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INFLUENCE OF WASTE INCINERATION RESIDUE ON SLAG VITRIFICATION DURING MEDICAL WASTE UTILIZATION

WPŁYW POZOSTAŁOŚCI PO PROCESACH SPALANIA NA WITRYFIKACJĘ ŻUŻLI WYTWORZONYCH PODCZAS UNIESZKODLIWIANIA ODPADÓW MEDYCZNYCH

Abstract: Vitrification is one of many methods of ashes treatment enabling receiving products with properties like glass. The slag received after medical wastes utilization (according to Purotherme Pyrolise) is difficult material for vitrification. Obtaing the product with glass-like properties requite applying of oxygen to the zone of reaction or applying materials supporting vitrification process. In the carried out test of slag and ash after combustion process were used as additives supporting vitrification process. In effect of treatment substrat with additives vitrificators were obtained. The best quality vitrificators in result of treatment of mixture of slag from medical wastes pyrolisys process and slag from municipal wastes combustion process (30 + 70%) and mixture of slag from medical wastes pyrolisys process and slag from municipal wastes combustion process (30 + 70%) and mixture of slag from medical wastes pyrolisys process and slag from municipal wastes combustion process (30 + 70%) and mixture of slag from medical wastes pyrolisys process and slag from municipal wastes combustion process (30 + 70%) and mixture of slag from medical wastes pyrolisys and sh from municipal wastes combustion process consisting 50% of each component were obtained. The vitrificators are characterized by amorphous structure, hardness (glass-like) 6–6.5 of scale Mohsa. Their density was above 2.6 g/cm³. The highest density (2.924 g/cm³) in the vitrificator obtained from mixture of slag from medical wastes pyrolisys and ash from municipal wastes combustion process was marked.

Keywords: medical wastes, pyrolisys, ash, slag, municipal wastes, combustion process, vitrification

At present the application of thermal processes for the utilization of waste becomes more and more favorable option for waste management. Thermal utilization of waste is associated with the formation of solid post processing residue, *ie* slag and ash. They can contain high concentrations of toxic substances from the input waste or formed during the process of utilization. If the amount of waste subjected to thermal utilization increases the amount of slag and ash requiring further processing will also increase. One of the methods applied for processing of waste incineration residue is vitrification [1–8]. This method allows to transform waste incineration residue into products with glass-a-like properties. Depending on the initial waste properties and applied processes

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for waste utilization the residue can show different properties and be more or less suitable for vitrification.

The slag generated during utilization of medical waste by the Purotherm Pyrolise technology (Fig. 1) was used for the investigation. Due to the specificity of pyrolisis this substrate showed high total carbon content which impairs the process of vitrification without the access of oxygen [9]. High temperature processing of the substrate in the presence of oxygen in the reaction zone can result in the formation of toxic gaseous compounds (dioxins and furans) [10]. Therefore the series of investigations was undertaken to vitrify the slag without introducing oxygen into the reaction zone. In order to do that some additional materials were used to facilitate the process of vitrification.



Fig. 1. Slag generated during the utilization of medical waste by Purotherm Pyrolise technology

Materials

Slag generated during the utilization of medical waste was subjected to the phase analysis which confirmed a significantly complex structure (heterogenic) of the substrate.

The composition of the substrate was predominated by: CaO - 27.13 %; $SiO_2 - 13.7 \%$; MgO - 5.1 %, $Al_2O_3 - 4.0 \%$; $Na_2O - 2.85 \%$; $Fe_2O_3 - 2.09 \%$. Slag showed deep gray color with black spots, non uniform granulation and contained incompletely incinerated ampoules, needles, lancets, bandage residues. The moisture content was 38 %.

To facilitate the process the selected additives, *ie* slag and ash generated from the incineration of municipal waste in a furnace, were applied. These materials showed a significant concentration of SiO_2 : 48.64 % (slag) and 40.89 % (ash).

Methods

Vitrification of the substrate was conducted in the following stages:

- self-transformation of the substrate,
- transformation of the mixture of substrate and slag after incineration,
- transformation of the mixture of the substrate and ash after incineration.

The mixtures of the substrate and the additives were prepared in the ratios presented in Table 1.

Table 1

The ratios of the substrate and the additives in the mixtures subjected to vitrification [%]

Substrate	Additives	
	Slag – the mixture No. I	Ash – the mixture No. II
80	20	20
50	50	50
30	70	70

The substrate and additives were weighed and transferred into a graphite crucible which was placed into the plasma reactor. Vitrification was conducted for 12 minutes by plasma forming gas using argon with the flow velocity of 14 dm³/min. The length of the plasma arc was 0.15 m. The I-U characteristics for the plasma reactor were selected based on the preliminary studies [1, 2].

Plasma reactor

Thermal transformation of slag and ash was conducted in the plasma reactor. The reactor is hermetic and can operate at partial pressure as well as overpressure up to 0.05 MPa which allows for conducting the process in the controlled atmosphere. The installation operates on the direct current which allows to reach the maximum arc power up to 150 kW at the regulated intensity for various voltage values. The torch inside the reactor can move vertically to alter the length of the arc up to 0.35 m. Ceramic or graphite crucibles with capacity up to 10 dm³ can be place on the arc-furnace electrode (anode). The reactor is equipped with the observation ports made of quartz glass allowing for the observation of the reaction zone. Argon was used as a plasma forming gas. Other gas ($eg O_2$) can be introduced into the reaction zone. Exhaust gases are removed through a condenser. The installation also consists of a power supply and water cooling systems.

Results

In the course of thermal transformation of the substrate a product (Fig. 2) with a dull and partly coarse surface both at the surface and in the fracture was obtained.

During the transformation of the mixtures with slag generated during pyrolisis of medical waste and slag remained after incineration of municipal waste (the mixture No. I), the input material underwent complete melting. Only in some cases insignificant amount of the material remained in the crucible which implies that it did not undergo the reaction. In most cases, the products obtained from the mixture No. 1 showed glossy surface and the fracture. However, some of them were characterized by a non uniform structure and a coarse surface. The quality of vertified products was diverse and



Fig. 2. The product obtained after the transformation of slag generated during pyrolisis of medical waste

depended on the individual components in the mixture (Fig. 3). The best results were obtained for the mixture of 30 % of slag after pyrolisis and 70 % of slag after incineration. The vertified product (referred to as Ic) obtained from this mixture is presented in Fig. 3c.



Fig. 3. The products obtained from the mixtures No. 1 (slag after pyrolisis + slag after incineration) in the following ratios: a -80 + 20 %, b -50 + 50 %, c -30 + 70 %

Also, as a result of the transformation of the mixtures No. I, apart from the vertified products, a clearly separated metal fraction of the product was obtained (Fig. 4).



Fig. 4. Metal fraction of the product obtained during transformation of the mixture No. I

In case of the mixtures No. II (slag after pyrolisis + ash after incineration) the substrates underwent a complete reaction and were transformed into the products with the properties typical for the vertified products. They were glossy on the surface and in the fracture and had a uniform structure. The products obtained from the mixtures No. II

were presented in Fig. 5. The best quality vetrified products were obtained during the transformation of the mixture containing 50 % of slag after pyrolisis and 50 % of ash after incineration. The vertified product (referred to as IIb) obtained from this mixture is presented in Fig. 5b.



Fig. 5. The products obtained from the mixtures No. II (slag after pyrolisis + ash after incineration): a - 80 + 20%, b - 50 + 50%), c - 30 + 70%

Based on the visual analysis the best vertified products (*ie* Ic and IIb) were subjected to hardness and density tests. The results are presented in Table 2.

Table 2

Density and hardness for the selected vitrified products

Vitrified product	Density [g/cm ³]	Hardness in the Mohs scale
Ic	2.637	6.0-6.5 (decreasing to 5)
IIb	2.924	6.0–6.5

The conducted X-ray analysis of the slag after pyrolisis of medical waste (Fig. 6) and obtained vitrified products shows the transformation of the substrates into the products with amorphous structure.

Figure 7 presents the X-ray diffractogram for the vertified product Ic. The diagram shows a characteristic nub of the diffractogram for the reflection angle in the range of $20-40^{\circ}$ which indicates the amorphous structure of the vertified product typical for glass.

Not too significant single peeks in the diagram indicate the presence of small quantities of the substances with a regular structure.

Mapping and chemical point rating analysis of the samples from the vitrified products were obtained by use of the scanning electron microscope. Figure 8 presents the EDS spectrum for the chemical composition of the glaze of the vertified products IIb and Ic. The basic compounds of the matrix glaze of these vertified products are Si, Al,O, Ca.

Figure 9 presents the morphology for the fracture of the vertified product IIb and the diversified chemical composition. The surface of the fracture is sufficiently smooth with



Fig. 6. The X-ray diffractogram for the slag generated during pyrolisis of medical waste



Fig. 7. The X-ray diffractogram for the vertified product Ic



Fig. 8. The EDS spectrum of the matrix glaze of the selected vertified products: a - vertified product IIb, b - vertified product Ic

few light round segmentations. The size of these segmentations does not exceed 20 micrometers (Fig. 9 a-d).

Apart from typical glass components there are sulfur and iron in their composition (Fig. 9e). Also, apart from bright segmentations there are some spots in irregular shapes with predominant content of carbon and NaCl (Fig. 9f).

The fracture surfaces of the vetrified product Ic are more diverse. Figure 10 shows two surfaces of the fracture. One of them (Fig. 10a) is covered with numerous,



Fig. 9. The analysis of the fracture structure of the vetrified product by the scanning electron microscope: a, b – the morphology of the surface (picture taken with a secondary electron detector), c, d – the chemical composition (picture taken with a backscattered electron detector), e, f – the EDS spectrum representing the chemical composition of the segmentations (e – bright segmentations, b – dark segmentations).



Fig. 10. The analysis of the fracture surface of the vetrified product Ic conducted with a scanning electron microscope: a, b - the morphology of the surface (the picture taken with a secondary electron detector), a_1 , $b_1 - the$ chemical composition (the picture taken with a backscattered electron detector).

half-rounded pits with a diameter from several to several hundred micrometers (about 100–300). These pits are empty and presumably are a result of the occurrence of gas bubbles. On the fracture surface (with a typical glaze composition) there are numerous dark spots and chips which are composed mainly of carbon. The morphology of the second surface is similar. Apart from the rounded pits on its surface there are some "wrinkles" (Fig. 10b), dark spots and chips composed mainly of carbon. Also, there are some small bright segmentations (up to 5 μ m) which are composed mainly of potassium chloride.

Conclusions

Waste residue generated during thermal utilization of medical waste by means of the Purotherm Pyrolise technology is rather difficult to transform by vitrification. Obtaining a good quality vetrified product requires introducing oxygen into the reaction zone or the addition of selected materials which facilitate the process.

The vetrified products obtained during the transformation of the mixtures of slag and ash after incinerating municipal waste show amorphous structure typical for glass. Similarly, the hardness and density characteristics of the vetrified products are typical for glass. The main components of the glaze were: Si, Al,O, Ca. Insignificant pockets of S, Fe, C, NaCl and KCl were observed in the matrix.

The transformation of the mixtures of the substrate and slag after incineration resulted in vetrified products with different quality due to the composition of the mixture. The best quality vetrified products were obtained from the transformation of the mixture containing 30 % of slag after pyrolisis and 70 % of slag after incineration. The hardness of the vetrified products obtained from this mixture was in the range of 6-6.5 according to Mohs scale with a decreasing tendency towards 5. The density of the vetrified product Ic was 2,637 g/cm³.

The morphology reflection of the fracture surface showed numerous empty pits (with a diameter in the range of (100; 300) μ m and some small spots which had different composition than the matrix.

The transformation of the mixture of the substrate and ash after incineration resulted in the products with smooth and uniform surface. The best results were obtained for the mixture containing 50 % of slag after pyrolisis and 50 % of ash after incineration. The hardness of the vetrified products obtained from this mixture were in the range of 6–6.5 according to the Mohs scale. The density of the vetrified product IIb was 2.924 g/cm³. The morphology reflection of the fracture surface examined with a scanning electron microscope showed smooth surface with few small segmentations.

The results of the study lead to the following conclusions:

1) good quality vetrified products from slag generated during pyrolisis of medical waste can be obtained after vetrification of the mixtures containing slag from pyrolisis and solid residue from incineration of municipal waste:

– in case of the mixtures containing slag generated after pyrolisis of medical waste and slag after incineration of municipal waste, the quality of the obtained vitrified products improves with the increase in the content of slag from incineration in the mixture whereas the best results were achieved for the mixture containing these components in the ratio of 30 % and 70 %; the pits remained after the occurrence of gas bubbles can indicate that the time of vitrification was too short,

– as for the transformation of the mixture containing slag after pyrolysis of medical waste and ash from incineration of municipal waste the best results were achieved for the mixtures with ratios of 50 % of each of the components, increasing or decreasing the content of these components deteriorates the quality of the obtained products,

2) the hardness of the vetrified products can be compared to the hardness of glass; in case of some vetrified products obtained during the transformation of the mixtures No. I, the hardness was lower (about 5 according to Mohs scale) than for the vetrified products obtained from the mixtures No. II,

3) the density of the vetrified products obtained from both types of mixtures was above 2.6 g/cm³ reaching 2.924 g/cm³ – which is typical for quartz glass – for the vetrified product obtained from the mixture of slag after pyrolisis and ash after incineration,

4) in case of the transformation of the mixtures containing slag after the pyrolisis of medical waste and slag from incineration of municipal waste, the recovery of metallic components is possible,

5) the addition of ash after incineration of waste allows for better results during the vitrification of slag after pyrolisis of medical waste than the addition of slag after incineration,

6) the best quality vitrified products were obtained from the transformation of the mixture containing slag after pyrolysis and ash after incineration in the ratio (by mass) of 50 % and 50 %, respectively.

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Abstrakt: Witryfikacja może być jedną z metod przekształcania stałych pozostałości po procesach termicznych, umożliwiającą uzyskanie z odpadów produktów o właściwościach szkłopodobnych. Żużel wytworzony w procesie unieszkodliwiania odpadów medycznych wg technologii Purotherm Pyrolise jest materiałem trudnym do witryfikacji. W celu ułatwienia procesu zeszkliwienia w badaniach zastosowano materiały wspomagające. Żużel po pirolizie odpadów medycznych przekształcano z pozostałościami po spalaniu odpadów komunalnych w piecu rusztowym. Najlepsze efekty osiągnięto przekształcając mieszanki zawierające 30 % żużla po pirolizie i 70 % żużla po spalaniu odpadów komunalnych oraz mieszanki

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zawierające 50 % żużla po pirolizie i 50 % popiołu po spalaniu odpadów komunalnych. Twardość uzyskanych witryfikatów była porównywalna do twardości szkieł i mieściła się w zakresie 6–6,5 w skali Mohsa. Gęstość witryfikatów otrzymanych z obydwu typów mieszanek wynosiła powyżej 2,6 g/cm³, osiągając wartość 2,924 g/cm³ w przypadku witryfikatu uzyskanego z mieszanki żużla po pirolizie i popiołu po spalaniu.

Słowa kluczowe: odpady medyczne, piroliza, popiół, żużel, odpady komunalne, spalanie, witryfikacja