Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 125 (2017) 56–62

Energy Procedia

www.elsevier.com/locate/procedia

European Geosciences Union General Assembly 2017, EGU Division Energy, Resources & Environment, ERE

Metallic Elements Occurrences in The Municipal Waste Incineration Bottom Ash

Piotr Rafał Kowalski[a,]*, Monika Kasina[a], Marek Michalik[a]

[a]*Institute of Geological Sciences, Jagiellonian University, Gronostajowa 3A, 30-387 Kraków, Poland*

Abstract

Bottom ash (BA) samples from a municipal waste incinerator in Poland were collected to investigate metallic components. Numerous metal-rich phases were present in the BA as a part of the incombustible waste fraction, concentrated and modified during thermal treatment. Metallic components in the BA occurred as heterogeneous assemblages of elements with various oxygen content. Fe- and Al-rich occurrences prevailed other types of compositions (e.g. Cu-, Zn- and Ti-rich). Elements in metal-rich phases co-occurred with each other (e.g. Fe occurred with Si, Ca, P, Al and Ti; Al occurred with Fe, Si and Ca; Zn occurred with Ca, Al and Si).

Peer-review under responsibility of the scientific committee of the European Geosciences Union (EGU) General Assembly 2017 – Division Energy, Resources and the Environment (ERE).

Keywords: waste incineration; MSWI bottom ash; metallic fragments; inclusions

1. Introduction

The increasing need for raw materials forces the mining industry to use low grade ores and allows the consideration of materials previously treated as waste, as a resource. In modern waste management, waste incineration residues represent significant volume of materials that need to be managed or landfilled (this is not recommended due to environmental and legislative issues). The main aim of using waste thermal treatment is to reduce its mass and volume with its simultaneous sanitization [1]. Waste thermal treatment allows additionally to recover thermal energy from the incineration. It is used to reduce incineration costs through production of electricity

* Corresponding author. Tel.: +48-663-307-850; fax: +48-12-664-43-05.
E-mail address: p.kowalski@doctoral.uj.edu.pl

1876-6102
Peer-review under responsibility of the scientific committee of the European Geosciences Union (EGU) General Assembly 2017 – Division Energy, Resources and the Environment (ERE).
10.1016/j.egypro.2017.08.060

or using heat in the technological processes or as additional source in a district heating. On average 30% of the waste mass remain in the form of solid post-process residues [2]. The BA is produced in the highest quantity and it is the main reservoir of the metallic elements taking into account its mass and elements absolute content [3].

The global trend in waste management is to recover or reuse as much as possible of valuable waste components to extend their lifetime and to follow the policy of Zero Waste. Selective waste collection and recycling is effective for these used products which are composed of pure metals or when it is easy to separate metallic components from others non-metallic parts. They often need cleaning and other purification steps before further use. Recovering of metals entrapped in the BA looks promising because of their concentration by flammable components removal during incineration. However, after incineration metals might be covered by ash material and/or oxidized, thus making it further processing more difficult. Incineration also significantly reduce the amount of waste which need to be processed for metallic elements recovery [4].

The BA from municipal solid waste incineration (MSWI) is a heterogeneous material composed of ash fraction (formed during the thermal treatment) and residual components barely affected in the furnace. The residual components are mostly composed of fragmented glass and ceramics and fragments of metal products (from few mm up to 3–5 cm in size). The BA chemical and mineral composition is to some extent diversified and mostly related to the composition of the waste in the incinerator operational area but also other factors (e.g. boiler characteristic, incineration temperature, used waste preparation technologies) [5-7]. That makes important the studies on the BA valuable components and their distribution in the material, in terms of their further processing.

The MSWI BA is an easily accessible material which can be used as a resource (e.g. mentioned metallic components) or as a raw material. The concentrations of some elements (e.g. Cu, Zn, Mg) in the BA were reported as comparable to low- and medium-grade ores [8]. By using valorization or extraction techniques it is possible to extend the range of its possible application [9]. The techniques of ferrous metal products separation using simple magnets and non-ferrous metal products using eddy current separators are widely used. To increase efficiency of the separation, techniques of grains size reduction should be applied (e.g. crushing, high voltage fragmentation) [10].

The aim of this study is to investigate metallic components of the BA to determine its usefulness as a resource of the metallic elements. Studies were based on the metallic components description: their chemical composition, sizes, distribution within the BA and characteristic of the metallic elements co-occurrences. The BA was characterized using chemical and mineralogical methods with quantitative determination of the amorphous and crystalline phase.

2. Materials and analytical methods

2.1. Bottom ash samples

To investigate distribution of metallic elements within metallic components in the BA, eight samples were collected in 2015 and 2016 (totally ca. 100 kg, 6–14 kg each sample). Material from municipal waste thermal treatment was obtained in the incineration plant in Poland situated in a big city (over one million of inhabitants), which incinerates 48 000–55 000 tons of waste per year. Three types of solid residues are produced there: the BA (Fig. 1a), the air pollution control residues (APC) and the fly ash (FA). Their ratio (wt%) is 91.5 / 7 / 1.5.

Fig. 1. (a) fresh BA stored on a heap; (b) metallic products separated from the BA using hand picking and magnetic separator.

The waste code of the collected BA is 19 01 12 and on the European List of Waste [11] it is categorized as "bottom ash and slag other than those mentioned in 19 01 11*" (*bottom ash and slag containing dangerous substances). After incineration wet bottom ash is stored on a heap under atmospheric conditions (Fig. 1a). The BA is composed of 60–80 wt% of ash material and 15–30 wt% of residual components (mostly represented by glass and ceramics) and 3–5 wt% of fragmented metal products.

2.2 Waste incineration technology

Incineration plant is using one incineration line based on Krüger W-Mark 5 shaft furnace. Before incineration collected mixed waste are controlled in order to avoid incineration of its potentially dangerous components (e.g. highly flammable or explosive). Waste (<8 t/h) is thermally treated for 30–120 minutes in temperatures ranging from 950 to 1100° C on the furnace grates. The hot BA is cooled with water and before storing on a heap, large fragments of metal products (<50 cm) are separated manually during transportation on the conveyor belt between the furnace and the separator where fragments in size below 20 cm are separated using magnets. These large fragments of the metal products (Fig. 1b) mixed with grainy BA material are effectively separated, whereas smaller fragments inherited in the BA grains and aggregates stay in the BA as its metallic components.

The FA and the APC are separated from flue gases in two stages of the air pollution control system. The process is performed to neutralize toxic and hazardous components of the flue gases (NO_X, SO_X, HCl, HF, toxic metallic elements, dioxins, furans and organic pollutants) using filters and reactions with ammonia vapors, $Ca(OH)_2$ and activated coke. At the second stage of the process in the recovery boiler overheated steam is produced and later used for the production of electricity (1.5–1.8 MW) and district heating (~9 MW) [12].

2.3 Analytical methods

The BA components were manually separated and three fractions were weighed: ash material, glass / ceramics and fragments of metal products. The BA chemical composition covering content of the main and trace elements were performed in the Bureau Veritas Upstream Minerals (formerly AcmeLabs Analytical Laboratories) in Vancouver, Canada. For multi-element analysis, inductively coupled plasma optical emission and mass spectrometry (ICP-OES, ICP-MS respectively) were used. The total content of C and S was measured using a LECO combustion analysis. Loss on ignition (LOI) was obtained using the thermal method.

The powder X-ray diffraction method (XRD) was used for qualitative and quantitative determination of the BA mineral composition. The measurements were performed in angles range of 2–70° 2Θ using Philips X'Pert APD diffractometer (goniometer PW3020, curved graphite crystal monochromator, CuKα radiation) with a step of 0.02° per 2 s for qualitative or 0.02° per 5 s for quantitative analyses. XRD patterns were interpreted using Philips X'Pert Graphics & Identify software (based on ICDD database) and the American Mineralogist Crystal Structure Database [13]. Quantitative calculations based on Rietveld refinement were made using SEIFERT AutoQuan software.

Internal structure of the BA grains was studied in a polished thin sections using Nikon Eclipse E600 POL optical microscope. The same thin sections (coated with carbon) were also used for microanalyses using field emission scanning electron microscope (FE-SEM) Hitachi S-4700 with Noran Nordlys microanalysis system of energy dispersive spectrometry (EDS). Metallic components size distribution was determined through measuring their sizes in two dimensions using SEM images.

3. Results and discussion

3.1. Chemical and mineral composition of the bottom ash

The BA is a material rich in Si and Ca and Fe, Al and Na present in smaller amounts (Table 1), what is a typical composition for this type of residue observed in various localities [14,15]. Residual materials separation results in lower content of Si, Ca and Na (main components of the fragmented glass and ceramics) and simultaneous increase, mostly in content of Fe and Al. The average content of the metallic elements in ash material (Al, Fe, Mg, Ti, Mn, Cr, Ni, Sc, Mo, Cu, Pb, Zn, Sn) is ~11 wt% [3] with domination of Al and Fe and elevated values of Mg and

Ti, Cu, Zn, which seem to be the most promising elements for the recovery. Most of these elements are reported as common in municipal waste incineration residues, nevertheless their concentration vary in a broad range [4,14,15,16]. They are distributed within amorphous and crystalline phase and metallic components of the BA. The overall content of metallic elements does not reflect their availability for the recovery [4]. The averaged value of ~11 wt% covers metallic elements present in all forms in the BA: in metallic fragments, as components of minerals or dispersed within them as well as components of the amorphous part of the BA.

Table 1 Chemical composition of the bottom ash.

element		Si	Ca	Na	Fe	Al	Mg	K	P	LOI	C_{tot}	S_{tot}
(*wt%*)	B	25.7	15.8	5.1	4.9	3.4	1.0	0.7	0.3	3.9	0.6	0.5
	R	23.8	12.3	4.1	5.4	4.4	1.0	0.7	0.4	4.8	0.9	0.7
element		Ti	Zn	Cu	Mn	Cr	Pb	Zr	Sn	Ni	Co	REE
(*ppm*)	B	3957	2359	1801	697	537	234	193	128	63	47	77
	R	4916	2815	1527	1007	469	364	156	131	127	61	90

B - bulk BA samples, R - BA samples after residual components removal. Values averaged from analysis of four samples for each type.

In the BA composition the amorphous phase is dominating and represents ~65 wt% (~53 wt% in the ash material) of each sample. It is mostly composed of silicate glass, which is the most common type of BA grains matrix [14,17]. Separation of residual materials results in 12% decrease of the amorphous phase content. Most of the mineral and metallic phases are entrapped within the BA grains glassy matrix, thus reducing their recovery potential. The glass was also reported as a phase prone to alteration e.g. in time of storage [6].

The BA contains various crystalline phases - silicates, aluminosilicates, oxides of non- and metallic elements, carbonates and sulphates (Table 2). It is a combination of residual (e.g. quartz, feldspars) and newly formed mineral phases (e.g. larnite, melilites).

Table 2 Mineral composition of the bottom ash.

Mineral	Chemical formula	BA (*wt%*)	Ash material* (*wt%*)
amorphous	$Si_{+ O, Ca, Na, Al, Fe, K, Mg, Ti}$	65.2	53.2
quartz	SiO_2	11.2	15.5
larnite	$Ca_2[SiO_4]$	6.3	7.9
calcite	$Ca[CO_3]$	4.8	6.3
feldspars	$K[AlSi_3O_8]$ - $Na[AlSi_3O_8]$ - $Ca[Al_2Si_2O_8]$	4.3	4.5
melilites	$Ca_2Mg[Si_2O_7]$ - $Ca_2Al[AlSiO_7]$	3.6	6.1
iron-oxides	Fe_xO_y	2.4	2.7
wollastonite	$(Ca_3[Si_3O_9])$, sulphates, phosphates, halite	<2	<2

*BA after separation of residual materials. Values averaged from analysis of four samples for each type.

3.2. Bottom ash and its metallic components

The BA is a heterogeneous grainy material composed of grains of diverse size, shapes and composition. The BA is composed of multi-component grains (Fig. 2a) usually present in fragile aggregates mixed with the fine fraction (Fig. 2b). That inhomogeneity is a remnant of the incinerated waste composition, which varied in a broad range and during incineration it is not possible to obtain high degree of unification due to irregular distribution of temperatures in the furnace and short time of exposure for high temperatures [5]. Nevertheless characteristics of the BA from different localities is comparable.

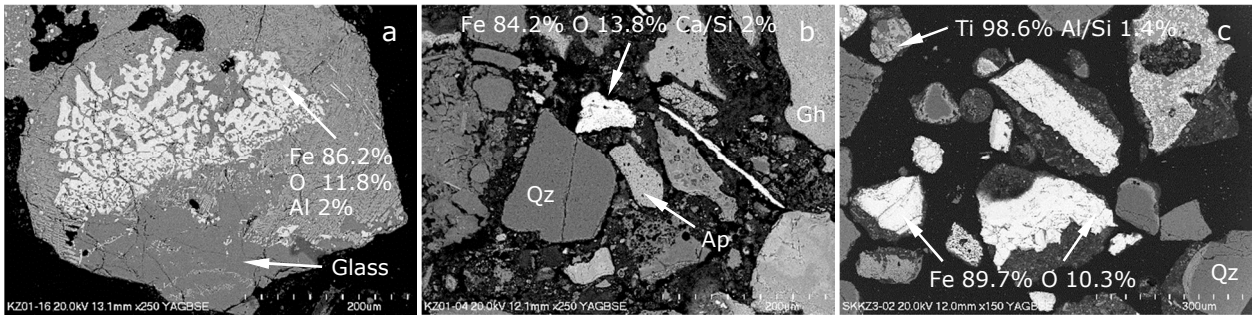

Fig. 2. Types of the BA internal structure: (a) grain with glassy matrix; (b) weakly bonded aggregate of grains [3]; (c) separate mineral and metallic grains covered by layers of amorphous material. Ap - apatite, Gh - gehlenite, Glass - silicate glass, Qz - quartz. SEM-BSE images, values of EDS analysis in wt%.

Metallic components of the waste concentrate in the incineration residues. Depending on their form of occurrence in waste and basic chemical properties they interact with melt in a different way. Some of them are barely affected by the thermal process and other are incorporated (mostly as inclusions and micro-inclusions) in the structure of newly formed mineral and amorphous phases. They are also irregularly distributed among the BA and ashes removed with flue gases, what was observed in various types of the waste incineration residues [3,18].

Two main forms of metallic element concentration within the BA were observed: inclusions within grains (Fig. 2a; 3a-d) or separated metallic grains (Fig. 2b,c; 3e) which were components of the fine fraction or aggregates. The inclusions had more regular shapes, often circular whereas the separate grains were often elongated and covered by thin layer of oxides or ash material (Fig. 2c; 3d).

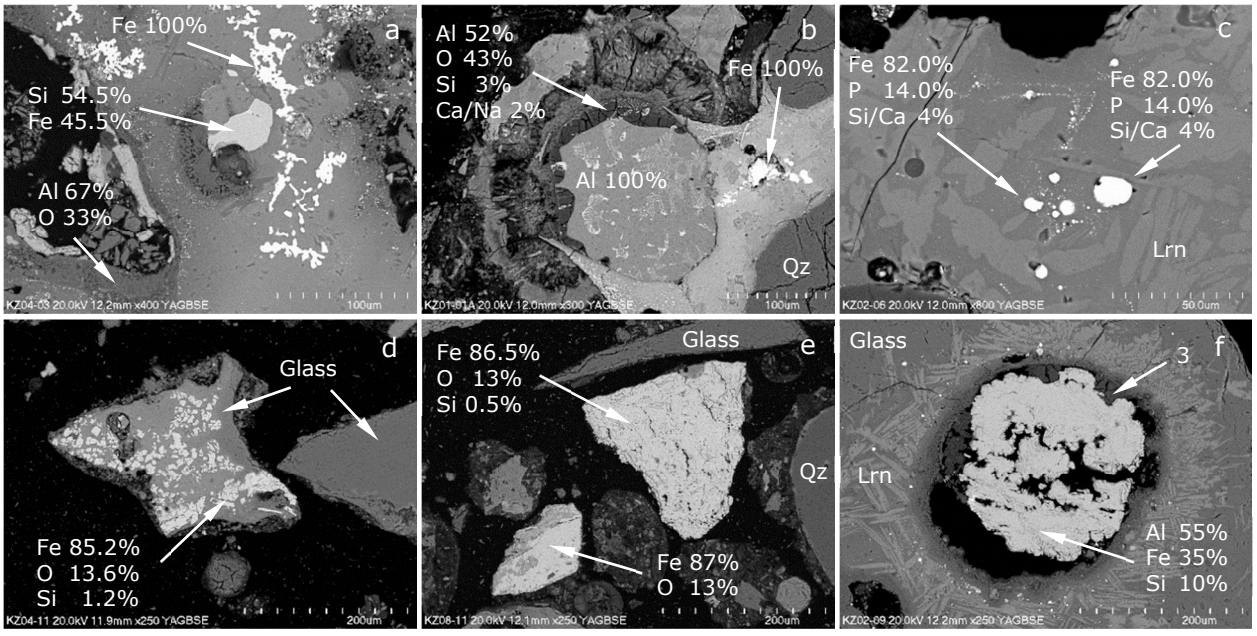

Fig. 3. Metallic components of the BA: (a-d) metallic inclusions within the BA grains; (e) accumulation of separate BA grains; (f) pore filled with metal-rich fragment (3 - Al 50%, O 46%, Ca 2.7%, S 1.3%). Glass - silicate glass, Lrn - larnite, Qz - quartz. SEM-BSE images, values of EDS analysis in wt%. (b) - [3].

In the glassy matrix large number of inclusions were present but their size usually did not exceed 10 μm and most of them were smaller than 5 μm (Fig. 4; 3c). Separate grains were larger than inclusions and more mass of the metallic elements were concentrated within them. The most of the separate grains were larger than 50 μm (Fig. 4) and were characterized by quite even grain size distribution in the range of sizes from 50 to 500 μm (Fig. 2bc; 3e).

Because of the sizes of the BA metallic components ant their physical properties, methods of gravity separation, floating, acid leaching were suggested to be used for their effective recovery [16].

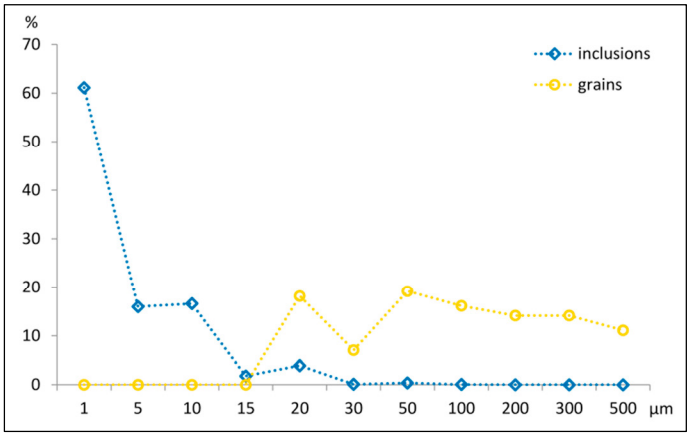

Fig. 4. Size distribution of metallic components in the BA.

The BA metallic components were characterized by their composition heterogeneity and various oxygen content. The most common were Fe-, Al- and Zn-rich occurrences, forming respectively 70%, 15% and 5% of the total amount of fragments. Fe occurred mainly as a component of metallic inclusions and separate grains. Al was mostly present in the metallic fragments on grains boundaries and also as separate grains (often oxidized). Moreover Al was important component of aluminosilicates and amorphous phase. Zn-rich metallic fragments were mostly in the form of separate grains. The content of oxygen in most of the metallic grains (except oxidised Al-rich fragments) was in a range from a few up to 15 wt%.

3.3. Metallic elements co-occurrence

In the composition of the metallic components one or two main elements dominates over others and rarely the single-element fragments occur. This is a remnant of a complex chemical composition of the waste metallic components where metallic elements are present mostly in the form of alloys or composites. Their final form and composition is a result of transformations which they undergo in a multi-component system during incineration. Processes of their melting and solidifying (if melting point of the phase was reached) supports incorporation of new elements. The thermal treatment in temperatures up to 1100 °C allows metal products to interact with others waste components and the multi-component character of the system can also influence incinerated metallic phases by lowering their melting temperatures.

Despite the diversity of the metallic components composition some regularities in elements co-occurrences were observed. The most common were co-occurrence of Fe with Si, Ca, P, Al and Ti co-occurrence of Al with Fe, Si and Ca and co-occurrence of Zn with Ca, Al and Si. Ability of metallic elements to interact with other waste components during incineration are based on their chemical properties: reactivity and chemical affinity. It is visible in newly formed or residual natural phases, which are present in the BA together with alloys and composites made on purpose by industry.

4. Summary and conclusions

The BA from the incineration of municipal waste is a heterogeneous material containing up to 65 wt% of the amorphous phase (mostly represented by silicate glass) and rich in metallic occurrences. In glass based grains and their aggregates, polymineral crystalline phase is irregularly distributed and co-occurred with metallic components in various forms. On average ~11 wt% of the BA are metallic elements, mostly concentrated in the form of metallic grains and inclusions but also partly dispersed within minerals and amorphous phases.

From the BA in a technological process large metallic products were effectively separated (by hand picking and using magnets) nevertheless up to 5 wt% of small fragments are still present in the BA. This BA components are easily extractable due to it weak bonding with ash material and its size from tenths of a millimeter to few centimeters. Smaller fragments are strongly bonded with ash material and are often entrapped within grains and their aggregates. The limiting factor of the recovery is the size of the metallic inclusions because ~85% of them are smaller than 5 µm. More promising for the recovery are easier accessible metallic grains which are larger (usually their size is in a range of 50 to 500 µm) thus concentrating more mass of the metallic elements.

The BA is a material rich in metallic components characterized by their multi-element form. Usually they were barely affected by the oxidation process (except Al-rich components), what is an additional value if their recovery would be applied. Forms and composition of the BA metallic components allows to evaluate the BA as a potential polymetallic resource. Beside high content of Fe and Al, the elevated content of Ti, Cu and Zn in the BA are promising from the point of view of their recovery. Additionally, recovery of the metallic components from the BA increases its raw material potential, by reducing the amount of elements which could be released from it in hazardous concentrations.

Acknowledgements

Research was funded by Polish National Science Centre (NCN) under grant No. UMO-2014/15/B/ST10/04171.

References

[1] Sabbas, Thomas, Alessandra Polettini, Raffaella Pomi, Thomas Astrup, Ole Hjelmar, Peter Mostbauer, Giovanna Cappai, Gabi Magel, Stefan Salhofer, Claudia Speiser, Soraya Heuss-Assbichler, R. Klein, and Peter Lechner. (2003) "Management of municipal solid waste incineration residues." *Waste Management* 23 (2003): 61-88.

[2] Chimenos, Josep, M., Mercè Segarra, Miguel A. Fernández, and Ferran Espiell. (1999) "Characterization of the bottom ash in municipal solid waste incinerator." *Journal of Hazardous Materials* 64.3 (1999): 211-222.

[3] Kowalski, Piotr, R., Monika Kasina, and Marek Michalik (2016) "Metallic elements fractionation in municipal solid waste incineration residues." *Energy Procedia* 97 (2016): 31-36.

[4] Kahle, Kristian, Bettina Kamuk, Jens Kallesøe, Edmund Fleck, Frans Lamers, Lars Jacobsson, and Jakob Sahlén. (2015) "Bottom ash from WtE plants - Metal recovery and utilization." *International Solid Waste Association Reports 2015.*

[5] Eusden, Dykstra, J., Taylor T. Eighmy, Kenneth Hockert, Elizabeth Holland, and Kimberly Marsella. (1999) Petrogenesis of municipal solid waste combustion bottom ash. *Applied Geochemistry* 14.8 (1999): 1073-1091.

[6] Bayuseno, Athanasius, and Wolfgang W. Schmahl. (2010) "Understanding the chemical and mineralogical properties of the inorganic portion of MSWI BA." *Waste Management* 30.8-9 (2010): 1509-1520.

[7] Kasina, Monika, Piotr R. Kowalski, and Marek Michalik. (2017) Seasonal changes in chemical and mineralogical composition of sewage sludge incineration residues and their potential for metallic elements and valuable components recovery. *Energy Procedia* (2017): (this issue).

[8] Funari, Valerio, Roberto Braga, Syed Nadeem Hussain Bokhari, and Tomas Meisel. (2015) "Solid residues from Italian municipal solid waste incinerators: A source for ''critical'' raw materials." *Waste Management* 45 (2015): 206-216.

[9] Lam, Charles H. K., Alvin W. M. Ip, John Barford, and Gordon McKay. (2010) "Use of Incineration MSW Ash: A Review." *Sustainability* 2 (2010): 1943-1968.

[10] "SELFRAG Revolutionises Incinerator Slag Recycling." [accessed 2017 May 10]. http://www.axt.com.au/incinerator-slag-recycling/

[11] Environmental Protection Agency. (2002) "European Waste Catalogue and Hazardous Waste List 2002." Ireland: *EPA*, (2002).

[12] Malczewski, Janusz, and Przemysław Nadulski. (2010) "Thermal treatment of wastes in ZUSOK - operational experience (in Polish)." *VII Conference: "Dla Miasta i Środowiska - Problemy Unieszkodliwiania Odpadów" - Conference materials*, (2010): 61-65.

[13] Downs, Robert, T, and Michelle Hall-Wallace. (2003) "The American Mineralogist crystal structure database." *American Mineralogist* 88.1 (2003): 247-250.

[14] Chandler, John, A, Taylor T Eighmy, Jan Hartlén, Ole Hjelmar, David S. Kosson, Steven E. Sawell, Hans A. van der Sloot, and Jürgen Vehlow. (1997) "Municipal solid waste incineration residues." *Studies in Environmental Science* 67 (1997).

[15] Wei, Yunmei, Takayuki Shimaoka, Amirhomayoun Saffarzadeh, and Fumitake Takahashi. (2011) Mineralogical characterization of municipal solid waste incineration bottom ash with an emphasis on heavy metal-bearing phases. *Journal of Hazardous Materials* 187 (2011): 534-543.

[16] Xia, Yi, Pinjing He, Liming Shao, and Hua Zhang. (2016) "Metal distribution characteristic of MSWI bottom ash in view of metal recovery." *Journal of Environmental Sciences* 52 (2016): 178-189.

[17] Saffarzadeh, Amirhomayoun, Takayuki Shimaoka, Yoshinobu Motomura, and Koichiro Watanabe. (2009) "Characterization study of heavy metal-bearing phases in MSW slag." *Journal of Hazardous Materials* 164 (2009): 829-834.

[18] Kasina, Monika, Piotr R. Kowalski and Marek Michalik. (2016) "Metals accumulation during thermal processing of sewage sludge - characterization of fly ash and air pollution control (APC) residues". *Energy Procedia* 97 (2016): 23-30.