FLAT GLASS WASTE EXPANDED WITH SILICON CARBIDE AND FLY ASH IN MICROWAVE FIELD

Bogdan FLOREA[1], Lucian PAUNESCU[2], Adrian IOANA[3], Dragos Florin MARCU[4*], Daniela TUFEANU[5]

The paper presents experimental results obtained in the microwave field manufacturing of an economic and ecological glass-ceramic foam using as raw materials clear flat glass waste and coal fly ash and silicon carbide as a foaming agent. The experiments have shown that under the influence of microwave irradiation, foamed products have a good microstructural homogeneity, although it is known from the literature that the flat glass is not suitable for a foaming with uniform pore distribution. The optimal sample of glass-ceramic foam sintered at 977 ºC had thermal insulation properties (apparent density of 0.42 g/cm^3 and thermal conductivity of 0.085 W/m·K) and high compressive strength of 2.4 MPa, being suitable for using as a thermal insulation building material. The product has the required characteristics of a thermal insulation material used in the field of construction and industrial. This material is a replacement for those commonly used. The advantages of using this product are: the low cost of the raw material consisting of a waste and an industrial by-product, the favorable ecological consequences and the low energy consumption of the unconventional manufacturing process.

Keywords: glass-ceramic foam, clear flat glass waste, microwave heating, coal fly ash, silicon carbide

1. Introduction

Recycling the glass waste has become a common practice in the world for the last 40-50 years. Initially, recycled waste was used only as a raw material in the industrial process of manufacturing the new glass allowing significant energy savings. Later, the high cost of the selecting process of glass waste by color, determined the industrial manufacturers refocusing to use this waste for

[1] Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: florea_b2004@yahoo.com
2. Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, corresponding author e-mail: lucianpaunescu16@gmail.com
3. Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: adyioana@gmail.com
4*. Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: dragos.marcu@arasnet.ro
5. Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: dana_tufeanu2003@yahoo.com

producing different types of glass foam as replacements of existing building materials. Generally, the post-consumer packaging bottle is the most used type of glass waste (soda-lime glass) as a raw material for the glass foam manufacture, being practically free of dangerous contaminants. Also, large quantities of glass waste are available in the world and their growth trend is obvious, the annual generation rate being very high.

One type of glass waste that exists massively in the world, although less available compared to packaging bottles, is the flat glass, mainly including window glass cullet, but also other forms of glass [1]. The United Kingdom produces 750,000 tons of flat glass annually, of which three quarters go into glazing products [2]. The mass proportion of recycled flat glass in this country reaches 20-30%. According to [3], the flat glass waste is less interesting for the production of glass foam due to the difficulty of obtaining an adequate structural homogeneity. The literature presents various methods of improving the quality of glass foams made from flat glass waste by using oxygen suppliers (MnO_2) to intensify the foaming [3]. MnO_2 improves the foaming ability of Si_3N_4, the expansion of the glass occurring at relatively low temperatures (800-850 ºC) and the mechanical strength of the foam significantly increases up to 4.4 MPa. According to the literature [4-6], the industrial use of the flat glass waste is practiced to a lesser extent compared to the post-consumer packaging bottle. The Austrian company Geocell Schaumglas currently uses a raw material mixture consisting of 90 wt.% colored packaging bottle and 10 wt.% flat glass waste and the German company Glapor Werk Mitterteich uses the two-glass waste either separately or together, the agent of foaming being predominantly glycerol.

2. Methodology

The heating techniques used both in the industrial processes of glass foam manufacturing and in the experiments mentioned above were conventional. The Romanian company Daily Sourcing & Research, which in the last four years has focused its experimental activity on the use microwave heating technique, also including testing the foaming of flat glass waste. In the work [7] two test groups were performed using glass waste and successively ($CaCO_3$) between 1.2-1.4 wt.% and silicon carbide (SiC) between 3.5-3.6 wt.% together with coal fly ash between 8.5-10.5 wt.%. The sintering temperatures varied from 820-833 ºC (first group) to 980-995 ºC (second group). The foamed products had an apparent density between 0.32-0.39 g/cm^3 and 0.32-0.42 g/cm^3 respectively, a compressive strength between 1.2-1.3 MPa and 1.4-2.1 MPa and homogeneous microstructures with pore sizes between 0.6-2 mm and 0.9-3 mm, respectively. In another paper [1], the flat glass waste foaming was performed with SiC as a foaming agent (between 2.5-3.5 wt.%) and coal fly ash (between 9.5-10.5 wt.%). The sintering/foaming temperature had values between 978-992 ºC, the heating rate being between 13.1-13.6 ºC/min. The characteristics of glass-ceramic foams were: apparent density between 0.25-0.31 g/cm^3, compressive strength between 1.27-1.35 MPa, thermal conductivity between 0.038-0.041 W/m·K, pore size being in the range 0.5-2.5 mm. The microstructure of the samples was characterized by a very good homogeneity.

The current work aims to improve the characteristics of glass-ceramic foam samples made from clean glass waste with the addition of fly ash and SiC. The heating technique adopted by the authors was unconventional, using the 0.8 kW microwave oven in the Daily Sourcing & Research company described also in other previous works presented in the literature. The basic method of foaming a glass-based powder mixture is to incorporate a foaming agent (solid or liquid) which releases at a high temperature a gas (or gaseous compound) into the thermally softened material with a suitable viscosity so that the gas is trapped under the shape of bubbles. By cooling after stopping the heating, the bubbles turn into a network of pores that characterizes the structure of a glass foam [8].

The use of various silicate wastes (metallurgical slag, coal fly ash, mud from zinc hydrometallurgy, different sludge types, etc.) together with glass waste and a foaming agent favors the controlled crystallization (devitrification) of the glass forming glass-ceramic foams [8, 9]. Uniquely combining adequate physical, thermal and mechanical characteristics, glass-ceramic foams are attractive as alternative building materials to similar materials on the market.

The foaming agent adopted was SiC. By its oxidation reaction (1) in the oxidizing atmosphere of the oven, which has the most favorable conditions in thermodynamic terms at temperatures around 900 ºC [8], carbon dioxide (CO_2) which contributes directly to the foaming process of glass and silicon dioxide (SiO_2) that is incorporated into the molten mass of the glass are released.

$$SiC + 2O_2 = SiO_2 + CO_2 \qquad (1)$$

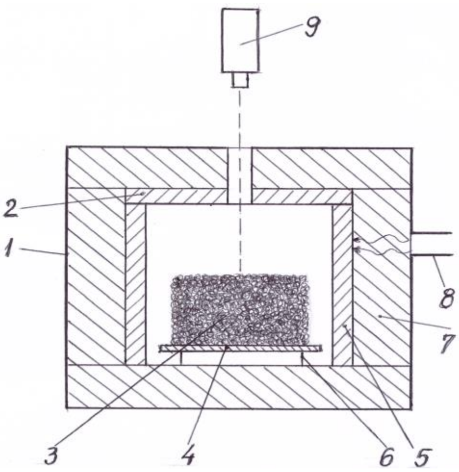
As noted above, the heating method adopted in experiments was the microwave irradiation. Although known for over 80 years, this technique recognized in the literature for its energy efficiency [10] has only been applied in low temperature drying or heating processes. The use of microwaves in industry is still in different experimental stages, although it has been found in the last decades that several types of materials (ceramics, organics, metals, glasses, polymers, etc.) are suitable for an efficient microwave heating [10]. Due to the very high SiO_2 content of the glass waste and to a lesser extent the coal fly ash that make up the raw material, the use of microwaves at low temperatures (up to 500 ºC) should not be adequate due to the microwave transparency of SiO_2 at these temperatures. However, this disadvantage is offset by the high presence of iron oxide (Fe_2O_3) in coal ash, which, although is a contaminant for the glass foam, has a good microwave susceptibility at room temperature [11], the efficiency of the microwave heating being very high since the beginning of the thermal process.

3. Equipment

The constructive solution of the experimental microwave equipment was influenced by the fact that the recycled commercial glass (soda-lime glass) is not suitable for a completely direct microwave heating, the microwave flux that irradiates the material subjected to heating tending to destroy its core structure at the foaming temperature [12]. According to the literature [11, 13], the direct microwave heating is initiated in the center of the irradiated material in the microwave oven. A feature of microwave heating is to avoid heating other components of the oven. It has been experimentally found that a screen made of a microwave material with SiC allows the intensity of the direct contact of the microwave flow with the material to be reduced to a level at which its foaming takes place properly, part of the emitted microwave field being absorbed by the thin wall of the screen (2.5-3.5 mm), converted into heat and transferred to the material by thermal radiation.

Fig. 1 presents the components of the experimental microwave equipment. The used oven was a 0.8 kW-microwave oven (1) adapted for operation at temperature up to 1200 ºC.

a



b

Fig. 1 The experimental microwave equipment
a – 0.8 kW-microwave oven; b – constructive scheme of the equipment: 1 – microwave oven; 2 – ceramic lid; 3 – pressed powder mixture; 4 – metal plate; 5 – ceramic tube; 6 – metal support; 7 – ceramic fiber thermal insulation; 8 – waveguide; 9 – pyrometer.

The oven was powered by only a microwave generator, whose waveguide (8) was placed in walls of the oven. The screen mentioned above was a ceramic tube made of a SiC and Si_3N_4 mixture with an outer diameter of 1250 mm, a height of 100 mm and a wall thickness of 2.5 mm (5). The wall thickness of the ceramic tube decreased from 3.5 mm [1, 7] to 2.5 mm contributed to the increase the heating ratio. The powder mixture (3) was deposited on a metal plate (4) which was on a ceramic fiber mattress (7). The pressed material was protected by coating with a ceramic cover (2). A very efficient thermal insulation from the ceramic fiber mattresses (7) was used around and above the ceramic tube and lid, avoiding the loss of heat outside. The radiation pyrometer (9) mounted above the oven on a vertical central axis allowed the temperature control of the irradiated material surface, visualized through holes provided on the central axis in the upper wall of the oven and the ceramic lid.

4. Materials

The solid components of the materials mixture used in the experiments were: clear flat glass cullet recycled from the demolition or rehabilitation of buildings, coal fly ash captured in electrofilters at the Paroseni (Romania) thermal power station and SiC, foaming agent. The glass waste was cleaned by washing, dried, broken, ground in a ball mill below 100 μm. The coal fly ash purchased from the Paroseni station at a grain size below 300 μm was ground in a ball mill and sieved at a grain size below 130 μm.

A typical chemical composition of the flat glass waste [2] and the chemical composition of coal fly ash are shown in Table 1.

Table 1

Chemical composition of flat glass cullet and coal fly ash

Component	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3
Clear flat glass cullet, wt.%	70.0-73.0	max. 1.5	8.0-9.7	3.5-4.5	13.4-14.6	-	max. 0.20
Coal fly ash, wt.%	46.5	23.7	7.9	3.2	6.0	4.1	8.6

The silicon carbide was purchased from the market with a very fine granulation below 40 μm and was used in experiments at this dimension.

4.1. Characterization of the samples

The glass-ceramic foam samples were subjected to the common methods for determination of the physical, thermal, mechanical and microstructural characteristics. The apparent density was measured by the gravimetric method [15, 16]. The porosity was calculated by the method of comparing the true and apparent density [17]. The thermal conductivity was measured by the heat-flow meter method (ASTM E1225-04) and the compressive strength was determined using a TA.XTplus Texture Analyzer (ASTM C552-17). The water absorption was determined for a time of 24 hours by the water immersion method (ASTM

D570). The microstructure configuration of the glass-ceramic foam samples was investigated with an ASONA 100X Zoom Smartphone Digital Microscope. The investigation of the crystallographic structure of the samples was performed with a X-ray diffractometer Bruker-AXS D8 Advance with CuKα radiation (EN 13925-2:2003 standard).

5. Results and discussions

According to the literature [14], a factor favouring the absorption of microwaves and implicitly, intensifying the foaming process is the presence in the raw material composition (flat glass waste and coal fly ash) of a rather high content of alkali metal oxides (Na_2O, K_2O). Thus, the coal fly ash content (8.5-13.5 wt.%) of the starting material was considered sufficient without the need of an oxygen supplier addition to intensify the foaming. The composition of the adopted experimental variants containing clear flat glass waste, coal fly ash as raw materials, silicon carbide as a foaming agent and water addition as a binder to facilitate the cold mixture pressing is shown in Table 2.

Table 2

Composition of the experimental variants

Variant	Clear flat glass waste (wt.%)	Coal fly ash (wt.%)	Silicon carbide (wt.%)	Water addition (wt.%)
1	82.5	13.5	4.0	10.0
2	85.4	11.0	3.6	10.0
3	86.5	10.0	3.5	10.5
4	87.0	9.7	3.3	10.5
5	87.7	9.2	3.1	11.0
6	88.5	8.5	3.0	10.5

The heat treatment of the powder mixture (in six experimental variants) was performed on the 0.8 kW-microwave oven described above. The main functional parameters of the process are shown in Table 3.

Table 3

The main functional parameters of the manufacturing process of glass-ceramic foam

Variant	Dry raw material/ glass foam amount (g)	Sintering/ foaming temperature (ºC)	Heating time (min)	Average rate, (ºC/min)		Index of volume growth	Specific energy consumption (kWh/kg)
				Heating	Cooling		
1	510/494	990	60	16.2	6.1	3.20	1.27
2	510/494	982	58	16.6	6.0	2.80	1.22
3	510/496	977	56	17.1	6.5	2.50	1.18
4	510/495	973	52	18.3	6.3	2.30	1.09

5	510/494	969	49	19.4	6.7	2.10	1.03
6	510/497	964	46	20.5	6.7	1.90	0.96

According to Table 3, the heating process for obtaining glass-ceramic foams had a temperature range between 964-990 ºC, the process duration varying between 46-60 min. The average heating rate increased from 16.2 ºC/min corresponding to the heat treatment up to 990 ºC (variant 1) to 20.5 ºC/min corresponding to the minimum value of the process temperature of 964 ºC (variant 6). The raw material expansion was maximum (3.20) in the case of variant 1 heated to 990 ºC, while in the case of variant 6 heated to 964 ºC the index of volume growth was much lower (1.90). Given that the level of maximum heating temperatures is high (almost 1000 ºC), the values of the specific energy consumption can be considered very economical (between 0.96-1.27 kWh/kg).

Images of the appearance of the six glass-ceramic foam samples are shown in Fig. 2.

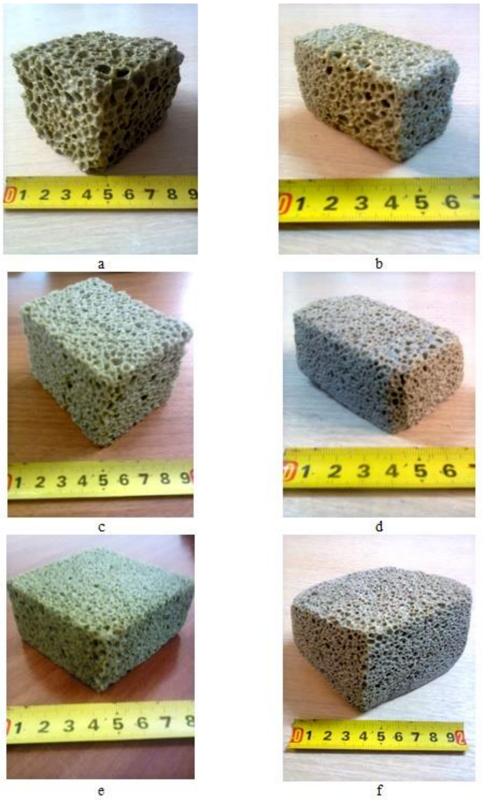


Fig. 2 Overall images of glass-ceramic foam samples
a – sample 1 heated at 990 ºC; b – sample 2 heated at 982 ºC;
a – sample 3 heated at 977 ºC; b – sample 4 heated at 973 ºC;
a – sample 5 heated at 969 ºC; b – sample 6 heated at 964 ºC.

Samples heated to the highest temperatures (a and b) have the appearance of materials with coarse porosity, but with closed pores. The pore size of samples heated to lower and lower temperatures tends to diminish, so that the appearance of samples e and f is satisfactory in terms of porosity. The main physical, thermal, mechanical, and microstructural characteristics of glass-ceramic foam samples are presented in Table 4.

Table 4

Main physical, thermal, mechanical and morphological characteristics of glass-ceramic foam samples

Variant	Apparent density (g/cm^3)	Porosity (%)	Thermal conductivity (W/m·K)	Compressive strength (MPa)	Water absorption (%)	Pore size (mm)
1	0.30	85.7	0.063	1.3	5.8	2.5-4.2
2	0.36	82.9	0.075	1.8	6.3	1.9-3.9
3	0.42	80.0	0.085	2.4	6.4	2.0-3.6
4	0.48	77.1	0.099	3.2	6.2	1.8-3.0
5	0.54	74.3	0.109	4.0	6.7	1.0-2.4
6	0.56	73.3	0.114	4.6	6.9	0.7-2.0

Determining the characteristics of the glass-ceramic foam samples highlighted the possibility of obtaining porous materials with compressive strength that can reach 4.6 MPa when using 8.5 wt.% coal fly ash and 3.0 wt.% SiC. Increasing the proportions of coal fly ash and SiC to 13.5 wt.% and 4.0 wt.% respectively, significantly reduces the compressive strength to a minimum of 1.3 MPa. The apparent density and thermal conductivity, whose values determine the thermal insulation character of the analyzed samples, are satisfactory in the range of samples 1-3. An apparent density between 0.30-0.42 g/cm^3 and a thermal conductivity between 0.063-0.085 W/m·K are considered excellent for a thermal insulation material. The compressive strength of samples 1-3 increases sharply from 1.3 to 2.4 MPa and the value corresponding to sample 3 (2.4 MPa) in combination with the density (0.42 g/cm^3) and thermal conductivity (0.085 W/m·K) are optimal characteristics for a very good thermal insulation material for buildings. For a deeper analysis of the characteristics of the glass-ceramic foam samples, it was necessary to investigate their microstructural configuration presented in Fig. 3.

Analyzing the pictures in Fig. 3, one can observe that the microstructural configuration of the samples is homogeneous with closed pores. The pore size is quite large, practically only samples 5 and 6 having normal dimensions (between 1-2.4 mm and 0.7-2 mm, respectively). The expanding intensification of the raw material due to the influence of the high content of alkali metal oxides in the composition of flat glass waste and coal fly ash was highlighted by the formation of microstructures with large pores. According to Fig.3, the sample 3 made of 86.5% glass waste, 10% coal fly ash and 3.5% SiC, considered optimal, has a homogeneous microstructure with pore size between 2-3.6 mm. The XRD analysis has identified wollastonite ($CaSiO_3$) as the main crystalline phase and to a lesser extent SiC and cristobalite (SiO_2).

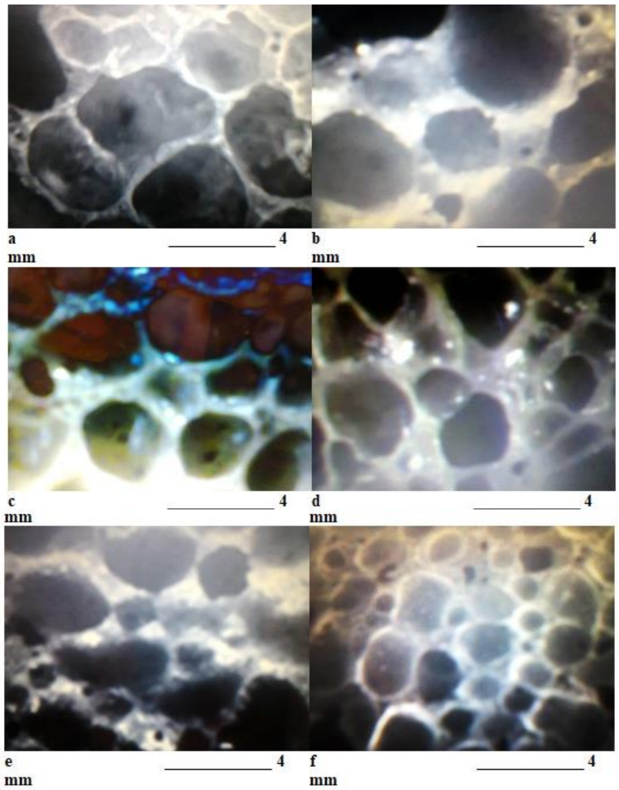


Fig.3. Microstructural configuration of the glass-ceramic foam samples
a – sample 1, b – sample 2; c – sample 3; d – sample 4; e – sample 5; f – sample 6.

The method of manufacturing a glass-ceramic foam from flat glass waste using the conversion of microwave energy into heat through predominant direct contact with the irradiated material, the raw material being glass waste and coal fly ash, showed that the conditions were met to obtain a product with a homogeneous microstructure. The intensification of the microwave absorption by the starting powder mixture due to the sufficiently high proportion of alkali metal oxides (Na_2O, K_2O) had an important role in achieving a uniform foamed structure. Given the difficulty reported in the literature of producing foamed materials with a uniform pore distribution using flat glass waste as a raw material, the ability to manufacture homogeneous microstructural products due primarily to use the microwave energy is a solution that can satisfactorily solve the inadequacy of flat glass for foaming processes. The glass-ceramic foams experimentally made have specific characteristics of thermal insulation materials (low apparent density, low thermal conductivity and high mechanical strength) and can successfully replace existing building materials on the market.

6. Conclusions

The paper presents the experimental research carried out with six variants of powder mixtures containing smooth glass waste (between 82.5-88.5% by weight), coal fly ash (between 8.5-13.5% by weight). SiC (3.0-4.0% by weight) was added as a foaming agent and water (10.0-11.0% by weight) was added as a binder. The experimental samples were sintered at 964-990 ºC in a 0.8 kW microwave oven to obtain glass ceramic foams. The compressive strength of glass-ceramic foam was strongly influenced by the decrease of coal fly ash and SiC contents and implicitly, of the sintering/foaming temperature in the ranges of tested values leading to a maximum of 4.6 MPa. The microstructural configuration of the product in all six experimental variants showed a good homogeneity, the pores having a uniform distribution. Analyzing the physical, thermal, mechanical and microstructural characteristics, variant 3 made of 86.5 wt.% flat glass waste, 10.0 wt.% coal fly ash, 3.5 wt.% SiC and 10.5 wt.% water addition by sintering at 977 ºC was adopted as the optimal sample. This sample characteristics were: apparent density of 0.42 g/cm^3, porosity of 80.0%, thermal conductivity of 0.085 W/m·K, compressive strength of 2.4 MPa, water absorption of 6.4% and pore size between 2.0-3.6 mm. The product has the required characteristics of a thermal insulation material usable in the building construction as a replacement for existing materials on the market. The advantages of using this product are: the low cost of the raw material consisting of a waste and an industrial by-product, the favorable ecological consequences and the low energy consumption of the unconventional manufacturing process.

R E F E R E N C E S

[1]. *M.F. Dragoescu et al*., The use of microwave fields in the foaming process of flat glass waste. International Journal of Engineering Sciences & Management Research. 5, 4, pp.49-5,2018.

[2]. Collection of flat glass for use in flat glass manufacture, Waste Protocols Project, A Good Practice Guide, Environment Agency, March (2008). [Accessed 15th January 2021]. Available from World Wide Web: http://www.wrap.org.uk/sites/files/wrap/WRAP_Flat_glass_GoodPractice_FINAL%(20)2.pdf

[3]. *A.S. Llaundis. et al.,* Foaming of flat glass cullet using Si_3N_4 and MnO_2 powders, Ceramics International. 35, 5, pp.1953-1959,2009.

[4]. *F. Cosmulescu at al.* , Comparative analysis of the foam glass gravel types experimentally produced by microwave irradiation. Journal of Engineering Studies and Research, 26, 3,pp. 58-68,2020.

[5]. *I. Butnariu , N. Constantin ., C. Dobrescu , T.Hepuţ ,* Research on the Recycling of Pulverulent Waste from the Ferrous and Non-Ferrous Industry in Order to Reduced the Pollution , Revista de Chimie (69), nr.5,pp.1066-1070 , 2018

[6]. *V.Rucai,, N.Constantin , C. Dobrescu* , Experimental research program regarding the influence of thermo-time treatment of multicomponent nibase melting on their properties in solid phase, University POLITEHNICA of Bucharest Scientific Bulletin Series B-Chemistry and materials science ,vol. 77,no. 4 ,pp. 359-364, 2015

[7]. *M.F. Dragoescu, , l. Paunescu, S.M. Axinte,,* Nonconventional heating method used to obtain glass foam from clear flat glass waste. Nonconventional Technologies Review. 22, 2,pp. 36-40, 2018.

[8]. *O.Donţu , N. Constantin , I. Butnariu,* Research Concerning reducing the Polluation Degrees in the Sectors of Production of Metal Materials, Revista de Chimie, vol.69, no.8, pp. 2129-2137 , 2018

[9]. *L. Paunescu ,N. Constantin , M.F. Dragoescu, A.Ioana , S.M. Axinte ,V. Rucai ,* Recycled glass waste expanded by a microwave heating technique, U.P.B. Sci. Bull., Series B, Vol. 82, . 4, pp.325-336,2020

[10]. *O.Kharissova , B.I. Kharissov, J.J. Ruiz Valdés* ,Review: The use of microwave irradiation in the processing of glasses and their composites. Industrial & Engineering Chemistry Research. 49, 4, pp.1457-1466, 2010.

[11]. *R. Buzduga , N. Constantin , A.Ioana* , Solutions to reduce the environmental pollution by the producers of refractories, U.P.B. Sci. Bull., Series B, vol. 80, no 1,pp.231-241 2018

[12]. *L. Paunescu, et al*., Testing the use of microwave energy to produce foam glass. European Journal of Engineering and Technology. 5, 4, pp.8-17, 2017.

[13]. *Kitchen et al*., Modern microwave methods in solid-state inorganic materials chemistry: From fundamentals to manufacturing. Chemical Reviews. 114, pp.1170-1206,2014.

[14]. *C.P.Mititelu ,M. Hritac , N.Constantin* , Experimental researches on briquetting and melting of fine ferrous waste, U.P.B. Sci. Bull., Series B, vol. 76, no. 4,pp.216-224, 2014

[15]. *Butnariu I., Constantin N.,* Protecţia mediului înconjurător şi microclimate, Universitatea "Politehnica" Bucureşti, 1994.

[16]. Metrology in laboratory. Measurements of mass and derived values, Radwag Balances and Scales (2013). [Accessed 10th February 2021] Available from World Wide Web: http://www.radwag.com

[17]. *L.M. Anovitz , D.R. Cole*, Characterization and analysis of porosity and pore structures. Review in Mineralogy and Geochemistry. 80., pp. 61-164,2005.