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CURRENT SITUATION IN SLOVAKIA REGARDING FLY ASH MANAGEMENT

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ABSTRACT

The present article describes the current situation in the Slovak Republic (SR) regarding fly ash management and provides a more detailed analysis of the yearly production of this type of waste, the total production of waste in the SR, and the methods of disposal of this type of waste. The article also presents the research results achieved in the field of high-temperature melting of fly ash in a plasma reactor.

KEYWORDS: plasma technology, glassy slag, fly ash.

INTRODUCTION

A common practice within the disposal of ash is mixing all ash types, i.e., cinder, slag, fly ash, waste from desulphurisation, and storing them at dumps. Such dumps and decanting plants have well-known negative effects on the environment (dustiness, leaching, damaging the vegetation); moreover, building dumps intended for permanent storage of such waste requires high investments [1].

The yearly production of solid waste from incineration in the Slovak Republic ranges from 600 to 900 thousand tonnes. From the environmental point of view it is therefore important to increase the efficiency of power units and reduce the production of these types of waste despite the fact that such waste may be used as a secondary raw material [1, 2].

Since 2010, there is an increasing trend among producers and consumers of reintroducing such waste into production processes. An increase in the material recovery of solid waste from incineration (fly ash) has become more intensive since 2005 [3].

According to the List of Waste [4], solid waste produced during combustion of various fuels is categorised depending on its characteristic properties. The waste categorization, in compliance with the applicable regulations, introduces three main types of waste, in particular: inert waste, other waste, and hazardous waste. In many cases, it is not possible to meet the criteria for inert waste due to the character and method of production of such waste. The vast majority of fly ashes, bottom ashes, and slags is thus categorised as other waste and a part thereof as hazardous waste, as follows [4, 5]:

Other waste

Category	*Category title*
10 01 01	Bottom ash, slag and boiler dust (excluding boiler dust mentioned in 10 01 04)
10 01 02	Coal fly ash
10 01 03	Fly ash from peat and (untreated) wood
10 01 15	Bottom ash, slag and boiler dust from co-incineration (other than those mentioned in 10 01 14)
10 01 17	Fly ash from co-incineration other than those mentioned in 10 01 16
19 01 12	Bottom ash and slag other than those mentioned in 19 01 11
19 01 14	Fly ash other than those mentioned in 19 01 13

Hazardous waste

Category	*Category title*
10 01 04	Oil fly ash and boiler dust
10 01 13	Fly ash from emulsified hydrocarbons used as fuel

10 01 14	Bottom ash, slag and boiler dust from co-incineration containing hazardous substances
10 01 16	Fly ash from co-incineration containing hazardous substances
19 01 11	Bottom ash and slag containing hazardous substances
19 01 13	Fly ash containing hazardous substances
19 04 02	Fly ash and other flue-gas treatment wastes

Solid products from co-incineration categorised as hazardous waste represent only about 0.15 to 0.25 % of the total production of fly ash. Disposal thereof should be paid higher attention due to the method of their disposal. Hazardous fly ashes are currently disposed of exclusively by dumping. The overview of the production of bottom ash, slag and fly ash in Slovakia in the period from 2010 to 2015 is presented in Fig. 1 where A represents the total waste production and B represents the material recovery of waste [3].

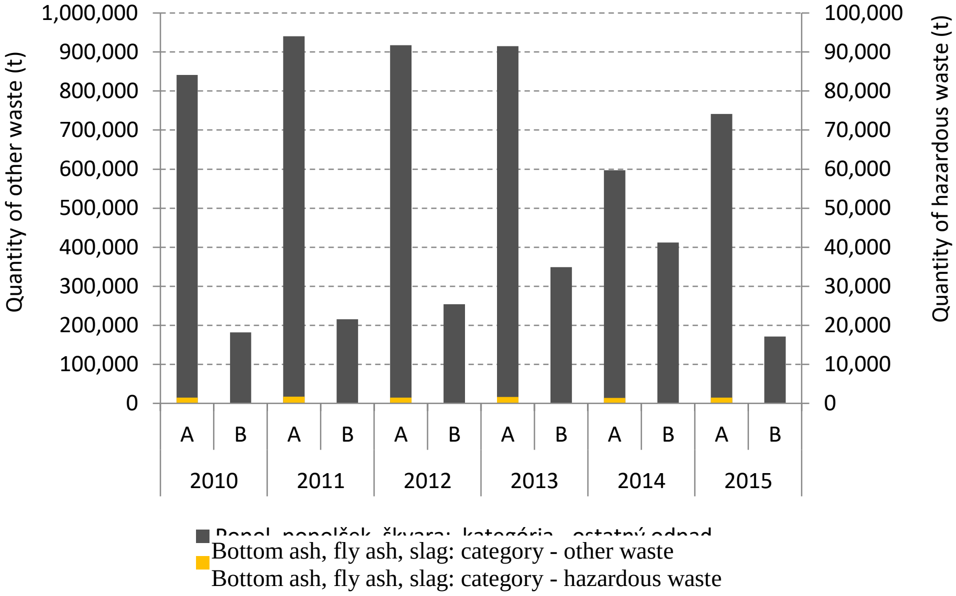

Figure. 1 Production of bottom ash, slag and fly ash in Slovakia in years 2010 to 2015

One of the methods of partial detoxification and decontamination of bottom ash and fly ash is the fixation with cement, extraction with acids, or stabilisation with chemical additives. The ultimate purpose of these processes is to strengthen the fine dust fraction of this type of waste. The stabilisation of fly ash by cementation and use of chemical additives does not result in the absolute inhibition of the release of toxic substances. Alkali chlorides contained in waste inhibit the hydration of cement. When comparing individual methods of fly ash disposal that are currently used, we may state that the objective is to search for a more efficient method of detoxification and decontamination of fly ash [6, 7].

At present, there is a new and intensively investigated method of efficient disposal of fly ash possessing hazardous characteristics, i.e., the transformation of fly ash in a thermal and chemical process, such as vitrification. During a vitrification process, fly ash is melted in an electric arc furnace, a rotary melting furnace, in a plasma reactor, or any other metallurgical aggregate together with fluxing agents at a high temperature so that oxidic slag melt is formed; such melt is subsequently granulated or casted into moulds. A glassy structure of the slag facilitates binding of a part of heavy metals and their compounds in an extremely stable glassy matrix [8]. The properties of the product of the above described process are suitable for further recovery. Fig. 2 presents the images of vitrified slag produced by processing various types of waste.

a)vitrified fly ash from municipal waste

b) vitrified Eternit roof tiles

c) vitrified fly ash from the production of FeMn

Figure. 2Vitrified slag

EXPERIMENTAL MELTING OF FLY ASH

In recent years, high-temperature processing of fly ash of various types in a plasma reactor has been subjected to the research activities carried out at the Department of Power Engineering. The main goal of the research is to minimise the amount of fly ash and its negative effects on the environment following from the very nature of this type of waste. The secondary subject of this research is also recovery of the produced glassy slag which often shows the properties suitable for applications as a secondary raw material.

The process of charge melting is carried out in a plasma reactor where the source of the heat is a low-ionised arc discharge excited between two electrodes connected in series. The processed charge, i.e., the already melted charge, actively contributes to sustaining the arc discharge. Images of the power part of the reactor and a 3D model of a 10 kVA laboratory plasma reactor are shown in Fig.3.

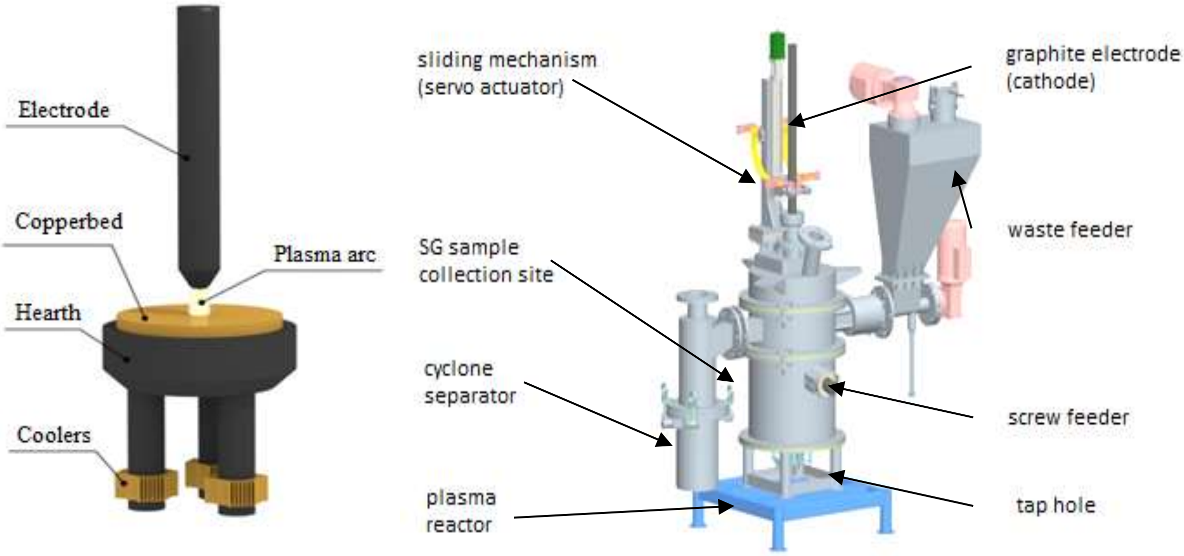

Figure.33D scheme of a 10 kVA laboratory plasma reactor

A plasma reactor consists of a steel casing lined with high-quality refractory aluminate lining, a sliding mechanism of the electrode, a graphite pot, and accessories providing the power supply. A hollow graphite electrode (cathode) is attached to a holder, with the supply of electric energy and plasma-forming gas (nitrogen), the holder arm is connected to the sliding mechanism with a software-controlled vertical movement of the cathode using a servo actuator. Electric current is supplied to the electrode via a flexible cable. Power supply to the anode is provided by three graphite and steel rods that are cooled at their ends by an air-cooler or by free cooling. A tap hole for tapping slag, as well as metal, is located in the graphite pot near the bottom of the reactor Fig. 1.

High-temperature waste processing in a plasma reactor is accompanied with the production of four products, i.e., synthesis gas, slag, alloy and fly ash. Processing of inorganic waste is characterised by the production of slag and fly ash as predominant products. Alloy is only formed when the reducing atmosphere is created. The percentages of alloy and fly ash are therefore largely determined by the marginal and reducing conditions at which a particular process of high-temperature melting is carried out.

Due to the nature of the research and the chemical composition of fly ashes processed so far, the main target product of melting was glassy slag with such properties that do not endanger the environment, or only to the minimum extent, in compliance with the applicable law. The used samples only included the samples of fly ash from co-incineration of municipal waste, fly ash from fluid boilers (from the process of black coal combustion), and power-plant fly ash. The resulting product of a melting process is usually stable glassy slag (see Fig. 2a). The chemical compositions of slags from various melting processes are listed in Tab. 1 and 2. A detailed description of the processes carried out within the experiments and the information characterising the marginal conditions of the given melting processes are provided in lit. 7.

Table 1. Chemical composition of fly ash

Component	MSW fly ash	MSW fly ash	Fly ash from fluid boilers
SiO_2	24.70	19.40	44.10
Al_2O_3	11.90	10.70	17.70
Fe_2O_3	4.11	2.49	7.28
CaO	32.50	37.40	7.53
MgO	2.98	2.96	1.66
MnO	0.18	0.20	0.19
TiO_2	1.75	2.11	0.71
Na_2O	2.31	2.21	0.40
K_2O	2.31	2.17	2.05
P_2O_5	1.35	1.44	0.30
SO_3	4.88	not determined	2.04
Annealing loss	10.90	10.30	15.60

Table 2. Results of the elementary and RFS analyses

Component	MSW fly ash	MSW fly ash	Fly ash from fluid boilers
Elementary analysis (wt.%)			
C	1.29	1.70	14.30
H	< 0.02	0.42	0.18
N	0.01	0.01	0.40
S_{total}	not determined	2.55	0.92
Contents of metals ($mg \cdot kg^{-1}$)			
As	18	35	8
Ba	1,910	3,003	1, 410
Cd	37	15	<2
Cr	329	350	67
Cu	427	250	38
Mo	< 10	28	3
Ni	82	65	85
Pb	---	513	39
Sr	406	520	355
V	42	89	9
Zn	6,800	5,758	82
Zr	131	183	345

Slag, being the main product of high-temperature melting of fly ash, represents a multicomponent system consisting of metal oxides and non-metallic elements that together form chemical compounds. In addition to the above listed components, slag may also contain, with regard to the course of waste melting and tapping, metal sulphides, gas components, tiny drops of a reduced metal component, etc.

With regard to the course of cooling the tapped slag (natural convection in small metal moulds, provided it is cooled in a water bath), the formed slags are usually amorphous or polycrystalline. Their melting temperature is also affected by, in addition to the chemical composition of the charge, the type of the used fluxing agents, or the composition of another type of inorganic waste that was used in the experiments. As an example we may present melting of fly ash from fluid boilers in the mixture containing also cement-asbestos roof tiles. By combining these two types of waste in the ratio of 1:1 and melting them in a plasma reactor at the temperature of 1,470 °C, two types of waste were disposed of.

Following the high-temperature processing of waste, it is important to identify the composition of the produced slag and its environmental impact. The assessment of the environmental impact of the produced vitrified slag was carried out on the basis of slag leaching testing in a water bath, carried out pursuant to Ministry of Environment of the SR Resolution 263/2010 Coll., as well as on the basis of ecotoxicity testing [9]. The results of the analyses, including the environmental standard data, are listed in Tab. 3. The results indicate that the samples of glassy slag obtained in the process of high-temperature plasma melting of fly ash, in the case of the mixture of fly ash and other types of inorganic waste, belong to the category of inert materials. They meet the current environmental standards and no longer possess the properties that endanger the environment.

Table 3. Results of the elementary and RFS analyses

Measured parameter	Concentration in the leachate Glassy slag from MSW fly ash ($mg \cdot l^{-1}$)	Concentration in the leachate Glassy slag from MSW fly ash ($mg \cdot l^{-1}$)	Concentration in the leachate Glassy slag from fly ash from fluid boilers ($mg \cdot l^{-1}$)
pH (1)	6.53	6.5	7.0
As ($mg \cdot l^{-1}$)	<0.001	<0.001	<0.0275
Ba ($mg \cdot l^{-1}$)	0.018	0.012	0.024
Cd ($mg \cdot l^{-1}$)	<0.0003	<0.002	<0.00060
Cr ($mg \cdot l^{-1}$)	0.003	0.002	<0.005
Cu ($mg \cdot l^{-1}$)	0.019	0.012	0.0515
Hg [$mg \cdot l^{-1}$)	<0.0001	<0.0001	0.001
Mo ($mg \cdot l^{-1}$)	<0.004	<0.005	<0.005
Ni ($mg \cdot l^{-1}$)	<0.002	<0.01	<0.005
Pb ($mg \cdot l^{-1}$)	<0.005	<0.01	0.0079
Sb ($mg \cdot l^{-1}$)	<0.001	<0.001	<0.001
Se ($mg \cdot l^{-1}$)	<0.001	<0.001	<0.001
Zn ($mg \cdot l^{-1}$)	0.012	0.022	0.00266
Chlorides ($mg \cdot l^{-1}$)	<1	<2	1.1
Fluorides ($mg \cdot l^{-1}$)	<0.1	0.03	<0.05
Sulphates ($mg \cdot l^{-1}$)	<2	<5	7
Phenol index ($mg \cdot l^{-1}$)	<0.03	<0.002	<0.01
CRL ($mg \cdot l^{-1}$)	34	38	105
Ecotoxicity	Negative	Negative	negative

Legend: a) If the identified CRL value is 400 $mg \cdot l^{-1}$, the values for chlorides and sulphates do not have to be identified b) The value for sulphates may be exceeded if the identified CRL value does not exceed 600 $mg \cdot l^{-1}$

It is assumed with regard to melting the mixture containing fly ash from fluid boilers and cement-asbestos roof tiles that despite a high melting temperature of pure chrysotile fibres (1,521 °C) [10] the chemical reactions running inside the melt result in their decomposition. The decomposition process is also significantly affected by the temperature at the site where the arc discharge is sustained while such temperature is significantly higher than the temperature of the melt located on the bottom of the reactor. The absence of chrysotile fibres in slag was confirmed by the examination of the grinds on the slag, using an electron microprobe, upon which the presence of chrysotile fibres was not detected in vitrified slag.

CONCLUSION
The high-temperature melting of fly ash in a plasma reactor aimed at stabilisation and future recovery of the produced glassy slag appears to be a promising method of disposal of this type of waste. Future applications of such thermal process of waste disposal are expected primarily in the management of the fly ash with hazardous properties. In addition to the possibility of stabilising the hazardous components of fly ash in an extremely stable matrix, the plasma melting technology also brings the possibility of a significant reduction of the initial amount of waste. The formed glassy slag, being the main product of melting, possesses the properties that make it appropriate for applications as a secondary raw material, mainly in the building industry. The potential recovery of such slag is particularly determined by the slag properties, categorisation as a secondary raw material, in compliance with the law, as well as the demand by consumers.

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