Analysis of the Selected Types of Waste Treatment by Plasma Technology - Part II

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Abstract**—** *The series of articles (Analysis of the selected types of waste treatment by plasma technology. Part I., Part II.) discusses the processing of selected three types of waste using plasma technology. In this second part of the article, the processing of fly ash from municipal waste, silicone rubber and asbestos-cement material using plasma reactor technology is presented. At the end of the article, the effectiveness or the contribution of individual experiments focused on the processing of the mentioned solid wastes using plasma technology.*

Keywords— Plasma Technology, Fly Ash from Municipal Solid Waste (MSW), Silicone Rubber, Asbestos-Cement Material.

I. INTRODUCTION

Plasma gasification and melting of waste commodities can be classified as a technology with wide-spectrum use of batch processing, whether from the field of metallurgy, but also various types of waste, either from the field of industry or municipal waste. The technology has been used for about 40 years. Its use is discussed in several experiments that have been published [1, 2]. Whether it is possible to talk about a universal technology for the treatment of any waste, we were convinced with the help of the plasma gasification and melting laboratory device at the Department of Energy Engineering, Faculty of Mechanical Engineering, Technical University of Košice.

II. LABORATORY PLASMA REACTOR

The experimental device of a plasma reactor with a power of 10 kVA and additional devices is presented through the table below with technical parameters (Table 1) as well as the resulting products from this technology, i.e. vitrified slag and synthesis gas.

TABLE 1
TECHNICAL PARAMETERS OF THE LABORATORY PLASMA REACTOR [3]

Volume of the reactor:	0,006 m^3
Operating voltage:	40 V
Operating electric current:	250 A
Electrical power of the source:	10 kVA
Plasma column temperature:	1400 – 2000 °C
Nitrogen flow rate:	5 – 8 $l \cdot min^{-1}$
Negative pressure in the reactor:	0,2 kPa

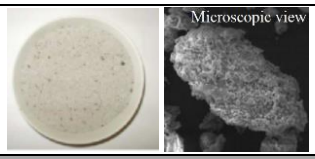
III. PROCESSING OF THE FLY ASH BY PLASMA TECHNOLOGY

The first type of waste processed by plasma technology was the fly ash obtained from the cyclone separators of the municipal waste incinerator. Fly ash from incineration of municipal waste is a fine-grained material of light grey colour, the basic

parameters of which are described in Table 2. Before the experiment itself, it was necessary to subject the fly ash to several analyses [3]:

- Determination of the percentage share of individual fly ash components,
- Determination of metal content using X-ray fluorescence spectrometric analysis,
- Determining the representation of slag-forming oxides,
- CHNS analysis.

TABLE 2
BASIC PARAMETERS OF PROCESSED WASTE – FLY ASH FROM MUNICIPAL WASTE

<table>
<tr><td colspan="2" rowspan="4"> 
</td><td>Grain size:</td><td>0,4 – 130 μm</td></tr>
<tr><td>Bulk density:</td><td>705 kg·m^{-3}</td></tr>
<tr><td>Moisture:</td><td>0,46 wt. %</td></tr>
<tr><td>Annealing loss:</td><td>10,9 wt. %</td></tr>
<tr><td colspan="2">Chemical composition of fly ash in wt. %</td><td colspan="2">Metal content in fly ash in mg·kg^{-1}</td></tr>
<tr><td>CaO</td><td>32,50</td><td>Zn</td><td>6800,0</td></tr>
<tr><td>SiO_2</td><td>24,70</td><td>Ba</td><td>1910,0</td></tr>
<tr><td>Al_2O_3</td><td>11,90</td><td>Pb</td><td>459,0</td></tr>
<tr><td>SO_3</td><td>4,88</td><td>Cu</td><td>427,0</td></tr>
<tr><td>Fe_2O_3</td><td>4,11</td><td>Sr</td><td>406,0</td></tr>
<tr><td>MgO</td><td>2,98</td><td>Cr</td><td>329,0</td></tr>
<tr><td>K_2O</td><td>2,31</td><td>Sb</td><td>189,0</td></tr>
<tr><td>Na_2O</td><td>2,31</td><td>Zr</td><td>131,0</td></tr>
<tr><td>TiO_2</td><td>1,75</td><td>Ni</td><td>82,0</td></tr>
<tr><td>P_2O_5</td><td>1,35</td><td>V</td><td>42,0</td></tr>
<tr><td>MnO</td><td>0,18</td><td>Cd</td><td>37,0</td></tr>
<tr><td>C</td><td>1,29</td><td>As</td><td>18,0</td></tr>
<tr><td>H</td><td>< 0,02</td><td>Y</td><td>13,0</td></tr>
<tr><td>N</td><td>0,01</td><td>Mo</td><td>< 10,0</td></tr>
<tr><td>Total S.</td><td>2,30</td><td>Hg</td><td>1,4</td></tr>
</table>

Based on the analysis of the ash, the melting temperature of the ash in the plasma reactor was determined. The presence of stable slag-forming oxides mainly affects the determination of the melting temperature of the fly ash sample. The most dominant compounds present in the fly ash sample with high affinity to oxygen are SiO_2, Al_2O_3, CaO. By converting their percentage representation to 100% state (35,75 wt.% SiO_2 – 17,22 wt.% Al_2O_3 – 47,03 wt.% CaO) and using the ternary phase diagram SiO_2 – Al_2O_3 – CaO, we obtain the approximate melting temperature of the fly ash sample.

In this case, it was a temperature of 1450 °C, but this intersection in the ternary diagram is located at the interface of 2 areas. A small change in the composition of the fly ash can cause a shift of this intersection to the area of higher temperatures in the range of 1500 – 1700 °C, which would represent an increase in the energy demand of the process. To avoid increasing the energy demand of the process, but not to disrupt the course of vitrification, the use of a suitable flux is required.

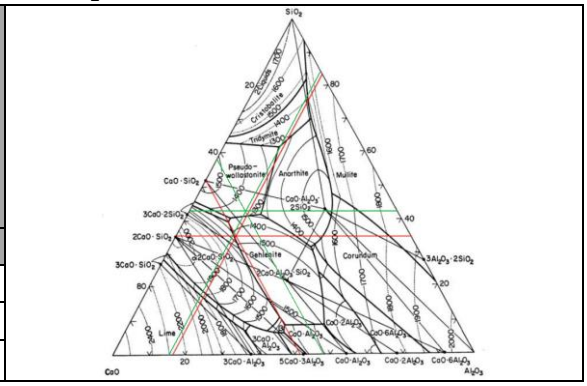
Fixation of fly ash "into the glass", more precisely into the glass matrix, is affected by the high content of alkaline CaO in the subject fly ash sample. For this reason, commonly available silica sand (alkaline flux) with a SiO2 content of 99.3 wt.% was chosen as flux. The ratio of fly ash and flux was determined from experience at 10:1.

The composition of the batch, even with the flux, after conversion to 100%, is shown in Table 3. The effect of adding flux to the fly ash sample lowered the reference melting point by approximately 100 °C, from 1450 °C to 1350 °C, as indicated by the green intersection in the ternary diagram (part of Table 3). By performing melting at a temperature increased by 50 °C, i.e. 1400 °C will be ensured:

- Formation of glassy vitrified slag (good viscous properties of the melt),
- Use of the afterburner presents in the fly ash as a reducing agent.

TABLE 3
DETERMINATION OF THE MELTING TEMPERATURE OF A SAMPLE OF FLY ASH FROM MSW INCINERATION WITH THE ADDITION OF SiO_2

Components	Percentage representation in the batch: FLY ASH + FLUX	Conversation to 100% condition	
	wt. %		
SiO_2	31,49	43,83	
CaO	29,54	41,12	
Al_2O_3	10,82	15,06	



The plasma gasification and melting experiment lasted 35 minutes at a melting temperature of 1400 °C. The charge mixture of fly ash and flux was dosed from the reservoir at 15-second intervals through a screw dosing device, while the charging time was set to 0,7 seconds based on the size of the reactor and ensuring the optimal mode of operation from the point of view of the existence of a plasma arc. A longer loading time as well as a larger amount of loaded dose would cause the loss of the plasma column, extinguishing of the arc and the end of the experiment. The process of adding fly ash was repeated until the tank was completely emptied, i.e. there were approximately 134 dosages of a batch weighing approx. 56 g. A total of 7,5 kg of the batch was remelted.

The specific energy consumption was determined to be 3,2 $kWh \cdot kg^{-1}$. The data on energy consumption is only indicative, as the heat losses of small reactors are significantly higher compared to plasma reactors with an output of several hundred kW and continuous operation.

The following products emerged from the experiment: synthesis gas and vitrified slag. The solid product from the experiment was a vitrified slag weighing 6,42 kg, with a specific gravity of 2810 $kg \cdot m^{-3}$.

The slag after tapping was allowed to cool freely in the air, then subjected to homogenization.

After its homogenization, the vitrified slag was subjected to chemical, X-ray fluorescence spectrometric analysis, ecotoxicity analysis and leachability of the slag in an aqueous solution.

TABLE 4
COMPOSITION OF VITRIFIED SLAG AS A PRODUCT OF PLASMA GASIFICATION AND MELTING OF FLY ASH FROM MSW

Chemical composition of the slag in wt. %		Metal content in the slag in $mg \cdot kg^{-1}$	
SiO_2	39,93	Ba	1570,0
CaO	32,93	Cu	1336,0
Al_2O_3	17,54	Cr	516,0
MgO	2,80	Sr	337,0
Fe_2O_3	2,79	Zn	163,0
TiO_2	1,83	Zr	136,0
P_2O_5	0,84	Pb	84,0
Na_2O	0,65	V	42,0
MnO	0,34	Ni	22,0
K_2O	0,16	Chlorides, Bromides, Y, Mo, ... < 20,0	

Synthesis gas production in the process of high-temperature gasification and melting of a mixture of fly ash from MSW and silica sand was 0,132$m^3 \cdot kg^{-1}$ of the batch, with a calorific value of 6,16 $MJ \cdot m^{-3}$.

IV. PROCESSING OF WASTE CONTAINING ASBESTOS BY PLASMA TECHNOLOGY

Another type of hazardous waste subjected to vitrification was asbestos-cement roofing. Processing this type of waste with plasma technology required the use of a flux. A flux that would be suitable for this purpose, i.e. to reduce the energy demand of the process, a waste product from coal combustion appeared, namely fly ash from fluid boilers.

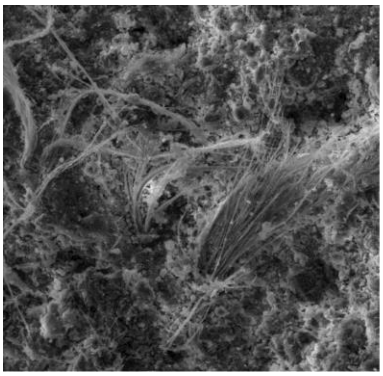
Waste that contains loosely bound asbestos (based on the structure, 2 basic forms of asbestos are distinguished – amphiboles and serpentines) are deposited in landfills after packaging (encapsulation). Covering the landfill with a sufficiently thick layer of soil is intended to prevent the leakage of fibres due to wind and water erosion. With the mentioned method of disposal of materials containing asbestos fibres, it is not possible to definitively destroy these fibres.

The samples subjected to experimental research contained asbestos fibres of the serpentine form, specifically chrysolite. As stated in the previous chapter III. it is necessary in practice to try to reduce the melting point, or of the temperature interval in which melting of debris occurs. The pure slag-forming oxides of which the slag is composed have high melting temperatures (t_{m}) [4]:

- t_{m_MgO} = 2 800 °C,
- t_{m_Al2O3} = 2 020 °C,
- t_{m_CaO} = 2 570 °C,
- t_{m_SiO2} = 1 723 °C.

Lowering the melting point of the asbestos roofing can be achieved by adding an acidic flux to the melting process. Acidic flux (majority SiO_2 content) is e.g. the mentioned product from thermal power plants – fly ash from fluid fires of coal-fired power plants. The chemical composition of the 4 major components of the sample (asbestos and fluid fly ash) is shown in Table 5.

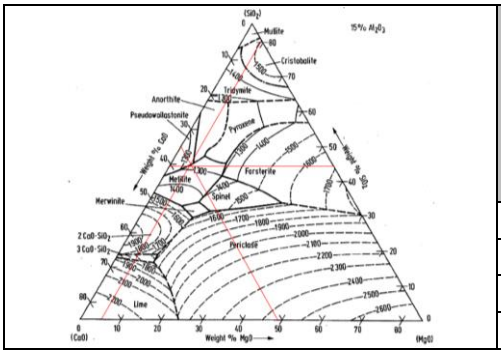
TABLE 5
BASIC PARAMETERS OF PROCESSED WASTE – ASBESTOS-CEMENT ROOFING (ASBESTOS) AND FLUID FLY ASH (FF ASH)



Chemical composition of ASBESTOS in wt. %		Chemical composition of FF ASH in wt. %	
CaO	42,50	SiO_2	44,10
SiO_2	21,30	Al_2O_3	17,70
MgO	5,94	CaO	7,53
Al_2O_3	5,09	Fe_2O_3	7,28
Fe_2O_3	2,29	MgO	1,66

The ratio of the batch mixture of crushed asbestos-cement roofing to a fraction < 5 mm and fly ash from the fluid fires of thermal power plants was 1:1. Using the quaternary diagram of the system Al_2O_3 – CaO – MgO – SiO_2, with a 15 wt.% Al_2O_3 content (Table 6), the melting temperature of the mixture was determined to be approximately 1300 °C (red intersection).

TABLE 6
DETERMINATION OF THE MELTING TEMPERATURE OF A SAMPLE ASBESTOS WITH FF ASH



Components	*Percentage in the batch*	*Conversion to 100% status*
	wt.%	
SiO_2	65,40	44,85
CaO	50,03	34,31
Al_2O_3	22,79	15,63
MgO	7,60	5,21

The experiment was carried out in two stages at a temperature of 1400 °C. The experiment was carried out in two phases under the same boundary conditions:

- I phase: tapping 5kg of melt,
- II phase: tapping 3 kg of melt.

The difference between I. and II. phase consisted in changing the cooling method of the taken sample of the resulting slag. In the first stage, the solidification of the slag sample took place by heat conduction and free convection on a concrete plate at an ambient temperature of 15 °C. In II. stage, the slag sample, after tapping into the cast iron mould, was then tipped out in the 30th minute into a water bath with a temperature of 15 °C.

During the experiment (I. and II. phase) vitrified slag with a total weight of 6,903 kg was produced. The specific weight of the vitrified slag was 2875 kg·m^{-3}. The vitrified slag was subjected to X-ray fluorescence spectrometric analysis.

TABLE 7
THE COMPOSITION OF VITRIFIED SLAG AS A PRODUCT OF PLASMA GASIFICATION AND MELTING OF THE MIXTURE – ASBESTOS-CEMENT ROOFING (ASBESTOS) AND FLUID FLY ASH (FF ASH)

Chemical composition of slag in wt. %		*Content of metals in the slag in mg·kg^{-1}*	
CaO	33,50	Ba	3651,0
SiO_2	32,10	Zr	827,0
Al_2O_3	27,50	Cu	585,0
MgO	4,33	Cr	44,0
TiO_2	0,58	V	11,0
Fe_2O_3	0,31	Br, Pb, Zn, Ni, ... < 10,0	

Synthesis gas production in the process of high-temperature gasification and melting (both phases of the process) was 0,116 m^3·kg^{-1} of the batch, with a calorific value of 8,205 MJ·m^{-3}, which enables its further energy use.

Asbestos fibres in the form of chrysolite (represented in asbestos-cement roof coverings) go through various stages of recrystallization under the influence of high-temperature treatment.

The melting bpd of chrysolite fibres is high, namely 1521°C [5]. Their decomposition due to chemical reactions taking place in the melt occurs because the temperatures at the place of maintenance of the arc discharge are significantly higher than the temperature of the melt, which is monitored by a sensor at the bottom of the reactor.

The impact of vitrified slag on the environment is assessed based on the results of analyses of the leachability of the slag in an aqueous solution.

V. PROCESSING OF WASTE SILICONE RUBBER BY PLASMA TECHNOLOGY

The last type of waste subjected to plasma treatment was discarded silicone moulds used for casting processes mainly in the automotive industry or in model making.

FIGURE 1: Processed waste – silicone rubber [6]

The general properties of silicone rubber include high binding energy. The siloxane bond (-Si-O-Si-) that forms the backbone of silicone (dimethylpolysiloxane) is very stable. Compared to the carbon bond (C-C) of 355 $kJ \cdot mol^{-1}$, the siloxane bond energy is 433 $kJ \cdot mol^{-1}$. Compared to common organic polymers, silicone rubbers have higher heat resistance and chemical stability. The material and thermal properties of silicone rubber are summarized in Table 8, the determination of moisture, ash and combustible content was based on thermogravimetric analysis [6].

TABLE 8
MATERIAL AND THERMAL PROPERTIES OF SILICONE RUBBER

Properties	Value
Dynamic viscosity of the sample	4000 mPa·s (or cP)
Tensile strength	6,5 MPa
Extension	120 %
Shrinkage	0,2%
Dielectric strength	19,7 $kW \cdot mm^{-1}$
Dielectric constant at 1 kHz	2,7
Working temperature range	–60 to +200 °C
Thermal conductivity	0,2 $W \cdot m^{-1} \cdot K^{-1}$
Combustion heat	14,39 $MJ \cdot kg^{-1}$
Moisture content of the sample	0,00 wt. %
Ash content of the sample	74,34 wt. %
The combustible content of the sample	25,66 wt. %

For the purposes of the experiment of plasma treatment of silicone rubber, the rubber sample was crushed, its weight was 0,477 kg. The batch was placed in the reservoir just before the experiment was carried out. It was necessary to prevent unwanted thermal decomposition of the batch in the reservoir during the heating of the reactor.

Batch dosing was started at the desired carbon bath temperature of 1150 °C. The plasma-forming gas nitrogen was fed into the reaction chamber with a volumetric flow rate of 0.005 $m^3 \cdot min^{-1}$. The experiment was carried out in two phases. In the first phase, the optimal dosing interval was set for maintaining the arc discharge between the cathode and the anode.

The second phase of the waste silicone rubber recovery experiment took place in the temperature range of 1360 – 1400 °C. In both phases, the batch was dosed at a rate of 0,02 $kg \cdot min^{-1}$

FIGURE 2: Inorganic residue of silicone rubber batch processed in a plasma reactor [6]

Figure 2 provides a complete idea of the success of the experiment. It is a view into the reaction chamber of the plasma reactor. A thermally decomposed charge weighing 256,36 g was identified in the lower part of the plasma reactor. It was a light grey fine-grained dust with a fine mesh structure.

In the cyclone separator of the technology and in the section between the separator and the reactor, a drift of grey-brown colour weighing 95,17 g was caught.

The samples of these solid products were subsequently subjected to thermal analysis.

TABLE 9
COMPOSITION OF SOLID PRODUCTS PRODUCED BY PLASMA PROCESSING OF WASTE SILICONE RUBBER

Component	*Mass fraction of processed waste from the reaction chamber (wt.%)*	*Mass fraction at the chimney exit (wt. %)*
SiO_2	82,7	78,04
Al_2O_3	6,74	0,09
TiO_2	4,99	0,04
Fe_2O_3	1,29	0,23
Na_2O_3	1,29	< 0,01
K_2O	0,63	0,02
CaO	0,47	0,15
P_2O_3	0,18	18,1
MgO	0,14	0,02
SO_3	0,10	0,05
MnO	0,06	0,03
Annealing loss	1,08	3,4

The high representation of SiO2 in waste solid products is the result of thermal decomposition of the main siloxane bond, in which silicon, characterized by a high affinity for oxygen, oxidizes to SiO2. The presence of phosphorus and titanium can be explained by the presence of colorants, vulcanizing agents and other additives in silicone rubber.

VI. CONCLUSION

The conducted experiments can be considered successful. In all cases of thermal treatment by plasma technology at high temperatures in a nitrogen atmosphere, the processed batch was decomposed into gaseous components and a solid residue in the form of chimney waste or product in a plasma reactor, or in the form of vitrified slag.

The energy recovery of the produced synthesis gas would be possible in all cases, but it is important to clean it before the actual use process. The calorific value of the produced synthesis gas for all types of input waste is shown in Table 10:

TABLE 10
AVERAGE CALORIFIC VALUE OF THE PRODUCED SYNTHESIS GAS

Waste batch for plasma treatment	The average calorific value of the produced synthesis gas in $MJ \cdot m^{-3}$
Fly ash from municipal waste	1,628
Asbestos-cement roofing	8,000
Silicone rubber	5,240

In the case of plasma processing of silicone rubber, the production of chimney waste represented an unexpected problem, i.e. the weight of the chimney waste to the weight of the batch was 20 wt. %. Chimney waste was mostly deposited in the chimney space of the reactor, and its deposition in some places caused almost 100% of the cross-section of the pipe system to be clogged.

From laboratory analyses in the case of vitrified slag as a product of plasma processing of fly ash from municipal solid waste and waste asbestos-cement roofing, it can be concluded that the vitrified slag represents inert waste without its further negative impact on the environment.

Only what concerns the plasma processing of silicone rubber, under the marginal conditions valid for the given experiment, is unjustified from an economic and ecological point of view. The processing of silicon waste in a plasma reactor does not exclude the formation of toxic products released during the chemical reactions occurring in the process of thermal decomposition of the batch. However, if the marginal conditions are changed, it is not excluded that the processing of silicone rubber by plasma technology would not bring the desired results for a more ecological solution for the disposal of this type of waste.

ACKNOWLEDGEMENTS

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