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Metallic Elements Fractionation in Municipal Solid Waste Incineration Residues

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Abstract

Municipal solid waste incineration residues from one of the Polish incineration plants were sampled to characterize the distribution of metallic elements among them. Those elements previously dispersed within the waste mass, as a result of incineration processes were unequally distributed to bottom ash (BA), fly ash (FA) and air pollution control residues (APC) due to their physical properties, form of occurrence and characteristics of the incineration system. Fe, Cu, Cr were concentrated in BA; Mg, Ti in FA; Pb, Sn in APC. Beside them several elements were equally distributed among BA and FA (Al, Mn), and FA and APC (Zn).

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1. Introduction

The composition of municipal waste is influenced by commonly used products and their components which become waste when their life cycle is over. Common usage of various metal-rich products makes metallic elements an important part of the municipal waste. A large amount of metal-rich products is collected separately or recycled from municipal waste, nevertheless these products dispersed within the waste mass as small fragments or as minor components in various non-recyclable products still remains in waste. Their concentration is obtained as side-effect of waste thermal treatment. High thermal resistance of waste components allows them to pass into the

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non-combustible phase. The process of waste incineration is commonly used worldwide as a solution to reduce significantly the amount of waste which need to be managed (e.g. landfilled). Through thermal treatment, the waste volume can be reduced up to 90% and its mass up to 70% [1].

As a result of municipal waste thermal treatment, municipal solid waste incineration (MSWI) residues are produced. They are represented usually by three main materials: bottom ash (BA), fly ash (FA) and air pollution control residues (APC). Within their mass, BA is dominating (80-90 wt%) [2,3]. The metallic elements content in MSWI residues is dependent on a number of factors (e.g. locality of the waste incineration plant, effectiveness of recycling). Also during thermal treatment elements considered as toxic are concentrated, nevertheless their content in residues is controlled and a number of techniques are used to reduce their toxicity. The concentrations of metallic and toxic elements are objects of concerns about the incineration residues impact on the environment but also gives the possibility to recover them, if their concentrations are high enough [4].

The process of MSWI residues formation is reported to be affected by various parameters including used technology, composition of waste, furnace type and distribution of temperature within it. Waste characteristic dependent on chemical composition, calorific value, level of averaging, melting/boiling points of the components (also volatility) is one of the most influential [3,5]. For the metallic elements also important are location and form of their primary occurrence in the incinerated waste [3,5,6].

The aim of this work was to investigate metallic elements distribution within municipal waste incineration residues (BA, FA and APC) to point out the type of residue where single elements concentrate and also to describe forms in which they concentrate. The important issue was to investigate also how physical parameters of metallic elements influence the process of their fractionation.

2. Materials and analytical methods

2.1 Samples of incineration residues and description of waste incineration plant

To investigate metallic elements distribution in MSWI residues, samples from one of the biggest MSWI plants in Poland were collected in two sampling campaigns (12.2015 and 05.2016). Each series covered BA, FA and APC produced at the same time. Based on European List of Waste [7], BA (waste code: 19 01 12) is classified as "bottom ash and slag other than those mentioned in 19 01 11*" (*bottom ash and slag containing dangerous substances). FA (waste code: 19 01 13*) is classified as "fly ash containing dangerous substances" and APC (19 01 07*) is classified as "solid wastes from gas treatment" (*also treated as hazardous material).

The plant is incinerating 48 000-55 000 tons of non-hazardous municipal waste per year using shaft furnace Krüger. Before incineration mixed waste are controlled in order to separate manually potentially dangerous components (e.g. those highly flammable or explosive). Furnace fed (<8 t/h) is thermally treated for 30-120 min in temperatures ranging from 950 to 1100° C. BA is cooled with water and before storing on a heap, large metallic fragments (<50 cm) are separated manually and smaller fragments (<20 cm) are separated using magnetic separator. FA and APC are separated from flue gases in two stages in the technological processes of energy recovery and controlling of air pollution through neutralization of toxic and hazardous components (NO_x, SO_x, HCl, HF, toxic metallic elements, dioxins, furans and organic pollutants) [8].

2.2 Analytical methods

Determination of samples mineral compositions were based on powder X-ray diffraction method (XRD), qualitative and quantitative using Rietveld refinement (calculations made using SEIFERT AutoQuan 2.62). Measurements (angles range: 2-70° 2 θ) were performed using Philips X'Pert APD diffractometer (goniometer PW3020, curved graphite crystal monochromator, CuK α radiation) with a step of 0.02° per 2 sec for qualitative analyses or 0.02° per 5 sec for quantitative analyses. XRD patterns were interpreted using Philips X'Pert Graphics & Identify v.1.2a software (based on ICDD PDF-2 database) and database of the Mineralogical Society of America [9]. Chemical analysis with emphasis on the metallic elements content were performed using inductively coupled plasma optical emission (ICP-OES) and mass spectrometry (ICP-MS) in AcmeLabs (Bureau Veritas Commodities Canada Ltd) in Vancouver.

For mineralogical analysis polished thin sections were used. Observations were made using a petrographic microscope (Nikon Eclipse E600 POL) and field emission scanning electron microscope (FE-SEM) HITACHI S-4700 (carbon-coated specimens) with NORAN Vantage microanalysis system of energy dispersive spectrometry (EDS). Elements were quantified using a “standardless” method with recalculation of results to a water free basis.

3. Results and discussion

3.1. Chemical and mineral composition of MSWI residues

The BA was grainy material rich in Si and Ca with elevated values of Al, Fe and Na (Table 1). Chemical composition of FA was dominated by Ca and Si with raised values of Al and S. APC was mostly composed of Ca with elevated values of Al, Na and K. It was also the material with the highest LOI value. In the composition of raw BA, beside ash material up to ~35 wt% of non-ash components were present. They were mostly represented by fragmented glass and ceramic and to a lesser extent (few wt%) macroscopically distinguishable metallic fragments. In this study samples of BA were analysed as received without separation of fragmented glass, ceramics etc., nevertheless BA after separation was also analysed (Table 1). Obtained results show that separation of residual components from the raw BA, resulted only in slight changes of its composition what allowed to compare studied BA to materials after separation described in the literature [6,10,11].

Table 1. Chemical composition of MSWI residues (values in wt%).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	LOI	C _{tot}	S _{tot}
APC	5.1	1.9	0.6	1.0	44.7	3.8	4.1	0.4	0.5	0.04	19.9	1.5	2.3
FA	19.4	7.4	1.8	2.3	35.2	3.9	3.8	1.9	1.5	0.1	6.1	0.3	6.1
BA	55.0	6.5	7.0	1.7	15.8	6.9	0.9	0.7	0.8	0.1	3.9	0.6	0.4
BA (without glass etc.)	50.9	8.4	7.7	1.7	17.2	5.6	0.9	0.8	1.1	0.1	4.8	0.9	0.7

All of the MSWI residues were characterized by a high share of amorphous phases (mostly represented by silicate glass): BA (~50 wt%) [11], FA (~45 wt%), APC (~60 wt%) and polymineral crystalline phase. BA was composed mostly of silicates (quartz SiO₂, larnite Ca₂[SiO₄], wollastonite Ca[SiO₃]), aluminosilicates (melilites Ca₂Al[AlSiO₇]-Ca₂Mg[Si₂O₇], feldspars K-Na[AlSi₃O₈]-Ca[Al₂Si₂O₈]), carbonates (mostly calcite CaCO₃) and in smaller extent apatite Ca₅(OH/F/Cl)(PO₄)₃, sulphates Ca[SO₄]*nH₂O and Fe-oxides Fe_xO_y [11]. Main mineral phases present in the FA were sulphates (anhydrite Ca[SO₄], gypsum Ca[SO₄]*2H₂O, syngenite K₂Ca[SO₄]₂*H₂O), quartz, chlorides (halite NaCl, sylvite KCl) and in smaller extent portlandite Ca[OH]₂ and Fe-oxides. In APC beside carbonates (mostly calcite), chlorides (halite, sylvite) and sulphates (anhydrite, bassanite Ca[SO₄]*0.5H₂O) present as main phases, small amounts of silicates (mostly quartz) were present.

3.2. Influence of metallic elements fractionation on the composition of MSWI residues

In a mass of BA 10.7 wt% were metallic elements, whereas in FA 9.4 wt% and in the APC 4.5 wt% of them were present. Main metallic elements present within residues were Al, Fe, Mg, Ti, Zn and in smaller amounts Cu, Mn, Pb, Sn and Cr. Elevated values of those elements in MSWI residues were also reported by Kirby and Rimstidt, Wei et al. and Saffarzadeh et al. [1,11,13].

The process of unequal distribution of elements among types of MSWI residues were described in the literature [3,11,13]. The elevated content of elements was usually present within one residue, nevertheless the situation of equal distribution among two of them was also noticed. In the BA the highest concentrations of Fe, Cu and Cr were observed, whereas in FA, Mg and Ti were preferably concentrated. In APC the highest content of Pb and Sn were noticed. Elements almost equally distributed between BA and FA were Al, Mn and between FA and APC was Zn.

Table 2. Content of main metallic elements present in MSWI residues and their selected physical properties [14]
(in bold - elements with the highest concentration).

residue/element	Sn (ppm)	Pb (ppm)	Zn (wt%)	Mg (wt%)	Al (wt%)	Cu (ppm)	Mn (ppm)	Fe (wt%)	Ti (wt%)	Cr (ppm)
APC	738	1956	0.81	0.58	0.98	426	271	0.40	0.26	160
FA	566	395	0.75	1.37	3.91	279	736	1.23	1.12	445
BA	128	234	0.24	1.03	3.43	1800	697	4.87	0.40	537
BA (without glass etc.)	131	364	0.28	1.00	4.43	1527	1007	5.36	0.49	469
melting temperature	232	327	420	650	660	1083	1247	1536	1660	1907
boiling temperature	2270	1755	907	1107	2467	2595	2061	2861	3287	2672
atomic mass	118.7	207.2	65.4	24.3	27.0	63.6	54.9	55.9	47.9	52.0

The process of metallic elements fractionation reflected in the chemical composition of incineration residues was observed in various types of materials introduced to a combustion system [2,3,15,16,17,18,19]. The process can be dependent on the physical properties of these elements such as their melting points [17], boiling points [16,20] etc. The correlation of these parameters are visible in Table 2.

According to Kasina et al. [17], the melting point seems to be the main factor which affects the volatility of elements and their distribution among FA and APC residues in fluidized bed incinerator. However this factor can be also applied for a distribution of elements between BA, FA and APC residues in shaft furnace. We also must keep in mind that the elements in waste and in incineration residues are very rarely present in the pure form. Usually they are present as part of various multi-component associations and thus their susceptibility on melting and/or volatilizing is different from those of single elements.

3.3. Metallic elements distribution among MSWI residues

Based only on absolute values of metallic elements concentrations in BA, FA and APC it seems that all of the materials are rich in metallic elements (Fig. 1a), nevertheless from the point of view of their recovery from the incineration residues, beside their concentration and forms of occurrence also an important factor is the amount of single residue produced (Fig. 1b). In studied MSWI incineration plant ~92% is BA, ~1.5% FA and ~6.5% APC is produced [personal communication with incineration plant staff].

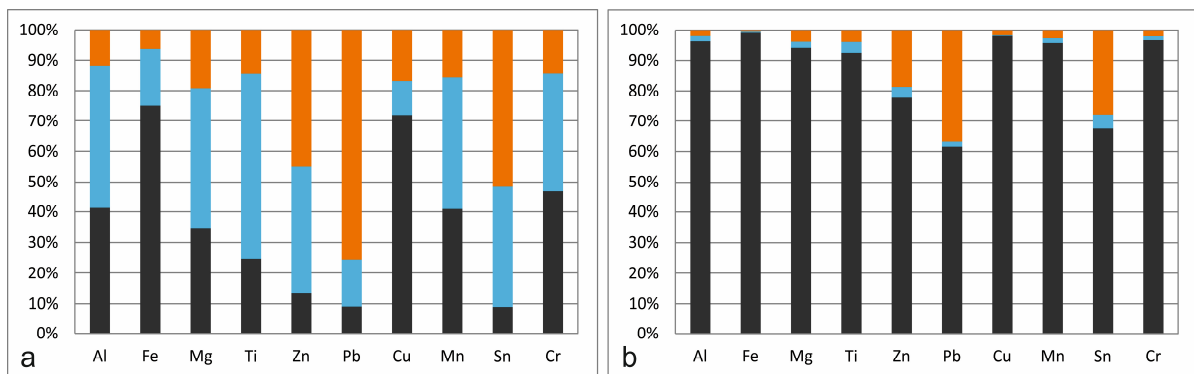


Fig. 1. Metallic elements distribution among MSWI residues; (a) relative content in BA (■) FA (■) and APC (■); (b) content of metallic elements in all residues calculated by mass of their produced amount.

If calculated metallic elements share using production rate for three types of residues, most of the metallic elements were concentrated in the BA (Fig. 1b) whereas only three elements (Pb, Zn and Sn) were present in the APC in elevated values (each 20-30% of the total). Thus only BA could be considered as a promising source of metallic elements.

3.4. Metallic elements-rich components of MSWI residues

Metallic elements in MSWI residues were mostly concentrated in the form of metallic fragments rich in few elements (Fig. 2). They were present within materials in several forms. Main were metallic grains and inclusions in the BA and FA [3] and metallic elements-rich grains in APC (Fig. 2e). Inclusions were dispersed within glassy background of grains often forming larger accumulations near edges or pores (Fig. 2a,d). Metallic components coexist with residual and newly formed mineral phases (Fig. 2a,c). BA fragments have the form of aggregates (Fig. 2b). Their size was in the range of 2-10 mm which was the main fraction of the material. FA and APC materials were of a finer fraction. In FA dominant were grains in the size of 0.25-0.1 mm, whereas in APC residues >95% of grains were smaller than 0.063 mm. All MSWI residues were characterized by the presence of similar mineral phases and multi component grains in various morphological forms (Fig. 2a-f). In FA grains were more regular and rounded (Fig. 2d) than in the BA (Fig. 2b) whereas in APC large amounts of fine grained material were present (Fig. 2f).

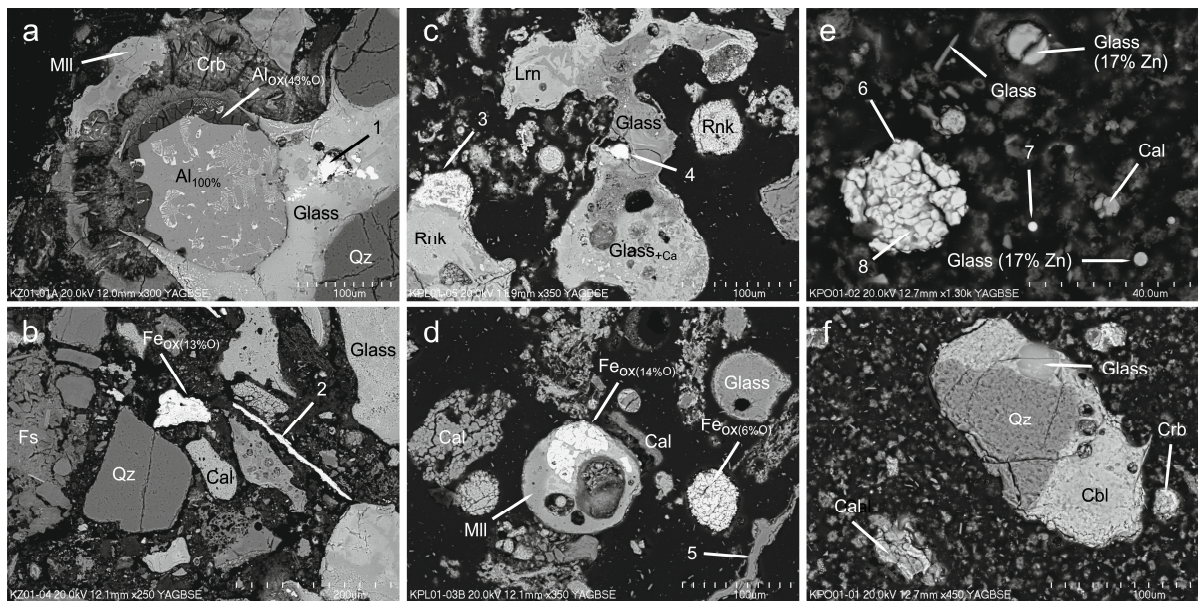


Fig. 2. Metallic components in MSWI residues, SEM-BSE images (results of EDS analysis in wt%); (a) multi-element BA grain with Al-rich fragments and metallic inclusions, 1 (95% Fe, 5% P); (b) accumulation of BA grains with separate metallic grains, 2 (84% Fe, 10% O, 6% Cr); (c) large FA grains with metallic inclusions, 3 (63% Fe, 24% Cr, 13% O), 4 (45% Fe, 55% Si); (d) rounded FA grains (with inclusions) and separate metallic grains, 5 (59% Al, 31% O, 10% Ca); (e) APC metallic element-rich grains 6 (83% Fe, 13% O, 2% Ca/Si), 7 (46% Fe, 31% Zn, 23% Ca), 8 (77% Fe, 8% Si/Ca, 7% O); (f) large three-component grain within fine grained APC material. Abbreviations: Cal - calcite, Cbl - cebolite $\text{Ca}_5\text{Al}_2(\text{SiO}_4)_3(\text{OH})_4$, Crb - carbonate, FeO_x - Fe oxide, Fs - feldspar, Glass - silicate glass, Lrn - larnite, Mll - melilite, Qz - quartz, Rnk - rankinite $\text{Ca}_3\text{Si}_2\text{O}_7$.

The high diversity in MSWI residues compositions were reported as inherited from waste, where large amounts of components were present and during incineration only a certain level of homogenization was obtained. It was mostly an effect of short time of incineration and characteristic of the shaft furnace where distribution of temperatures is unequal with possible presence of hotter and colder spots [5].

4. Conclusions

Fractionation of metallic elements within MSWI residues was observed. Depending on metallic elements properties (physical parameters, forms of occurrence in waste) and processes that occurred in the furnace they were preferably concentrated in the BA (Fe, Cu, Cr) or in the fraction removed from the furnace with the flue gases: in FA (Ti, Mg) or APC (Pb, Sn). Beside that several elements present in MSWI residues in the highest concentrations were equally or semi-equally distributed among two of the materials: BA/FA (Al, Mn) and FA/APC (Zn). Metallic elements were concentrated within MSWI residues in the form of metallic fragments or phases rich in those elements. They were characterized by a multitude of forms of their occurrences and diversified chemical composition with significant domination of the most common metallic elements: Al, Fe, Zn, Cu and Pb/Ti. Considering the amount of produced residues only the BA could be attractive from the point of view of metallic elements recovery.

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