MIDDLE POMERANIAN SCIENTIFIC SOCIETY OF THE ENVIRONMENT PROTECTION
ŚRODKOWO-POMORSKIE TOWARZYSTWO NAUKOWE OCHRONY ŚRODOWISKA

Annual Set The Environment Protection
Rocznik Ochrona Środowiska

Volume/Tom 15. Year/Rok 2013 ISSN 1506-218X 181–191

Vitrification and Devitrification of Ash after Sewage Sludge Combustion

Katarzyna Wystalska, Jolanta Sobik-Szołtysek, January B. Bień
Czestochowa University of Technology

1. Introduction

The purpose of the vitrification processes is obtaining final products with the structure similar to the structure of glass. Transition into the state with amorphous structure depends on sufficient cooling rate [8] and the content of glass-forming substances. The specific properties of glass materials are: hardness (5–7 on the Mohs scale) and brittleness. Higher contents of the amorphous phase in the glass cause that the glass becomes less brittle and more meltable. The basic raw material for glass production is quartz sand ((SiO_2). The most popular additions include Na_2CO_3, $CaCO_3$ and fluxes such as B_2O_3 and PbO. In practice, a crystalline phase observed in a particular substance often coexists with the vitreous phase. In such substances, the domains of the crystalline phase are observed as mixed with the domains of the amorphous phase.

According to [2], in order to obtain crystalline phases from vitrified materials, an aggregate of atoms, ions or particles must be created at the initial phase of crystal forming, termed crystallization nucleus. In crystallization of alloys, the precondition for initiation of the process of nucleation is supercooling. A number of studies on treatment of solid residues after the thermal processes have been oriented at vitrification of post-combustion ash and subsequent obtaining the vitroceramic materials with improved mechanical properties [3–5, 10–12]. An essential factor in the processes of transformation of vitreous (vitrified) materials into vitroceramics is precise determination of the temperatures which stimulate nucleation and crystallization [12]. This is presented in Table 1.

Table 1. Temperatures and times for crystallization of ash after waste combustion
Tabela 1. Zestawienie temperatur i czasu krystalizacji popiołów ze spalania odpadów

Type of Waste	Crystallization Temperature (°C)	Crystallization Time (h)
Volatile ashes after combustion of solid municipal waste [10]	870	10
Volatile ashes from sludge combustion [12]	1100	2
Ashes after combustion of solid municipal waste [11]	870	10
Volatile ashes [3]	950	2
Ashes from combustion of dangerous waste [7]	800	1

2. Methodology

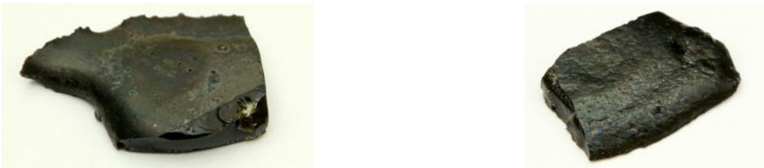
2.1. Materials Used in the Study

The authors used ashes from combustion of sewage sludge at the temperature of 850°C in a fluidized-bed furnace. This substrate exhibited fine, homogeneous grain and orange-red colour (Fig. 1). The material used as an addition during ash vitrification was the post-floatation waste obtained during flotation-based enrichment of zinc-lead ores that mainly contained dolomites (ca. 70%). According to [6], typical chemical composition of this type of waste is: 23–32% CaO, 12–17 % MgO, 1–2% Al_2O_3, 2–4.5% SiO_2, 0.5–5 % S, 2.5–8% $Fe_{całk.}$, 1–3% Zn, 0.1–0.9%.

Fig. 1. Ash obtained after fluidized-bed combustion of sewage sludge
Rys. 1. Popiół uzyskany po fluidalnym spalaniu osadów ściekowych

2.2.Vitrification and Devitrification

The ash from sewage sludge combustion was subjected to plasma modification, either alone or with 20% (wt%) addition of dolomite post-floatation waste, according to the methodology presented in previous studies [1,9]. Plasma modification of the substrates used in the study allowed authors to obtain the products as presented in Fig. 2.



a b

Fig. 2. Vitrificates obtained during plasma modification: (a) ash after sewage sludge combustion; (b) ash after combustion of sewage sludge with the 20% addition of dolomite post-floatation waste

Rys. 2. Witryfikaty uzyskane podczas modyfikacji plazmowej: (a) popiołu po spalaniu osadów ściekowych, (b) popiołu po spalaniu osadów ściekowych z 20% dodatkiem dolomitowych odpadów poflotacyjnych

The obtained vitrificates were subjected to thermal analysis in order to determine the respective crystallization temperatures. The authors used the differential scanning calorimetry method (DSC), which means measuring the differences in heat transfer, and the thermogravimetric method (TG) that measures changes in mass of the sample.

On the next stage of the study, the vitrificates, in order to be devitrified, were heated in a muffle furnace for 3 hours at the temperatures adopted based on the thermal analysis. After the set time, the products were left to be slowly cooled down.

The vitrificates and the products obtained during heating were subjected to X-ray analysis in order to examine their structure.

3. Results

The plasma modification of the substrates allowed for their transformation into the vitrified products with amorphous structure, which is confirmed by the diffractograms obtained for the ash after combustion of sewage sludge and its mixture with dolomite post-flotation waste (Fig. 3).

a

b

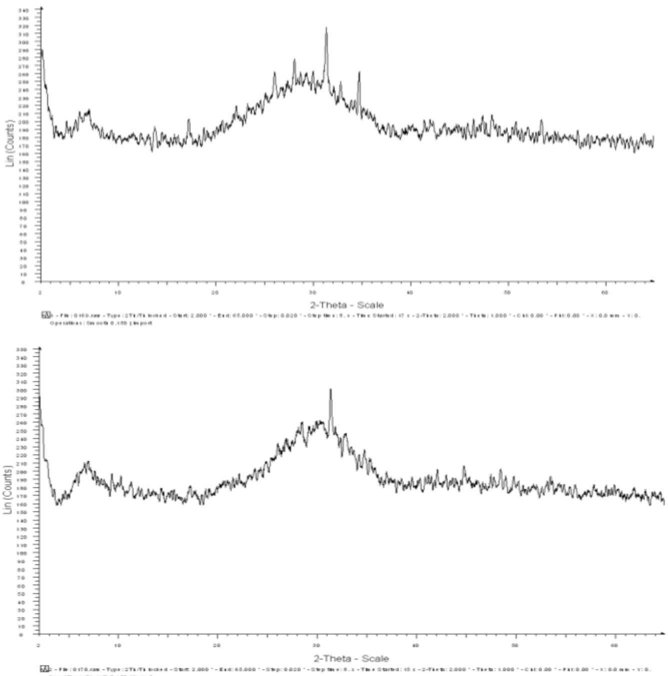


Fig. 3. The diffractograms of the vitrificates obtained from: (a) ash after sewage sludge combustion; (b) ash after combustion of sewage sludge with the addition of dolomite post-floatation waste
Rys. 3. Dyfraktogramy witryfikatów uzyskanych: (a) z popiołu ze spalania osadów ściekowych, (b) z popiołu ze spalania osadów z dodatkiem dolomitowych odpadów poflotacyjnych

Hardness of the vitrificates obtained on the Mohs scale was at the level of 6.5. The products obtained during vitrification of the ash after sludge combustion were more brittle than the products obtained during vitrification with the addition of dolomite post-floatation waste.

The thermal analysis (TG-DSC) of the obtained vitrificates allowed for determination of crystallization temperatures. For the vitrificate obtained from the ash after sewage sludge combustion, the initial point of the crystallization effect was set at 1096.7°C (Fig. 4a). For heating the vitrificate in order to carry out devitrification, the authors adopted the temperature of 1150°C. Furthermore, in the case of the vitrificate obtained from the ash with the addition of dolomite post-flotation waste, the exothermic effect is initiated at the 870.9°C and 985.5°C (Fig. 4b). For heating the vitrificates in order to carry out devitrification, the authors adopted the temperatures of 871°C and 986°C.

a

b

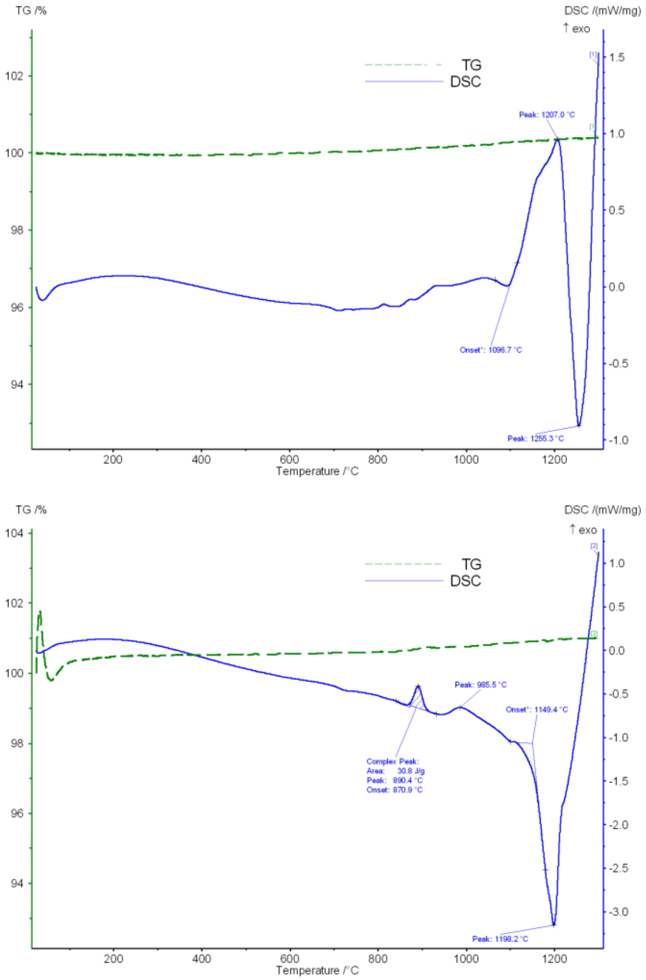


Fig. 4. Thermal analysis of the vitrificates obtained from: (a) ash after sewage sludge combustion; (b) ash after combustion of sewage sludge with addition of dolomite post-floatation waste

Rys. 4. Analiza termiczna witryfikatów uzyskanych: (a) z popiołu ze spalania osadów ściekowych, (b) z popiołu ze spalania osadów z dodatkiem dolomitowych odpadów poflotacyjnych

Heating of the vitrificates at the set temperature yielded the products presented in the Fig. 5. These products were subjected to X-ray analysis. The results of this analysis are presented in Fig. 6.

Fig. 5. Devitrification products for the vitrificates obtained from: (a) ash after sewage sludge combustion (crystallization temperature: 1150°C); (b) ash after combustion of sewage sludge with the addition of dolomite post-floatation waste (crystallization temperature: 871°C); (c) ash after combustion of sewage sludge with the addition of dolomite post-floatation waste (crystallization temperature: 986°C)

Rys. 5. Produkty odszklenia witryfikatów uzyskanych: (a) z popiołu ze spalania osadów ściekowych (temperatura krystalizacji 1150°C), (b) z popiołu ze spalania osadów z dodatkiem dolomitowych odpadów poflotacyjnych (temperatura krystalizacji 871°C), (c) z popiołu ze spalania osadów z dodatkiem dolomitowych odpadów poflotacyjnych (temperatura krystalizacji 986°C) a

b

c

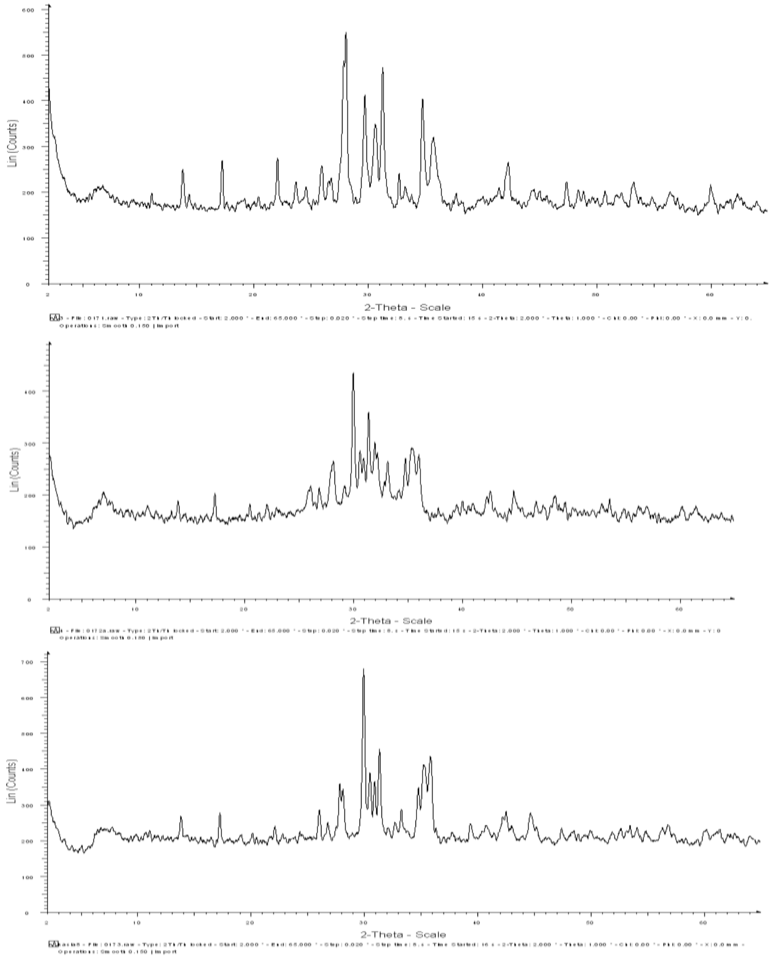


Fig. 6. Diffractograms of the devitrification products for the vitrificates obtained from: (a) ash after sewage sludge combustion (crystallization temperature: 1150°C); (b) ash after combustion of sewage sludge with addition of dolomite post-floatation waste (crystallization temperature: 871°C); (c) ash after combustion of sewage sludge with addition of dolomite post-floatation waste (crystallization temperature: 986°C)

Rys.6. Dyfraktogramy produktów odszklenia witryfikatów uzyskanych: (a) z popiołu ze spalania osadów ściekowych (temperatura krystalizacji 1150°C), (b) z popiołu ze spalania osadów z dodatkiem dolomitowych odpadów poflotacyjnych (temperatura krystalizacji 871°C), (c) z popiołu ze spalania osadów z dodatkiem dolomitowych odpadów poflotacyjnych (temperatura krystalizacji 986°C)

At this stage of the study, the authors did not carry out the identification of the crystallized phased and their quantitative proportion.

4. Discussion

Analysis of the results obtained in the study leads to the conclusion that the ashes after fluidized sewage sludge combustion are a good material for vitrification. Application of plasma as a specific source of heat allows for transformation of these materials into the products in the form of a homogeneous solid with vitreous fracture. The characteristic convexity noticeable in the diffractograms (Fig. 3) for the angle of reflection of 20–40° suggests the amorphous structure of the obtained products, which is typical of glass. The hardness of the vitrificates (6.5 on the Mohs scale) is also within the range of hardness typical of glass. The visual evaluation of the quality of the vitrificates did not reveal considerable differences in the quality of the vitrificates obtained from ash alone compared to the ashes obtained from the ash with the addition of dolomite post-flotation waste. Lower brittleness of the vitrificates obtained from the ash with the addition of dolomite post-flotation waste might suggest higher share of the amorphous phase and their improved meltability and the role of a stabilizer in the process of vitrification played by the waste used.

Thermal analysis (TG-DSC) of the obtained vitrificates revealed that the addition of dolomite waste caused a shift in the crystallization temperature from the level of 1096°C (vitrificate obtained from the ash after sludge combustion) to the level of 870°C (vitrificate from the ash after combustion of sludge with the addition of dolomite waste). In the case of the vitrificate obtained from the ash with the addition of dolomite post-flotation waste, apart from the exothermic effect at the temperature of 870.9°C, the second exothermic effect was also observed at the temperature of 985.5°C, which might suggest that different phases are crystallized at different temperatures.

This thesis was confirmed by the analysis of the diffractograms presented in Fig. 6b and 6c. The diagram presented in Fig. 6b a small convexity can be observed for the angle of reflection of 20–40°, which suggest presence of the amorphous phase. For comparison, the diagram obtained for the same sample (Fig. 6c) but heated at higher temperature reveals lack of the convexity for the angle of reflection of 20–40°. X-ray analysis (Fig. 6a) of the product obtained during heating of the vitrificate (at the temperature of 1150°C) obtained from the ash after sewage sludge combustion leads to the conclusion that it was devitrified, which confirms the presence of a number of clear peaks that point to the presence of phases with ordered structure. The products after devitrification are characterized by different colour, ranging from dark graphite (Fig. 5a) to orange-brown (Fig. 5bc). This might suggest crystallization of different phases which at the present stage of the research have not been identified yet.

5. Final Conclusions

The study confirmed that vitrification is a good method for treatment of ash after sewage sludge combustion, particularly in the context of the increasing popularity of thermal method in processing the sewage sludge in Poland. The use of dolomite post-flotation waste as an addition to the process of vitrification opens up opportunities for processing the waste obtained after flotation of zinc-lead ores. The use of dolomite post-flotation waste as an addition to the process of vitrification opens up opportunities for crystallization of target phases in the material after devitrification. The process of devitrification of the vitrificates obtained from the ash with the addition of dolomite post-flotation waste, carried out at different temperatures (871°C and 986°C) allows for crystallization of different phases with the ordered structure, characterized by presumably different properties. In order to ensure the comprehensive analysis of the process of devitrification, it is necessary to identify the crystallized phases and examine their properties.

This study was financed from BS/PB – 401-301/11

References

1. **Bień J., Białczak W., Wystalska K.:** *Solid waste vitrification using a direct current plasma arc.* Environmental Engineering – Pawłowski, Dudzińska & Pawłowski. Proceedings of The Second National Congress of Environmental Engineering, Lublin, Poland, 4–8 September 2005. Taylor & Francis Group, London, 307–310 (2005).
2. **Bolewski A., Kubisz J., Manecki A., Żabiński W.:** *Mineralogia ogólna (Fundamentals of Mineralogy).* Wydawnictwa Geologiczne, Warsaw, 1990.

3. **Cheng T.W., Chen Y.S.:** *Characterisation of glass ceramics made from incinerator fly ash*. Ceramics International, 30, 343–349 (2004).
4. **Cheng T.W., Ueng T.H., Chen Y.S., Chiu J.P.:** *Production of glass-ceramic from incinerator fly ash*. Ceramics International, 28, 779–783. (2002).
5. **Endo H., Nagayoshi Y., Suzuki K.:** *Production of glass ceramics from sewage sludge.* Wat. Sci. Tech., 36, 11, 235–241 (1997).
6. **Girczys J., Sobik-Szołtysek J.:** *Odpady przemysłu cynkowo-ołowiowego (Waste from Zinc-Lead Industry)*. Publisher: Częstochowa University of Technology Monographs No. 87 (2002).
7. **Kavouras P., Kaimakamis G., Ioannidis Th.A. et al.:** *Vitrification of lead-rich solid ashes from incineration of hazardous industrial wastes.* Waste Management, 23, 361–371 (2003).
8. **Wasylak J.:** *Specyfika stanu szklistego (Specific Nature of the Vitrous State)*. Szkło i Ceramika (Glass and Ceramics), 55, 5 (2004).
9. **Wystalska K.:** *Vitrification of Sludge and Ash from Thermal Waste Utilization*. Polish journal of environmental studies. Vol.2, pp. 248–253 (2010)
10. **Young J.P., Jong H.:** *Conversion to glass-ceramics from glasses made by MSW incinerator fly ash for recycling*. Ceramics International, 28, 689–694 (2002).
11. **Young J.P., Jong H.:** *Corrosion behavior of glass and glass-ceramics made of municipal solid waste incinerator fly ash*. Waste Management, 24 , 825–830 (2004).
12. **Young Jun Park, Soon Ok Moon, Jong Heo.** *Crystalline phase control of glass ceramics obtained from sewage sludge fly ash*. Ceramics International, 29, 223–227. 2003

Zeszkliwianie i dewitryfikacja popiołów po spalaniu osadów ściekowych

Streszczenie

W artykule zaprezentowano wstępne wyniki badań procesu zeszkliwiania i dewitryfikacji popiołów po spalaniu osadów ściekowych. Pierwszy etap, zeszkliwianie – realizowano z wykorzystaniem plazmy, przekształcając popioły po spalaniu osadów samodzielnie i z dodatkiem dolomitowych odpadów poflotacyjnych przemysłu cynku i ołowiu. Zarówno samodzielne przekształcanie popiołów pochodzących z procesu spalania osadów ściekowych jak i popiołów z dodatkiem dolomitowych odpadów poflotacyjnych skutkowało otrzymaniem produktu stanowiącego jednolitą, zwartą bryłę, szklistą w przełamie, o budowie

amorficznej. Twardość uzyskanych produktów oznaczona w skali Mohsa była na poziomie 6,5. Produkty uzyskane podczas witryfikacji popiołów po spalaniu osadów były bardziej kruche od produktów uzyskanych w prosie witryfikacji popiołów z dodatkiem dolomitowych odpadów poflotacyjnych. Analiza termiczna (TG-DSC) uzyskanych produktów pozwoliła stwierdzić, że dodatek dolomitowych odpadów poflotacyjnych spowodował przesunięcie temperatury krystalizacji z poziomu 1096°C (witryfikat z popiołu po spalaniu osadów) do poziomu 870°C (witryfikat z popiołu po spalaniu osadów z dodatkiem dolomitowych odpadów poflotacyjnych). Kolejnym etapem badań było wygrzewanie witryfikatów w wyznaczonych temperaturach w celu dewitryfikacji. Przeprowadzona analiza rentgenowska potwierdziła odszklenie produktów – obecność faz o budowie uporządkowanej.