Solidification of MSWI fly-ash with regard to hazardous metals leaching

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This study was concerned with solidification/stabilisation (S/S) process of municipal solid waste incineration (MSWI) fly-ashes produced in the plant located in Košice (Slovakia) by cementation with a special interest in binding leachable heavy metals. Waste incineration is a commonly used technique for waste processing and disposal connected to production of MSWI fly-ash. Fly-ash is classified as hazardous waste due to high heavy metals content, and very fine particles. Two types of MSWI fly-ashes, collected from the cyclones (assigned as C) and from the filters (assigned as F) of the flue gas cleaning plant, were studied. By the S/S process using Portland cement both the fly-ashes were stabilised and the highest fly-ash:cement ratio to prepare firm stabilised samples were found to be 1:1.45 and 6:1 for the fly-ashes F and C, respectively. These differences were caused by different composition of the fly-ashes that significantly influence the S/S process, especially low chlorides content, and presence of sulphates and quartzin the fly-ash C and high chlorides and sulphides and low quartz content, absence of sulphates, and higher contents of lead and zinc in the fly-ash F. Special interest was paid on Ni, Cr, Cd, Cu, Zn, and Pb leaching from both the non-stabilised and the stabilised MSWI fly-ashes. Ni showed the highest and Zn the lowest leaching ratios for both the non-stabilised MSWI fly-ashes. All the monitored heavy metals leached from both the stabilised MSWI fly-ashes in concentrations below 0.03 mg.l^{-1}. The leachates of both the solidified MSWI fly-ashes showed a significant immobilisation of the heavy metals in the stabilised product with a decrease of the leaching ability by more than 99 %. The stabilised MSWI fly-ashes can be deposited in landfills for inert waste.

Key words: *MSWI fly-ash, solidification/stabilisation process, Portland cement, leaching, heavy metal*

Introduction

Waste is, in various forms and states, an everyday part of life of the whole population. Waste generation is an undesirable consequence of human activity related to the life-cycle of any material. Waste is produced in a range of social and production processes including extraction of raw materials, their treatment by technological processing into products and the use of products. After consumption commercial products also become waste. Concerning the environmental perspective solid waste is a major problem as current gas cleaning technology and wastewater treatment are converting pollutants into solid form which is deposited in landfills.

In Slovakia, about one and a half million of tons of municipal solid waste (MSW) are produced every year. The overall production of waste which includes MSW, other waste, and hazardous waste, has been decreasing due to economic recession that has started in 2009, as reported in Waste Management Programme (2010). The production of MSW and the share of MSW on the overall waste production have, however, increased, as shown in Fig. 1 based on the data from Slovak Environmental Agency (2003-2010). Effective waste management and utilization are major concern in Slovakia (Malidžáková, 2011). Incineration is one of the techniques used for waste treatment due to its capacity of waste mass reduction and volume reduction as well as, it is also associated with energy recovery from waste, in some cases. In general, two main types of ash, namely bottom ashes and fly-ashes, are produced by municipal solid waste incineration (MSWI). These fly-ashes are classified as hazardous waste according to the Slovak legislation on waste (Act No. 223/2001 Coll. 2001) due to its high heavy metals contents and, in some cases, toxic chlorinated organics.

MSWI is also connected to air pollution though the topic of air pollution is not the main interest of this study but is not negligible. The main sources of air pollution, except for MSWI, are industrial plants from metallurgy, engineering, mining and energy industries. In the Košice region the air quality is significantly influenced by emissions of SO_X, NO_X and CO_2 as well as solid pollutants. The most significant producers are the metallurgical manufacturing plant U. S. Steel Košice, the lime works Carmeuse Slovakia - plant Košice, the heating plant TEKO, Košice, the cement works V.S.H., Turňa nad Bodovou, etc. (Pavovlová et al., 2012; Leššo et al., 2009; Laciak et al., 2012).

In this study, the stabilisation of MSWI fly-ashes produced in TEKO a.s., Košice (SK), the heating plant for the city of Košice by cementation as S/S process, was studied, with special attention on heavy metals leaching from the MSWI fly-ash before and after the S/S/cementation process.

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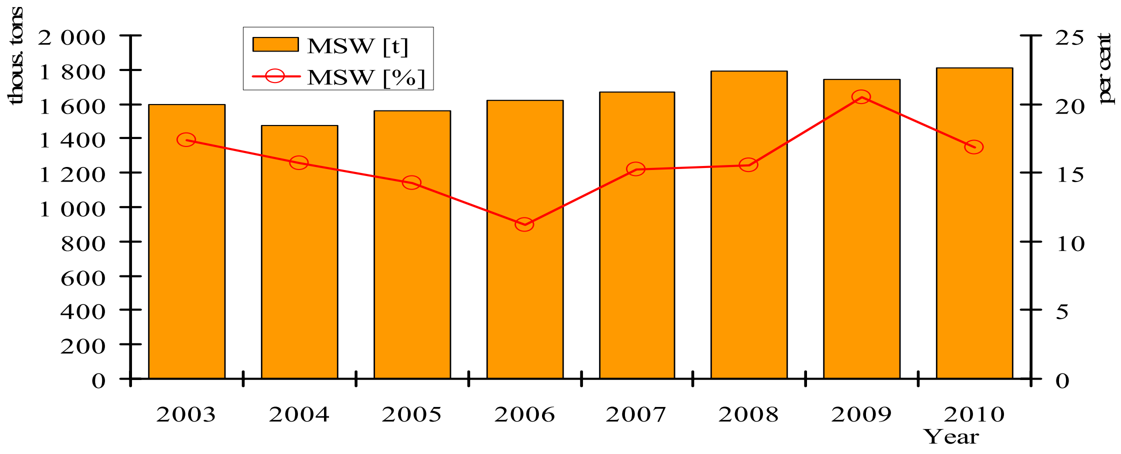

Fig. 1. MSW production in Slovakia in selected period.
Source: prepared according to the Slovak Environmental Agency (2003-2010).

Waste incineration

The basic methods for processing and disposal of waste (other than landfill) include thermal (incineration of organic waste, pyrolytic decomposition of organic substances, melting into slag, thermal decomposition), physical (evaporation, distillation, extraction by liquid or gaseous medium, filtration, heat sublimation), chemical (oxidation, neutralization, reduction and chemical precipitation), physical-chemical (special technologies – solidification/stabilisation, desalination and degradation by ionizing radiation) and biological (anaerobic digestion, bacterial decontamination, mechanical-biological treatment, mechanical-biological stabilization, mechanical-physical stabilization (physical drying) methods (Kozáková, Zeleňák, 2007; Šolc, Mikloš, 2007).

The process of waste incineration allows disposal of waste of different origins - municipal waste, waste from agricultural or industrial activities. Incinerated waste is a heterogeneous mixture, which has different physical and chemical properties (Kozáková, Zeleňák, 2007).

Municipal waste, according to the Slovak legislation (Act No. 223/2001 Coll., 2001), is defined as household waste generated in a municipality by activities of individuals and waste of similar characteristics and composition generated by a corporate body or an entrepreneur except for waste produced in direct performance of activities covering the objects of entrepreneurship or activities of a corporate body or an entrepreneur.

Incineration is a destructive process with a significant reduction of the amount of waste. A large part of the components is disintegrated and changes into relatively less harmful substances remaining in the ash and the flue gas (Miháliková, Králiková, 2005). The waste mass can be reduced by 70 % and the volume by 90 %. Certain recovery of energy from waste can be provided by electricity generation (Lam, 2010). When incineration is realised using stabilising and additional fuel, solid and liquid waste containing carbon is oxidised to carbon dioxide, water and fly-ash. In the combustion process the remaining chemicals can produce harmful emissions to be separated. The incineration plant is a stationary or mobile technical device used for thermal treatment of wastes with or without recovery of the generated combustion heat. The disadvantages of incineration, as reported by Eštoková et al. (2009) and in KOSIT (2009), include high investment and operating costs and the need to use special technological equipment for collection, storage, transport and sorting of waste. Further on waste gases are produced; therefore, each incineration plant is a source of air pollution.

Solidification/Stabilisation of MSWI fly-ash

For solidification/stabilisation (S/S) process an additive or a binder was used to chemically and/or physically fix the hazardous content in the fly-ash (Wiles, 1966; Mangialardi, 2003). The main goal of the S/S process was minimization of solubility and toxicity of the fly-ash and its components. In this study Portland cement was used for the process. Though this method has been reviewed by Lam et al. (2010) and evaluated and studied by e.g. Mangialardi (2003) and Mangialardi et al. (1999) using MSWI from Italian plants, Auer et al. (1995) using MSWI from a French plant, Qian et al. (2006) using MSWI from Malaysian plants, Youcai et al. (2002) using MSWI from a Chinese plant, Derie (1996) using MSWI from a Belgian plant, and by other authors in different countries, the process varies due to different composition of MSW over time and country that can be caused by different lifestyle and/or waste recycling processes introduced in each country, as Lam et al. (2010) state. S/S process using cement has also been successfully used for fly-ash from coal burning documented by a previous study of Kołodziejczyk et al. (2012) and for sulphide-rich copper/zinc mine tailings documented by a previous study of Yilmaz et al. (2011).

Materials

MSWI fly-ashes

The two types of MSWI fly-ash used in this study were collected from the cyclones (C) and from the filters (F) of the flue gas cleaning plant of MSWI plant in Košice (SK). These two different types of fly-ashes were selected due to their negative impact on the environment if improperly treated.

The designed capacity of one incineration line is 75,000 tonnes of thermally disposed waste per year. The composition of annual mixed municipal waste from the city of and the vicinity of Košice, shown in Fig. 2, indicates that the share of biodegradable municipal waste is up to 67 % (KOSIT, 2009).

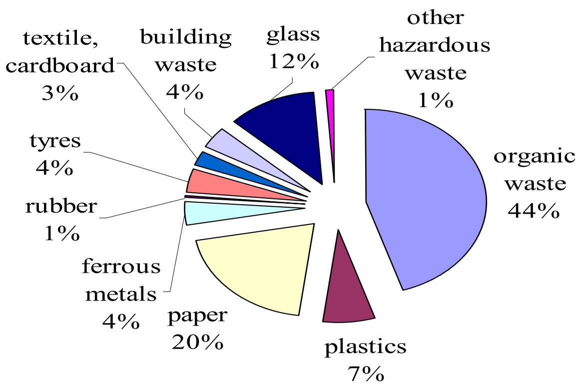

Fig. 2. Composition of annual mixed municipal waste.

The assessment of physical and chemical properties of fly-ash is important, as Eusden et al. (1999) and Dhadse et al. (2008) state, for evaluation of the possibility of further use of MSWI fly ash. The most important properties of MSWI fly-ash, according to Lam et al. 2010, are presented in Tab. *1*. For S/S process and the leaching of the stabilised MSWI fly-ash not all these properties were considered. Only particle size distribution, moisture content, chemical composition (including chloride content), loss on ignition (LOI) and leachability were estimated due to main concern in S/S process and transformation of hazardous waste into non-hazardous or inert waste. LOI was considered only to a certain extent as explained in the Results and Discussion section.

The colour, structure and granularity of flay-ashes are different based on their visual evaluation (Fig. 3):

- fly-ash C – bright-brown colour, sandy structure,
- fly-ash F – grey colour with shade of blue, powdery.

Tab. 1. Main physical and chemical properties of MSWI fly-ash (Lam et al. 2010).

Physical properties	**Chemical properties**
Particle size distribution	Chemical composition
Moisture content	Loss on ignition
Bulk density	Heavy metals and leachability
Compressive strength	Organic constituents
Permeability	Chloride content
Porosity	

The mineralogical composition of both the fly-ashes was determined by X-ray diffraction (XRD) performed using DRON 2.0 (Techsnabexport, Russia). The main mineralogical constituents of each fly ash were different, as presented in Tab. 2. Sylvite, halite, calcite-magnesium, and muscovite were the common constituents for both fly-ashes C and F. A significant content of quartz was recorded in fly-ash C; however, no content of quartz was recorded in fly-ash F. Anhydrite, aphthitalite, chalcopyrite, calcium hydroxide, scrutinyite, were other constituents of fly-ashes C (not found in fly-ash F) and sphalerite, portlandite were other constituents of fly-ashes F (not found in fly-ash C). The only heavy metal in atomic form detected by XRD was cadmium in fly-ash F. The rest of heavy metals were present in the form of compounds not detectable by or in amounts under detection limits of XRD (amorphous phases, crystalline phases at concentration levels below XRD detection limit, or impure, complex crystalline compounds). The XRD spectra are presented in Figure 4. and the particle size distribution is given in Figure 5.

a) ***b)***

Fig. 3. Fly-ashes a) C and b) F.

The basic chemical composition of tested samples was investigated by X-ray fluorescence analysis (XRF). The XRF was performed using SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10 000 pulses. The primary beam was polarized by Bragg crystal and Highly Ordered Pyrolytic Graphite - HOPG target. The samples were measured during 300 s at voltage of 25 kV and 50 kV at current of 0.5 and 1.0 mA, respectively under helium atmosphere by using the standardized method of fundamental parameters for powder samples. The analysis showed results as follows. Calcium is the predominant metal in both the fly-ashes (>20 %). In fly-ash C it is followed by metals magnesium, aluminium, iron, and potassium (>1 %). In fly-ash F it is followed by metals potassium and zinc (>1 %). Zinc in fly-ash C and magnesium, aluminium, and iron in fly-ash F are also present yet in concentrations below 1 % (>0.2 %). Other metals present in concentrations below 0.2 % in both the fly-ashes are Cu, Mn, As, Pb, Cr, Co, Ni, Cd, Sb, Ti, Rb, Sr, Mo, Sn, and Ba. The predominant non-metal is silicium in fly-ash C and chlorine in fly-ash F (>10 %). Sulphur is present in both the fly-ashes whereas chlorine in fly-ash C and silicum in fly-ash F are also present (>1 %). Other non-metals present in concentrations below 1 % in both the fly-ashes are P, and Br. The analysis of chemical composition corresponds to the mineralogical composition.

Tab. 2. Mineralogical constituents of fly-ashes (by XRD).

Fly-ash F	**Fly-ash C**
sylvite - KCl	
halite - NaCl	
calcite-magnesium - $Mg_{0.03}Ca_{0.97}CO_3$	
muscovite-2M1, vanadian barian - $(K,Ba,Na)_{0.75}(Al,Mg,Cr,V)_2(Si,Al,V)_4O_{10}(OH,O)_2$	
sphalerite - ZnS	quartz - SiO_2
portlandite - $Ca(OH)_2$	anhydrite - $CaSO_4$
cadmium - Cd	aphthitalite - $(K,Na)_3Na(SO_4)_2$
	chalcopyrite - $CuFeS_2$
	calcium hydroxide - $Ca(OH)_2$
	scrutinyite - PbO_2

LOI at 825°C is 4.52 % and 18.64 % for fly-ash C and F, respectively. The moisture content is 1.23 % and 2.01 % for fly-ash C and F, respectively.

Cement

In the experiments, Portland cement – CEM III/ A 32,5 N – was used which is blast furnace cement with an increased content of blast furnace slag. The average chemical composition is given in Tab. 3. The loss on ignition, the insoluble fraction and the content of blast furnace slag of the cement are 2.2 ± 0.5 %, 0.6 ± 0.5 % and 44.9 ± 3.2 %, respectively.

Methods

Cementation methods of fly-ash originating from the incineration of municipal waste were tested. For cementation the fly-ashes C and F were used separately and mixed with cement. The fly-ash was stabilised by solidification/cementation process. The MSWI fly-ash samples and the stabilised samples were leached and in the leachate heavy metal concentrations were measured.

Tab. 3. Mean composition (% wt.) of the Portland cement CEM III/A 32,5 N.

CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	Na_2O	K_2O	MgO	Cl^-
51.4 ±0.9	28.0 ±0.8	5.6 ±0.3	2.0 ±0.2	3.0 ±0.2	0.37 ±0.03	0.57 ±0.08	5.8 ±0.4	0.039 ±0.012

Solidification/stabilisation process

Homogenization of fly ash and cement was performed under intense stirring of dry substances. After stirring distilled water was added to the mixture. The mixture of water, fly-ash and cement was poured into a mould and allowed to solidify spontaneously at ambient temperature (20 ± 3 °C) for 48 hours.

Two types of moulds were used. The first one (assigned as first mould further on) with dimensions 2.5x2.5x2 cms was used to prepare samples for visual and compactness testing. The fly-ash : cement weight ratios were selected between 20 : 1 and 1 : 20 and are presented in Tab. 4. The second one (assigned as second mould further on) with dimensions 10.5x6.5x5 cms was used to prepare samples for leaching which complied with compactness testing from the first mould, i.e. did not disintegrate after the compactness testing; therefore the fly-ash : cement weight ratios were the same as for the first mould (Tab. 5). In all the homogenisation experiments the water : solid weight ratio was set to 1:2.5.

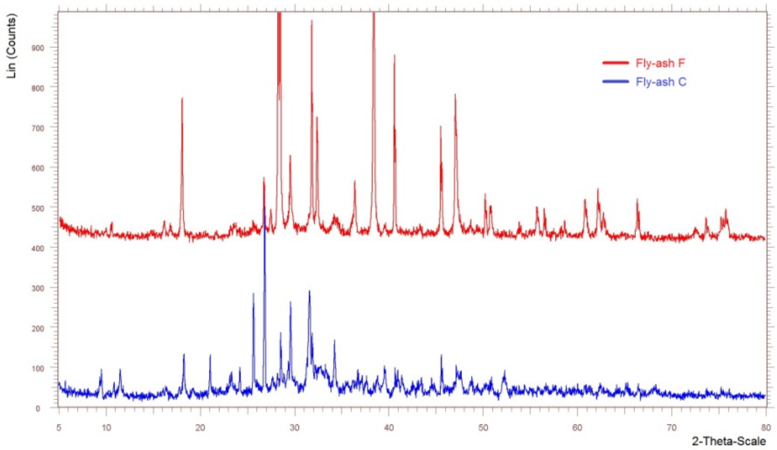

Fig. 4. XRD spectra of fly-ashes C and F.

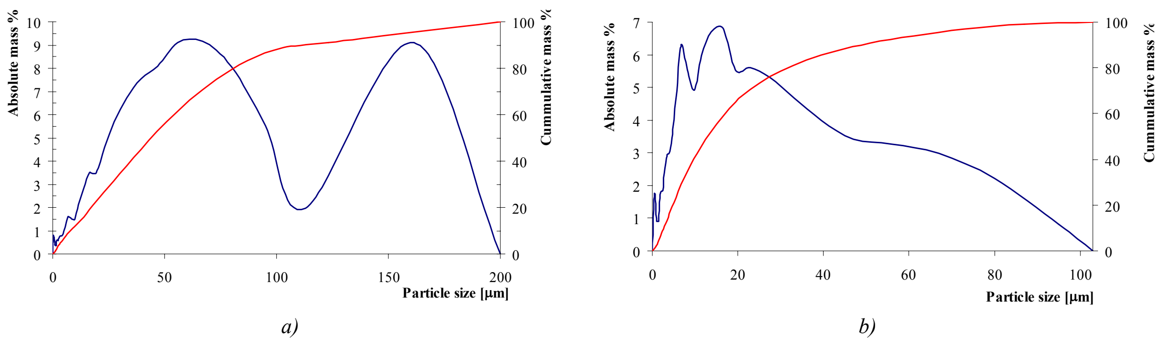

Fig. 5. Particle size distribution of fly-ashes a) C and b) F.

Visual and compactness testing

As the determination of the compactness of the stabilised samples was a tool for setting the maximum fly-ash : cement weight ratio, the hardened samples were tested for compressive strength and mechanical stress on material immediately after the end of the S/S process as well as after leaching in distilled water for 24 hours. The solidified samples were also visually checked for cracks, defects and disintegration.

Leaching of non-stabilised MSWI fly-ash

The leaching of the MSW was carried out according to unified methods for the analytical control of waste described below (Act No. 223/2001 Coll., 2001).

Dry residues for the tested MSWI fly-ashes at 105 °C were first estimated by standard procedure. Amount of waste corresponding to 100 ± 0.001 g of dry residue was weighed from the prepared analytical sample. The weighed sample was quantitatively brought over into a wide-neck 2000 ml bottle with a well-fitting lid. Exactly 1000 ml of deionised water was added to the sample. The bottle was sealed and placed in an upright position on a laboratory shaker. The intensity of shaking was set to 200 ± 5 rpm to reach intensive shaking of MSWI fly-ash. The leaching was carried out at ambient temperature, i.e. 20 ± 3 °C. Total time of contact between the sample and water was 24 hours. For the first 6 hours the leaching was carried out by shaking of the contents of the bottle on the shaker. After this time the shaking was stopped. The content of the bottle was left at rest till the end of the 23rd hour starting from the first contact of MSWI fly-ash and the leachant. The last hour the sample was leached by shaking under the same conditions as the first 6 hours.

Immediately after the leaching the solid phase was separated from the liquid one by filtration through filters with an average pore size of 0.45 mm under vacuum. The filters were rinsed with water before use. Turbid filtrates were centrifuged.

Tab. 4. The fly-ash : cement weight ratios used in the first mould.

Sample No.	Fly-ash : Cement Weight Ratio	Visual and compactness testing for **fly-ash F**	Visual and compactness testing for **fly-ash C**
1	20 : 1	disintegrated	disintegrated
2	10 : 1	disintegrated	disintegrated
3	9 : 1*	not tested	disintegrated
4	8 : 1*	not tested	disintegrated
5	7 : 1*	not tested	disintegrated
6	6 : 1	disintegrated	**firm**
7	5 : 1	disintegrated	firm
8	4 : 1	disintegrated	firm
9	3 : 1	disintegrated	firm
10	2 : 1	disintegrated	not tested
11	1 : 1	disintegrated	not tested
12	1 : 1.25**	disintegrated	not tested
13	1 : 1.35**	disintegrated	not tested
14	1 : 1.45**	**firm**	not tested
15	1 : 1.55**	firm	not tested
16	1 : 1.65**	firm	not tested
17	1 : 1.85**	firm	not tested
18	1 : 2	firm	not tested
19	1 : 3	firm	not tested
20	1 : 5	firm	not tested
21	1 : 10	firm	not tested
22	1 : 20	firm	not tested

**These ratios were prepared additionally to find the most suitable fly-ash : cement ratio between 6 : 1 and 10 : 1 for fly-ash C as explained below.*

***These ratios were prepared additionally to find the most suitable fly-ash : cement ratio between 1 : 1 and 1 : 2 for fly-ash F as explained below.*

Tab. 5. The maximum fly-ash : cement weight ratios used in the second mould.

Fly-ash F : cement	1 : 1.45
Fly-ash C : cement	6 : 1

Leaching of stabilised MSWI fly-ash

The main potential for contamination of the environment from stabilised fly-ash product is considered to be leaching (through contact with infiltrating rain water or groundwater). The potential for leaching is a function of the waste properties and the effectiveness of the S/S technology, as stated by Mačáková et al., (1996). The leaching of the stabilised MSWI fly-ash by S/S/cementation was carried out according to unified methods for the analytical control of waste described below (Act No. 223/2001 Coll., 2001).

The stabilized sample was leached under defined conditions using deionised water and the undissolved share was separated by filtration or centrifugation.

A closed circulatory system made up of wide-neck bottle (with the outlet just above the bottom of the bottle) and a rotary peristaltic pump for continuous pumping of leachant (with a capacity of 10 L per hour) i.e. deionised water (Fig. 3) was used to prepare the leachate of the stabilised samples.

The outlet of the bottle was sealed by silicone rubber tube. The tube was placed into the peristaltic pump and the other end was inserted through a hole in the stopper into the bottle. The samples of specified dimensions were suspended approximately 10 cms above the bottom of the bottle filled with water by a sufficiently strong polymer fibre thus the entire surface of the sample was submerged in the leachant during leaching. First, the sample was allowed to soak for three hours at ambient temperature (20 ± 3) °C. After the three hours, the pump was turned on. The performance of the pump was adjusted to allow pump the volume of water used for leaching 6 to 8 times within 24 hours, i.e. the sample was leached under constant circulation of water for 24 hours. After this time the extract obtained from the stabilized fly-ash leaching was filtered under the same conditions as for solid waste.

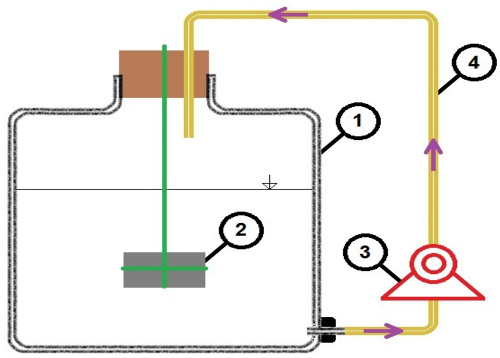

Fig. 3. Scheme of apparatus for leaching.
Key: 1 - vessel for leaching, 2 - tested sample of the stabilised MSW, 3 - peristaltic pump, 4 - silicone rubber tube.

All the leaching tests, both for MSW and the stabilised samples, were carried out in triplicate and the results were determined as the average of three measurements. The coefficients of variation for measurements of leaching within a set were always less than 5 %.

Heavy metals analyses

The concentrations of selected heavy metals in the leachates were determined by atomic absorption spectrometry (AAS) performed using iCE 3300 (Thermo Scientific, USA) within 24 hours from the end of the leaching process. AAS is an optical method based on absorption of electromagnetic radiation in the range of wavelengths 190 to 850 nm and is ranked among the most common methods for the determination of heavy metals in environmental samples. Heavy metals contents - nickel, chromium, cadmium, copper and zinc were measured in the extracts.

Results and Discussion

The aim of fly ash cementation experiments was to find the maximum weight ratio (fly-ash : cement), in which the resulting stabilised fly-ash product reached satisfactory strength properties and the leachate meets the legislative requirements (Tab. 4 and Tab. 5).

The first set of samples was prepared for weight ratios 3 : 1, 4 : 1, 6 : 1, 10 : 1 and 20 : 1 for both F and C fly-ashes in the first mould. They were tested visually and for compactness. Based on these tests all the samples disintegrated for the fly-ash F; however the sets of samples 3 : 1 to 6 : 1 remained firm whilst the sets of samples 10 : 1 and 20 : 1 disintegrated for the fly-ash C. This situation could be expected due to different composition of both the fly-ashes as discussed above.

Further on sets of the samples for weight ratios 2 : 1 and 1 : 1 were prepared for the fly-ash F. However, both the sets of samples disintegrated. For this reason another set of samples was prepared for weight ratios between 1 : 2 and 1 : 20. All these samples remained firm therefore the final weight ratio was found in the final set of samples between 1 : 1 and 1 : 2.

In order to find the best weight ratio for the fly-ash C sets of samples were prepared for ratios 7 : 1, 8 : 1 and 9 : 1. All the samples from these sets disintegrated. Each set of samples consisted of three samples prepared under the same conditions.

According to these results the stabilised fly-ash cement samples were prepared in triplicate each in the second mould with the best fly-ash : cement weight ratios for both the fly-ashes (Tab. 5). All the stabilised MSWI fly-ash samples were leached and leachates were analysed for heavy metals contents.

The average values of heavy metals in the non-stabilised and stabilised MSWI fly-ash leachates are shown in Tab. 6.

Tab. 6. Heavy metals concentrations in MSWI fly-ash leachates.

Fly-ash	**non-stabilised** [mg.l^{-1}]		**leaching ratio** [%]		**stabilised** [mg.l^{-1}]		**leaching ratio** [%]		**limit*** [mg.l^{-1}]	**binding capacity** [%]	
	F	**C**	**F**	**C**	**F**	**C**	**F**	**C**		**F**	**C**
Ni	4.5268	8.5896	66.57	76.69	0.0207	0.0163	0.30	0.15	0.04	99.54	99.81
Cr	8.3454	7.6571	22.68	9.75	0.0101	0.0292	0.03	0.04	0.05	99.92	99.74
Cd	2.0123	1.9789	10.54	3.72	< 0.0113**		0.06	0.02	0.004	> 99.44	> 99.43
Cu	29.8140	29.2145	17.54	16.23	< 0.0330**		0.02	0.02	0.2	> 99.89	> 99.89
Zn	36.5841	29.6980	3.10	4.18	< 0.0100**		0.00	0.00	0.4	> 99.97	> 99.97
Pb	10.5698	11.5890	29.77	4.53	< 0.0100**		0.03	0.00	0.05	> 99.91	> 99.91

**based on Slovak legislation for leachates of waste for landfills of inert waste issued by Decree No. 283/2001 Coll. (2001)*
***amounts not detectable by AAS (detection limits used)*

The MSWI S/S process can occur as macro-encapsulation, micro-encapsulation, ion exchange in the lattice, absorption, and adsorption (Vempati et al., 1995; Qian et al., 2001). Regardless of the way of S/S mechanism the goal of the process is minimization of heavy metals and toxic compounds release from MSWI fly-ash.

Chlorides at low concentrations enhance the S/S process. On the contrary, as Mangialardi (2003), Tayler (1990) and Park (2009) state, chlorides at high concentrations negatively influence the cementation products thus it was necessary to use more cement to get a solid non-friable product. In addition, as Hou et al. (2006) and Hamernik, Frantz (2001) state, high content of chlorides and sulphides in MSWI fly-ash has a negative impact on cement hydration. As to the chlorides contents based on the XRD analysis both the fly ashes contain KCl and NaCl, further fly-ash C also contains $CuFeS_2$ and fly-ash F also contains ZnS. Nevertheless the content of both chlorine (only occurring in the form of chlorides) and sulphur (mostly occurring in the form of sulphides, less in the form of sulphates) in the fly-ashes is different. Fly-ash F contains 7.494 % and 19.360 % of S and Cl, respectively, whereas fly-ash C contains 3.485 % and 3.640 % of S and Cl, respectively.

Sulphates, only occurring in fly-ash C, positively influence the cementation products by enhancing the hydration, as state Mangialardi et al. (1999) and Tayler (1990).

Carbonates also contained in both the fly-ashes may also improve the fixation of heavy metals as MSWI fly-ash with contents of heavy metals has an increased tendency to carbonation (Smith, Walton, 1991; Malviya, Chaudhary, 2006).

Quartz, based on XRD analysis, is only present in fly-ash C; however, the chemical analysis indicated that silicium (probably in the form of quartz in concentration level below XRD detection limit) though in a low concentration of about 1% is also present in fly-ash F. Regardless of the quartz presence in fly-ash F there is a significant amount of quartz in fly ash C, confirmed by chemical analysis (content of Si almost 12 %). Quartz is also the main component in Portland cement used for S/S process thus its higher content may enhance the process.

Heavy metals chromium, cadmium, nickel, and mercury in the forms of oxides and salts have no significant influence on the S/S process as they are likely to be bound in the entire cement matrix, report Mangialardi (2003), Komarneni et al. (1988), and Ortego (1990). However, Thomas et al. (1981), and Ortego et al. (1989) in their studies report, that lead and zinc compounds have a notable negative influence on the process as lead forms a lead-based colloid phase around silicates; moreover, Arliguie, Grandet (1990), Yousuf et al. (1993), and Mangialardi (2003) also confirm, that zinc forms an amorphous gel layer around the cement particles.

LOI indicates the contents of organic compounds of MSWI fly-ash. Nevertheless, Ecke (2003) states, that the contents of both physically and chemically bound water can significantly influence this value and cause its failure up to one order of magnitude. In spite of this fact, LOI is commonly used to determine the content of unburned carbon and even the effectiveness of the incineration process. According to the results, LOI was 4.52 % and 18.64 % for fly-ashes C and F, respectively, but we do not reckon these figures for the content of unburned carbon even if the moisture is deducted.

These differences also significantly influence the S/S process resulting in much higher fly ash : cement weight ratio of fly-ash C (acceleration due to low chlorides content, and presence of sulphates and quartz) than of fly-ash F (retardation due to high chlorides and sulphides and low quartz content, absence of sulphates, and higher contents of lead and zinc [about twice and seven times, respectively, more than in fly-ash C]).

As presented in Tab. 6 the leachates of non-stabilised MSWI fly-ashes do not meet the requirements of the Slovak legislation, issued by the Decree No. 283/2001 Coll. (2001) and the Act No. 223/2001 Coll. (2001) for landfills of inert waste. The leaching ratios have been calculated for the monitored heavy metals from both the non-stabilised and stabilised MSWI fly-ashes. The results of leaching expressed according to the requirements of the unified methods for the analytical control of waste which can be compared with the valid legislation for leachates of wastes for landfills, i.e. the results expressed in $mg.l^{-1}$ showed different data from the results expressed as leaching ratio which is a percentage of the content of heavy metal estimated by XRF leached into the leachate prepared according to the methods described above, i.e. the results expressed in %.

In the leachates of non-stabilised MSWI fly-ashes Cu, and Zn leached in the highest amount of about 30 $mg.l^{-1}$, Pb, Cr, and Ni in the amount of about 10 $mg.l^{-1}$ and Cd in the lowest amount of about 2 $mg.l^{-1}$. According to the Slovak legislation both the non-stabilised MSWI fly-ashes do not meet the requirements for leachates of waste for landfills of inert waste therefore they have to be deposited in landfills for hazardous waste. In the leachates of stabilised MSWI fly-ashes Cd, Cu, Zn, and Pb concentrations were in amounts not detectable by AAS, and the Ni and Cr concentrations were below 0.03 $mg.l^{-1}$; therefore, the leaching ratios were also very low for both the fly ashes. The results show a very high binding capacity of the S/S process for all the monitored heavy metals. The binding capacity was above 99 % for all the heavy metals. The leachates were up to standard of the Slovak legislation for inert waste within the monitored pollutants.

The results expressed as leaching ratio (%) showed different results that also deserve attention though they are not comparable to the legislation. In the leachates of non-stabilised MSWI fly-ashes Zn showed the lowest leaching ratio for fly-ash F and Cd for the fly-ash C (about 3 %). Zn leaching ratio was also low for the fly-ash C (above 4 %). The highest leaching ratios were obtained for Ni from both the fly-ashes (above 66 %).

The results also show difference between the fly-ashes as to the leachability. Cr, Cd, and Pb leached in amounts with a difference of less than 1 $mg.l^{-1}$ for each metal between fly-ash F and fly-ash C whilst the leaching ratios from fly-ash F were about three times the ratios from fly-ash C. Ni, Cu, and Zn leached in amounts roughly corresponding to leaching ratios. Comparing these figures to the basic chemical and mineralogical compositions, Cr, Cd, and Pb can be found in the fly-ash C in mineralogical forms less leachable than from the fly-ash F as the content of these metals in both the fly-ashes is less than 0.2 %.

Conclusion

Waste incineration process is a commonly used technique for waste processing and disposal connected to production of MSWI fly-ash. Fly-ash is classified as hazardous waste due to high heavy metals content, and very fine particles. Due to these parameters this type of waste has to be disposed at landfills of hazardous waste which is economically demanding. Nevertheless, the S/S process using cement can be used for its stabilisation and turning into a non-hazardous or inert waste.

The S/S process of MSWI fly-ash from the filters and the cyclone of the Košice MSWI plant using Portland cement was proved to be an effective means of stabilisation of this material. The process was effective in immobilizing heavy metals (Ni, Cr, Cd, Cu, Zn, and Pb) present in the fly-ashes and the fly-ash leachates. The use of this process is environmentally friendly as it helps decreasing the environmental load with heavy metals and very fine particles.

The simple S/S method incorporating mixing the fly-ash, and cement, and adding water can successfully remove the harmful contaminants and concurrently aggregate the fine particles. The stabilised MSW contains heavy metals bound in immobilised form and the size of final product can be influenced by the size of mould used for stabilisation. The immobilisation of heavy metals has also been investigated in this study. According to the presented results the leachates of stabilised MSWI fly-ash contain heavy metals in concentrations below the limits for landfills of inert waste.

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