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Investigation of A Porous Structure Formation Mechanism of a Foamed Slag Glass Based On the Glycerol Foaming Mixture.

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ABSTRACT

The necessity of heat loss reduction by usage of high-quality thermal insulating materials has been examined. One of the most promising thermal insulating materials – a foam glass – has been described. Compositions of the foam glass based on a thermal power plant slag waste– the foamed slag glass – have been determined. A new type of foaming agent for the foam glass synthesis – glycerol foaming mixture – has been developed. The behavior of the foamed slag glass samples during heat treatment has been studied. Basic processes that occur during the synthesis of materials have been discovered using DTA–TGA. Structure and properties of the samples have been determined. Mechanism of the porous structure formation during the synthesis of foam glass materials based on a glycerol foaming mixture has been formulated. Relationship between material viscosity and structure formation has been investigated, threshold viscosity values corresponding to qualitative changes in the structure and properties of the samples have been discovered.

Keywords: slag waste, thermal insulation, foam glass, thermal expansion, porous structure.

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INTRODUCTION

Energy efficiency in buildings - current situation

One of the primary reasons for excessive consumption of natural energy resources is a great heat loss through the roof and walls of the building, due to the insufficient thermal insulation of the commodity construction materials. Reducing of heat loss through the building envelope in civil and industrial construction, as well as in the heat transfer systems requires using of high-quality thermal insulation materials (World Business Council for Sustainable Development, *n.d.*).

The most widespread thermal insulating materials nowadays are organic polymers (expanded polystyrene, polyurethane foam, and the products that are based on them), which have several advantages: low price, good insulation properties, low density. Yet, these materials have also some significant drawbacks – extreme flammability, emission of smoke and toxic compounds when burning, impossibility of recycling, low chemical resistance, and short life span, etc.

One of the most promising thermal insulating materials is a foam glass – cellular glass with a foam structure. The resulting product is essentially a pure glass. Consequently, it has all the benefits of glass: moisture- and vapor permeability, complete fire safety, dimensional stability at high temperatures, resistance to the action of rodents, pests and bacteria, ease of installation, environmental friendliness, and many others. The service life of a foam glass is virtually unlimited, and the physical properties do not change over time, as in conventional glassware. The main disadvantage of a foam glass is its high cost associated with the use of glass cullet as the main raw material.

Foam glass based on the slag waste

Works on replacing the glass cullet with other materials are carried out all over the world, with special attention paid to various industrial wastes. Research works in this field are dedicated to the use of metallurgical slag (Ding *et al.*, 2015; Ponsot & Bernardo, 2013; Suzuki *et al.*, 2014), waste glass (Fernandes *et al.*, 2014; König *et al.*, 2015; Fernandes *et al.*, 2009; Lee, 2013), coal combustion products (Chen *et al.*, 2010; Bai *et al.*, 2014; Kaz'mina *et al.*, 2009; Leroy *et al.*, 2001; Kaz'mina *et al.*, 2009) and even reservoir sediments (Liao & Huang, 2013). It should be noted that the variety of industrial wastes suitable for use as raw materials is very wide and widely differs in chemical and phase composition, as well as in a particle size. According to the investigations on the composition and structure of wastes used as raw material in the production of building materials, slag waste from coal combustion on thermal power plants (TPP slag waste) was recognized as the most suitable to replace glass cullet in the foam glass technology (United States Environmental Protection Agency, *n.d.*; The American Coal Ash Association, *n.d.*; Recycled Materials Resource Center, *n.d.*).

The selection of TPP slag as the raw material for the foam glass is explained by its stable chemical composition with prevalence of SiO_2 and glass-like structure, which is due to the principle of slag generation: refractory inorganic part of the coal during its combustion is flowing underneath the combustion chamber in the form of a melt, where it is quenched to obtain non-crystalline amorphous solid.

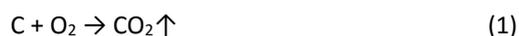
Moreover, the problem of TPP slag waste disposal is particularly relevant for countries and regions with developed mining and processing industry. For example, the Novochoerkassk State District Power Plant – thermal power plant producing more than 90 % of the Russian Southern Federal District' electricity – has a volume of accumulated waste of more than 40 million tons occupying the area of 250 hectares. This plant generates 800-1000 thousand tons annually. The volume of slag recycling does not exceed 10 % of its production.

In this regard, we have developed the technology of a foam glass production with a partial replacement of the initial glass with TPP slag waste – foamed slag glass (FSG) (Yatsenko *et al.*, 2014; Yatsenko *et al.*, 2015). A number of optimal compositions has been developed for manufacturing materials and products with insulation and bearing properties. The use of slag in this case was from 20 to 50 wt. %. Additionally, it has been found possible to change the main properties (density, strength, thermal conductivity) by varying a temperature-time synthesis mode.

However, due to the presence of refractory oxides (mainly, Al₂O₃) in the slag composition, using of conventional inorganic foaming agents (anthracite, chalk, etc.) led to significant increase in the synthesis temperature. This is due to the relatively high decomposition temperature of these foaming agents (700-900 °C), as well as the necessity of their additional ultrafine grinding to obtain uniform structure.

Foaming agents for foam glass production

According to Pittsburgh Corning (1992), traditional foaming agents in foam glass technologies are divided into two groups: carbon and carbonate. Carbon foaming agents include graphite, anthracite, soot, and other carbon-based materials. Pore formation occurs due to the oxidation (combustion) of carbon according to the reaction (1). Resulting gas foams the material.



Carbonate foaming agents are most commonly presented by limestone and chalk, as the cheapest of carbonates. Other carbonate materials such as marble or even dolomite could also be used as carbonate foaming agents. Pore formation occurs due to the gas generated by the thermal decomposition of carbonates according to the reaction (2).



The use of various foaming agents leads to a different structure of the resulting material. So, for example, carbonate foaming agents lead to channel-like pores which give additional sound insulating properties to the material. However, no data related to the joint use of different foaming agents were found.

It has been found that easily flammable organic compounds can be used as a foaming agent. Pore formation here occurs similarly to the reaction (1), because any organic compound burns with the formation of CO₂ and water vapor. One such type of foaming compounds for the foam glass production is “waterglass – glycerol” mixture (hereinafter – glycerol foaming mixture). This mixture allows obtaining a uniform porous structure immediately upon reaching the desired glass viscosity. This possibility is due to the low combustion temperature of glycerol (≈ 260 °C) and the liquid state of the mixture, so there is no need to grind the foaming agent for porosity improvement.

Although it has been discovered that the porous structure formation requires both components of foaming mixture, but the research of their interaction process had not been previously conducted. Thus, the aim of this research is to study the mechanism of porous structure formation of the foamed slag glass based on the glycerol foaming mixture.

METHODS

Production of foamed slag glass (FSG) samples was conducted by a standard powder method. Raw materials (glass cullet, TPP slag waste, flux) were pre-dried at 120 °C. The resulting dry powders were milled to 420 microns fraction (mesh No. 40) (Aldrich Chemicals - Technical Library, *n.d.*). Chemical composition of the glass powder and slag waste was found using energy dispersive X-ray fluorescence spectrometer ARLQUANT'X and is presented in Table 1.

Table 1. Chemical composition of raw materials

Material	Chemical composition*, wt. %						
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
Slag	57.5	23.0	10.8	1.9	1.2	3.6	0.9
Glass	71.2	2.70	0.8	3.4	7.6	0.8	13.2

* Oxides, content of which is less than 0.2%, are not shown.

Glycerol foaming mixture was prepared in a separate vessel by mixing the components in the following ratio, wt. %: waterglass – 4, glycerol – 4, water – 2. Then, prepared raw materials were composed and mixed according to the established batch compositions, wt. %:

- FSG-2: glass – 70, slag – 20, glycerol mixture – 10;
- FSG-5: glass – 40, slag – 50, glycerol mixture – 10, flux – 10 over 100.

Then samples from composed batches were molded into cubes with edge length of 20 mm and mass of 10 g (volume $8 \cdot 10^{-6} \text{ m}^3$, density 1250 kg/m^3). Then samples were loaded into a furnace for heat treatment according to Figure 1.

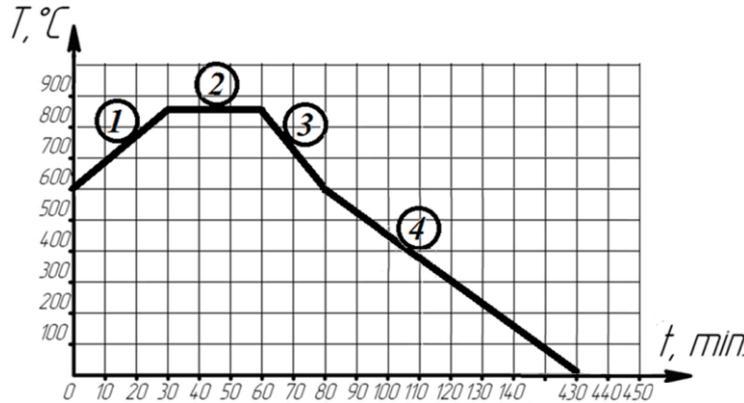


Figure 1 – FSG synthesis mode:

- 1 - heating, 2 – foaming, 3 – rapid cooling with structure stabilization (quenching), 4 - slow cooling (annealing).

When the air inside the furnace cooled to room temperature, the samples were removed from the furnace and subjected to mechanical processing (filing) to give them the regular shape. Further, weight of the samples of given shape was determined. Then calculations of the volume, density and foaming coefficient were performed based on the obtained data according to (3)-(5), respectively.

$$\text{Volume } V = a \cdot b \cdot c \quad (3)$$

$$\text{Density } d = m / V \quad (4)$$

$$\text{Foaming Coefficient } FC_T = V_{R^T} / V_I \quad (5)$$

where a – sample length, cm; b – sample width, cm; c – sample height, cm; V – sample volume, cm^3 ; m – sample mass, g; V_{R^T} – resulting sample volume after heat treatment at foaming temperature T, cm^3 ; V_I – initial sample volume before heat treatment, cm^3 .

Each recorded testing value was the mean of the results from five samples.

Differential thermal and gravimetric analyses (DTA–TGA) were carried out on Q-1500D equipment of MOM Company (Hungary). Measurements were done under synthetic air, using platinum crucibles and sample’s mass of 300 mg.

The viscosity was determined by calculations according to the method of M.V. Okhotin (Okhotin *et al.*, 1967; Flom & Kofman, 1985), which established that the temperature T, corresponding to a specific viscosity η , can be determined by the formula (6):

$$T_{\eta} = X \cdot x + Y \cdot y + Z \cdot z + K \quad (6)$$

where X, Y, Z, K – calculated coefficients; x – mass fraction of Na_2O in the glass, %; y – mass fraction of $\text{CaO} + \text{MgO}$ in the glass, %; z – mass fraction of Al_2O_3 in the glass, %.

RESULTS

FSG samples were subjected to heat treatment according to Figure 1 at various foaming (Stage 2) temperatures. Photographs of obtained samples depending on the temperature and viscosity are shown in Figure 2, changes of density and foaming coefficient – in Figure 3.

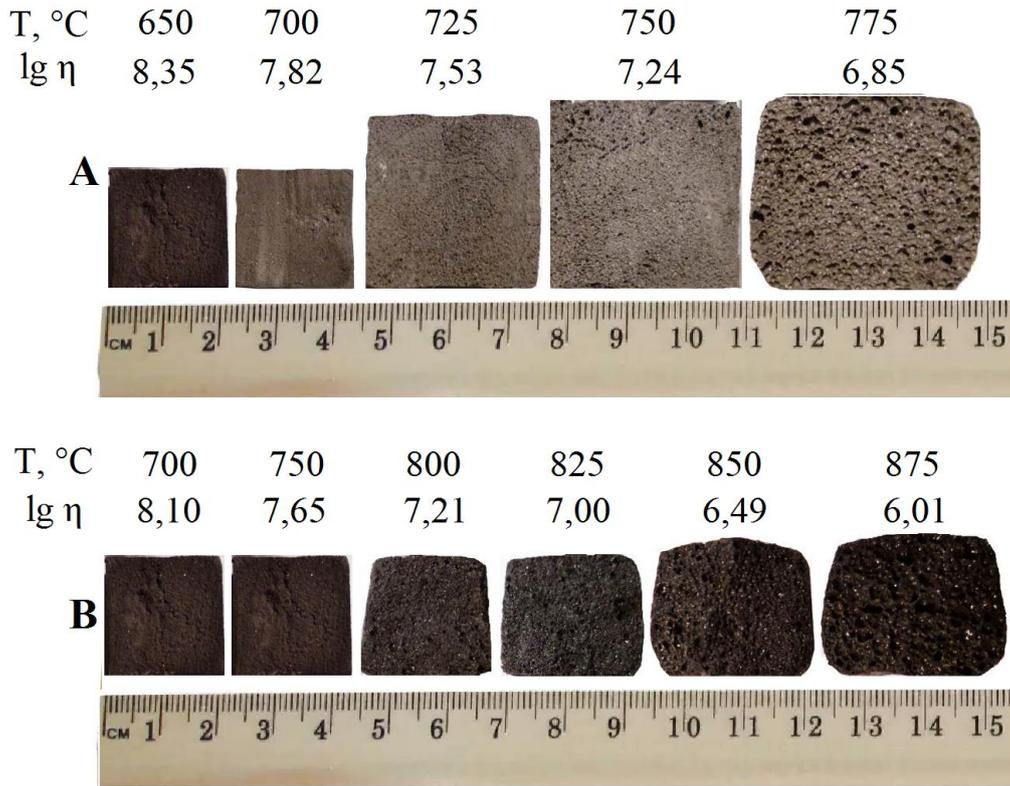


Figure 2 – Macrostructure observation of cross-section of (A) FSG-2 samples and (B) FSG-5 samples

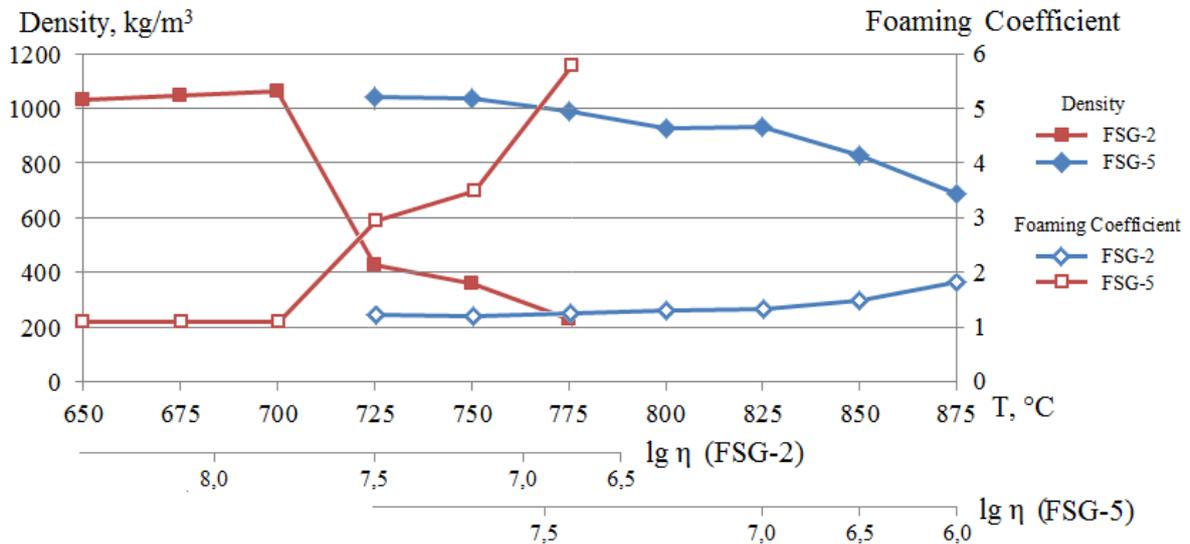


Figure 3 – Dependence of density and foaming coefficient change on the temperature and FSG viscosity

DTA-TGA analyses were carried out to explain the processes occurring during the heat treatment. Composition based on pure glass cullet (glass – 90 wt. %, glycerol mixture – 10 wt. %) was used as a model. Resulting curves are shown in Figure 4.

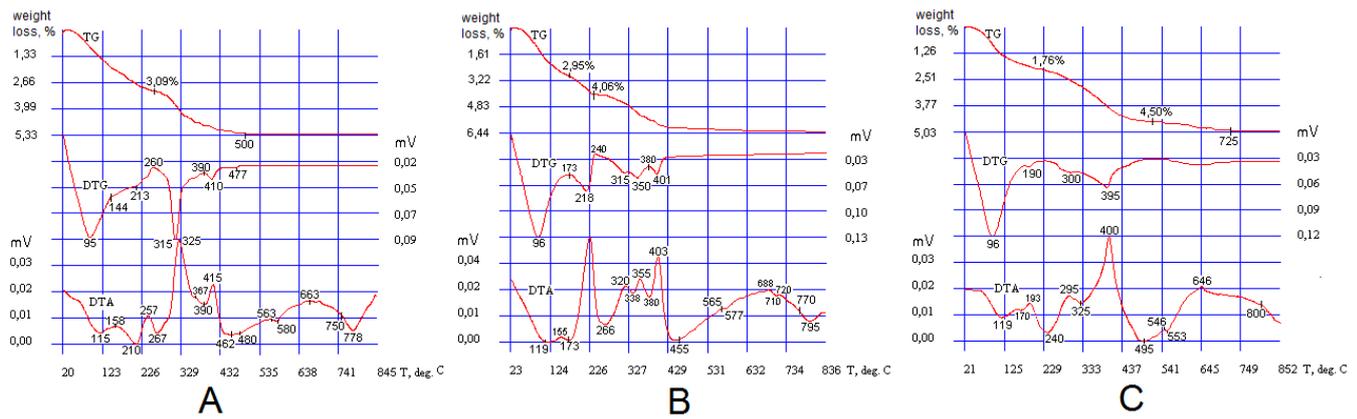


Figure 4 – DTA-TGA curves of foamed slag glass compositions: A – model, B – FSG-2, C – FSG-5

DISCUSSION

The foaming process of batches was identified (Figure 5) by examining and comparing the DTA-TGA curves, and by taking into account the synthesis mode, structure and properties of the synthesized materials.

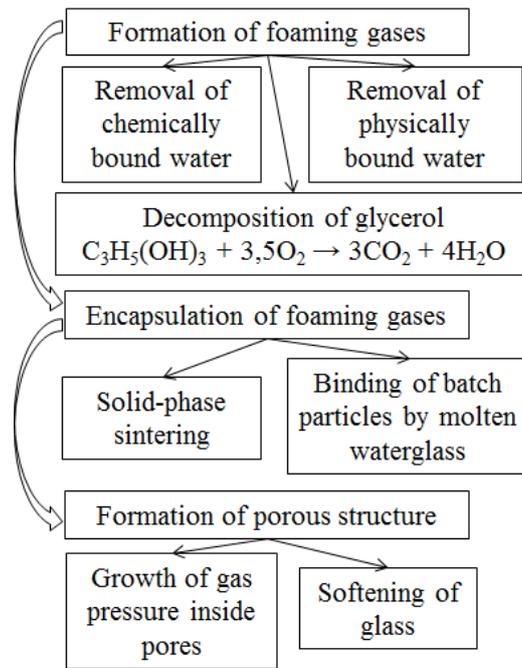


Figure 5 – Foaming mechanism of batches based on glycerol mixture

According to Figure 1, samples are loaded in a furnace preheated to 600 °C. As the result, all of the low-temperature processes (evaporation of physically and chemically bound water, glycerol decomposition) begin to occur simultaneously. The resulting gases are removed from surface layers of the sample, and then from the inner part by capillary actions. At the same time with the gas formation, solid-phase sintering begins.

The sintering process slows removal of gases from the sample by converting the outer and, afterwards, the inner layers into tightly sintered material. Thus, gases remained in the sample are encapsulated in the form of very fine (less than 100 microns) pores. Encapsulation process is particularly improved by waterglass, which after evaporation of chemical and physical water became a viscous melt, preventing gas removal from the sample by binding the batch particles and eliminating capillaries between them.

At 650 °C, samples of both compositions already became tightly sintered materials where all fusible and flammable compounds are removed from the surface layers. Further heating continues the sintering process that causes slight increase in density and decrease in volume due to the contraction of the particles.

Since the gas pressure in the pores is higher than atmospheric pressure and keep growing with temperature growth, the foaming of material is expected. It does not occur, though, until the glass viscosity falls to values suitable for the ductile state. Additionally, as can be seen on the Figure 2, the processes of foaming of the studied compositions differ.

In the FSG-2 samples (Figure 2A), after reaching viscosity of $10^{7.6}$ Pa·s (≈ 715 °C), the processes of liquid-phase sintering and pore formation begins in the softened glass mass with following sharp density decrease (≈ 2 times). Further heating to 750 °C leads to a linear change in the volume and density. Upon reaching viscosity of $10^{7.0}$ Pa·s (≈ 760 °C) the second abrupt change occurs, leading to the uniform porous structure formation. Further heating and a corresponding decrease in viscosity does not lead to qualitative changes in the structure, only the size and uniformity of the pore distribution are changing.

The key feature of the FSG-5 composition (Figure 2B) is the presence of large amounts of slag waste, which strongly influences the behavior of the samples. Therefore, when the viscosity reaches $10^{7.6}$ Pa·s (≈ 755 °C), sharp increase of sample's volume does not occur. Although pore cores are formed, density at 930 kg/m^3 is retained until the viscosity of $10^{7.0}$ Pa·s (825 °C) is reached. Further, similarly to FSG-2 composition, there is the linear increase in the sample volume and consequent reduction in the sample density.

It should be noted that the quantitative characteristics of the above changes (density, foaming coefficient, etc.) depend strongly on the material composition and deteriorate with increasing slag waste content. This problem was solved by the introduction of fluxes, which reduce the melting point of the batch and intensify the structure formation processes.

CONCLUSION

Possibility of TPP slag waste use as a raw material for the production of foam glass-based materials – foamed slag glass – has been established. Foaming mixture to obtain foamed slag glass at lower temperatures – glycerol foaming mixture – has been developed. This mixture allows obtaining products with uniform porous structure without additional grinding of foaming agent and at foaming temperatures lower than such for the traditional foaming agents (anthracite, chalk).

Mechanism of the porous structure formation of foam glass materials based on glycerol foaming mixture has been developed. Entering a sample into the temperature zone of 600 °C during rapid heating leads to reduction of intensity of removal of gaseous reaction products (water vapor, glycerol decomposition products) provided by their encapsulation in the pores smaller than 0.1 mm and formation of viscous waterglass melt eliminating capillaries between the pores.

Two qualitative changes in the structure and properties of the samples corresponding to the threshold values of viscosity $10^{7.6}$ Pa·s and $10^{7.0}$ Pa·s have been established. Upon reaching the viscosity of $10^{7.6}$ Pa·s, processes of liquid-phase sintering and pore formation begin in the softened glass mass resulting in sharp increase in volume and decrease in density. Then upon reaching viscosity of $10^{7.0}$ Pa·s second sharp change occurs, leading to the formation of uniform porous structure. Further heating and corresponding viscosity decrease does not lead to qualitative changes in the structure, changing only the pore size and distribution uniformity.

For a more complete description of the porous structure formation mechanism of the foam glass based on TPP slag waste and glycerol foaming mixture it is advisable to investigate the physical and chemical processes of the glycerol mixture components interaction between each other and with other batch materials. Besides it is necessary to determine the influence of each raw material particle size on batch melting and porous structure formation.

The proposed technology can be used to obtain modern thermal insulating foam glass materials with reduced cost through the use of TPP slag waste. It is possible to obtain various products based on these

materials (granules, blocks, rubble, etc.). Moreover, their structure and mechanical properties can be varied within wide limits.

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REFERENCES

- [1] Energy Efficiency in Buildings: Business Realities and Opportunities (Summary Report) (2016, June 08). In World Business Council for Sustainable Development Retrieved June 10, 2016 from <http://www.c2es.org/docUploads/EEBSummaryReportFINAL.pdf>.
- [2] Ding, L., Ning, W., Wang, Q., Shi, D. and Luo, L. (2015). Preparation and characterization of glass-ceramic foams from blast furnace slag and waste glass. *Materials Letters*, 141, 327–329. DOI:10.1016/j.matlet.2014.11.122.
- [3] Ponsot, I & Bernardo, E. (2013). Self glazed glass ceramic foams from metallurgical slag and recycled glass. *Journal of Cleaner Production*, 59, 245–250. DOI:10.1016/j.jclepro.2013.06.029.
- [4] Suzuki, M., Tanaka, T. and Yamasaki, N. (2014). Use of hydrothermal reactions for slag/glass recycling to fabricate porous materials. *Current Opinion in Chemical Engineering*, 3, 7–12. DOI:10.1016/j.coche.2013.08.006.
- [5] Fernandes, H.R., Ferreira, D.D., Andreola, F., Lancellotti, I., Barbieri, L. and Ferreira, J.M.F. (2014). Environmental friendly management of CRT glass by foaming with waste egg shells, calcite or dolomite. *Ceramics International*, 40 (8), 13371–13379. DOI:10.1016/j.ceramint.2014.05.053.
- [6] König, J., Petersen, R.R. and Yue Y. (2015). Fabrication of highly insulating foam glass made from CRT panel glass. *Ceramics International*, 41(8), 9793–9800. DOI:10.1016/j.ceramint.2015.04.051.
- [7] Fernandes, H.R., Tulyaganov, D.U. and Ferreira, J.M.F. (2009). Preparation and characterization of foams from sheet glass and fly ash using carbonates as foaming agents. *Ceramics International*, 35 (1), 229–235. DOI:10.1016/j.ceramint.2007.10.019.
- [8] Lee, C.-T. (2013). Production of alumino-borosilicate foamed glass body from waste LCD glass. *Journal of Industrial and Engineering Chemistry*, 19 (6), 25, 1916–1925. DOI:10.1016/j.jiec.2013.02.038.
- [9] Chen, H.J., Wang, S.Y. and Tang, C.W. (2010) Reuse of incineration fly ashes and reaction ashes for manufacturing lightweight aggregate. *Construction Building Materials*, 24, 46–55. DOI:10.1016/j.conbuildmat.2009.08.008.
- [10] Bai, J., Yang, X., Xu, S., Jing, W. and Yang, J. (2014). Preparation of foam glass from waste glass and fly ash. *Materials Letters*, 136, 52–54. DOI:10.1016/j.matlet.2014.07.028.
- [11] Kaz'mina, O.V., Vereshchagin, V.I., Abiyaka, A.N., Mukhortova, A.V. and Popletneva, Yu.V. (2009). Temperature regimes for obtaining granular material for foamed crystal glass materials as a function of the batch composition. *Glass and Ceramics*, 66 (5-6), 179-182. DOI:10.1007/s10717-009-9160-4.
- [12] Leroy, C., Ferro, M.C., Monteiro, R.C.C. and Fernandes, M.H.V. (2001). Production of glass-ceramics from coal ashes. *Journal of the European Ceramic Society*, 21 (2), P. 195-202. DOI: 10.1016/S0955-2219(00)00193-X.
- [13] Kaz'mina, O.V., Vereshchagin, V.I. and Abiyaka, A.N. (2009) Assessment of the compositions and components for obtaining foam-glass-crystalline materials from aluminosilicate initial materials. *Glass and Ceramics*, 66, 3–4. DOI:10.1007/s10717-009-9133-7.
- [14] Liao, Y.-C. & Huang, C.-Y. (2013). Glass foam from the mixture of reservoir sediment and Na₂CO₃. *Ceramics International*, 38 (5), 4415–4420. DOI:10.1016/j.ceramint.2012.01.080.
- [15] Coal Ash Basics (2016, June 08). In US EPA - United States Environmental Protection Agency. Retrieved June 10, 2016 from <http://www2.epa.gov/coalash/coal-ash-basics>.
- [16] Coal Combustion Products Production & Use Statistics (2016, June 08). In ACAA - The American Coal Ash Association. Retrieved June 10, 2016 from <http://www.acaa-usa.org/Publications/Production-Use-Reports/>
- [17] Coal Bottom Ash/Boiler Slag - Material Description (2016, June 08). In RMRC - Recycled Materials Resource Center. Retrieved June 10, 2016 from <http://rmrc.wisc.edu/ug-mat-coal-bottom-ash-boiler-slag/>

- [18] Yatsenko, E.A., Zubekhin, A.P., Gol'tsman, B.M., Smolii, V.A. and Kosarev A.S. (2014). Investigation of the factors influencing the properties and structure of foamed slag glass. *Glass and Ceramics*, 71 (3-4), 111-114. DOI:10.1007/s10717-014-9630-1. DOI:10.1007/s10717-014-9630-1.
- [19] Yatsenko, E.A., Zubekhin, A.P., Smolii, V.A., Grushko, I.S., Kosarev, A.S. and Gol'tsman, B.M. (2015) Resource-Conserving Technology of Heat-Insulation-Decorative Glass-Composite Material Based on Ash-Slag Wastes. *Glass and Ceramics*, 72 (5), 216-219. DOI:10.1007/s10717-015-9759-6.
- [20] Pittsburgh Corning. (1992). *Foamglas Industrial Insulation Handbook*. Waterloo: Editions TECHNIP, 1992
- [21] Particle Size Conversion Table (2016, June 08). In Aldrich Chemicals - Technical Library. Retrieved June 10, 2016, from <http://www.sigmaaldrich.com/chemistry/stockroom-reagents/learning-center/technical-library/particle-size-conversion.html>.
- [22] Okhotin, M.V., Raevskaya, E.I. and Tuzikov, A.I. (1967) An experiment on the industrial determination of the viscosity of the glass melt in the feeder of a tank furnace. *Glass and Ceramics*, 24 (12), 682-684. DOI:10.1007/BF00673521.
- [23] Flom, Z.G. & Kofman, A.G. (1985) Calculation of glass viscosity in the temperature interval of formation. *Glass and Ceramics*, 42 (7), 302-304. DOI:10.1007/BF00694601.