European Geosciences Union General Assembly 2016, EGU
Division Energy, Resources & Environment, ERE

Metals Accumulation During Thermal Processing of Sewage Sludge - Characterization of Fly Ash and Air Pollution Control (APC) Residues

Monika Kasina[a,*], Piotr R. Kowalski[a], Marek Michalik[a]

[a]Institute of Geological Sciences, Jagiellonian University, Oleandry 2a, 30-063 Krakow, Poland

Abstract

Sewage sludge thermal utilization leads to production of fly ash and APC residues which may contain elevated amounts of some metallic or toxic elements (Fe, Zn, Pb, Sn, Au, Hg, Cd, As). Distribution of these elements in studied fly ash and APC residues was unequal and dependent on their melting temperature. Metals in fly ash are present as Fe-rich grains and rims around Si-glass whereas in APC metallic components are mostly represented by Sn-rich inclusions dispersed in matrix, Ca-phosphates or as separate micro-grains. Elements concentrations were elevated but overall content was low thus disqualifying the material in terms of recovery.

Keywords: thermal utilization; sewage sludge; fly ash, air pollution control residues; metallic components

1. Introduction

Due to increasing mass of sewage sludge produced in wastewater treatment, problems in its management have appeared in Poland. Over years sewage sludge was landfilled, however due to the European Landfill Directive 1999/31/EC [1] it is not an option anymore due to the fact that sewage sludge contains materials regarded as hazardous.

────────

* Corresponding author. Tel.: +48-607-443-607; fax: +48-12-633-22-70.
  E-mail address: monika.kasina@uj.edu.pl

Highly concentrated metallic and harmful elements, toxic organic substances and biological components (e.g. parasites, microbes) disqualify this material for landfilling. In addition EU-member states obliged themselves with accordance to that directive to reduce the amount of biodegradables waste landfill by 65% in comparison to the amount from 1995 [2]. Some of the EU countries (Germany, The Netherlands, Sweden, Austria, Denmark and Belgium) achieved the goal already in 2010 by combining material recycling, biological treatment and waste-to-energy technology [2], however in Poland still over 50% of waste is landfill [3].

Currently in Europe one of the most reasonable method for sewage sludge treatment is incineration [4,5]. This process results in the utilization of sewage sludge by thermal destruction of toxic compounds [6] with minimum energy consumption and thus minimize the costs of managing waste generated in the process. In addition energy is recovered due to high calorific value of sewage sludge, almost equal to that of brown coal [5]. Nevertheless even the incineration has advantages due to the reduction of sewage sludge volume and lower disposal costs it is not a complete method [7] since almost 30% of the solids remain in incineration residues as fly ash and air pollution control (APC) residues.

The goal of this study was to characterize chemical and mineral composition of fly ash and APC residues as well as to attempt to characterize fractionation of metallic and toxic elements and their accumulation within residue materials in terms of their potential recovery.

2. Materials & methods

2.1 Characteristic of sewage sludge thermal utilization plant – technological approach

Dewatered sludge is transported directly from wastewater treatment plant by conveyors to the dewatered sludge silo, where it is further transported to the node for sludge membrane drying system down to 22% dry mass. The dryer is supplied with heat in the form of hot steam, which is recovered from the incineration process. Dried sludge is incinerated in the fluidized bed furnace Pyrofluid™ which is characterized by high turbulence of the fluidized bed at a constant temperature and constant intensity of the process which provides complete incineration of organic matter, constant operating temperature in the range of 850-900º C what ensures a longer life time of the furnace and the effective reduction of NO_x emission. In addition the heat exchange area within the fluid bed allows to reduce the size of the installation. A thermal utilization station is equipped with a heat exchanger, responsible for pre-cool of flue gases and the production of saturated steam to power the drying node [8].

2.2 Materials characteristic and preparation for analyses

During the process of sewage sludge thermal utilization a fly ash, classified as non-hazardous waste[1] and by-products from the cleaning of exhaust gases so called air pollution control residues (APC) residues, classified as hazardous waste[2] were produced.

Fly ash was a reddish, fine-grained material, containing ~ 30 wt% of particles within 0.25-0.063 mm size range and very low soluble material content (~ 1 wt%), whereas APC residues were light grey, very fine-grained material, where particles between 0.25-0.063 mm size constitute over ~ 99 wt% and the soluble material content was ca. 98 wt%.

Due to high content of soluble material in APC residues a soluble fraction was removed by dissolution in deionized water (APCc), what caused significant mass reduction of 98% and additional concentration of potentially valuable or toxic metals.

----

[1] Fly ash (waste code: 19 01 14) with accordance to the Regulation of the Minister of the Environment of 9 December 2014 (Dz.U. 2014 poz. 1923) is defined as: "ash other than those mentioned in 19 01 13 (fly ash containing dangerous substances)".

[2] APC residues (waste code: 19 01 07*) with accordance to the Regulation of the Minister of the Environment of 9 December 2014 (Dz.U. 2014 poz. 1923) is defined as: "solid waste from gas treatment".

2.3 Analytical methods

The chemical composition of sewage sludge incineration residues was analyzed using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) methods performed in the ACME Analytical Laboratories Ltd, Vancouver, Canada. The main mineral composition was determined using a Philips X'Pert Diffractometer (APD type) with a PW 3020 vertical goniometer. The analytical range for XRD analyses was 2-64° θ, Cu Kα radiation, a step size of 0.02° and a time of 1 s/step were applied. For phase identification, the Philips X'Pert Graphics and Identify v.1.2a software with the ICDD PDF2 database was used. To characterize the form of occurrences of metallic components and their composition a field emission scanning electron microscope (FE-SEM) Hitachi S-4700 was used. Quantitative analyses of the chemical composition of the metallic particles was performed using an energy dispersive spectrometer (EDS). The fly ash, and APC residues, prepared as thin sections, were carbon coated and examined with FE-SEM operating at an accelerating voltage of 20 kV, using the back scattered electrons (BSE) mode.

3. Results and discussion

3.1. Mineral and chemical composition of fly ash and APC residues

The fly ash was a SiO_2-P_2O_5-Fe_2O_3-CaO dominated material (35 wt% SiO_2, 17.92 wt% P_2O_5, 15.85 wt% Fe_2O_3 and 12.63 wt% CaO). The XRD analyses indicated the presence of quartz (SiO_2), apatite ($Ca_5(PO_4)_3(OH,F,Cl)$), hematite (Fe_2O_3) and feldspar ($K(AlSi_3O_8)$-$Na(AlSi_3O_8)$-$Ca(Al_2Si_2O_8)$) as main mineral phases. However in the literature whitlockite ($Ca_3(PO_4)_2$) is mentioned more often than apatite [9]. The content of metallic and toxic elements in fly ash was high. Contents of these elements are compared in Table 1 to the upper continental crust [10].

Table 1. Content of selected metallic and toxic components in fly ash, APC residues and APCc
(in bold – highly concentrated elements in studied materials).

Element	Unit	Fly ash	APC residues	APCc	Upper continental crust composite [10]
Fe	%	**11.09**	0.06	1.42	5.544
Ti	%	0.59	0.01	0.09	0.64
Mn	%	0.09	0.001	0.02	0.1
Mo	ppm	25.5	1.1	4.5	1.1
Ni	ppm	**119.5**	1.6	43.3	47
Cr	ppm	**1047**	0.001	89	92
Zn	ppm	**4472**	164	**6326**	67
Cu	ppm	**665.5**	12.2	**476.6**	28
Pb	ppm	138.0	14.8	**514.3**	17
Sn	ppm	364	66	**2465**	2.1
Co	ppm	27.2	0.3	8.6	17.3
As	ppm	16.2	0.4	15.4	4.8
Cd	ppm	7.0	0.5	20.3	0.09
Sb	ppm	6.9	2.1	64.6	0.4
Hg	ppm	0.01	10.05	**50.00**	0.05
Au	ppm	**0.9**	0.00018	0.00005	0.00015

The APC residues composition was dominated by soluble minerals, mostly thenardite ($Na_2(SO_4)$). Thenardite could form in the reaction of sodium bicarbonate ($NaHCO_3$) which was used as a reagent during the purification of flue gases (i.a. removal of SO_x). A significant mass reduction of 98 wt% related to the removal of soluble material by dissolution in deionized water caused 30-fold additional concentration of some elements. Main mineral phases detected in APC residues after removal of soluble materials (APCc) were quartz, calcite ($Ca(CO_3)$) and apatite. In Table 1 are listed the metallic and toxic components present in APC residues and highly concentrated in APCc.

The concentration of REE and other critical elements was very low, and in comparison to the upper continental crust significantly depleted. However [11] indicated in crust-normalized REE pattern of sewage sludge ash produced in Japan is slightly enriched with Sm, Eu, and Tb. Nevertheless we must keep in mind that sewage sludge incineration residues can differ in composition and content of various elements depending on the local environmental conditions, level of environmental awareness, economic development, and also social needs and society education in each region.

3.2. Elements fractionation between fly ash and APC residues

The partitioning behavior of elements was widely studied for coal combustion. Three main classes are distinguished based on the element volatility [12,13]: non-volatile, partially volatile and highly volatile.
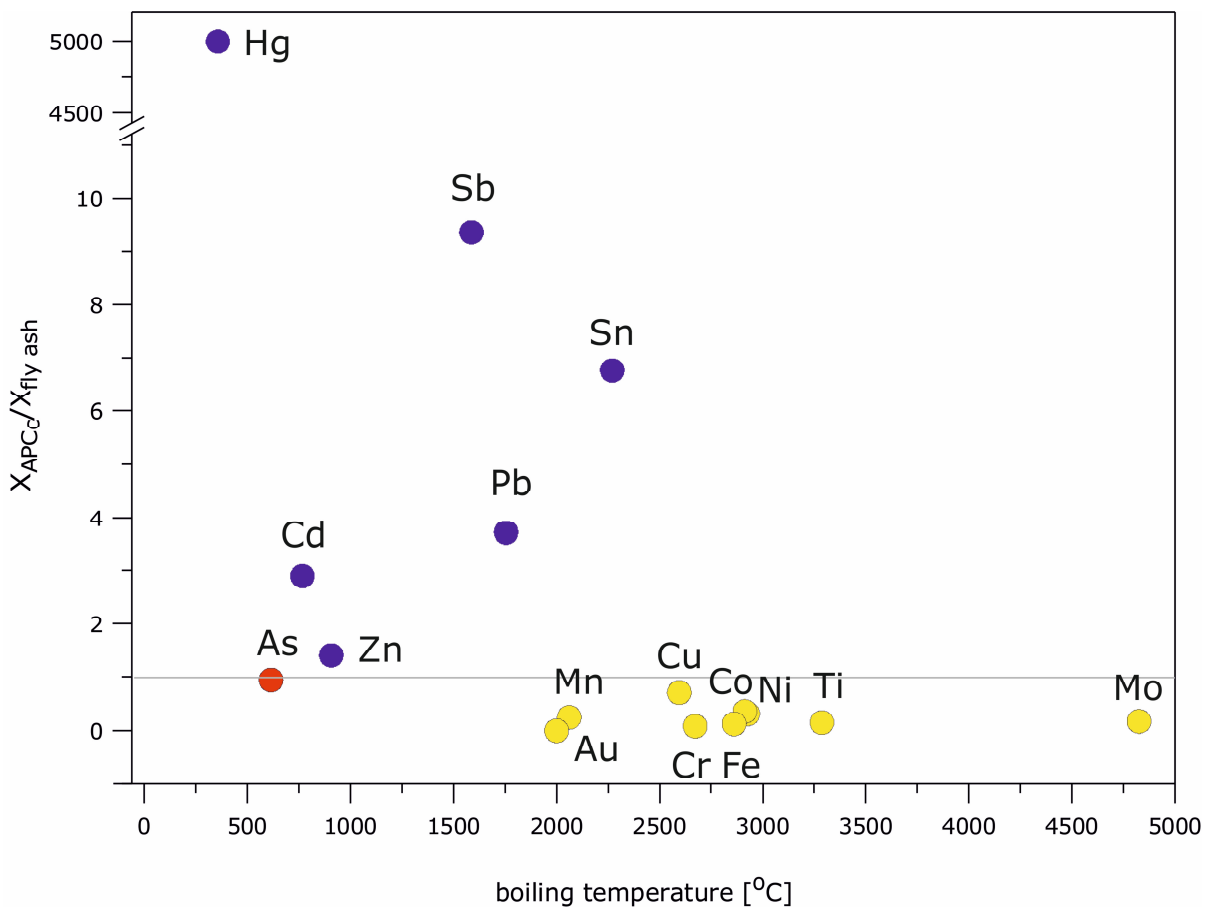

Fig. 1. Metal fractionation of sewage sludge incineration residues. ● - relative enrichment of elements in APCc; ● - relative enrichment of elements in fly ash; $X_{APCc}/X_{fly\ ash}$ for As was ~ 1; boiling temperatures of elements from [14].

Some elements can overlap between these three groups depending on e.g. combustion conditions and combustor type what can cause different ranges of volatility of the elements as well as fluid dynamics and kinetic factors within the incinerator [15].

Even though the range of volatility of the elements can be large as suggested by [13] at some point it was possible to notice similarities in elements volatility series in sewage sludge thermal incineration residues and coal combustion residues.

The distribution of metals in fly ash and APC residues after incineration in the fluidized bed furnace was analyzed by comparing metal concentrations in the fly ash and APCc. A metal enrichment factor was calculated from the ratio of concentration of given element in APCc to concentration in fly ash ($X_{APCc}/X_{fly\ ash}$). The values below 1 indicated the concentration of elements in fly ash whereas the values above 1 indicated the enrichment of elements in the APC residues (Figs. 1, 2).

The boiling and melting temperature were examined to show the correlation of $X_{APCc}/X_{fly\ ash}$ with temperature in order to demonstrate which of these factors was responsible for metal distribution between fly ash and APC residues.
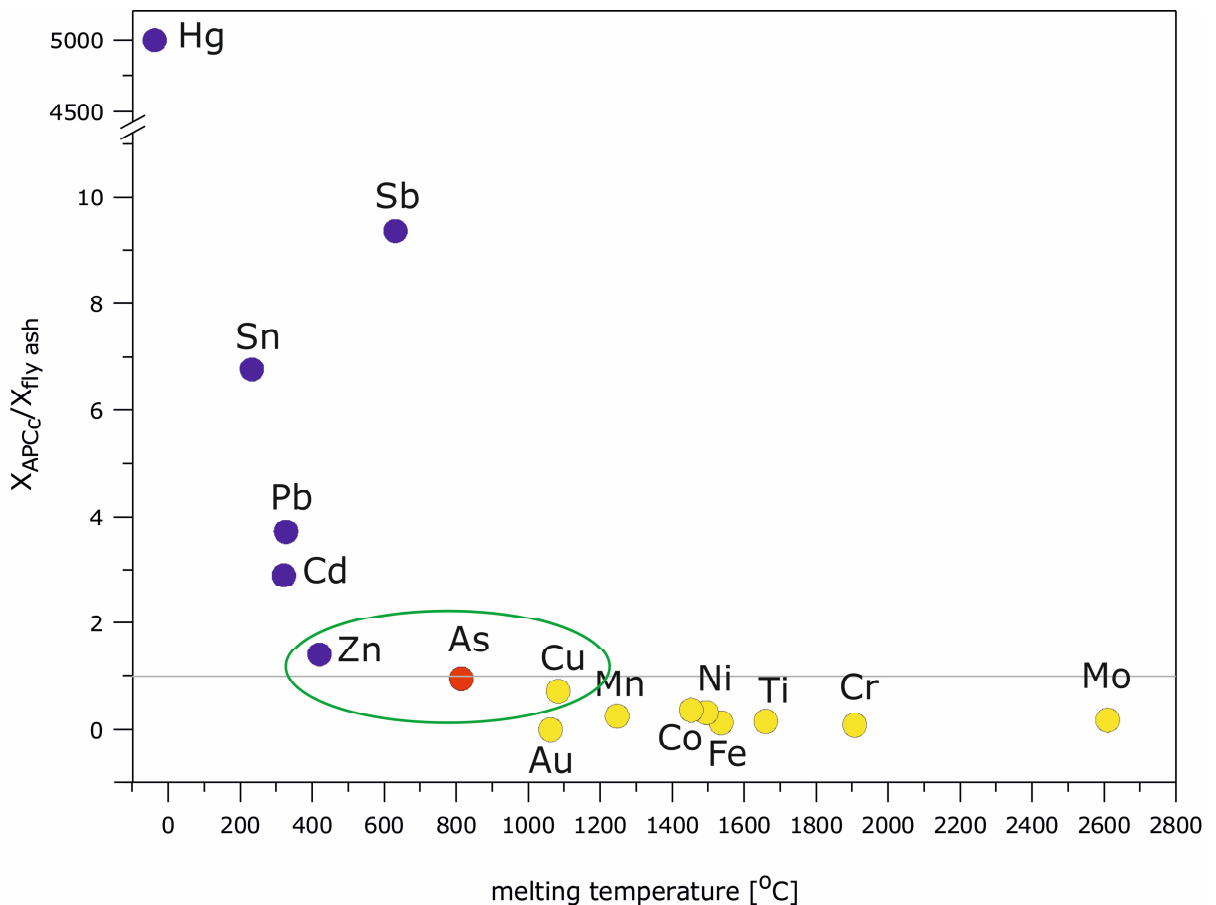

Fig. 2. Metal fractionation of sewage sludge incineration residues. ● - relative enrichment of elements in APCc; ● - relative enrichment of elements in fly ash; ⬭ - almost equally distributed elements; $X_{APCc}/X_{fly\ ash}$ for As was ~ 1; melting temperatures of elements from [14].

Boiling temperature poorly correlated with the $X_{APCc}/X_{fly\ ash}$ could be applied only to some elements (Fig. 1). According to [13], volatility of elements usually shows a positive correlation with their boiling points. However in that study enrichment of fly ash in comparison to bottom ash was shown. For sewage sludge incineration residues discrepancies were observed, mostly due to the fact that bottom ash was not produced at all and the fraction of the fly

ash and APC residues was much finer. As suggested by Wilczyńska-Michalik et al. and Mardon and Hower [16,17] elements concentrate more easily on a finer particles due to larger surface area of a fraction and can be dependent on both melting or boiling temperature. Nevertheless other factors responsible for metal fractionation between fly ash and APC residues shall also be considered in the further studies.

Melting temperature of elements correlated with the $X_{APCc}/X_{fly\ ash}$ ratio and seemed to be the main factor governing their partitioning in fly ash and APC residues (Fig. 2). Elements characterized by high melting temperature were mostly concentrated in fly ash (e.g. Mo, Cr, Ti, Fe, Ni, Co, Mn, Cu, Au), these of a lower melting temperature could be led out from the furnace in the volatile form and concentrated in APC residues. Only As, Zn and Cu were distributed equally between fly ash and APC residues. These findings were in agreement with Elled et al. [18] who also suggested Hg, Cd, Sb, As and Pb to be volatilized during the incineration and their condensation on ash surface during the temperature drop down related to the flue gases heat recovery [19].
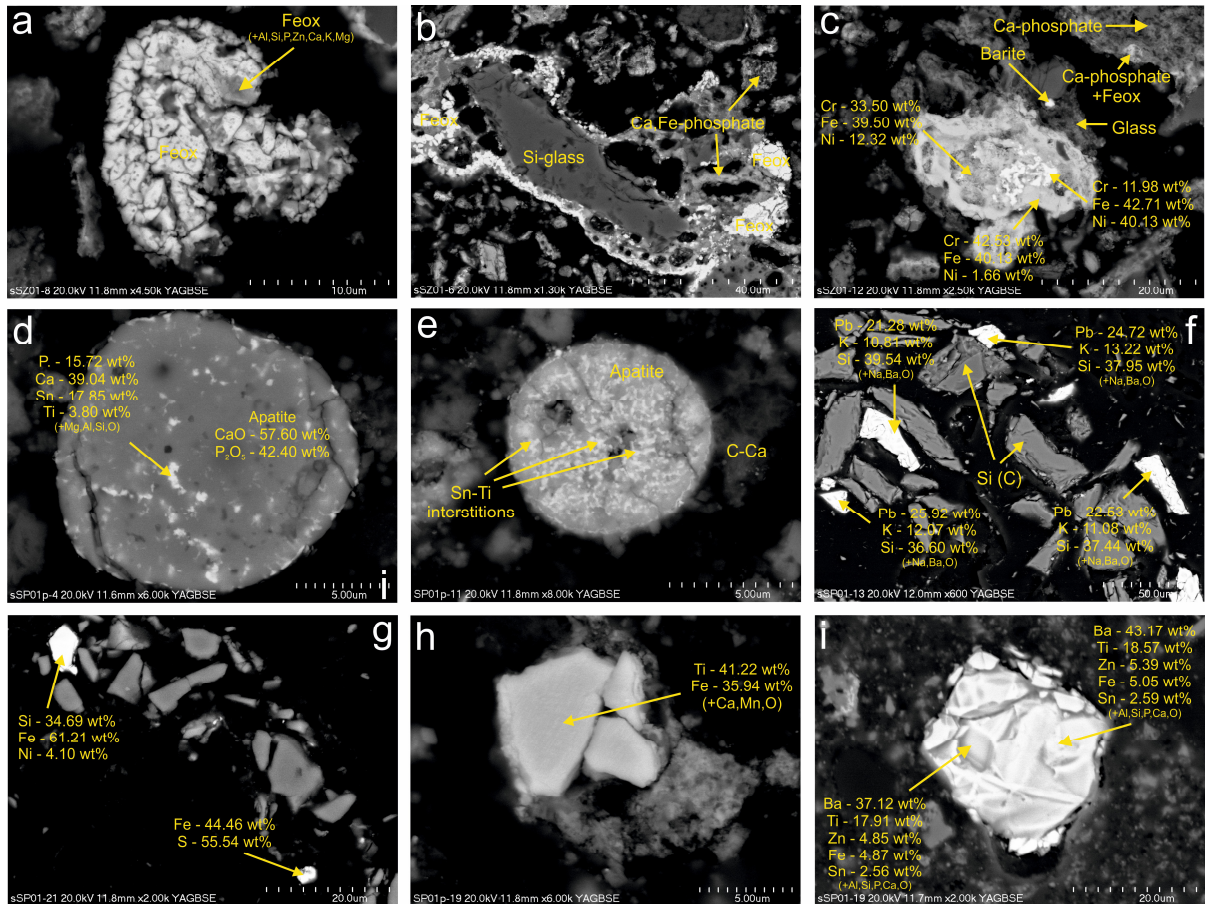

Fig. 3. (a) grain of Fe_ox; (b) rims around silica glass composed of Fe_ox; (c) Ni-Fe-Cr alloys; (d) rounded phosphate with Sn-Ti rich inclusions; (e) rounded phosphate with Sn-Ti rich interstitions; (f) grains containing Si, Pb, K (Pb-K silicide); (f) grains containing Si, Fe, Ni (Fe-Ni silicide); (g) Ti-Fe alloy; (h) multi-metallic grain rich in Ba, Ti, Zn and Fe.

3.3. The forms of occurrence of metallic components in fly ash and APC residues

Iron oxides (Fe_ox) in the form of separate grains up to 20 µm in size (Fig. 3a) or in the form of rims around grains of silica glass or other matrix components of fly ash (Fig. 3b) were the most common metal occurrences in fly ash. Fe_ox were often dispersed within Ca-phosphates. Single grains of Fe-phosphates were also detected. Other single

grains containing metals were rich in Cr, Fe and Ni which in composition were the nearest to Ni-Fe-Cr alloys (Fig. 3c).

In APC residues metallic components were dispersed chaotically in the matrix in the form of inclusions. Rounded phosphate grains up to dozens of µm in diameter which contain inclusions (Fig. 3d) or interstitions (Fig. 3e) composed of Sn with admixtures of Ti were common. Metallic components were also present in the form of separated elongated grains up to 50 µm in size which were composed of Si, Pb and K (Fig. 3f) or Si, Fe and Ni (Fig. 3g). Grains were preliminary identified as silicides of Pb and K or Fe and Ni. The existence of silica-rich phases can be explained by the fact that, in fluidized bed incinerators, the combustion bed material usually consists of silica sand, nevertheless sewage sludge itself can contain high concentration of silica which originate from the city sewage system into which water together with the street sand can flow in. Also single examples of Ti-Fe alloys up to µm in size (Fig. 3h), as well as multi-element grains rich in Ba, Ti, Zn, Fe and Sn, cubic, with a size up to 40 µm (Fig. 3i) were found.

4. Conclusions

The metallic elements accumulated in the sewage sludge incineration residues were present either in the form of separate grains or multi-element mixtures as well as rimming Si-rich components, however the overall content of them was not high. Although the incineration residues were enriched in comparison to the average composition of upper continental crust in metals and toxic elements such as Cu, Zn, Pb, Ni, As, Cd, Au, Hg, Sn, Cr, Sb, Co, the overall concentration of metals was very low. In fly ash the total concentration was not higher than 12 wt%, whereof 11 wt% was Fe. In APCc the total content of metals hardly exceeded 2 wt%. The partitioning of metals between fly ash and APC residues was related to the melting temperature of elements and conditions within the incineration chamber.

Due to low content of valuable metals their recovery is not an economically justified options. However due to a quite high phosphate content and low content of potentially hazardous elements the fly ash can be considered as suitable material for fertilizer. In case of APC residues further processing is required to adapt material for further usage due to high content of undesirables elements e.g. Hg, As, Cr.

Acknowledgements

References

[1] Council Directive 199/31/EC of 26 April 1999 on the landfill of waste. Official Journal of the European Communities1999;L182,1-19.
[2] Caneghem Van J, Brems A, Lievens P, Block C, Billen P, Vermeulen I, Dewil R, Baeyens J, Vandecasteele C. Fluidized bed waste incinerators: Design, operational and environmental issues. Prog Energy Combust Sci 2012;38(4),551-582. doi:10.1016/j.pecs.2012.03.001.
[3] http://ec.europa.eu/eurostat/statistics-explained/index.php/Waste_statistics.
[4] Stasta P, Boran J, Bebar L, Stehlik P, Oral J. Thermal processing of sewage sludge. Appl Therm Eng 2006; 26(13):1420-1426. doi:10.1016/j.applthermaleng.2005.05.030.
[5] Fytili D, Zabaniotou A. Utilization of sewage sludge in EU application of old and new methods-A review. Renew Sust Energ Rev 2008; 12:116-140. doi:10.1016/j.rser.2006.05.014.
[6] Khiari B, Marias F, Zagrouba F, Vaxelaire J. Analytical study of the pyrolysis process in a wastewater treatment pilot station. Desalination 2004; 167:39-47. doi:10.1016/j.desal.2004.06.111.
[7] Malerius O, Werther J. Modelling the adsorption of mercury in the flue gas of sewage sludge incineration. Chem Eng J 2003; 96:197-205. doi:10.1016/j.cej.2003.08.018.
[8] Grabowski Z. Incineration of sewage sludge based on STUO Krakow. Fourth Forum of the sludge management 2011.
[9] Cyr M, Coutand M, Clastres P. Technological and environmental behaviour of sewage sludge ash (SSA) in cement-based materials. Cem Concr Res 2007; 37:1278-1289. doi:10.1016/j.cemconres.2007.04.003.
[10] Rudnick R, Gao S. Composition of the continental crust. In: Rudnick, R.L. (Ed.), The Crust. In: Holland, H.D., Turekian, K.K. (Eds.), Treatise on Geochemistry, vol. 3. Elsevier–Pergamon, Oxford; 2003, p. 1-64.
[11] Zhang F-S, Yamasaki S, Kimura K. Rare earth element content in various waste ashes and the potential risk to Japanese soils. Environ Int 2001; 27(5):393-398. doi:10.1016/S0160-4120(01)00097-6.
[12] Ratafia-Brown JA. Overview of trace element partitioning in flames and furnaces of utility coal-fired boilers. Fuel Process Technol 1994; 39:139-157. doi:10.1016/0378-3820(94)90177-5.

[13] Wang W, Qin Y, Wang J, Li J, Weiss DJ. A preliminary method for determining acceptable trace element levels in coal. Energy 2010; 35:70-76. doi:10.1016/j.energy.2009.08.028.

[14] Lenntech Periodic table. http://www.lenntech.com/Data-sheets/Periodic-table-chart-of-all-chemical-elements.pdf.

[15] Corella J, Toledo JM. Incineration of doped sludges in fluidized bed. Fate and partitioning of six targeted heavy metals. I. Pilot plant used and results. J Hazard Mater 2000; B80:81-105. doi:10.1016/S0304-3894(00)00280-6.

[16] Wilczyńska-Michalik W, Moryl R, Sobczyk J, Michalik M. Composition of coal combustion by-products: The importance of combustion technology. Fuel Process Technol 2014; 124:35-43. doi: 10.1016/j.fuproc.2014.02.016.

[17] Mardon, SM, Hower JC. Impact of coal properties on coal combustion by-product quality: examples from a Kentucky power plant, Int J Coal Geol 2004; 59:153-169. doi:10.1016/j.coal.2004.01.004.

[18] Elled AL, Amand LE, Leckner B, Andersson BA. 2007. The fate of trace elements in fluidised bed combustion of sewage sludge and wood. Fuel 2007; 86:843-852. doi:10.1016/j.fuel.2006.08.014.

[19] Van de Velden M, Dewil R, Baeyens J, Josson L, Lanssens P. The distribution of heavy metals during fluidized bed combustion of sludge (FBSC). J Hazard Mater 2008; 151(1):96-102. doi: 10.1016/j.jhazmat.2007.05.056.