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THE TREATMENT OF INCINERATION WASTES
WITH A CARBONATE WASTE FRACTION
FROM THE ZINC-LEAD INDUSTRY

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Abstract: The article presents the results of plasma vitrification of solid remnants from thermal waste treatment with and without the addition of a carbonate fraction obtained from lead-zinc ore flotation. The substrates used in the research were slags and ashes from medical waste treatment, incineration of municipal waste, sewage sludge as well as hazardous and industrial wastes.

The plasma treatment resulted in acquiring products of different quality depending on the processed substrate. Most of the obtained products were of vitreous and homogenic build. Treatment of remnants from incineration of hazardous and industrial wastes resulted in obtaining heterogeneous and rough surfaced products. A 20% share of the carbonate fraction enabled the obtaining of a vitrified product with a glassy surface and fracture. Hardness of the obtained products was rated in Mohs scale and ranged from 6 to 6,5. Leaching tests showed a decrease in heavy metal concentration in the leachates from vitrificates with the addition of carbonate fraction compared to the ones with it.

INTRODUCTION

The constantly increasing amount of landfilled waste as well as their illegal or inappropriate storage are a serious threat to the health of people and the environment. The need of regulating the waste management system results in the growing “popularity” of thermal waste treatment by incineration, pyrolysis and gasification. The wastes are converted into ashes, slags and gases, accumulating many chemical compounds, which were present in them before incineration and new ones, which were formed during incineration. The increasing amount of thermal treated wastes results in an increased amount of produced slags and ashes which need to be utilized. Their storage in landfills is a hazard for the environment due to the harmfulness of their leachates. One of the thermal waste treatment methods is vitrification which allows for obtaining products of glasslike qualities.

Vitrification is the formation of a stable and impermeable, glassy structure in effect of heating substances to a semi-fluid state and their fast cooling. Inclosing of components such as heavy metals from the treated substance in an impenetrable structure prevents their migration. Treatment of hazardous substances is carried out by their binding in a crystalline glass structure, as well as their encapsulation [9].

Vitrification is an effective way of treating hazardous waste. Usually vitrification is carried out for wastes with unfavourable physical properties and complex chemical composition hard to utilize with other methods, e.g., medical wastes, nuclear wastes, slimes, polluted earth, asbestos, slags and ashes [4, 10, 11].

By vitrification of certain wastes one can obtain products of qualities allowing for their reuse, mostly in the ceramic and building industries.

The advantages of vitrification products are:

- low chemical reactivity and non-toxicity,
- mechanical strength,
- no dusting,
- possibility of attribute modification [2, 3, 12].

Vitrification requires specific heating systems and large quantities of heat energy. Different kinds of installation may be used for waste vitrification, for example plasma systems [8, 11].

Vitrification of slags and ashes from waste incineration requires glass forming additives such as SiO_2 , B_2O_3 or agents lowering the melting temperature. In the experiment a rich in CaO carbonate fraction from the zinc and lead industry was used in order to lower the melting temperature of the substrates.

SUBSTRATES

In the experiment the following were used: slag from municipal waste incineration, slag from medical waste treatment, slag from incineration of hazardous and industrial wastes, ash from sewage sludge incineration and waste carbonate fraction.

Slag from municipal waste incineration is generated during a process in which wastes meant for incineration are directed to the feed chute from which they are fed to the incinerator grate. Wastes are incinerated in the temperature range of 850–1150°C. The slag is discharged into a chute with a water curtain where it is cooled down. The slag is of grey colour and irregular granulation (Fig. 1a).

The next substrate used is slag from medical waste treated with Purotherm Pyrolyse Technology. This technology is carried out in 2 stages. In the first stage after loading wastes to the pyrolysis chamber their conversion at about 800°C to a flammable gas is carried out, which is followed by its incineration in the post-combustion chamber in the second stage. This process is carried out at about 1200°C for a minimum of 2 seconds. The slag remaining after medical waste treatment is of grey colour and irregular granulation with visible remnants of metal parts (needles) (Fig. 1b).

Slag from industrial and hazardous waste incineration is generated during incineration of wastes in a rotary kiln, in a temperature of up to 1250°C. This substrate is also of irregular granulation and gray colour with hints of rust (Fig. 1c).

Ash from sewage sludge incineration is generated during incineration of sewage sludge at 850°C in a fluidized-bed furnace without any additional fuel. Hot air heated

up by *heat exchangers* serves as the fluidization agent. The possibility of carrying out autothermic incineration (without additional fuel) is dependent on the amount of moisture and inorganic compounds in sewage sludge. The obtained ash was of homogenous, fine granulation and orange-red colour (Fig. 1d).

The material used for lowering the vitrification temperature was the waste carbonate fraction from the zinc-lead industry. This fraction consists mostly of dolomite (ca. 70%) whereas the average chemical composition of flotation wastes is as follows: 23–32% CaO, 12–17% MgO, 1–2% Al₂O₃, 2–4.5% SiO₂, 0.5–5% S, 2.5–8% Fe_{catk.}, 1–3% Zn, 0.1–0.9% Pb [6, 7].

Loss on ignition for the used substrates, heavy metal content in leachates (water eluates according to PN-EN 12457-2), pH and conductivity were analysed. The results

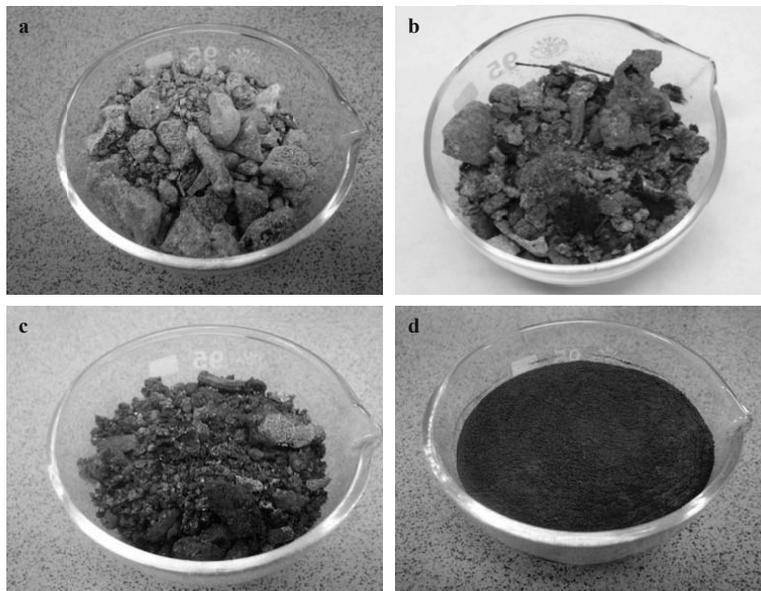


Fig. 1. Substrates: **a** – slag from municipal wastes grate furnace incineration, **b** – slag from medical waste Purotherm Pyrolyse treatment, **c** – slag from industrial and hazardous waste kiln incineration, **d** – ash from sewage sludge fluidized-bed furnace incineration

Table 1. Waste characterization before plasma modification

Parameters	Slag from municipal wastes	Slag from medical wastes	Slag from hazardous and industrial wastes	Ash from sewage sludge	Carbonate fraction
Loss on ignition %	1.16	1.06	3.37	0.19	2.01
pH (leachate)	9.59	9.14	9.08	9.31	7.54
Conductivity (μs) (leachate)	1240	1267	5690	1165	1208

Table 2. Heavy metal concentration in leachates (converted to *dry-weight basis*) from the substrates and limiting values for admitting wastes to storage in the landfills of inert wastes

Concentration Unit	Metal	A	B	C	D	Carbonate fraction	Limit value
mg Zn/kg	Zinc	1.0	3.4	2.3	2.1	14	4
mg Cu/kg	Copper	2.0	3.1	3.2	1.2	1.2	2
mg Cd/kg	Cadmium	<0.05	<0.05	<0.05	<0.05	0.15	0.04
mg Ni/kg	Nickel	0.20	0.06	0.35	<0.05	0.05	0.4
mg Pb/kg	Lead	<0.1	0.17	<0.1	<0.1	0.95	0.5
mg Cr/kg	Chromium	0.09	0.10	0.15	0.06	<0.05	0.5

A – slag from municipal wastes; *B* – slag from medical wastes; *C* – slag from hazardous and industrial wastes; *D* – ash from sewage sludge.

are shown in Tables 1 and 2. Heavy metal concentrations in leachates were compared to the limiting values for admitting wastes to storage in the landfills of inert wastes [5].

Metal concentration results (Tab. 2) showed an exceeded concentration of copper for the slag from medical wastes (3,1 mg Cu/kg) and slag from hazardous and industrial wastes (3,2 mg Cu/kg). High concentration of Cd, Pb and Zn was noted for the carbonate fraction. The concentration of these metals is due the origin of this waste.

RESEARCH METHODICS AND TEST BENCH

Weighed amounts of substrates (50 g) were placed in graphite pots and were treated with plasma. The vitrification lasted for 15 minutes, argon was used as the plasma gas. The processed substrates were as follows: slag from municipal waste, slag from medical waste, slag from hazardous and industrial waste, ash from sewage sludge, next the aforementioned substrates were processed with a 20% addition of carbonate fraction from the lead-zinc industry.

The experiment was carried out in a plasma arc furnace (Fig. 2), which is a shut tight device and operational at *underpressure* and *overpressure of up to 0.05 MPa which allows for carrying out the process in a controlled atmosphere* DC powered. The plasma torch is able of changing its vertical position, in order to adjust the length of the arc up to 0.35 m. There is the possibility of placing graphite or ceramic pots of volume up to 10 dm³ on the lower electrode (anode). The reactor allows for monitoring of the reaction area through a viewfinder made of quartz glass [1].

RESULTS

The plasma treatment of the substrates resulted in obtaining dense, glassy masses. The treatment of ash from sewage sludge resulted in obtaining products of homogenous build with a glassy surface and fracture (Fig. 3a). Products obtained from medical waste slag and municipal waste slag treatment had a rough surface, with a partly glassy fracture (Fig. 3b–c). Products obtained from hazardous and industrial waste slag had a heterogenous rough surface, with numerous pores in the fracture (Fig. 3d).

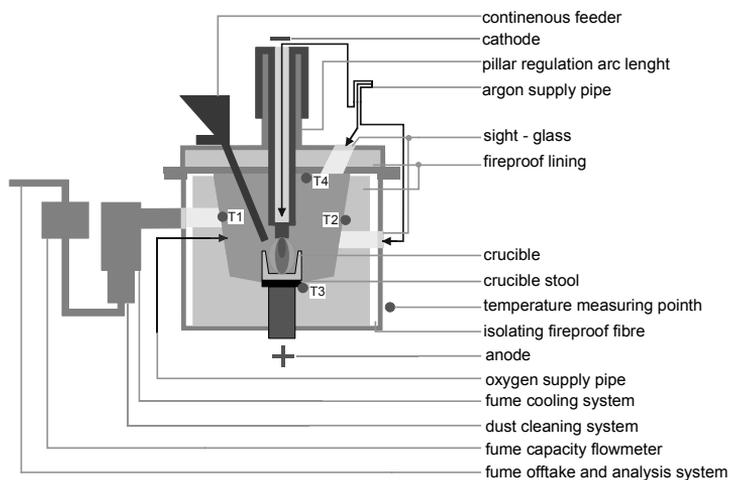


Fig. 2. Plasma arc furnace [1]

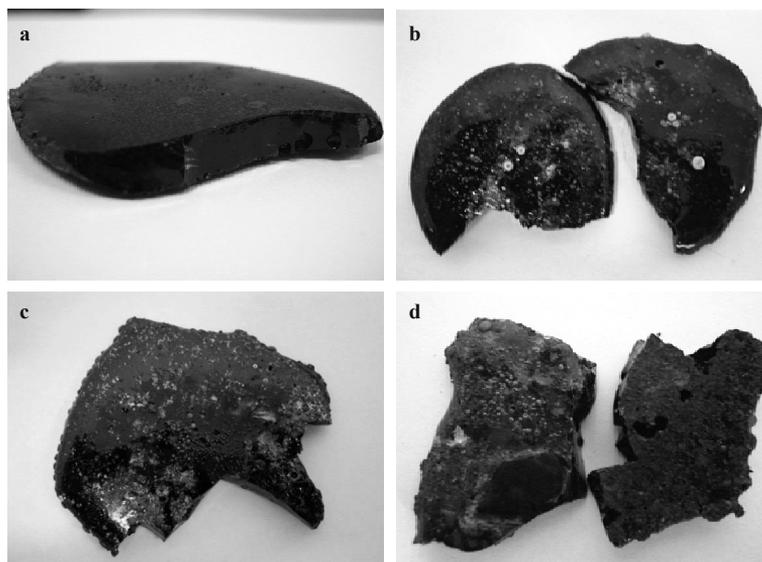


Fig. 3. Products of waste plasma vitrification: a – vitrificate from sewage sludge ash, b – vitrificate from municipal waste slag, c – vitrificate from medical waste slag, zd – vitrificate from hazardous and industrial waste slag

Treatment of wastes with the carbonate fraction also allowed for obtaining dense, vitrified masses. Products obtained from sewage sludge incineration ash and carbonate fraction had a dull surface, glassy fracture and uniform built (Fig. 4a). Processing of other substrate mixtures with the carbonate fraction allowed for obtaining a more uniform, homogenous and glassy products. The greatest effect of carbonate fraction addition was

noted for slag from hazardous and industrial wastes. The obtained vitrificate with the addition of carbonate fraction was more glassy and had a homogenous built (Fig. 4d).

In the obtained vitrificates high concentrations of some heavy metals (Tab. 3) were noted. The highest concentrations were found for Cu, Ni, Cr.

For the acquired products leaching tests were performed in order to verify their resistance to heavy metal leaching (Tab. 4).

Heavy metal concentrations in the leachates do not exceed the limiting values for storage in *Inert waste landfills*. The results in Table 4 show that the heavy metal

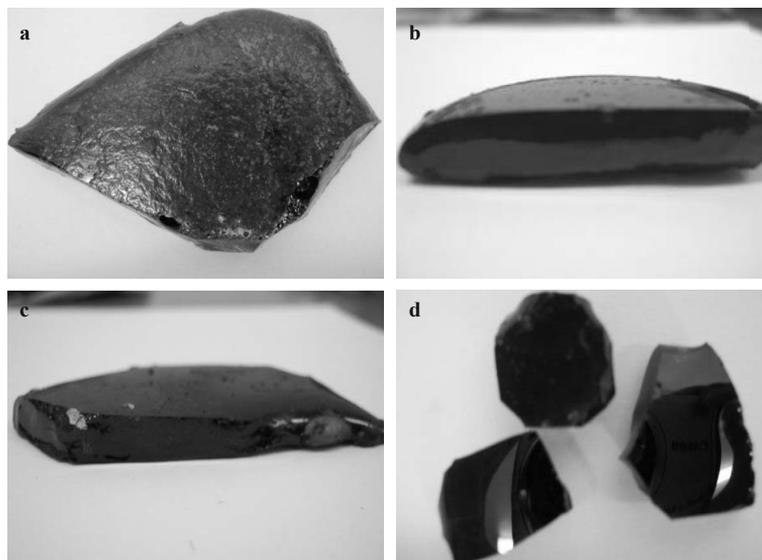


Fig. 4. The products of plasma treated wastes: **a** – ash from sewage sludge (40 g) + carbonate fraction (10 g), **b** – slag from municipal waste (40 g) + carbonate fraction (10 g), **c** – slag from medical waste (40 g) + carbonate fraction (10 g), **d** – slag from hazardous and industrial waste (40 g) + carbonate fraction (10 g)

Table 3. Heavy metal concentration in the acquired vitrificates

Concentration Unit	Metal	A	B	C	D	E	F	G	H
mg Zn/kg	Zinc	24.0	23.0	28.0	14.0	51.0	36.0	26.0	37.0
mg Cu/kg	Copper	290.0	5600.0	5600.0	300.0	210.0	3500.0	4700.0	130.0
mg Cd/kg	Cadmium	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
mg Ni/kg	Nickel	21.0	92.0	1000.0	38.0	23.0	160.0	1200.0	22.0
mg Pb/kg	Lead	1.3	<1.0	5.8	<1.0	<1.0	<1.0	<1.0	<1.0
mg Cr/kg	Chromium	14.0	50.0	920.0	450.0	51.0	190.0	620.0	120.0

Vitrificates: A – slag from municipal waste; B – slag from medical waste; C – slag from hazardous and industrial waste; D – ash from sewage sludge; E – slag from municipal waste + carbonate fraction; F – slag from medical waste + carbonate fraction; G – slag from hazardous and industrial waste + carbonate fraction; H – ash from sewage sludge + carbonate fraction

Table 4. Heavy metal concentration in leachates from vitrificates

Concentration Unit	Metal	A	E	B	F	C	G	D	H
mg Zn/l	Zinc	0.053	0.033	0.092	0.11	0.15	0.074	0.031	0.035
mg Cu/l	Copper	0.093	0.056	0.13	0.071	0.082	0.13	0.079	0.075
mg Cd/l	Cadmium	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
mg Ni/l	Nickel	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.006	0.006
mg Pb/l	Lead	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
mg Cr/l	Chromium	0.008	0.020	0.007	<0.005	0.007	0.047	0.016	0.016

Vitrificates: A – slag from municipal waste; B – slag from medical waste; C – slag from hazardous and industrial waste; D – ash from sewage sludge; E – slag from municipal waste + carbonate fraction; F – slag from medical waste + carbonate fraction; G – slag from hazardous and industrial waste + carbonate fraction; H – ash from sewage sludge + carbonate fraction

concentration in leachates from vitrificates obtained with the addition of carbonate fraction is lower than in the leachates from the raw substrates.

After vitrification a mass reduction of the processed substrates (Fig. 5) was noted. The highest reduction was present for ash from sewage sludge, and the lowest for the slag from municipal waste with the addition of carbonate fraction.

Vitrificate hardness ranged from 6 to 6,5 in Mohs scale. Hardness rating of 6.0 was noted for the vitrificate from medical waste pyrolysis slag, other vitrificates had a hardness rating of 6.5.

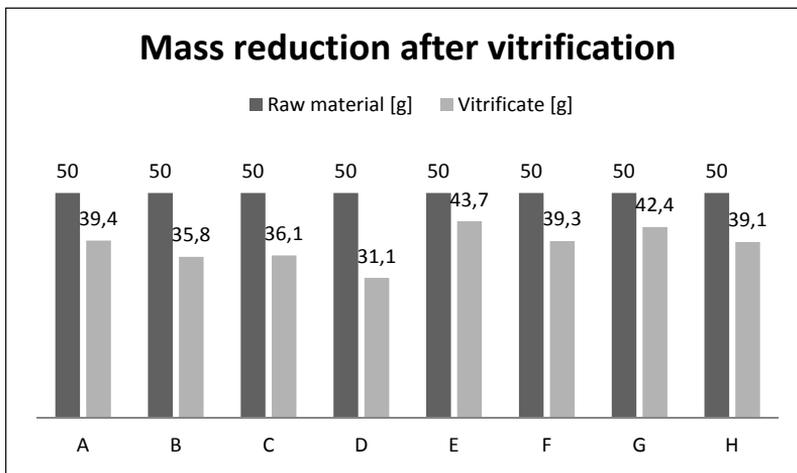


Fig. 5. Raw material mass reduction after vitrification

Vitrificates: A – slag from municipal waste; B – slag from medical waste; C – slag from hazardous and industrial waste; D – ash from sewage sludge; E – slag from municipal waste + carbonate fraction; F – slag from medical waste + carbonate fraction; G – slag from hazardous and industrial waste + carbonate fraction; H – ash from sewage sludge + carbonate fraction

CONCLUSIONS

Plasma treatment of the substrates resulted in obtaining homogenous masses of varying morphology depending on the kind of processed material. Processing of ash from sewage sludge incineration led to obtaining a homogenous, uniform mass with a glassy surface and fracture. Products obtained from the processing of slag from medical waste treatment and slag from municipal waste incineration had a rough-glassy surface and partly glassy fracture. The treatment of remnants after industrial and hazardous waste incineration resulted in obtaining heterogeneous porous masses with a rough surface. The addition of carbonate fraction clearly affected the quality of the obtained products, which were of uniform and glassy character (excluding the vitrificate from sewage ash, which had a dull surface). The most noticeable effect of the addition of carbonate fraction was noted for the vitrificate from hazardous and industrial waste incineration slag from which a glassy and uniform product was obtained.

Heavy metal analysis for the acquired vitrificates showed high concentration of Cu, Ni and Cr. These metals have high boiling temperatures exceeding 2500°C and could not be transformed into gaseous products (tab. 3).

Heavy metal analysis for the leachates from the obtained vitrification products show that the addition of carbonate fraction might have influenced the leaching of metals from the vitrificates due to the high concentration of Ca and immobilizing the metals in a glass matrix (Tab. 4). Metal concentrations in the leachates from the vitrificates do not exceed the limiting values for admitting wastes to storage in the landfills of inert wastes.

The acquired products' hardness ranged from 6 to 6.5 in Mohs scale and was in the hardness range of glasses.

The results and their analysis allowed for the following conclusions to be drawn:

- vitrification is a process which allows for treatment of slags and ashes from thermal waste treatment and obtaining glasslike products;
- the addition of the carbonate fraction improves the vitrification effects and allows for obtaining products of better quality with limited metal leaching properties;
- the use of the carbonate fraction as an additive in the vitrification process allows for utilisation of the waste created during flotation of zinc-lead ores.

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UNIESZKODLIWIANIE ODPADÓW POSPALENIOWYCH Z ODPADOWĄ FRAKCJĄ WĘGLANOWĄ Z PRZEMYSŁU CYNKOWO-OŁOWIOWEGO

W artykule przedstawiono wyniki badań dotyczących plazmowej wityfikacji stałych pozostałości po termicznej utylizacji odpadów, którą realizowano bez i z dodatkiem odpadowej frakcji węglanowej wytworzonej podczas flotacji rud cynkowo-olowiowych. Substratami wykorzystanymi do badań były żużle i popioły pochodzące z unieszkodliwiania odpadów medycznych, ze spalania odpadów komunalnych, osadów ściekowych, odpadów niebezpiecznych i przemysłowych.

W efekcie plazmowego przekształcania uzyskano produkty o różnej jakości w zależności od rodzaju przekształcanego substratu. W większości otrzymano produkty zeszkliwione o jednolitej budowie. W wyniku zeszkliwiania pozostałości po spalaniu odpadów przemysłowych i niebezpiecznych uzyskano produkty o niejednolitej, chropowatej powierzchni. Dopiero 20% dodatek frakcji węglanowej pozwolił na uzyskanie produktu zwityfikowanego, charakteryzującego się szklistą powierzchnią oraz przełamem. Twardość uzyskanych produktów oznaczona w skali Mohsa była w zakresie 6–6,5. Analiza wymywalności metali z wityfikatów wykazała mniejsze stężenia metali ciężkich w wyciągach wodnych sporządzonych z wityfikatów z dodatkiem frakcji węglanowej w porównaniu do stężeń metali w wyciągach wodnych z wityfikatów uzyskanych z materiałów wyjściowych.