

**UNIVERSITY OF BELGRADE
TECHNICAL FACULTY IN BOR
CHAMBER OF COMMERCE AND
INDUSTRY OF SERBIA**

PROCEEDINGS



**XIII International
MINERAL PROCESSING and
RECYCLING CONFERENCE**

Editors:

Grozdanka Bogdanović

Milan Trumić

Belgrade, Serbia, 8 – 10 May 2019



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**PRODUCTION OF GLASS - CERAMICS FROM COAL FLY ASH AND
LIMESTONE**

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ABSTRACT – The results of laboratory scale experiments of vitrification of fly ash collected from the coal fired power plant are presented. The final glassy material was obtained by melting a mixture of ash and limestone at T= 1450 °C and quenching the melt in air. To convert the waste into useful and environmentally acceptable material the crystallization of fly ash glass was performed by powder route processing. The properties of the resultant glass-ceramic indicate a potential various application such as building materials, ceramics tiles, etc.

Key words: vitrification, fly ash glass, glass-ceramic

INTRODUCTION

The increasing production of fly ashes from carbon combustion in thermal power plants has compounded environmental and economical problems worldwide. Many efforts have been made to improve the environmental quality of residues from coal combustion and to recycle or utilise at least part of it.

The recovery of waste matrices otherwise destined for disposal allows to save resources, reducing the need for natural raw materials. Considering that recycling has priority over disposal/deposition in landfill sites and the use of secondary raw materials reduces costs and conserves resources, it is a need in the processing of waste materials into utilisable secondary raw materials [1-3].

Coal combustion generate large amounts of ashes, which are disposed in open pits or landfills. Usually, fly ashes contain appreciable amounts of heavy metals (Pb, Hg, Cd, Cr, etc.) which can be accumulated in surrounding soil and water sources causing a huge environmental damage. Unfortunately, only small amount of fly ashes were recycled and reused and therefore, it is necessary to seek new options to solve this problem. Over the past few decades, coal fly ash has mainly been used in concrete

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[4], cement [5], paper making [6], steam-cured bricks [7], ceramics and other related industries. Because the chemical contents of coal fly ash are close to those of ceramic raw materials, research into using fly ash in applications similar to other ceramic products has attracted much attention. As one of promising solution the vitrification of fly ashes could be considered.

By this process the waste toxic components are bonded within the glass structure and the obtained durable material is environmentally stable for a long time. Also, the vitrification greatly reduces the volume of waste and by using appropriate technologies the waste can be converted to useful materials. As reported earlier the different fly ashes without or with addition of other waste inorganic materials, can be transformed in glasses by melting technique. It has been demonstrated that is possible to prepare a glass-ceramics with good chemical and mechanical durability by controlled crystallization of the parent waste fly ash glasses [8-10].

This paper reports the results of vitrification of waste fly ash collected from the open pit near the TPS „Nikola Tesla” - Republic of Serbia. Also, the possibility of obtaining the glass-ceramics by sintering and crystallization of powder parent vitrified fly ash was presented.

MATERIALS AND METHODS

The raw sample of fly ash was dried and then analyzed. To determine chemical composition of fly ash a wet chemical method and AAS (Perkin Elmer 703) were employed. The phase composition was defined by the XRD - Philips PW-1710 automated diffractometer with a Cu K α radiation tube operating at 40 kV and 32 mA.

The grain size was determined using Warman cyclosizer M4. Vitrification procedure was realized by melting of the mixture of fly ash and powdered raw limestone (60:40) at $T = 1450$ °C for 2 h in an electrical furnace Carbolite BLF 1700 using zirconate crucible. As confirmed by XRD the melt which was cooled in air on steel plate solidified as a homogenous black glass.

For DTA measurement the powder glass was prepared by crushing and grinding the bulk glass in agate mortar, and then sieving it up to grain size of < 0.038 mm. Netsch STA 409 EP DTA device was used, and sample (100mg) was heated at $v = 10$ °C min $^{-1}$ up to $T = 1000$ °C.

For the crystallization experiments the glass powders (< 0.074 mm) were pressed at $P = 50$ MPa in the form of pellets ($d = 5$ mm). The test samples were sintered in an electric furnace at the temperature of 1000 °C for 2 h. The phase composition of the resultant glass-ceramics was examined by XRD using Philips PW- 1710 automated diffractometer.

RESULTS AND DISCUSSION

The chemical composition of the fly ash sample is shown in Table 1.

Table 1. Chemical composition of the fly ash sample

Oxides	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	(Fe ₂ O ₃) _u	TiO ₂	P ₂ O ₅	S	L.o.i
Mass %	58.52	24.03	3.31	2.11	0.32	1.08	6.23	0.87	<0.02	0.33	3.16

The XRD and microscopic analyses revealed a complex phase composition of fly ash. The glassy phase (> 30 %) appears in the sample in a form of pearls of different colors with dimension up to 1mm. The large porous aggregates (> 40 %) belong to the burned clay (chamotte) with inclusions of coal and iron oxides. As can be seen from the XRD patterns (Figure 1), the crystalline phases determined in the sample are: quartz, feldspar, mullite, melilite, cristobalite and anhydrite.

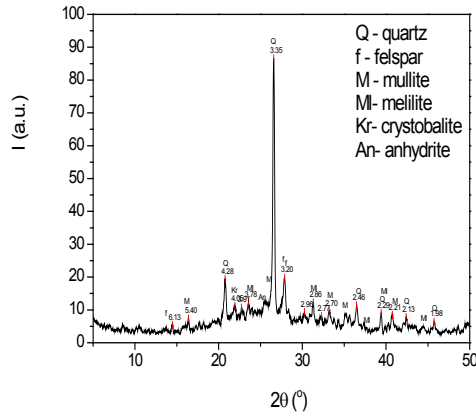


Figure 1. XRD patterns of the fly ash sample

The grain size of the fly ash is shown in Figure 2.

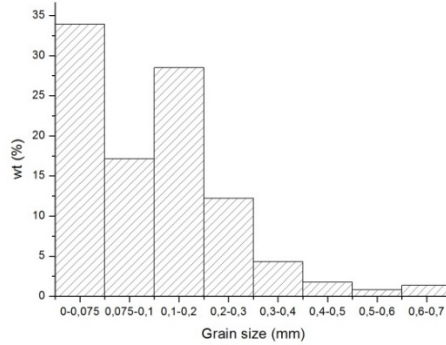


Figure 2. Grains size analysis of the fly ash sample

The melting experiments have shown that is not possible to obtain an appropriate melt of the raw fly ash at temperatures $T \leq 1500$ °C. At $T = 1500$ °C, the melt remains highly viscous and could not be cast. To vitrify the fly ash properly, the mixture of limestone and fly ash was melted at $T = 1450$ °C for 2 h. The parent homogenous black glass was obtained by melt casting on steel plate and it is shown in Figure 3. The chemical composition of the glass sample is shown in Table 2, and DTA curve in Figure 4.

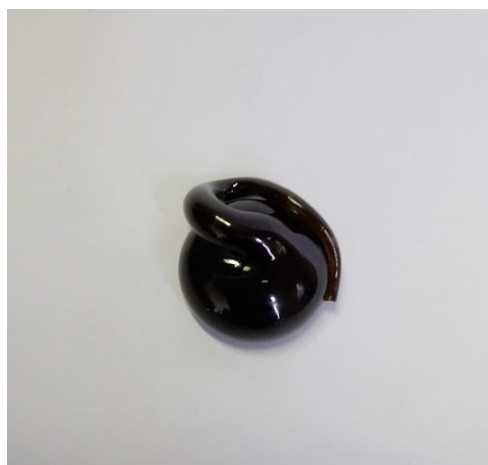


Figure 3. Parent glass sample

Table 2. Chemical composition of the parent glass sample

Oxides	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	(Fe ₂ O ₃) _u	TiO ₂	L.o.i
Mass %	46.83	18.97	26.33	1.49	0.29	0.67	4.18	0.68	0.58

The cations of heavy metal of fly ash were bonded into the parent glass network structure. From the DTA curve (Figure 4), the glass transformation temperature $T_g = 740$ °C and the peak crystallization temperature $T_p = 966$ °C were determined.

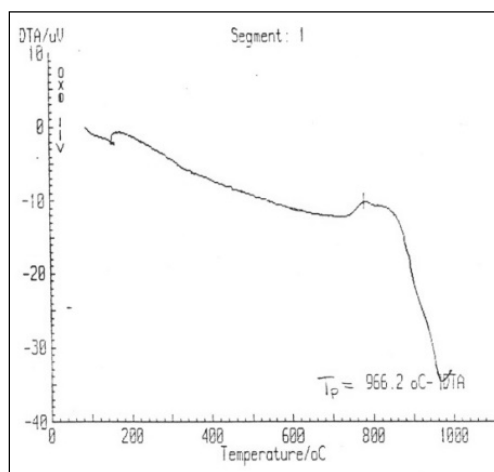


Figure 4. DTA curve of the parent glass sample

The results of sintering showed that the glass pellets shrink significantly during heating. The appearance of the untreated cold pressed sample and sintered at $T = 1000$ °C for 2h is present in Figure 5.

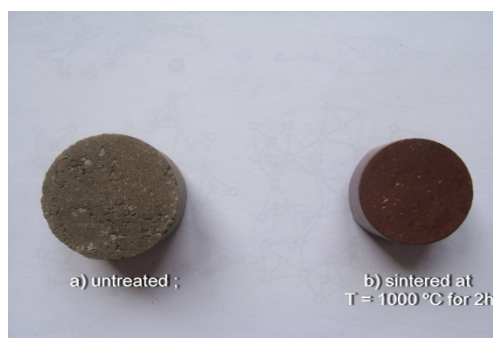


Figure 5. Appearance of glass pellets

By sintering process a dense dark-brown body with glassy appearance was obtained. The XRD analysis showed the crystallization of the sample. The extent of crystallization is small and only one crystalline phase (anorthite) was determined in the sintered sample (Figure 6).

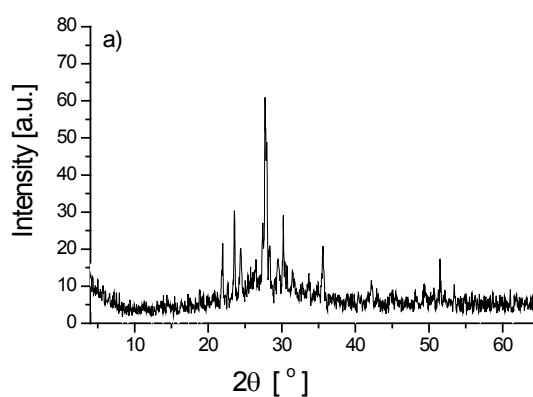


Figure 6. XRD patterns of the sample sintered at $T = 1000\text{ °C}$ for 2h

This result demonstrated that the sintering and crystallization processes take place simultaneously during heating of sample. These glass-ceramic material could be applied for production of building materials, ceramics tiles and waste disposal matrix.

CONCLUSION

The subject of this study was the vitrification of waste coal fly ash from thermo-power station. The results of laboratory experiments have shown that the vitrification process can be considered as promising solution for waste management. This process enables the conversion of toxic and environmentally dangerous waste material into a inert glass which can be used for production of useful glass-ceramics with potential wide application.

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References

1. Barbieri, L., Manfredini, T., Queralt, I., Rincon, J and Romero, M., Vitrification of fly ash from thermal power station., *Glass Technology*, 38 (1997) 165,
2. Barbieri, L., Lancellotti, T., Manfredini, T., Queralt, I., Rincon, J and Romero, M., Glasses and glass-ceramics from coal fly ashes., *Fuel* 78 (1999) 271,
3. L. Maccarini Schabbac, F. Andreola, E. Karamanova, I. Lancellotti, A. Karamanov, L. Barbieri, Integrated approach to establish the sinter-crystallization ability of glasses from secondary raw material, *Journal of Non-Crystalline Solids* 357 (2011) 10–17,
4. W. Wang, C. Lu, G. Yuan, Y. Zhang, Effects of pore water saturation on the mechanical properties of fly ash concrete, *Constr. Build. Mater.* 130 (2017) 54–63,
5. M. Rafieizonooz, J. Mirza, M.R. Salim, M.W. Hussin, E. Khankhaje, Investigation of coal bottom ash and fly ash in concrete as replacement for sand and cement, *Constr. Build. Mater.* 116 (2016) 15–24,
6. M. Zhang, Q. Li, S. Song, N. Hao, G. Liu, Increase of paper strength and bulk by co-flocculation of fines and fly ash-based calcium silicate, *Bioresources* 11 (2016) 7406–7415,
7. Qian, G., Song, Y., Zhang, Y., Xia, Y., Zhang, H., Chui, P., Diopside based glass-ceramics from MSWI fly ash and bottom ash, *Waste Management.*, 26 (2006) 1462,
8. Park, Ch., Yoon, S., Yun, Y., The characterization of glass-ceramics made from waste glass and fly ash, *J. Ceram. Process. Res.*, 8 (2007) 435,
9. Kim, J., Kim, H., Processing and properties of a glass-ceramic from coal fly ash from a thermal power plant through an economic process, *J. Eur. Ceram. Soc.*, 24 (2004) 2825,
10. Leroy, C., Ferro, M., Monteiro, R., Fernandes, M., Production of glass-ceramics from coal ash, *J. Eur. Ceram.Soc.*, 21 (2001) 195.