c, 6d, 7a, 7b), and the compounds as a separate phase was found in the X-rays only in one sample of bottom ash BA-3 (Fig. 2).

Taking Ba content into account (Table 2) it can be observed that its maximal amount was not always connected with the presence of Ba phases, which could be identified using XRD or SEM.

Regardless of this, the presented research showed that heavy metals had a tendency to accumulate in the structures of secondary phases (ettringite) present in the bottom ashes (BA-1 and BA-2) (Figs. 8a and 8b).

On the contrary, as in the case of bottom ash, fly ash is mostly composed of very fine, densely packed clusters (Fig. 9a, 9b).

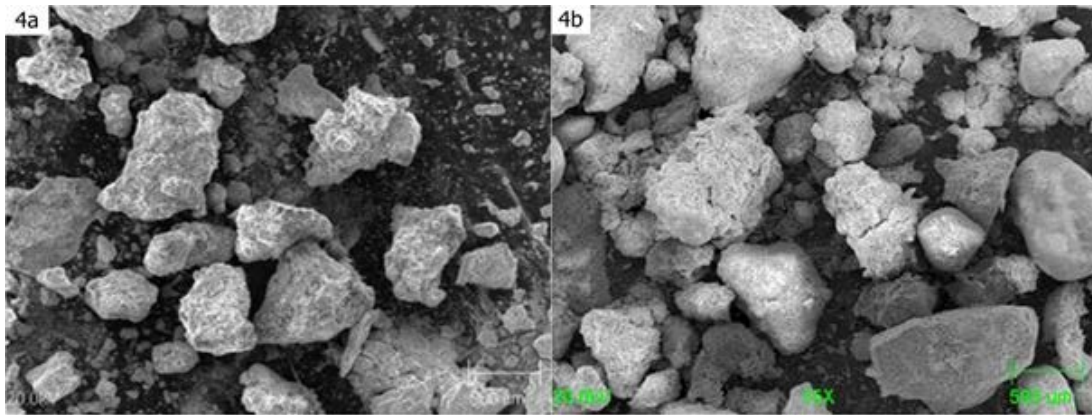


Fig. 4. SEM (x35) micrographs of bottom ash: a) BA-1, b) BA-3

Rys. 4. Morfologia ziaren żużli a) BA-1, b) BA-3

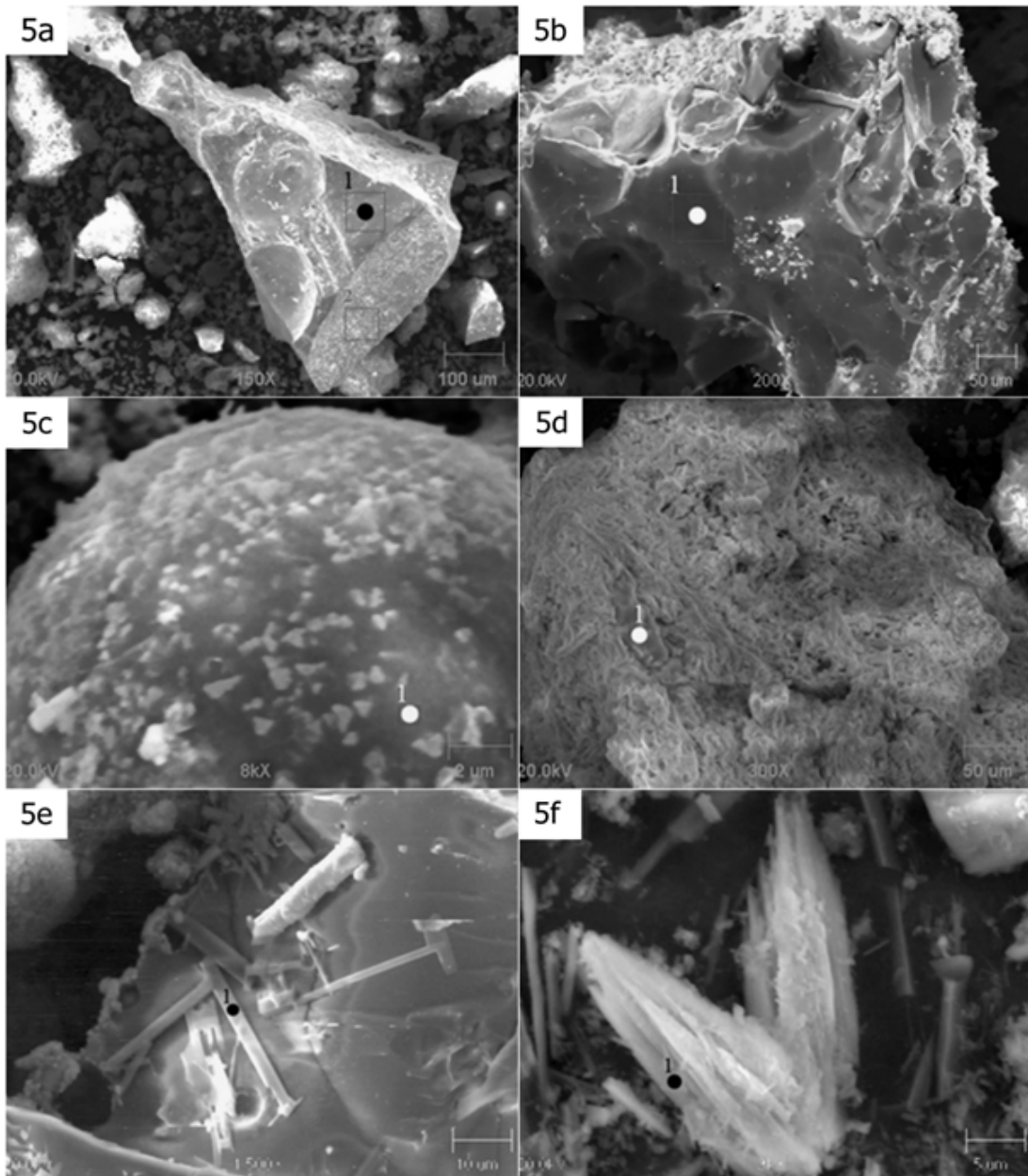


Fig. 5. SEM/EDS micrographs of glaze: a) BA-5, point 1 (% wt.): O: 23, Na: 1, Al: 4, Si: 26, K: 1, Ca: 8, Fe: 9, Cu: 1, Zn: 1, Hg: 6, Pb: 15; b) BA-5, point 1 (% wt.): O: 42, Na: 2, Al: 4, Si: 32, K: 2, Ca: 7, Ti: 1, Cr: 1, Fe: 2, Cd: 1; c) BA-2, point 1 (% wt.): C: 2, O: 28, Mg: 2, Al: 3, Si: 10, P: 1, Ca: 7, Ti: 5, Fe: 8, Ba: 14, Hg: 5, Pb: 10; d) BA-3, point 1 (% wt.): C: 16, O: 37, Na: 1, Al: 4, Si: 15, Ca: 14, Ti: 2, Mn: 1, Cu: 1, Zn: 1, Ba: 1; e) BA-5, point 1 (% wt.): O: 32, Na: 1, Al: 4, Si: 28, S: 7, K: 8, Ca: 10, Ti: 1, Cr: 1, Fe: 1; f) BA-1, point 1 (% wt.): C: 16, O: 31, S: 2, Ca: 40, Fe: 3, Ba: 3

Rys. 5. SEM/EDS szkliwa w żużlach

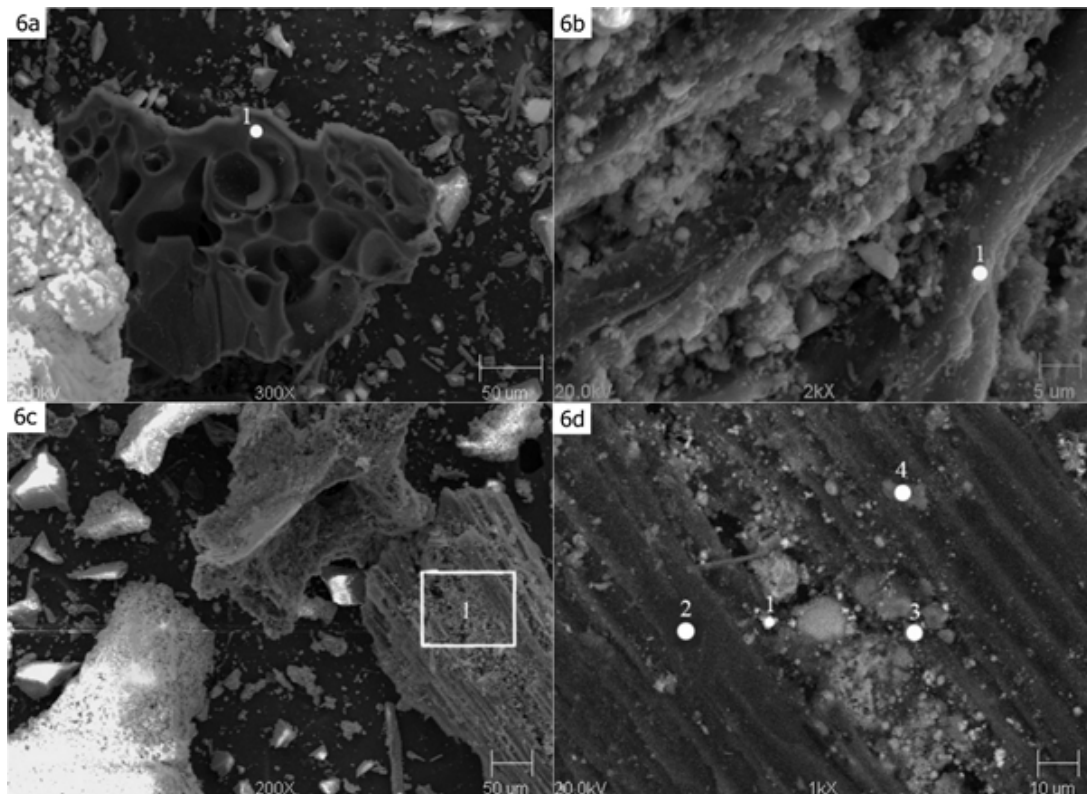


Fig. 6. SEM/EDS micrographs of unburned carbon: a) BA-4, point 1 (% wt.): C: 65, O: 25, Fe: 2, Ca: 1, Ba: 1; b) BA-6, point 1 (% wt.): C: 85, O: 10, Fe: 1; c) BA-2, area 1 (% wt.): C: 43, O: 14, S: 1, Cl: 3, Ca: 9, Ti: 1, Fe: 7, Ba: 3, Hg: 4, Pb: 7; d) BA-2, point 1 (% wt.): C: 28, O: 34, Si: 1, S: 4, Ca: 4, Fe: 1, Ba: 15, Hg: 4.3, Cu: 1.5; point 2 (% wt.): C: 68, O: 15, Si: 1, S: 1, Ca: 3, Fe: 3, Ba: 2; point 3 (% wt.): C: 1, O: 4, Si: 1, S: 2, Ca: 31: Fe: 8, Ba: 10, Pb: 10, Hg: 7, Zn: 1, Ti: 14; point 4 (% wt.): C: 13, O: 15, S: 1, Ca: 38, Fe: 4, Ba: 5, Pb: 9, Hg: 6.

Rys. 6. SEM/EDS substancji niespalonej w żużlach

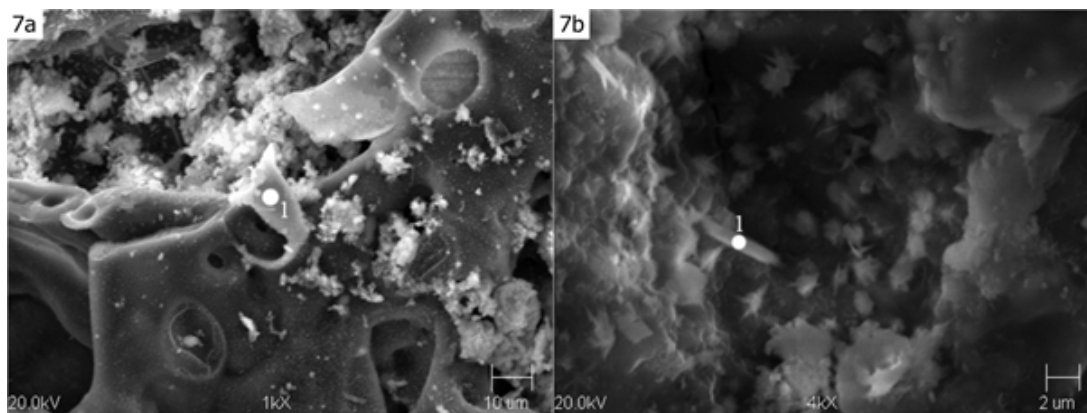


Fig. 7. SEM/EDS micrographs of barium compounds: a) BA-2, point 1 (% wt.): P: 1, Cl: 9, K: 2, Ca: 27, Cd: 9, Ba: 50; b) BA-3, point 1 (% wt.): C: 8, O: 45, Al: 7, S: 5, Ti: 1, Ba: 17, Hg: 6, Pb: 4

Rys. 7. SEM/EDS połączeń baru w żużlach

The amorphous phase present in the fly ash formed mainly elongated forms often attached to other components of fly ash. Rarely, sharp edged and/or rounded grains were observed. Regardless of their shape, the grains were covered principally by Ca and chlorine compounds. The presence of Ba and Cd, as well as Pb, Hg and Zn, was detected in the examined covering phase (Figs. 10a–d).

Regardless of the small amount of amorphous phase, the examined fly ashes were composed of loosely bound and/or joined together fine-grained, poorly developed salt crystals, mainly calcium chloride (Fig. 11a), halite (Fig. 11b, 11c), sylvite (Fig. 11d) and anhydrite (Fig. 11e). Often accompanied by considerable amounts of heavy metals such as Pb, Hg, Zn and Cd (Figs. 11a–f). Unburned substance was rarely observed (Figs. 12a, 12b).

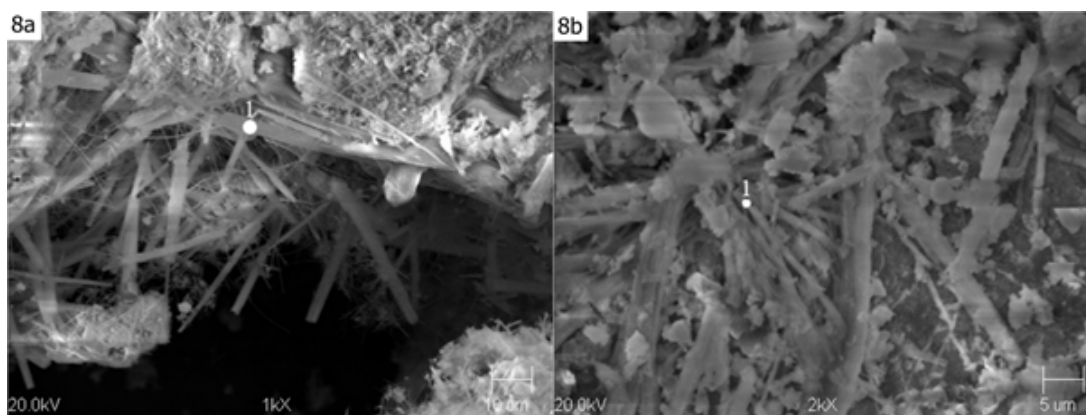


Fig. 8. SEM/EDS micrographs of ettringite: a) BA-1, point (% wt.): O: 27, Al: 6, S: 7, Ca: 39, Cu: 1, Zn: 2, Hg: 4, Pb: 8; b) BA-2, point 1 (% wt.): C: 16, O: 38, Na: 1, Al: 5, S: 4, Cl: 10, Ca: 15, Hg: 1, Pb: 3.

Rys. 8. SEM/EDS ettringitu w żużlach

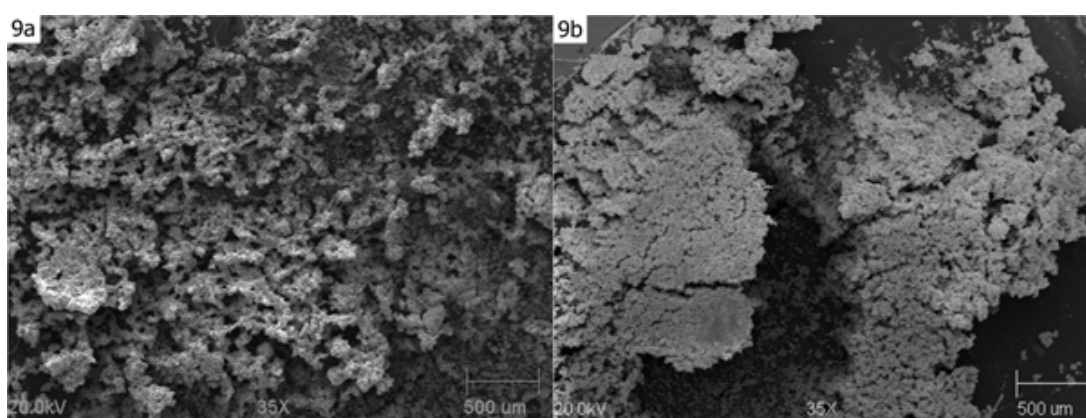


Fig. 9. SEM (x35) micrographs of fly ash: a) FA-1, b) FA-3

Rys. 9. Morfologia ziaren popiołów lotnych

### Leaching test

The results of leaching tests were shown in Tables 5 and 6 together with criteria for waste acceptable at landfills for hazardous waste. These criteria were listed in the Council of the European Union's decision [22]. The presented data indicated that bottom ashes meet the requirements. The leachability of heavy metals from fly ash samples was significantly higher than the bottom ash samples. This results from the abovementioned different volatility of metals present in samples, the incorporation of some metals into the glaze phase (bottom ashes), as well as their incorporation into highly insoluble calcium crystal structures.

The highest concentration of leached metals was measured for Zn, Mg, Cd and Pb. The average concentrations of metals leached from fly ash samples exceeded acceptable values established for landfills for hazardous waste. Only Ni concentration was below the criteria threshold.

Solid residues revealed strong variability of both chemical composition and leachability behavior. The relationship between the highest content and maximal

leachability was observed in particular for elements such as: Zn, Ni, Cd, Hg, Cl and SO<sub>3</sub>/SO<sub>4</sub> found in fly ashes. For bottom ash the correlation was observed in the case of the elements Pb, Cu, Cd, Cl and SO<sub>3</sub>. The lowest leachability of elements from fly ash samples in which their concentration was lowest was observed for Pb, Ni, Hg and Cl. The same observation was noted for Cl present in bottom ash samples. It is worth emphasizing that the proportional relationship between the amount of a particular element and its leachability from individual samples of solid residues was rarely noted.

### Conclusions

The presence of heavy metals in solid residues from the thermal treatment of HW leads to the formation of wastes that can prove harmful for the natural environment, and subsequently for human health. Taking this into account it seems that, apart from the examination of the chemical and mineral composition of solid residues, data on the leachability of heavy metals from wastes is also highly important.



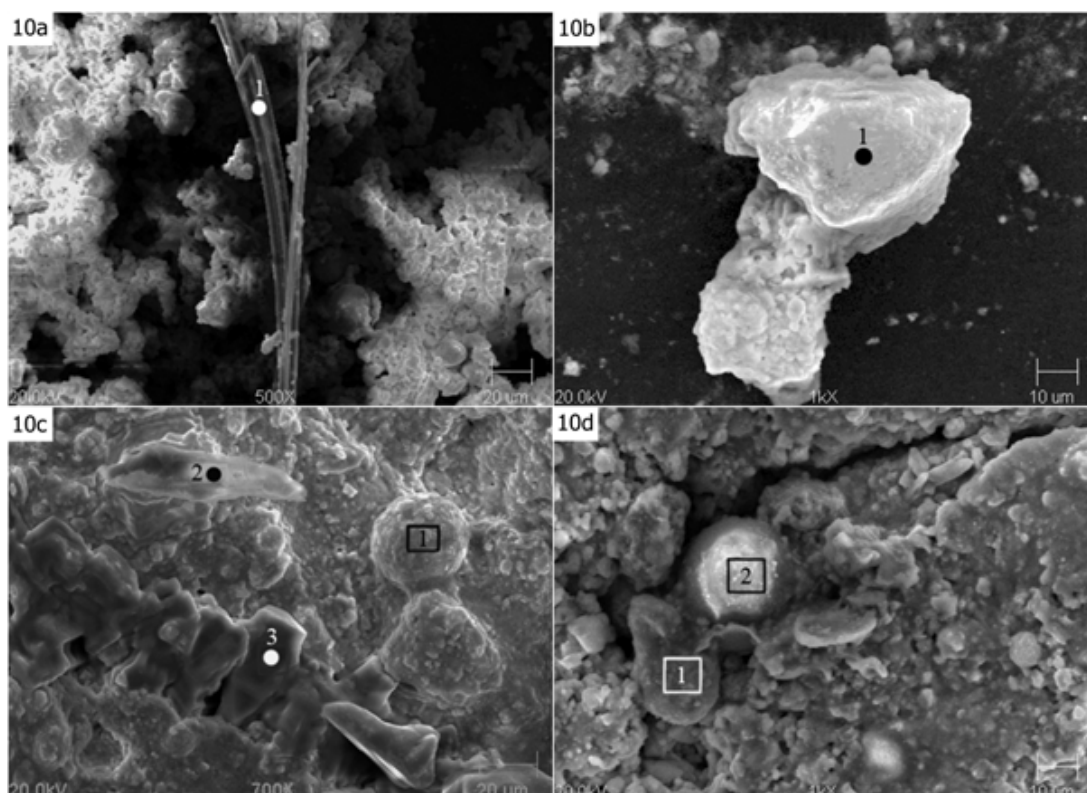


Fig.10. SEM/EDS micrographs of amorphous phase in fly ashes: a) FA-1, point 1 (% wt.): C: 8, O: 33, Na: 1, Mg: 5, Al: 6, Si: 16, Cl: 2, Ca: 12, Ti: 1, Cr: 1, Fe: 4, Cd: 1, Ba: 3; b) FA-5, point 1 (% wt.): O: 28, Al: 6, Si: 30, S: 2, Cl: 2, Ca: 17, Ti: 1, Cr: 1, Mn: 1, Fe: 7, Cd: 1; c) FA-2, area 1 (% wt.): O: 20, Na: 2, Al: 4, Si: 9, P: 2, S: 4, Cl: 9, Ca: 15, Ti: 1, Fe: 15, Zn: 5, Ba: 7; point 2 (% wt.): 2: C: 44, O: 24, Cl: 15, K: 1, Ca: 6, Zn: 2; point 3 (% wt.): O: 26, Mg: 8, Cl: 45, K: 10, Fe: 1, Co: 1, Ni: 1; d) FA-2, area 1 (% wt.): C: 2, O: 31, Na: 1, Al: 1, Si: 7, S: 6, Cl: 16, K: 1, Ca: 20, Cr: 1, Fe: 1, Cu: 1, Ba: 7; area 2 (% wt.): C: 4, O: 38, Mg: 2, Al: 7, Si: 17, Cl: 1, Ca: 21, Fe: 4, Ba: 2.

Rys. 10. SEM/EDS fazy amorficznej w popiołach lotnych

Tab. 5. Leaching test of bottom ashes

Tab. 5. Wymywalność zanieczyszczeń chemicznych z żużli

Elements	Concentrations of leached elements (mg/kg)						Average	Criteria for waste acceptable at landfills for hazardous waste
	BA1	BA2	BA3	BA4	BA5	BA6		
Ca	832	468	424	432	1793	940	815	-
Cd	0.067	0.002	0.012	0.065	1.140	0.025	0.218	5
Cr	0.070	0.490	0.042	0.038	0.120	0.072	0.139	70
Cu	0.019	0.018	0.024	0.015	2.380	0.049	0.418	100
Hg	0.010	0.003	0.017	0.005	0.004	0.054	0.016	2
K	296	119	107	69	1 171	357	353	-
Mg	5.20	1.10	5.00	25.90	187.40	6.40	38.50	-
Na	2 170	182	686	122	1 261	2 996	1 236	-
Ni	0.820	0.009	0.010	0.550	1.180	0.003	0.429	40
Pb	0.150	0.006	0.035	0.013	0.420	0.085	0.118	50
Zn	0.90	0.05	0.63	0.43	113.60	0.42	19.34	200
Cl	6080	1 607	374	237	1 042	6 880	2 703	25 000
SO <sub>4</sub> <sup>2-</sup>	1 630	132.5	1 559	620	10 270	1 081	2 549	50 000
pH	10.4	11.34	10	7.15	8.11	8.2	9.2	-

In contrast to solid residues that result from the combustion processes of fossil fuels or municipal solid wastes (MSW), a significant variability of the chemical and mineralogical composition was observed here.

This phenomenon was also noted for leaching tests.

As is already known, leachability results depend on element concentration, pH, forms of appearance and the leachability test itself. Nevertheless a correlation

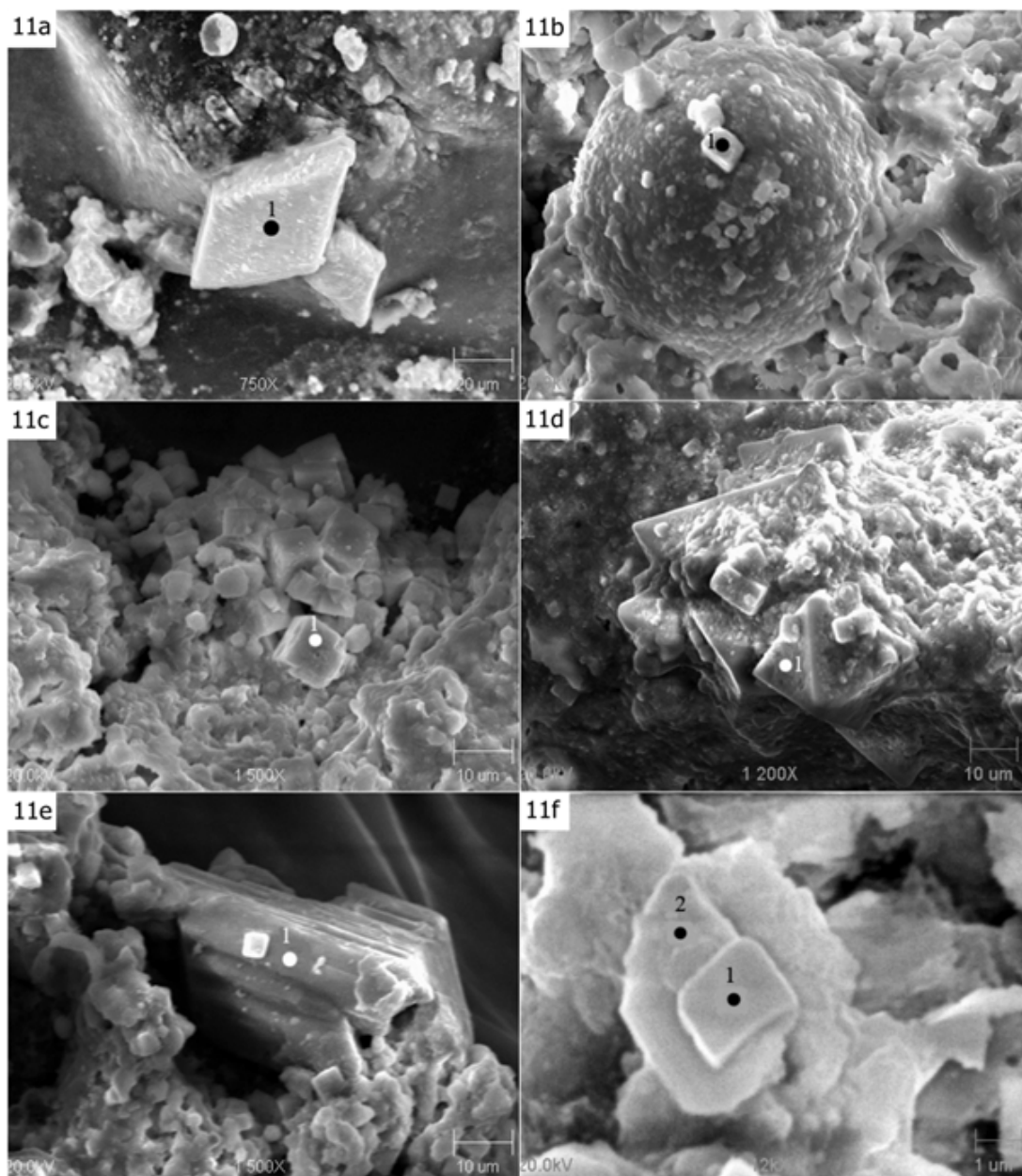


Fig. 11. SEM/EDS micrographs of crystals phase in fly ashes: a) FA-3, point 1 (% wt.): O: 32, Al: 1, Si: 1, S: 9, Cl: 21, Ca: 33; b) FA-3, point 1 (% wt.): C: 17, Na: 26, Cl: 44, Ca: 1, Co: 1, Ni: 1, Zn: 1; c) FA-3, point 1 (% wt.): C: 11, Na: 33, Cl: 47, Zn: 1; d) FA-2, point 1 (% wt.): Cl: 51, K: 18, Ca: 4, Mn: 2, Fe: 2, Co: 1, Ni: 4, Cu: 2, Zn: 5, Ba: 3; e) FA-3, point 1 (% wt.): C: 10, O: 22, S: 18, Ca: 25, Ni: 1, Cu: 1, Zn: 1, Hg: 3, Pb: 6; f) FA-1, point 1 (% wt.): Na: 1, S: 1, Cl: 9, K: 1, Ca: 5, Co: 1, Ni: 1, Cu: 3, Ba: 4, Hg: 8, Pb: 59.

Rys. 11. SEM/EDS fazy krystalicznej w popiołach lotnych

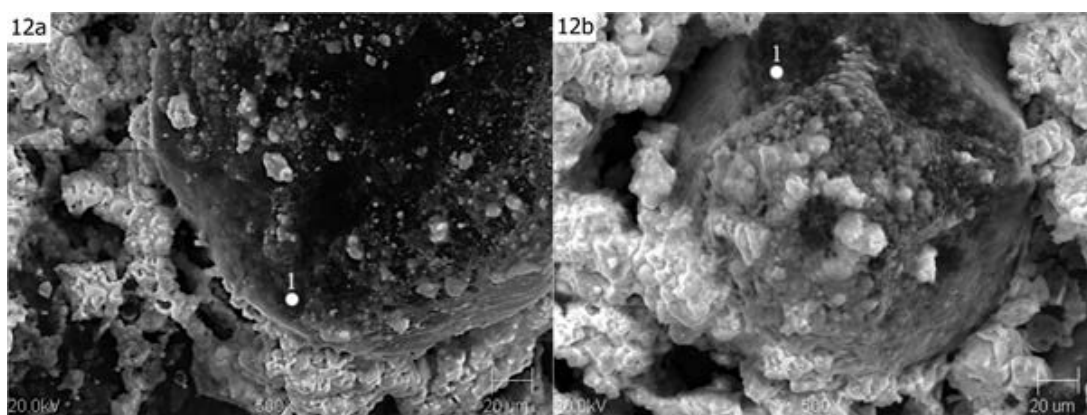


Fig. 12. SEM/EDS unburned carbon: a) FA-3, point 1 (% wt.) C: 77, O: 19, Cl: 2, Ca: 1; b) FA-3, point 1 (% wt.): C: 74, O: 25.

Rys. 12. SEM/EDS substancji niespalonej w popiołach lotnych

Tab. 6. Leaching test of fly ashes

Tab. 6. Wymywalność zanieczyszczeń chemicznych z popiołów lotnych

Elements	Concentrations of leached elements (mg/kg)						Average	Criteria for waste acceptable at landfills for hazardous waste
	FA1	FA2	FA3	FA4	FA5	FA6		
Ba	2.33	3.26	4.77	1.30	1.59	2.47	2.62	300
Ca	25 670	18 330	94 510	6 572	251 000	24 090	70 029	-
Cd	110.00	56.90	84.40	667.00	2.61	0.23	153.52	5
Cr	0.45	0.70	3.25	0.84	0.56	10.10	2.65	70
Cu	9.33	11.88	4.61	14.62	22.92	0.16	10.37	100
Hg	8.54	26.80	9.86	0.09	72.20	6.23	20.62	2
K	7 200	8 676	25 944	58 730	1 071	8 800	18 404	-
Mg	1 460	773.1	2197	384	3 571	1 376	1 627	-
Na	24 470	13 370	43 230	76 700	2 372	55 800	35 990	-
Ni	13.10	2.69	3.40	4.28	0.87	1.12	4.24	40
Pb	120.00	22.88	153.10	7.25	2.84	8.91	52.50	50
Zn	5 800	2 022	6 489	19 019	307.2	9.88	5 608	200
Cl <sup>-</sup>	109 890	87 230	249 300	37 750	450 660	136 610	178 573	25 000
SO <sub>4</sub> <sup>2-</sup>	29 950	10 250	8 932	271 200	6 186	9 680	56 033	50 000
pH	6.9	7.0	6.7	6.6	6.9	11.7	7.6	-

between concentration and leachability was observed. It was more frequently noted for fly ash samples where metals possess their own phases or cover grain surfaces. In turn, in the case of bottom ash samples, the presence of glaze was observed in which heavy metals were bound. This fact was confirmed by SEM observations and, as an effect, heavy metals were isolated from the dissolving agent.

The metals in the solid residues mainly appear as salts (chlorides, silicates, aluminosilicates and chlorates) or as oxides (magnetite, Al<sub>2</sub>O<sub>3</sub>).

Heavy metals such as Zn, Pb and Cd were accumulated in higher amounts in samples of fly ash than in bottom ash, which was connected with their higher volatility in comparison to Cu, Cr, Fe and Al.

Heavy metals were found in higher amounts in fly ash samples, which led to a better correlation with

leachability than in the case of bottom ash samples.

The leachability test often provides information that helps to decide about the future processing of the HW. This may be their direct use or conversion into more environmentally friendly forms and/or conversion into forms possessing features that render them reusable.

The combustion process did not lead to the destruction of heavy metals present in the HW but led to changes in their chemical composition.

#### Acknowledgments

The part of results of the researches shown in the article have been developed within the realization of the statute work no. 11.11.100.482.

## Literatura – References

1. Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives.
2. BREF 2006. European Commission, Integrated Pollution Prevention and Control: Reference Document on the Best Available Techniques for Waste Incineration. August 2006.
3. Saxena S.C., Jotshi C.K., 1996. Management and combustion of hazardous wastes. *Prog. Energ. Combust.* 22, 401-425.
4. Gidarakos E., Petrantonaki M., Anastasiadou K., Schramm K.-W., 2009. Characterization and hazard evaluation of bottom ash produced from incinerated hospital waste. *J. Hazard. Mater.* 172, 935–942.
5. Kępys W., 2008. Trial of recovery of fly ash and bottom ash from thermal treatment of wastes as artificial aggregates. *Mineral Resources Management*, Vol. 24, Issue 3, 149-156.
6. Kępys W., Pomykała R., Pietrzyk J., 2013. Properties of fly ash from thermal conversion of municipal sewage sludge. *Inżynieria mineralna*, Vol. 14, Issue 1, 11-18.
7. Sabbas T., Poletini A., Pomi R., Astrup T., Hjelmar O., Mostbauer P., Cappai G., Magel G., Salhofer S., Speiser C., Heuss-Assbichler S., Klein R., Lechner P., 2003. Management of municipal solid waste incineration residues. *Waste Manage.* 23, 61–88.
8. Hasselriss, F., Licata, A., 1996. Analysis of heavy metal emission data from municipal waste combustion. *J. Hazard. Mater.* 47, 77-102.
9. Jung, C.H., Matsuto, T., Tanaka, N., Okada, T., 2004. Metal distribution in incineration residues of municipal solid waste (MSW) in Japan. *Waste Manage.* 24, 381–391.
10. Li M., Xiang J., Hu S., Sun L.-S., Su S., Li P.-S., Sun X.-X., 2004. Characterization of solid residues from municipal solid waste incinerator. *Fuel* 83, 1397–1405.
11. Chimenos J.M., Ferná'ndez A.I., Cervantes A., Miralles L., Ferná'ndez M.A., Espiell F., 2005. Optimizing the APC residue washing process to minimize the release of chloride and heavy metals. *Waste Manage.* 25, 686–693.
12. Meharg A.A., French M.C., 1995. Heavy metals as markers for assessing environmental pollution from chemical warehouse and plastic fires. *Chemosphere* 30, No. 10, 1987-1994.
13. Mulder K.F., 1998. Sustainable Consumption and Production of Plastics? *Technol. Forecast. Soc.* 58, 105-124.
14. Sabiha-Javied Tufail M., Khalid S., 2008. Heavy metal pollution from medical waste incineration at Islamabad and Rawalpindi, Pakistan. *Microchem. J.* 90, 77–81.
15. Stempkowska A., Kępys W., Pietrzyk J., 2015. The influence of incinerated sewage sludge ashes physical and chemical properties in possibility of usage in red ceramic. *Mineral Resources Management*, Vol. 31, Issue 2, 109-121.
16. Bakoglu M., Aykan K., Savas A., 2003. Partitioning characteristics of targeted heavy metals in IZAYDAS hazardous waste incinerator. *J. Hazard. Mater.* B99, 89–105.
17. Anastasiadou K., Christopoulos K., Mousios E., 2012. Solidification/stabilization of
18. fly and bottom ash from medical waste incineration facility. *J. Hazard. Mater.* 207–208, 165–170.
19. Cobo M., Gálvez A., Conesa J.A., Montes de Corre C., 2009. Characterization of fly ash from a hazardous waste incinerator in Medellin, Colombia. *J. Hazard. Mater.* 168, 1223–1232.
20. Zhao L., Zhang F.-S., Chen M., Liu Z., Wu D.B.J., 2010. Typical pollutants in bottom ashes from a typical medical waste incinerator. *J. Hazard. Mater.* 173, 181–185.

21. Bodenan F., Deniard Ph., 2003. Characterization of flue gas cleaning residues from European solid waste incinerators: assessment of various Ca-based sorbent processes. *Chemosphere* 51, 335–347.
22. Vassilev S.V., Vassileva Ch.G., Karayigit A.I., Bulut Y., Alastuey A., Querol X., 2005. Phase–mineral and chemical composition of composite samples from feed coals, bottom ashes and fly ashes at the Soma power station, Turkey. *Int. J. Coal Geol.* 61, 35–63.
23. Council Decision of 19 December 2002 (2003/33/EC) establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC.

*Badania chemiczne popiołów lotnych i żużli ze spalania odpadów niebezpiecznych*

*Zawartość metali ciężkich w stałych pozostałościach ze spalania odpadów niebezpiecznych powoduje, że są to odpady mogące negatywnie wpłynąć na jakość środowiska naturalnego jak i na zdrowie ludzi. Dodatkowo właściwości często decydującą o dalszym postępowaniu z tymi odpadami, polegającymi na ich bezpośrednim wykorzystaniu czy też przekształceniu w formę bezpieczną dla środowiska i/lub posiadającą cechy umożliwiające ich wykorzystanie. Z tego względu przebadano właściwości fizykochemiczne popiołów lotnych i żużli pochodzących z przemysłowej spalarni odpadów niebezpiecznych. W artykule przedstawiono wyniki badań zawartości głównych składników i metali ciężkich, analizy mineralogicznej i morfologicznej oraz wymywalności. Badania pokazują, że dominującymi składnikami są SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>, Cl. Zaobserwowano różnice w lokowaniu się metali ciężkich jak Cr, Cu, Zn, Ni, Pb i Cd pomiędzy popiołami lotnymi a żużlami. Wyniki wymywalności wskazują na mniejszą ilość wymywanych metali ciężkich z żużli niż z popiołów lotnych w efekcie występowania ich w fazie szklistej żużli.*

*Słowa kluczowe: odpady niebezpieczne, termiczne przekształcanie, popiół lotny, żużel*



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