USE OF NATURAL DOLOMITE AS A CHEAP FOAMING AGENT FOR PRODUCING GLASS FOAMS FROM GLASS WASTE IN THE MICROWAVE FIELD

LUCIAN PAUNESCU[*1], MARIUS FLORIN DRAGOESCU[1], SORIN MIRCEA AXINTE[1, 2]

[1]*Daily Sourcing & Research SRL, 95-97 Calea Grivitei, sector 1, Bucharest, 010705, Romania*

[2]*Department of Applied Chemistry and Materials Science, University "Politehnica" of Bucharest, 1-7 Gh. Polizu street, sector 1, Bucharest, 011061, Romania*

Abstract: The paper presents experimental results obtained in the process of making glass foam from glass waste using a cheap foaming agent (natural dolomite). The originality of the work is the application of the microwave energy, unlike the conventional techniques commonly used in the world. The main advantage highlighted by the experiments is the very low specific energy consumption (below 1.5 kWh/kg), due to the peculiarities of the microwave heating technique. The foamed product has physical, mechanical and morphological characteristics (density between 0.30-0.32 g/cm^3, thermal conductivity between 0.064-0.067 W/m·K, compressive strength in the range 2.2-2.6 MPa), which are similar to those of foams made by conventional methods and are suitable for its use as insulating material in construction.

Keywords: glass foam, microwave, natural dolomite, cheap foaming agent, energy

1. INTRODUCTION

Given the high rate of accumulation of glass waste in the world, especially in developed and developing countries, their recycling is an economic solution with ecological effects. In the last decades this activity has gained increasing interest. Apart from the main specialized consortia in the glass industry (Misapor Switzerland, Pittsburgh Corning, Geocell Schaumglas, etc.), which industrially produce different kinds of porous materials by foaming glass waste, which can be used as substitutes for building materials on the market, there is an intense concern from the researchers for the development of new manufacturing techniques, so far on an experimental scale. Due to their remarkable physical and mechanical characteristics (low density, low thermal conductivity, relatively high mechanical resistance, fire resistance, impermeability and resistance to other various external aggressions of rodents, insects, bacteria etc.) the glass foams have already proved their viability especially in the field of building construction, of pavements, road construction, foundations, but also as filters, absorbers, gas sensors, etc. [1-3].

The basic principle of the process of foaming glass waste (in the form of powder) is the use of foaming agents, which, embedded in the mass of the waste, release by decomposition, oxidation or other chemical reactions at high temperature a gas that remains blocked in the form of bubbles in the mass of the material. A correlation

[*] Corresponding author, email: lucianpaunescu16@gmail.com

between the temperature at which the reaction occurs and the reaching the softening temperature of the waste is required so that the gas does not leave the material. According to the literature [2], to obtain a maximum porosity and a minimum apparent density of the glass foam, the optimum range of the viscosity value of the softened material is between 10^5–10^3 Pa·s. By cooling, the gas bubbles form a homogeneous porous structure constituting the glass foam.

A variety of foaming agents, especially solids, are used: carbon powder, black carbon, calcium carbonate, sodium carbonate, calcium sulphate, silicon carbide, silicon nitride, titanium nitride, etc., adopted depending on the nature of the glass waste as well as for economic reasons [2].

Worldwide, both on an industrial scale and on an experimental scale, heating techniques for sintering and foaming glass waste are conventional (by burning fossil fuels or with electrical resistances). The Romanian company Daily Sourcing & Research Bucharest has performed in recent years numerous experiments for the production of glass foams using exclusively microwave energy [4, 5]. Given that the design data of a microwave energy-efficient industrial oven are currently being finalized, the profitability criteria of the process involve adopting a cheap foaming agent. According to the literature information, the market price of white natural dolomite sorts varies between 35-180 USD/ton [6], compared to the price of industrial calcium carbonate (between 10-50 USD/kg [7]) or that of silicon carbide powder (between 1-50 USD/kg [8]). The results of the tests for evaluating the effectiveness of the use of natural dolomite as a foaming agent are presented below.
In the world, the use of the natural dolomite as a foaming agent for glass waste is applied only to a small extent. More commonly, dolomite is used for foaming metal aluminum [9, 10]. The literature [11] refers to experimental results obtained in the process of foaming the transparent soda-lime glass waste using natural dolomite as a foaming agent. The powder mixture was fired in an electric oven with heating speeds between 5-10 ºC/min up to 600 ºC, and then, with 1.7-2.5 ºC/min up to the final experimental fired temperatures (800-900 ºC). The weight proportion of the dolomite was in the range 3-5 %. The thermographic and differential analysis of dolomite (TG-DTA) showed that the material has an initial mass loss of around 30 % at about 800 ºC due to the release of carbon dioxide. The dolomite decomposition begins at this temperature and reaches a maximum at 900 ºC. The hydroxyls loss from the antigorite structure ($H_{10}Mg_3O_9Si_2$) occurs between 500-700 ºC. In another bibliographic source [12] is presented a technique for the manufacture of glass foam from glass waste, fly ash (20 wt %) and a sludge based on dolomite and calcite ($CaCO_3$) as a foaming agent in the weight proportion of 1-2 %. The sintering and foaming temperature was 850 ºC. The foamed product had the apparent density between 0.36-0.41 g/cm^3 and the compressive strength in the range 2.4-2.8 MPa. Natural dolomite as a foaming agent is used as one of the variants that include egg shell waste or calcite in the process of foaming the panel and funnel glasses from cathode ray tube (CRT) [13]. The foaming temperature had relatively low values (650-750 ºC). The glass foam obtained had an apparent density of 0.29 g/cm^3 and the compressive strength 2.34 MPa, the weight proportion of the foaming agent being 3 %.

The originality of the paper consists in the use of an unconventional heating technique of the raw material by its irradiation in microwave field. This heating mode is faster and more economical compared to the conventional techniques used exclusively in the world. Although the advantages of the microwave using in heating processes are known, their industrial application is still extremely limited. Moreover, in the field of glass foaming this technique is not even used in tests on an experimental scale.

2. METHODS AND MATERIALS

2.1. Methods

The experiment was performed using a 0.8 kW-domestic microwave oven adapted for operating at high temperature (up to 1200 ºC). Because the oven is equipped with only one microwave generator placed on one of the sidewalls, the rotary device functionality was maintained, being adapted also to the high thermal stress. A bed from ceramic fiber mattresses protected this mechanism, without obstructing its rotation motion. The sample subjected to the heating process, composed from the homogeneous powder mixture of glass waste and natural dolomite, previously pressed into a metal mold at about 15 MPa, was placed on a 1 mm-stainless plate placed on the surface of the ceramic fiber bed, being raised with 18 mm with a metal support. A silicon carbide ceramic tube with the wall thickness of 10 mm was installed on the bed surface equidistantly protecting the sample. The role of the tube made of a high microwave susceptible material, is to absorb the electromagnetic radiation, being fast and intense heated and to transfer the heat by thermal radiation to the sample. The indirect heating system was adopted based on previously experimental results, which indicated that the direct microwave glass heating is not suitable, severely affecting the material macrostructure. The ceramic tube was covered with a 10 mm-silicon carbide lid. To avoid the heat loss outward, the tube and the lid were protected with more layers of ceramic fiber mattresses. The control of the sample temperature during the heating process was achieved with a Pyrovar type radiation pyrometer placed above the oven at about 350 mm in its central ax. The upper wall of the oven as well as the ceramic lid and the corresponding ceramic fiber layer have provided a hole Ø 30 mm each in order to be viewed the upper surface of the sample with the pyrometer. Figure 1 shows the composition of the experimental equipment for producing glass foam from glass waste and natural dolomite.

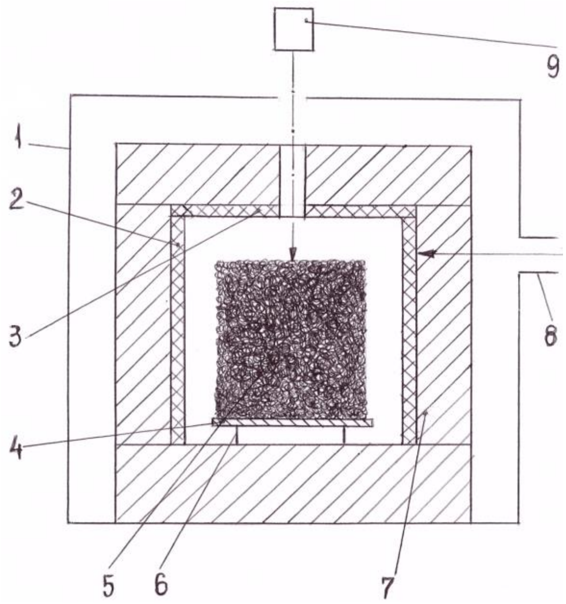


Fig. 1. Composition of the experimental microwave equipment: 1- microwave oven; 2 - ceramic tube; 3 - ceramic lid; 4 - stainless plate; 5 - sample; 6 - metal support; 7 - ceramic fiber protection; 8 - waveguide; 9 - pyrometer.

The heating method of the powder mixture tested in experimental conditions is close to the simulation of the conditions provided for the industrial installation. It will have the sidewalls and the vault covered with a 10 mm-silicon carbide layer and the material will be loaded in metal trays, which will be moved on a roller track inside the oven.

The basic principle of the foaming process is the thermal decomposition of the foaming agent (dolomite) in two stages, according to the TG-DTA analysis previously determined. The first stage begins at 440 ºC and the second begins at 740 ºC. The two stages occur according the following chemical reactions [14-16].

$$CaMg(\mathrm{CO_3})_2 = Ca\,\mathrm{CO_3} + MgO + \mathrm{CO_2} \quad (1)$$

$$Ca\,\mathrm{CO_3} = CaO + \mathrm{CO_2} \quad (2)$$

2.2. Materials

The raw material used in the manufacturing process of glass foam is a mixture of green, colorless and amber packaging glass waste, the weight proportion of the green glass being predominant (about 80%). The glass waste was broken, ground into a ball mill and sieved at a granulation below 130 μm. The natural dolomite was used as a foaming agent. The dolomite was ground at size smaller 130 μm. The chemical composition of the glass waste [17] and the foaming agent [11] is shown in Table 1. The glass waste and the foaming agent were mixed and homogenized into a small dimension’s laboratory device. Then, moistening the powder mixture with water in weight ratio of 16% was performed. The wet material was loaded into a metal mold and axially pressed at about 15 MPa and then, was removed from the mold, being introduced in the oven.

Table 1. Chemical composition of glass waste and natural dolomite.

Material	Chemical composition, wt %										
	SiO_2	CaO	MgO	Na_2O	K_2O	Al_2O_3	SO_3	Fe_2O_3	TiO_2	Cu_2O	LOI
Glass waste (80% green glass)	73.7	8.3	2.3	13.0	0.4	1.9	-	0.2	0.1	-	-
Natural dolomite	-	74.3	21.4	1.3	-	1.1	0.9	0.3	0.1	0.1	0.5

2.3. Characterization of the samples

The investigation of the main physical, mechanical and morphological characteristics of the foamed samples (apparent density, porosity, thermal conductivity, compressive strength, water absorption and hydrolytic stability) was carried out in laboratory in the companies Daily Sourcing & Research and Cosfel Actual as well as in the Department of Applied Chemistry and Materials Science of the University "Politehnica" of Bucharest, using common methods of analysis. Thus, the apparent density was determined with a pycnometer by the gravimetric method [18]. The porosity was calculated by the comparison method of the true and apparent density of the material, experimentally measured [19]. The compressive strength was determined with a uniaxial press for ceramics and the thermal conductivity was measured by the guarded-comparative-longitudinal heat flow technique (measurable in the temperature range 90-1300 K), according to ASTM E 1225-04. The hydrolytic stability of the samples was determined by the standard procedure ISO 719: 1985 [20, 21]. The water absorption of the sample was measured by the method of its immersion in water.

3. RESULTS AND DISCUSSION

3.1. Results

During the experiments four compositional variants, presented in Table 2, were tested, where the weight proportion of glass waste varied between 94-97% and that of natural dolomite between 3-6%, while the water addition was maintained constant at 16%. For guidance, the variation limits of dolomite/ glass waste ratio were adopted taking into account the experimental results presented in literature.

Table 2. Tested compositional variants.

Variant	Glass waste wt %	Natural dolomite wt %	Water addition wt %
1	97.0	3.0	16.0
2	96.0	4.0	16.0
3	95.0	5.0	16.0
4	94.0	6.0	16.0

As noted above, the tests were performed in an experimental oven operating with the microwave energy, unlike the conventional heating technique used worldwide. The functional parameters of the sintering/ foaming process of glass waste using natural dolomite as a foaming agent are shown in Table 3.

Table 3. Functional parameters of the process.

Variant	Raw material quantity, g		Process temperature ºC	Process duration min	Glass foam quantity g	Index of volume growth	Specific consumption of electricity kWh/kg
	dry	wet					
1	480	556.8	820	46	465	1.9	1.32
2	480	556.8	829	48	467	2.0	1.37
3	480	556.8	837	50	464	2.2	1.44
4	480	556.8	848	52	468	2.5	1.48

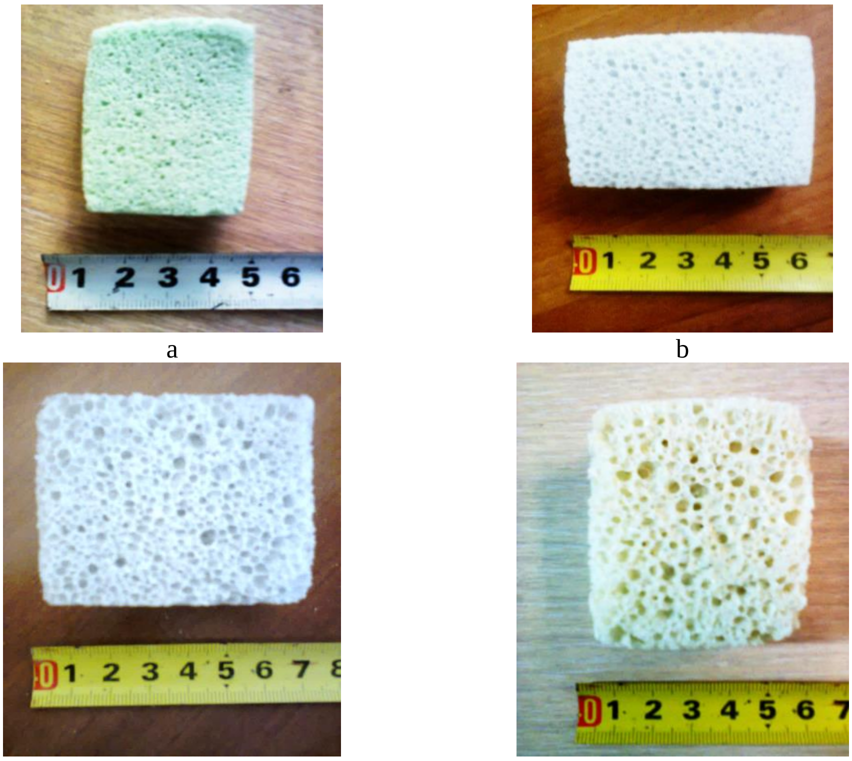
According to the data from Table 3, equal quantities of raw material including glass waste and natural dolomite (480 g as a dry material and 556.8 g as a wet material, respectively) were used in wall variants. These quantities were adopted taking into account the energy capacity (0.8 kW) of the microwave oven. The temperature of the sintering foaming process was between 820-848 ºC, reached in 46-52 min, with a specific consumption of energy below 1.5 kWh/kg. The index of volume growth of the powder glass waste was in the range 1.9-2.5, the highest value corresponding to the maximum ratio (6 wt %) of natural dolomite used as a foaming agent.

The physical, mechanical and morphological characteristics of glass foams produced in microwave field from glass waste and natural dolomite are presented in Table 4.

Table 4. Physical, mechanical and morphological characteristics of glass foam.

Var.	Apparent density g/ cm^3	Porosity %	Compression strength MPa	Thermal conductivity W/m·K	Water absorption %	Pore size mm
1	0.32	85.5	2.6	0.067	0.8	0.8-1.5
2	0.30	86.4	2.4	0.065	1.0	1.0-1.7
3	0.31	85.9	2.3	0.065	1.1	1.5-2.5
4	0.30	86.5	2.2	0.064	1.2	1.8-3.3

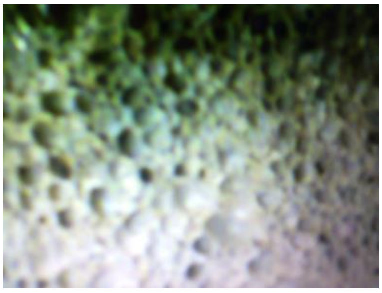
The glass foam obtained after the thermal treatment of the powder mixture has physical and mechanical characteristics appropriate for its usage as an insulating material for applications in construction: apparent density between 0.30-0.32 g/cm^3, porosity over 85.5%, thermal conductivity between 0.064-0.067 W/mK, water absorption below 1.2%. The compressive strength of the material, between 2.2-2.6 MPa is suitable for the field of applicability. The macrostructural analysis in the longitudinal section of the glass foam (Figure 2) showed a relatively homogeneous structure with closed pores whose size varied between 0.8-1.5 mm (sample 1, corresponding to the variant 1) and between 1.8-3.3 mm (sample 4, corresponding to the variant 4). From the point of view of the physical, mechanical and morphological characteristics, all the glass foam samples obtained by the unconventional technique of the use of microwaves are similar to those produced by the usual conventional techniques.



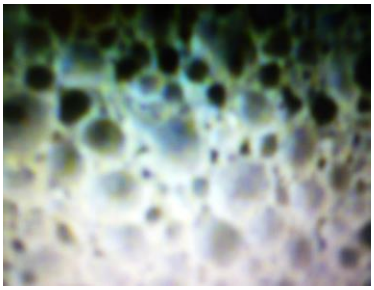
a b c d

Fig. 2. Images of the sample's macrostructure in longitudinal section: a – sample 1; b – sample 2; c – sample 3; d – sample 4.

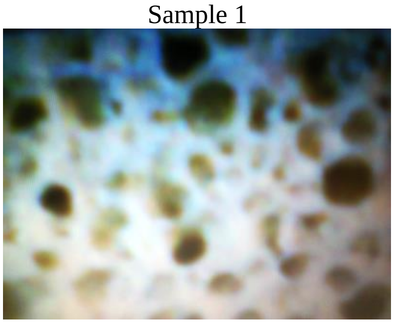
The images of the microstructural configuration of the samples viewed with a Smartphone Digital Microscope are shown in Figure 3.



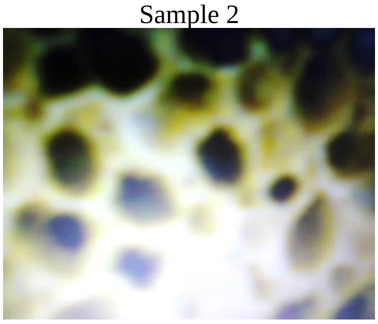
Sample 1



Sample 2



Sample 3



Sample 4

Fig. 3. Images of the microstructural configuration of the samples.

The test for determining the hydrolytic stability was performed according to the standard procedure ISO 719: 1985 with 0.15 mL of 0.01 M HCl solution. The test result showed that the stability of the glass foam samples corresponds to the hydrolytic class no. 2.

3.2. Discussion

Previous tests of direct microwave heating of the powder mixture based on glass waste carried out in the company Daily Sourcing & Research Bucharest have unequivocally demonstrated that this system is not suitable for obtaining a homogeneous porous structure of the foamed material [22]. The peculiarities of the heating in microwave field, completely different compared to the conventional heating techniques, consisting of the fast and intense initiation of the process in the core of the material, the thermal transfer being made from the inside to its peripheral areas, generate the complete destruction of the sample macrostructure in the central area. The heating speed reaches very high values (over 35 ºC/min) seriously affecting the foaming process of the glass waste. For this reason, the microwave heating methods for obtaining glass foams with physical, mechanical and morphological characteristics similar to those produced by conventional techniques were exclusively indirect methods.

The main advantage of using microwaves in the process of sintering/ foaming the glass waste is due to the way in which the heating is produced. Thus, only a microwave susceptible material is rapidly heated. In the case of indirect heating of a sample, this material is either a thin ceramic wall placed between the microwave generating source and the sample subjected to heating (as in the experiments described above), or a ceramic layer applied on a microwave transparent material. The heat transfer to the sample is carried out by radiation and convection, in conditions where the ceramic wall or layer is not in direct contact with the sample. A ceramic fiber thermal protection of the outer surface of the ceramic wall is necessary to avoid heat loss to the outside. This heating system is theoretically more economical compared to the conventional one, because it is no longer necessary the initial heating of the massive components of the oven, which then transfers the heat to the material subjected to the heating. Practically, it is achieved so-called "selective heating", which allows only the material subjected to this process to be heated. Thus, the energy is no longer wasted for global heating, specific to the conventional heating ovens [23].

The specific energy consumption of the sintering/ foaming process, achieved by the microwave irradiation of the powder mixture, has very low values (1.32-1.48 kWh/kg). The literature does not specify the level of energy

consumption of industrial processes, but theoretically, it is significantly higher due to the advantage of "the selective heating" of the microwave technique mentioned above. In addition, according to [24], the industrial application of the microwave technology has at least 25% higher energy efficiency compared to processes carried out in a small capacity oven, such as the 0.8 kW-oven used in the experiments described in this paper.
The comparison between the physical, mechanical and morphological characteristics of the samples obtained experimentally by the unconventional method and materials obtained by conventional techniques indicates their similarity. Thus, materials obtained from glass waste and fly ash by using a sludge based on dolomite and calcite (1-2%) as a foaming agent [12] had the apparent density between 0.36-0.41 g/cm^3 and the compressive strength between 2.4-2.8 MPa. Another porous material presented in the literature [13], made from CRT waste with natural dolomite and calcite (or eggshell waste) as a foaming agent (3%), had the apparent density of 0.29 g/cm^3 and the compressive strength of 2.34 MPa. By comparison, the samples made in the microwave field had the apparent density between 0.30-0.32 g/cm^3 and the compressive strength between 2.2-2.6 MPa. Their thermal insulation property was given by the homogeneity of the pore distribution in the section.

4. CONCLUSIONS

The experimental results obtained in the sintering and foaming process of glass foam using a cheap foaming agent (natural dolomite) are presented in the work.

The originality of the process is the microwave energy application, unlike the common use of the conventional techniques in the world.

The peculiarities of the microwave heating of raw material have as effect a very low specific energy consumption (below 1.5 kWh/kg) compared to the conventional heating techniques.

The physical, mechanical and morphological characteristics of the glass foams (apparent density 0.30-0.32 g/cm^3, thermal conductivity between 0.064-0.067 W/mK, compressive strength between 2.2-2.6 MPa) similar to the foams made by conventional methods, are suitable for using as an insulating material in construction.

REFERENCES

[1] Rawlings, R.D., Wu, J.P., Boccaccini, A.R., Glass-ceramic: Their production from waste-A review, Journal of Materials Science, vol. 41, no. 3, 2006, p. 733-761.
[2] Scarinci, G., Brusatin, G., Bernardo, E., Glass Foams in Cellular ceramics: structure, manufacturing, properties and applications, Scheffler, G., Colombo, P. (eds), Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany, 2005, p. 158-167.
[3] Hurley, J., Glass - Research and Development, Final report, A UK market survey for foam glass. Banbury, Oxon, Great Britain: The Waste and Resources Action Programme Publication, 2003.
[4] Paunescu, L., Grigoras, B.T., Dragoescu, M.F., Axinte. S.M., Fiti, A., Foam glass produced by microwave heating technique, Bulletin of Romanian Chemistry Engineering Society, vol. 4, no. 1, 2017, p. 98-108.
[5] Paunescu, L., Axinte, S.M., Grigoras, B.T., Dragoescu, M.F., Fiti, A., Testing the use of microwave energy to produce foam glass, European Journal of Engineering and Technology, vol. 5, no. 4, 2017, p. 8-17.
[6] http://www.alibaba.com/showroom/dolomite-prices.html (30.09.2019).
[7]http://www.alibaba.com/product-detail/Industrial-Calcium-carbonate-CAS-471-34_62163533054.html (01.10.2019).
[8] http://www.alibaba.com/showroom/price-of-silicon-carbide.html (03.10.2019).
[9] Papadopoulus, D.P., Omar, H., Stergiou, F., Tsipas, S.A., Michailidis, N., The use of dolomite as foaming agent and its effect on the microstructure of aluminium metal foams-Comparison to titanium hydride, Colloids and Surfaces A: Physochemical and Engineering Aspects, vol. 382, no. 1-3, 2011, p. 118-123.
[10] Mandrino, D., Paulin, I., Krzmanc, M.M., Skapin, S.D., Physical and chemical treatments influence on the thermal decomposition of a dolomite used as a foaming agent, Journal of Thermal Analysis and Calorimetry, September 2017.

[11] Pokorny, A., Vicenzi, J., Bergmann, C.P., Influence of heating rate on the microstructure of glass foams, Waste Management & Research, vol. 29, no. 2, 2011, p. 172-179.

[12] Fernandes, H.R., Tulyaganov, D.U., Ferreira, J., Preparation and characterization of foams sheet glass and fly ash using carbonates as foaming agents, Ceramic International, vol. 35, no. 1, January 2009, p. 229-235.

[13] Fernandes, H.R., Ferreira, D.D., Andreola, F., Lancellotti, I., Environmental friendly management of CRT glass by foaming with waste egg shalle, calcite or dolomite, Ceramic International, vol. 40, no. 8, September 2014, p. 13371-13379.

[14] Olszak-Humienik, M., Jablonski, M., Thermal behavior of natural dolomite, Journal of Thermal Analysis and Calorimetry, vol. 119, no. 3, 2015, p. 2239-2248.

[15] Koizumi, T., Kido, K., Kita, K., Mikado, K., Foaming agent for powder metallurgy production of aluminium foam, Materials Transactions, vol. 52, no. 4, April 2011, p. 728-733.

[16] Weast, R.C., CRC Handbook of Chemistry and Physics (59th edition), West Palm Beach, Florida, CRC Press, 1978-79, p. B-133.

[17] Dragoescu, M.F., Paunescu, L., Axinte, S.M., Fiti, A., Influence of the color of bottle glass waste on the characteristics of foam glass produced in microwave field, International Journal of science and engineering Investigations, vol. 7, no. 72, 2018, p. 95-100.

[18] http://www.deu.ie/sites/default/files/mechanical_engineering/pdf/manuals/DensityDeterminationmanualpdf (17.03.2017).

[19] Anovitz, L.M., Cole, D.R., Characterization and analysis of porosity and pore structures, Review in Mineralogy & Geochemistry, vol. 80, no. 1, 2015, p. 61-164.

[20] ISO 719: 1985 (reviewed and confirmed in 2011), Glass-Hydrolytic resistance of glass grain at 98 ºC-Method of test and classification.

[21] http://glassproperties.com/chemical_durability (15.04.2017).

[22] Paunescu, L., Grigoras, B.T., Dragoescu, M.F., Axinte, S.M., Fiti, A., Foam glass produced by microwave heating technique, Bulletin of Romanian Chemical Engineering Society, vol. 4, no. 1, 2017, p. 98-108.

[23] Jones, D.A., Lelyveld, T.P., Mavrofidis, S.D., Kingman, S.W., Miles, N.J., Microwave heating applications in environmental engineering – a review, Resources, Conservation and Recycling, vol. 34, 2002, p. 75-90.

[24] Kharissova, O., Kharissov, B.I., Ruiz Valdés, J.J., Review: The use of microwave irradiation in the processing of glasses and their composites, Industrial & Engineering Chemistry Research, vol. 49, no. 4, 2010, p. 1457-1466.