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High-Temperature Melting Ash from the Incineration of Municipal Waste Versus the Cementation Method

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ABSTRACT

It appears that the prospective way of an eco-friendly disposal of fly ash originating from the incineration of municipal waste (MSW fly ash) is its high-temperature melting in a reactor with a plasma arc. During the process of a high temperature melting, solidification and stabilization of the fly ash occur. The main target product of the process is a glassy slag, categorized as an inert product which, moreover, has the characteristics of a secondary raw material, suitable for the construction industry. Synthesis gas is considered to be a by product.

The following article dissertates the results of the experiment of the high-temperature ash melting whereby the ash is obtained as a by-product of the municipal waste incineration process. Furthermore, the article indicates the results of the stabilization ash cementation method and compares both methods from the environmental point of view

Keywords: MSW fly ash, cementation method, vitrification, plasma technology

INTRODUCTION

Combustion as a thermal method of the disposal of municipal waste (MSW) is, after landfilling, considered as one of the oldest methods of waste disposal. Thermal treatment of municipal solid waste has become a common practice in waste volume reduction and resource recovery consisting in a recovery of the energy content of the waste [1,2].

An increased use of thermal methods within a municipal waste management system can be recorded mainly in the founding states of the EU. The main objective of the construction of modern incinerators is an energy recovery from the waste as well as a significant reduction of its volume. Despite the drastic reduction in the volume of waste after the thermal treatment, combustion is not the ultimate way of disposal. During the treatment process, by-products are created. Slag, bottom ash and fly ash form solid products of the combustion process, the disposal of which is provided mainly in the form of landfilling.

Unwanted waste from the municipal waste combustion process is the fly ash. Fly ash constitutes a fine-grain fraction of the waste. Due to its large surface, the fly ash is able to bond with most of the heavy metals, persistent organic pollutants, and the like. The legislation of the European Union is progressively restricts the regulations regarding the treatment of the waste prior to its landfilling and increasing the fees for storing the ashes that are categorized as **hazardous waste.** Organizations are forced to deal with the treatment of the fly ash before it is landfilled, making use of different technologies. Part of the introduction of new technologies is particularly high investment costs that the organizations must consider along with the economic assessment of the given technology [3,4].

Use of the fly ash as a secondary raw material is in some cases complicated because of the variability of its mineralogical and chemical composition [5]. Therefore, only a small amount of fly ashes is being processed. In addition, none of the producer of the fly ash is able to ensure a constant quality (composition) of the final fly ash, since that is subject to the variability of the quality of the raw material. The distance between the source where the ash is produced and the actual place of use as well as the transportation are yet other important factors that a potential buyer must consider.

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According to § 21, sect. 8, of the Law 223/2001 on waste, as amended, the obligation to stabilize the waste prior its landfilling (Annex no. 6), entered into the force in January 2005. For this reason, fly ash, categorized as hazardous waste must be stabilized prior to it being deposited in a landfill with a controlled regime [6]. Concept or concepts, respectively, of stabilization and solidification are terms of the waste management vocabulary that are considered to be the most controversial and not always well understood. The terms express the treatment of the waste (including industrial) whereby the waste is a complex mixture of several components of an unknown composition.

The goal of this paper is to describe the experiment of ash melting using a high temperature melting method, whereby the ash is produced by the incineration of the municipal waste. An additional goal is to compare the obtained results with the results of the experiment using the cementation method, and all mainly from the environmental viewpoint.

MSW FLY ASH

For the purpose of the experimental research on the stabilization and solidification, the ash from the incineration of the municipal solid waste (MSW fly ash) was selected. A selected type of the fly ash is collected in a cyclone separator of the MSW incinerator operated in the region of Košice. This type of fly ash was selected due to its negative impact on the environment if improperly treated. Fly ash collected in a cyclone separator of the incinerator represented a coarse fraction with a grain size from 0.4 to 130 microns. This is the coarsest fraction of the entire system of the flue gas cleaning. Micro-picture of the ash is shown in Figure 1 (Image provided by the scanning electron microscope MIRA3 TESCAN) [7,8].

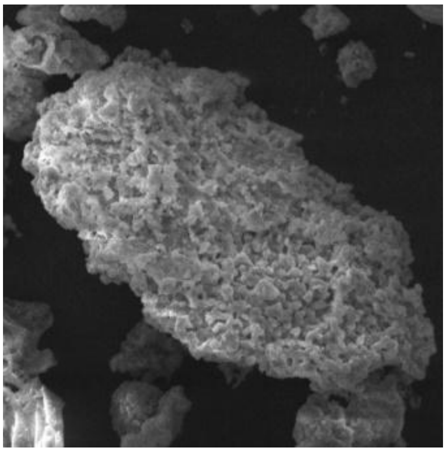


Figure1. *MSW fly ash from cyclone – a visible field of the micro-picture of 133 microns*

The particles of the fly ash from the combustion of the MSW (Figure 1) are characterized by irregular shapes and various sizes, with some spherical particles being coated by crystals or by micro-particles that:

- arise from condensation of vapour in the combustion zone, and
- contain harmful and toxic elements.

The fly ash sample included in the experimental research is subjected to the chemical analysis. Chemical analysis of samples was performed by the atomic absorption spectrometry (ASS), atomic emission spectrometry with inductively coupled plasma (ICP-AES), elemental analysis with thermal conductivity detector (EA) and gravimetric analysis. A summary of major and minor components of the fly ash, as well as the results of the elemental analysis of carbon, hydrogen, nitrogen, and S (CHNS), are shown in Table 1 [8].

Table1. *Chemical analysis of the ash sample from the MSW incineration process*

Compound	Chemical composition (hm.%)	Element	Amount of metals in the ash X-rays analysis($mg\cdot kg^{-1}$)
SiO_2	24.70	V	42
Al_2O_3	11.90	Cr	329
Fe_2O_3	4.11	Ni	82
CaO	32.50	Cu	427
MgO	2.98	Zn	6800

TiO_2	1.75	As	18
MnO	0.18	Sr	406
K_2O	2.31	Y	13
Na_2O	2.31	Zr	131
P_2O_5	1.35	Mo	< 10
SO_3	4.88	Ag	< 1
Loss by annealling	10.90	Cd	37
C	1.29	Sb	189
H	< 0.02	Ba	1910
N	0.01	Hg	1.40
S_{total}	2.30	Pb	459

SOLIDIFICATION AND STABILIZATION OF THE MSW FLY ASH

Solidification and stabilization of the ash analyzed in this paper was carried out by using plasma reactor technology. The technology allows for processing of various kinds of waste with a temperature limit in the reaction chamber of up to 1750°C. The maximum temperature of the outer lining is limited by the type of the lining used, which in this case is aluminate. The source of the heat in the process of a high temperature melting is a plasma arc discharge excited between the graphite electrodes in a dependent connection. A more detailed specification of the technology is available in [2].

When considering the percentage of the three most dominant oxides in the ash (SiO_2, Al_2O_3 and CaO) and when using the ternary diagram system SiO_2-Al_2O_3-CaO, the ash melting point is, in terms of the energy intensity of the process, high (around 1800 °C). In order to reduce the melting point of the ash itself, it was decided to use a flux with the amount of SiO_2 above 96 wt.% (silica sand). The weight ratio of the fly ash and silica sand was 5:1. The approximate melting temperature was thus lowered to about 1370°C when pre-treatment was used [8, 9].

The temperature smelting of the batch took place in a reducing atmosphere at an average temperature of 1409°C. For the process of a weakly ionized plasma arc, nitrogen was used. The speed of dosing was 12.1 $kg \cdot min^{-1}$, enabling a smooth running of the process. The specific energy consumption per kilogram of the batch was quantified to 0.65 $kWh \cdot kg^{-1}$.

During the high temperature melting, three products were formed: synthesis gas, glassy slag and flue dust. The synthesis gas was rich in hydrogen and carbon monoxide. The overall amount of the two types of gases in the synthesis gas was more than 60 vol.%. The measured volume production of the syngas was of an average value of 0.018 $m^3 \cdot kg^{-1}$ and the calorific value was 7.38$MJ \cdot m^{-3}$. The particulates generated by the process were not analyzed due to the small amount of the melted batch [8].

The target product is a glassy slag melt exhibiting an inert character. The inertness of the product was investigated by leaching tests, which is used to measure the toxicity of materials. The analysis of the leachate from the leachate tests, according to the regulation Nr. 263/2010 of the Codex of the Ministry of the Environment, along with standards for the landfilling of the inert waste, is shown in Table 2.

Table2. *Results of the leaching tests and standards for landfilling*

Measured paramater	Unit	Concentration in the leachate from the vitrified slag	Landfill Class SMIW Leaching class I.
pH		6.5	6 - 12
arsenic (*As*)	$(mg \cdot l^{-1})$	<0.001	0.05
baryum (*Ba*)	$(mg \cdot l^{-1})$	0.012	2
cadmium (*Cd*)	$(mg \cdot l^{-1})$	<0.002	0.004
Chrome total (*Cr*)	$(mg \cdot l^{-1})$	0.002	0.05
copper (*Cu*)	$(mg \cdot l^{-1})$	0.012	0.2
mercury (*Hg*)	$(mg \cdot l^{-1})$	<0.0001	0.001
molybdenum (*Mo*)	$(mg \cdot l^{-1})$	<0.005	0.05
nickel (*Ni*)	$(mg \cdot l^{-1})$	<0.01	0.04
lead (*Pb*)	$(mg \cdot l^{-1})$	<0.01	0.05

antimony (*Sb*)	(mg·l^{-1})	<0.001	0.006
selenium (*Se*)	(mg·l^{-1})	<0.001	0.01
zinc (*Zn*)	(mg·l^{-1})	0.022	0.4
chlorides	(mg·l^{-1})	<2	80$^{b)}$
fluorides	(mg·l^{-1})	<0.03	1
sulfates	(mg·l^{-1})	<5	100$^{b)c)}$
phenol index	(mg·l^{-1})	<0.002	0.1
CRL	(mg·l^{-1})	38	400

The results of the high-temperature melting of the ash generated in the incineration of the municipal waste will be further compared with the results of the scientific team of the Faculty of Mining, Ecology, Process Control and Geotechnology (TUKE). The conducted experiments used the same fly ash type and of the same origin as in the above mentioned research. The stabilization and the solidification of the ash was ensured by the cementation method [5].

RESULTS AND DISCUSSION

By the melting of the charge consisting of a mixture of the fly ash and the silica sand, mixed in a weight ratio of 5:1, the target product, glassy slag was obtained. The vitreous slag exhibiting an amorphous structure consists predominantly of stable slag-forming oxides (SiO_2, Al_2O_3, CaO, MgO, TiO_2, Cr_2O_3, and the like.) characterized by a high affinity to oxygen. Oxides of easily reducible metals like CuO_2, Fe_2O_3, NiO, CdO, SnO_2, and PbO depending on the temperature, pressure, and reducing conditions, are for the most part reduced into metal. Metals with a high boiling point and a low metal vapor pressure (Fe, Cu, Sn, and Ni) might be concentrated on the bottom of the reactor as an individual metal phase if there is a sufficient quantity of a melted batch. Metals with a low boiling point and a high vapor pressure (Hg, Cd, Zn, and Pb) partially evaporate in the synthesis gas from which they condensate and are subsequently collected as a light ash in the gas cleaning equipment. Similarly, for metals with a low boiling point and a high vapor pressure. Non-reduced and unevaporated metals residues are bonded in the silica matrix, preventing its leaching (Table 3).

The above mentioned assumptions concerning the inertness of the created product following the plasma melting, confirm the results of the leachate test (Table 2) and the eco-toxicity. The product is environmentally friendly. When comparing the results of the analysis in the extract obtained in the leachate test of the glassy slag with limiting values of the harmful substances that can be deposited to landfill, it can be stated that all specified values obtained through the analysis are significantly below the limits set by Regulation Nr. 263/2010 of the Codex of the Ministry of the Environment.

Table3. *X-ray fluorescence spectrum analysis of the vitrified slag*

Element	Chemical composition (mg·kg^{-1})
V	89
Cr	350
Ni	65
Cu	250
Zn	5758
As	35
Br	184
Rb	36
Sr	520
Y	15
Zr	183
Nb	17
Mo	28
Ag	5
Cd	15
Sn	419
Sb	259
Ba	3003
Hg	<2
Pb	513

Some of the most important indicators of a high-temperature processing of the fly ash in the plasma reactor are the weight and the volume reduction. The weight reduction of the batch at 20 wt.% is associated with the presence of alkali metal oxides, metal oxides of a low melting point and mechanical losses. The presence of carbon in the batch supports the weight reduction as well, as it helps to oxidize the batch into carbon monoxide or dioxide, respectively. At the process of fly ash melting, chlorine is removed, in the form of metal chlorides, or as elemental chlorine. Sulfur in the syngas is represented in the form of S_2O or S_2.

$$volume\ reduction\ (\%) = \frac{m_{batch} \cdot \rho_{slag} - m_{slag} \cdot \rho_{batch}}{m_{batch} \cdot \rho_{slag}} \tag{1}$$

Volume reduction according to the equation (1) has been set to 58 vol.%. Comparing to the method of cementation, where there is an increase in volume, in the case of processing the fly ash in the plasma reactor, we observe a significant savings of the space set for the waste storage.

Research concerning the produced slag into the cementation area was as follows. Homogenization of the ash and the Portland cement was made by an intensive mixing of the two materials in the dry state within a range of ratios 20: 1 to 1:20, per weight unit. A mixture of the fly ash, cement and water was placed into molds with dimensions of 10.5 x 6.5 x5 cm, wherein the curing took place spontaneously at a room temperature for 48 hours. During the research, the mechanical properties as well as leachability were tested. Leaching tests were carried out in distilled water (according to the methodology set out in the Reg. No. 223/2001 Coll.) and lasted 24 hours. Additional limiting conditions for the samples production of the stabilization product, as well as the process of their testing are mentioned in [5].

Completed experiments are in regards to the procedure intended at the fixation of heavy metals into the silicate matrix using the cementation method (Table 4). Similarly, as in the case of the vitrification, the final results are, from the environmental viewpoint, very favorable [5]. Leaching of heavy metals is greatly suppressed, if compared with the samples of the stabilized waste. Problems, however, arise in particular in determining the correct mixing ratio of the fly ash and the Portland cement, which has a major impact on the integrity and leachability of samples [5].

Table4. *Heavy metals concentrations in MSWI fly ash leachates [5]*

Fly ash	Non-stabilised [$mg \cdot l^{-1}$]	Leaching ratio [$mg \cdot l^{-1}$]	Stabilized [$mg \cdot l^{-1}$]	Leaching ratio [$mg \cdot l^{-1}$]	Limit* [$mg \cdot l^{-1}$]
	C	C	C	C	
Ni	8.5896	76.69	0.0163	0.15	0.04
Cr	7.6571	9.75	0.0292	0.04	0.05
Cd	1.9789	3.72	< 0.0113**	0.02	0.004
Cu	29.2145	16.23	< 0.0330**	0.02	0.2
Zn	29.6980	4.18	< 0.0100**	0.00	0.4
Pb	11.5890	4.53	< 0.0100**	0.00	0.05

C – MSWI fly ash from cyclones

** 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)*

Heavy metals such as chromium, cadmium, nickel and mercury in the form of oxides and salts have no significant impact on the process of the ash stabilization and solidification with the cementation method. The compounds of zinc and lead can cause substantial negative effects on the process of solidification, as it is in the case with a high percentage of sulfides and chlorides are found in the fly ash. On the contrary, the sulfates improve the hydration process [5].

Processing of the fly ash with the plasma reactor technology brings, in addition to the positive impact on the environment, many other benefits. Compared with the cementation method, wherein the overall effect is not only the fly ash stabilization but also an obvious increase in the volume of the material, at the high-temperature ash melting using the plasma reactor technology we observe a considerable volume reduction. The highly reduced volume of the initial batch reflects in a reduced floor space required for the storage. Moreover, the amorphous glassy slag has extra features that offer a possible further use – mineral wool and foam glass.

Research into the stabilization of the fly ash, treated by the heat, inside the amorphous glassy slag, was carried out by the Department of the Power Engineering in collaboration with the Institute of Inorganic Chemistry Bratislava, and it focused on the production of the foam glass. The results confirm the significance of the development of research activities in that area.

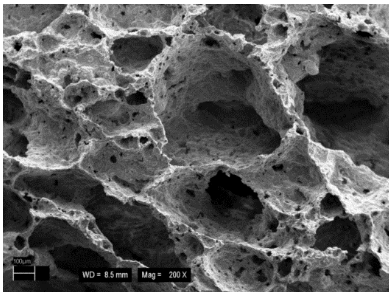
The first phase of the research was focused on a possible production of a foam glass. The crushed glassy slag (VS - vitrified slag) with a particle size below 100 microns was mixed with $CaSO_4$ at a weight ratio of 99:1. The decomposition temperature of the foaming agent, at the formation of gaseous components, is specified in the literature in the range of 700-1000 °C. In the case of this experiment, the initial heating temperature of the batch and $CaSO_4$ was set to 1000°C. The choice was made based on the DSC analysis (onset of phase transformations, crystallization from about 900°C).

At this temperature, not only the decomposition of foaming agent ($CaSO_4$) may be expected but also the optimal viscosity of the sample, which is a condition for the successful course of the foaming process. The parameters of the final product are shown in Table 5.

Table5. *Parameters of foam glass prepared from the pre-mixed sample of VT + 1% $CaSO_4$*

Density of the sample before heating ρ_0 ($g\cdot cm^{-3}$)	2.89
Density of the sample after heating ρ_t ($g\cdot cm^{-3}$)	0.99
Porosity $\Delta\rho$ (%)	cca 65 %

The structure made of foam glass was observed under an electron scanning analytical microscopy JEOL JSM-7600 F / EDS / WDS / EBSD. Images on the Figure 2 offer a glance of not only the structure made of foam glass from the pre-mixed sample of VT + 1% $CaSO_4$ (Figure 2a), but also the structure of industrially produced foam glass (Figure 2b).



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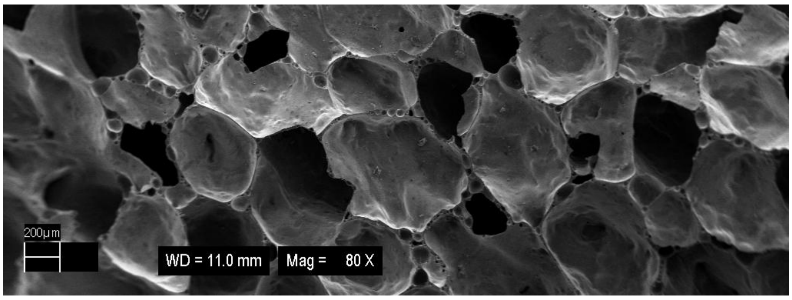

b,

Figure2. *The structure of the foam glass under the microscope*

The microscopic structure of the synthetic sample of the insulation confirms more homogeneous pore structure. Porosity as well as a uniform bubble- like pore distribution within the foam glass made of a vitrified slag requires continued research and further refinement of the boundary conditions of the foaming process.

CONCLUSION

The rather widespread method of the fly ash stabilization has become the *cement method* in which, following the mixing of the ash with certain additives and liquid reagents and subsequent drying of the mixture, the fixation of pollutants into the produced silicate matrix occurs. However, this method of stabilization tackles only the problem related to the safer storage of the fly ash in landfills with the controlled regime. As an environmentally acceptable way of stabilizing the ashes, with a possible use of the final product generated from the process of stabilization, a high temperature smelting process of the waste using a plasma reactor technology may be considered. The target product of melting, which is a glassy slag, is an inert product; hence does not have features, which could affect the environment. A significant benefit of the processes is the achievement of the volume reduction of the charge to about 58 vol. % which is, in the case of the cementation method, inaccessible. In addition, properties of the glassy slag predetermine its use in the construction industry in a form of a secondary raw material - insulation material.

Based on actual results we can conclude that the plasma technology intended for the disposal of the fly ash is suitable from the technological viewpoint; however, further experiments and tests shall confirm its economic justification. The fact that the technology is environmentally friendly has been established based on the results of the analysis; nonetheless, to justify the uniqueness of the hypothesis requires more thorough analysis of the composition of the gaseous products formed in the process of the vitrification.

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