USING A SODIUM SILICATE SOLUTION TO PRODUCE IN MICROWAVE FIELD A HIGH-STRENGTH POROUS GLASS FOAM

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ABSTRACT: Another experimental application of the nonconventional microwave heating technique in the manufacturing process of a porous glass foam with high mechanical strength confirmed the high energy efficiency of this procedure compared to the conventional techniques. The specific energy consumption of the manufacturing process was very low (0.72-0.73 kWh/kg). Due to its physical, thermal, mechanical and microstructural characteristics (apparent density of 0.23-0.27 g/cm^3, porosity of 87.7-89.5%, thermal conductivity of 0.063-0.070 W/m·K, compressive strength of 6.4-6.8 MPa and pore size between 0.2-0.6 mm) the product can enter in the foam glass gravel category usable as a thermal insulating material in construction in application fields that require mechanical, chemical and thermal shock resistance.
KEYWORDS: glass foam, microwave heating, glass waste, sodium silicate solution, sodium borate, mechanical strength.

1. INTRODUCTION

Sodium silicate is a global name that includes chemical compounds of the general formula $(Na_2O)_x(SiO_2)_y$. In this category mainly sodium metasilicate (Na_2SiO_3) and also sodium orthosilicate (Na_4SiO_4) and sodium pirosilicate ($Na_6Si_2O_7$) fall. Sodium metasilicate is also known as "water glass". Commercially, it is available in aqueous solution or in solid state. In industry, different types of sodium silicate are used, being classified according to the SiO_2/Na_2O weight ratio, which can have values between 1/2 and 3.75/1. Ratios below 2.85/1 identify the alkaline sodium silicates and those over this value, the neutral sodium silicates [1].

According to the literature [2], the water glass swells by heating at low temperature (150-250 ºC), its volume growing 50-70 times by forming a highly porous structure. Due to this feature, the product can be used as a thermal insulating material, having low apparent density and low thermal conductivity. The foam produced from sodium silicate is chemically and biologically inert, non-toxic and is characterized by low water absorption (less than 5%). Its compressive strength is acceptable with values over 0.7 MPa. The research presented in the paper [2] followed the process of pore formation in the water glass mass during heat treatment and found that increasing its density leads to increased foaming ability. The experimental results showed that even from high-density water glass it is possible to obtain porous pellets with an arbitrary shape (not spherical) without an outer crust. In order to obtain a granular material with uniform porosity, the difficulty was to obtain spherical microporous pellets with compacted outer crust. The solution found by the authors was to carry out a process of silica gel coagulation from alkali metal salt electrolytes. Several additives were tested: hydrochloric acid, phosphoric acid, sodium chloride, sodium nitrate, sodium hydroxide, etc. The optimal variant for obtaining the minimum pellets density (0.22 g/cm^3) was experimentally determined being the use of sodium silicate aqueous solution (with the density of 1.51 g/cm^3) and an addition of 3-10% of its mass of sodium chloride as a modifying additive. The green pellets were prepared using a rotating disk pelletizer. The heat treatment of the pellets was performed in an electric oven at 300 ºC for 10 min. The product had a pellet core density of 0.22 g/cm^3, an apparent density of 0.15 g/cm^3, a splitting strength of 0.07 MPa and a water resistance factor of 0.3.

Another way to use sodium silicate solution ($Na_2SiO_3·9H_2O$) in the form of water glass in the manufacturing process of glass foam was experimentally tested and presented in the paper [3]. Colored container glass waste (colorless, green and amber) as a fine powder raw material mixed with aqueous solution of sodium silicate as a foaming agent in successive proportions of 12 and 19 wt.% and water addition as a binder were sintered at different temperatures between 750-900 C for 30 min. The optimum processing parameters for producing foam glass with thermal insulating properties were the sintering temperature of 850 ºC, water glass weight ratio of 12%, holding time at the

sintering temperature of 30 min and glass powder grain size of 75 μm. By sintering at 850 ºC, the porosity reached 90%, the compressive strength had a relatively high value (1.62 MPa) compared to other glass foams and the thermal conductivity was low (0.078 W/m·K). The bulk density reached a minimum of 0.25 g/cm^3 and the most uniform distribution of pores in the material structure was obtained. The variation of the holding time of the foamed product at 850 ºC led to the modification of the compressive strength value: 3.13 MPa for 10 min and 1.60 MPa for 40 min. In the temperature range 750-800 ºC, the bulk density of the product had higher values (0.37-0.61 g/cm^3), and the compressive strength was very high (up to 18.68 MPa). At 900 ºC, the pore size increased (0.50-1.10 mm) and the tendency of pores to join together was observed.

According to the literature [4], another technique for improving the compressive strength of glass foam is the use of sodium silicate solution as a binder in a powder mixture consisting of 80% industrial glass waste (from the manufacture of flat glass), 20% coal fly ash and 1% calcium carbonate as a foaming agent. According to [5], the sodium silicate solution (or water glass) is the most important of the soluble silicates. This material used as a binder contributes to the significant increasing of mechanical strength. The physical and mechanical characteristics of the glass foam were: compressive strength of 6 MPa, apparent density of 0.42 g/cm^3 and water absorption of 2.1%. The role of the sodium silicate solution incorporated in a powder glass waste is to homogenize its chemical composition and the most important technological properties of the material. Some silicates containing chemically bound water are formed by the reaction between water glass and the surface of glass waste particles. The water is released at 600-620 ºC and facilitates the foamed product formation. Water glass in the powder mixture increases the amount of vitreous phase and reduces the tendency of glass to crystallize [6].

Water glass has the ability to be used as a foaming agent without the contribution of other common foaming agents. Experimentally, glass foams with fine porosity were obtained, with closed pores with a diameter from 4 μm to 800 μm and mechanical strengths up to 1.7 MPa [7].

A very recently published paper [8] presented experimental results obtained in sintering/foaming processes of glass waste, the foaming agent being glass water in a weight proportion of 15%. The raw material was of a mixture of powder container glass of different colors (colorless, green, amber) and the grain size of the glass waste was varied between 75 - 250 μm. The heating temperature had values of 800 ºC and 850 ºC, respectively. The test results showed that the use of a fine-grained raw material leads to obtaining glass foams with more homogeneously distributed pores. The heating temperature influences the pore size of the foamed product. Larger pores correspond to a higher temperature. Fine-grained glass waste leads to a decrease in the compressive strength of glass foam. The products obtained by sintering/foaming, having the parameters mentioned above, correspond to the standard requirements imposed on the insulating materials used in construction, their thermal conductivity not exceeding 0.250 W/m·K.

In the industrial production, the aqueous solution of sodium silicate (water glass) is used as a binder in association with a liquid foaming agent (glycerol) for the manufacture of foam glass gravel from glass waste. This type of glass foam is manufactured in a tunnel furnace powered by conventional heating techniques (electrical resistances or burning a fossil fuel). The products are pieces with maximum dimensions of 70-80 mm and are obtained by breaking the cooled mass of glass foam at the cold end of the conveyor belt. The final material is characterized by a very low bulk density of 0.10-0.20 g/cm^3, very fine porosity with pore size below 1 mm, thermal conductivity in the range 0.06-0.08 W/m·K and high compressive strength up to 6 MPa [9, 10]. The foam glass gravel is suitable as a thermal insulating material in special areas of application that involve a fairly high mechanical stress such as road and railway construction, thermal insulating for long-distance heating pipelines, underground storage tanks, insulating for swimming pools and tunnels, thermal insulating of roof for platforms and terraces including also green roof with drainage function, etc.

There is not much information in the literature on manufacturing recipes of the industrial manufacturers. Glapor Werk Mitterteich company uses 87% recycled glass (flat glass or container glass), 1% glycerol, 12% sodium silicate solution and below 5% kaolin [11]. Glamaco company, although it is only a manufacturer of ovens and industrial equipment, in particular, for thermal processes of glass foam production, recommends a recipe that includes 95% glass waste (below 100 μm), 5% glycerol, calcium carbonate and sodium silicate solution as well as water and very low kaolin ratio [9, 12, 13].

In recent years, the Romanian company Daily Sourcing & Research has conducted experiments on

the manufacture of glass foam using sodium silicate solution together with glycerol as a liquid foaming agent or calcium carbonate as a solid foaming agent as well as glass waste as raw material. Unlike the experiments or industrial manufacturing processes presented above, which used conventional heating techniques, the production of foam glass gravel made by the Romanian company was performed using the microwave radiation. The paper [9] presented in the literature shows a comparative analysis of several solutions adopted by the authors for the manufacture of foam glass gravel in the microwave field.

Three groups of manufacturing recipes were tested experimentally. The recipes in the first group included glass waste, calcium carbonate (1.5%), sodium borate (between 3-8%) and sodium silicate solution (3-8%). Sodium borate was used as a fluxing agent. The sintering temperature varied between 835-855 ºC, the process duration being between 38-44 min. The specific energy consumption was between 0.92-1.07 kWh/kg. The foam glass gravel characteristics were: apparent density between 0.45-0.80 g/cm^3, porosity between 63.6-79.5%, thermal conductivity in the range 0.071-0.105 W/m·K, compressive strength between 3.5-9.5 MPa and the pore size from 0.8-1.0 mm up to 2.0-3.5 mm. The second experiments group was based on the use of glycerol (1.0-1.8 wt.%) associated with sodium silicate (between 5.3-7.5 wt.%) and water (between 7.7-10.0 wt.%). Colorless flat glass waste (between 83.0-83.7 wt.%) was used as raw material. The sintering temperature varied between 810-824 ºC, the process duration being between 39-42 min. The specific energy consumption was between 0.81-0.88 kWh/kg. The manufactured products had apparent density between 0.20-0.26 g/cm^3, porosity between 85.5-88.2%, thermal conductivity in the range 0.056-0.070 W/m·K, compressive strength between 4.6-5.8 MPa and pore size from 0.3-0.8 mm up to 0.8-1.1 mm. The third tests group was almost similar to the previous, the major difference being the use of a mixture of container glass waste (colorless, green and amber in the 50/20/30 ratio) between 82.3-83.0 wt.%. The glycerol varied between 1.0-1.6 wt.%, the sodium silicate was between 8.0-10.1 wt.% and the water between 6.0-8.0 wt.%. The process parameters were: the temperature between 815-823 ºC, the duration between 40-42 min and the specific energy consumption between 0.83-0.88 kWh/kg. The foam glass gravel had apparent density between 0.21-0.24 g/cm^3, porosity between 89.1-90.5%, thermal conductivity in the range 0.057-0.063 W/m·K, compressive strength between 4.8-5.9 MPa and pore size from 0.3-0.6 mm up to 0.7-0.9 mm.

The current work aimed to obtain with high energy efficiency light foamed products with high mechanical strength using sodium metasilicate (water glass) as a foaming agent and borax as a fluxing agent. The heating technique adopted was nonconventional based on the microwave radiation, still in an experimental stage in the Romanian company Daily Sourcing & Research.

2. METHODS AND MATERIALS

2.1 Methods

Generally, the technique of manufacturing glass foam from silicate waste is known and is based on the release of a gas in the pressed powder mass of the raw material subjected to a heat treatment at high temperature. The gas is released by a chemical reaction of a foaming agent incorporated in the raw material mass. There should be a good correlation between the temperature range in which the reaction occurs and the temperature at which the glass-based mixture is softened and has an adequate viscosity so that the released gas spreads in the mass of the material forming bubbles, but not leaves it. Subsequently, by cooling, a porous structure is formed [14].

The experimental manufacturing process was based on the use of commercial container glass waste (soda-lime glass) as a raw material, an aqueous solution (36.8% concentration) of sodium metasilicate (water glass) as a foaming agent (between 11-31 wt.%), sodium borate (borax) as a fluxing agent (5 wt.%) and water addition (between 8-15 wt.%) as a binder. The sodium borate has been used as a fluxing agent due to its high Na_2O content, which is the most important chemical compound with fluxing properties, especially for the glass industry [15].

The mechanism of the foaming process of glass waste using sodium metasilicate (water glass) as a foaming agent is slightly different from the mechanism with other common foaming agents. By heating to 100-300 ºC, the sodium metasilicate loses its crystallization water, releasing it. According to some authors [16], the sodium metasilicate hydrolyzes to free ions of sodium and silicic acid (synonym for silica). According to [17], the transition temperature of soda-lime glass is around 570 ºC. At this temperature, the sintering process of the glass particles begins, causing very small internal voids. The liquid phase formed into the material prevents the release of gases resulting from the foaming reaction that occurs at over 620 ºC. The

small voids begin to grow in the form of bubbles. As the process temperature increases, the viscosity of the glass waste decreases. The gas pressure inside the bubbles increases due to the increase of the process temperature, forcing the material expansion. The massive release of chemically bound water in the form of vapors (above 620 ºC) inside the mass of molten glass with sufficiently low viscosity contributes to the formation of glass foam. As in all powder foaming processes, cooling the expanded material leads to the formation of a porous structure. The sodium borate ($Na_2B_4O_7{\cdot}10H_2O$) added in the starting powder raw material has a crystalline structure. At over 100 ºC, it loses the crystallization water and at over 400 ºC, it turns into anhydrous sodium tetraborate. Increasing the borax content of the mixture, the glass viscosity decreases. Also, the fraction of open porosity in the foam decreases [18].

Due to its specific structure with vitreous network, the boron in borax (about 11%) used in experiments, has an important influence on the characteristics of glass, contributing significantly to the increase of mechanical strength, chemical resistance and thermal shock resistance of glass foam [19, 20].

The microwave equipment used in the experiments was the same 0.8 kW-microwave oven of the type commonly used in the household, adapted for high temperature operation, which was used in recent years by the Daily Sourcing & Research company for the manufacture of glass foams [21].

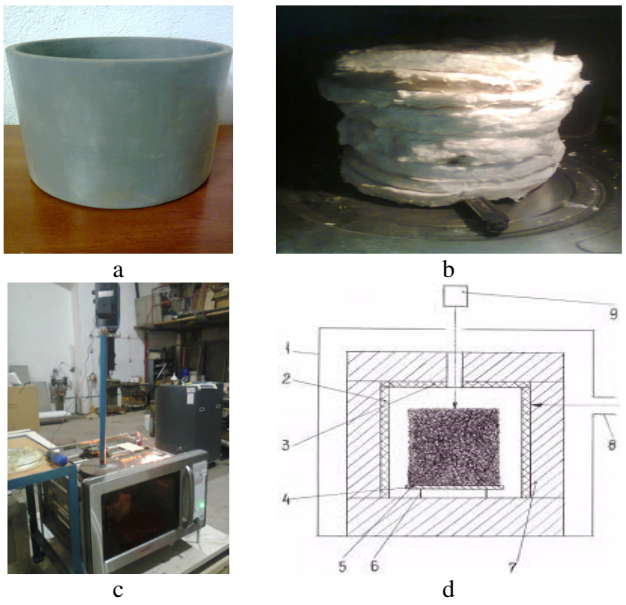

Figure 1. The experimental microwave equipment a – ceramic tube; b – ceramic fiber thermal protection; c - overall image of the microwave equipment; d – constructive scheme of the equipment: 1 – 0.8 kW-microwave oven; 2 – ceramic tube; 3 – ceramic lid; 4 – metal plate; 5 – pressed mixture of raw material; 6 – metal support; 7 – ceramic fiber mattress; 8 – waveguide; 9 – radiation pyrometer.

The other components of the equipment that includes the microwave oven are: a bed of ceramic fiber mattresses placed at the base of the oven, a 1 mm-thick metal plate placed 15-20 mm above the bed by means of a metal support, the pressed powder material deposited freely on the plate, a ceramic tube (with a outer diameter of 125 mm, height of 100 mm and a wall thickness of 2.5 mm) with a ceramic lid from a high microwave susceptible material (SiC and Si_3N_4 in 80/20 weight ratio) also placed on the ceramic bed containing inside the pressed sample. The entire assembly is thermally protected with ceramic fiber mattresses to avoid the heat loss outside the system. A radiation pyrometer mounted above the oven having the possibility to visualize the upper surface of the material ensures the control of its temperature (Figure 1).

The tube and the ceramic lid have the role to reduce the impact intensity of the microwave field with the sample. The thickness of the 2.5 mm-tube wall allows the predominantly direct microwave heating. Partially, the waves are absorbed in the mass of the tube wall, which heats up quickly and transfers heat by thermal radiation (indirect heating) [21].

The main advantages of the microwave direct heating are the volumetric heating (from the sample core to the peripheral areas in its entire volume) [22] and the heating selectivity (being heated only the vised material) [23].

2.2 Materials

The materials used within the experiments were: post-consumer container glass as the main raw material, sodium borate (borax) as a fluxing agent, an aqueous solution of sodium metasilicate (water glass) as a foaming agent.

The waste glass was composed of colorless, green and amber glass in equal weight ratios. The chemical composition of this three glass types is shown in Table 1.

Table 1. Chemical composition of the glass waste types

Chemical composition	**Glass waste type, wt.%**		
	Colorless	Green	Amber
SiO_2	71.7	71.8	71.1
Al_2O_3	1.9	1.9	2.0
CaO	12.0	11.8	12.1
Fe_2O_3	-	-	0.2
MgO	1.0	1.2	1.1
Na_2O	13.3	13.1	13.3
K_2O	-	0.1	0.1
Cr_2O_3	0.05	0.09	-
TiO_2	-	-	0.05
SO_3	-	-	0.05

The glass waste was selected by color and weighed with a laboratory balance.. Then, it was broken, ground in a ball mill and sieved at a grain size below 100 μm.

Purchased from the market at a grain size below 400 μm, the sodium borate (borax) was ground in an electrical laboratory device and sieved at below 130 μm.

The aqueous solution (36.8% concentration) was purchased from the market being used as a liquid foaming agent. The solution was supplementary diluted by water addition, not only for this purpose, but also as a binder for cold pressing the powder mixture of glass waste and sodium borate. The water addition to the sodium silicate solution was performed in a separate vessel before being discharged to the solid powder mixture.

3. RESULTS AND DISCUSSION

3.1 Results

As mentioned above, four experimental manufacturing recipes were tested on the 0.8 kW-microwave oven. Post-consumer container glass (colorless, green and amber) between 64-84 wt.%, sodium borate (5 wt.%) as a fluxing agent, aqueous solution sodium silicate between 11-31 wt.% as a foaming agent and water addition between 8-15 wt.% as a binder were used according Table 2.

The main functional parameters of the manufacturing process of glass foam are shown in Table 3. The total amount of wet raw material used in the four variants was kept constant at 570 g.

The accentuated increase of sodium silicate solution ratio from 11 to 31 wt.% and constant keeping at 5 wt.% the sodium borate ratio led to a gradual decrease in the sintering/foaming temperature from 847 ºC up to 836 ºC. Implicitly, the heating process time was reduced from 32 to 30 min. The average heating rate had high values between 25.8-27.2 ºC/min. What is remarkable is the very low level of the specific energy consumption between 0.72-0.79 kWh/kg, the lowest value being achieved in variant 1. Unlike the technique of manufacturing glass foam by conventional heating methods, in which the soaking time of the hot material is very important to obtain the required physical, mechanical and microstructural characteristics, in the case of manufacturing by the nonconventional method, the heating of the expanded material is stopped, followed by a slow cooling under the thermal protection conditions provided in the oven, because the ceramic fiber has a very low thermal inertia. Thus, the average cooling rate of glass foam had quite high values (6.5-6.7 ºC/min).

Table 2. Composition of the experimental variants

Variant	Container glass waste wt.%	Sodium silicate solution wt.%	Sodium borate wt.%	Water addition wt.%
1	84	11	5	8
2	77	18	5	10
3	69	26	5	12
4	64	31	5	15

Table 3. The main functional parameters of the manufacturing process of glass foam

Variant	Wet 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	570/461	847	32	25.8	6.5	1.30	0.72
2	570/440	842	31	26,5	6.7	1.40	0.73
3	570/418	839	30.5	26.9	6.6	1.60	0.76
4	570/398	836	30	27.2	6.7	1.70	0.79

Table 4. The main physical, thermal, mechanical and microstructural characteristics of the glass foam sample

Variant	Apparent density g/cm³	Porosity %	Thermal conductivity W/m·K	Compressive strength MPa	Water absorption %	Pore size mm
1	0.27	87.7	0.070	6.8	1.6	0.2 – 0.5
2	0.23	89.5	0.063	6.4	1.8	0.2 – 0.6
3	0.24	89.1	0.065	5.2	1.9	0.6 – 1.0
4	0.26	88.2	0.069	5.4	1.7	0.5 – 1.2

The same methods for determining the characteristics of glass foam samples used in previous similar experimental works were applied. The apparent density was measured by the gravimetric method [24] and the compressive strength was determined using a Stable Micro Systems TA XT Plus Texture Analyzer. The thermal conductivity was measured by the guarded-comparative-longitudinal heat flow (ASTM E1225-04 standard) and the porosity was calculated by the method of comparing the true and apparent density [25]. The water absorption was determined by the water immersion method (ASTM D570 standard). The samples microstructure was examined with a Smartphone Digital Microscope. The main physical, thermal, mechanical and microstructural characteristics of the glass foam sample are shown in Table 4.

Analyzing the data in Table 4, the low values of the apparent density (between 0.23-0.27 g/cm^3) and thermal conductivity (between 0.063-0.070 W/m·K) as well as the high values of porosity (between 87.7-89.5%) could be observed. These are physical characteristics specific to thermal insulating materials. Simultaneously, the compressive strength of glass foams was very high (between 5.2-6.8 MPa). On the one hand, the aqueous solution of sodium silicate as a foaming agent contributed both to increasing the material porosity and to decreasing the density and thermal conductivity. It also influenced the obtaining of products with high mechanical strength. In turn, the sodium borate through its boron content (11 wt.%) contributed to the increase of mechanical strength, chemical resistance and thermal shock resistance.

For sodium silicate weight proportions of 11 and 18 % the values evolution of the physical and thermal characteristics of samples 1 and 2 was normal. At higher proportions (26 and 31 wt.%) of sodium silicate corresponding to samples 3 and 4, a slight increase in density and thermal conductivity and a slight decrease in compressive strength were observed. To explain this behavior it was necessary to examine the microstructural images. Pictures of the four samples produced by the nonconventional heating technique are presented in Figure 2 and the microstructural images of these samples are shown in Figure 3.

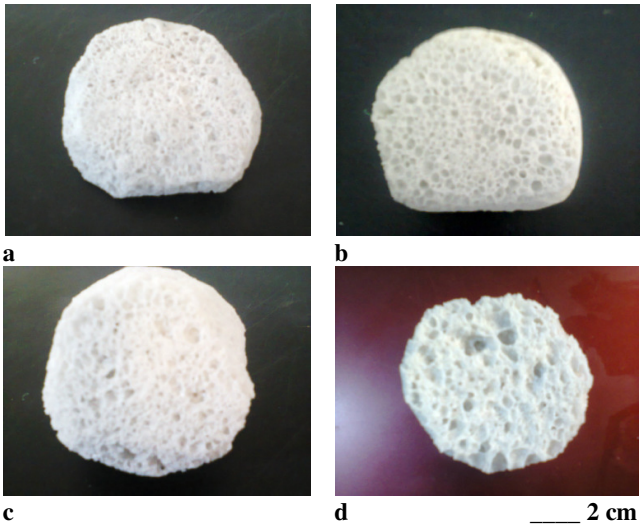

Figure 2. Picture of the glass foam samples
a – sample 1 heated at 847 ºC; b – sample 2 heated at 842 ºC; c – sample 3 heated at 839 ºC; d – sample 4 heated at 836 ºC.

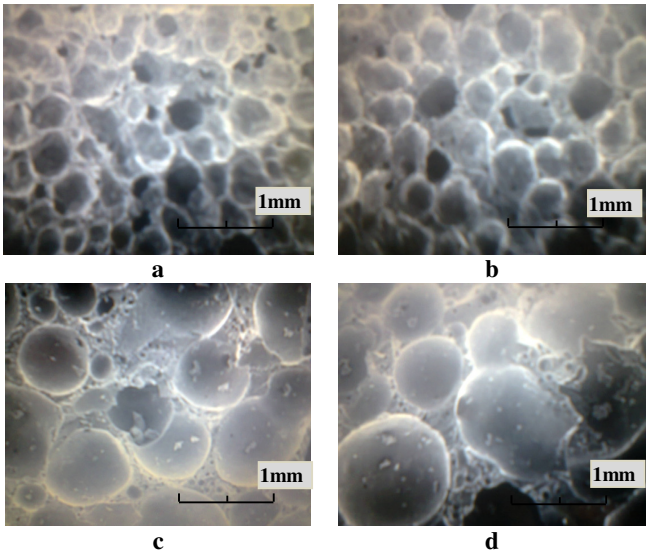

Figure 3. Microstructural images of the glass foam samples
a – sample 1; b – sample 2; c – sample 3; d – sample 4.

Figures 3a and 3b show homogeneous microstructures with low pore size (0.2-0.5 mm and 0.2-0.6 mm, respectively) uniformly distributed. At high proportions of sodium silicate according to Figures 3c and 3d, the pore size increased to 0.6-1.0 mm and 0.5-1.2 mm, respectively, having the tendency to intercommunicate between large neighboring pores by channels through dense struts between cells. In this way, although the large pore size could indicate a reduction of the glass foam density, in reality it increases due to the dense struts

between the cells. By default, the value of compressive strength remains high.

3.2 Discussion

Taking into account the experimental results the best samples are 1 and 2. The physical and thermal properties of sample 2 are slightly better, however the compressive strength of sample 1 is slightly higher. Both samples have excellent characteristics specific for a foam glass gravel.

Therefore, the main physical, thermal, mechanical and microstructural characteristics of the optimal glass foam samples manufactured by sintering the glass waste at 842-847 ºC were: apparent density between 0.23-0.27 g/cm^3, porosity between 87.7-89.5%, thermal conductivity in the range 0.063-0.070 W/m·K, compressive strength between 6.4-6.8 MPa and pore size between 0.2-0.6 mm. The heating rate obtained by the predominant direct microwave heating technique was between 25.8-26.5 ºC/min. The cooling of the glass foam was slow (6.5-6.7 ºC/min) being done in the oven after stopping its power supply. The specific energy consumption was very low of only 0.72-0.73 kWh/kg.

By comparison with the characteristics and functional parameters of the same type materials made in other conditions and with other additive types presented in the literature [3-13], it can be concluded that in qualitative terms the samples obtained and described in this paper are almost similar and can be assimilated with foam glass gravels.

In energy terms, the comparison with other manufacturing processes of this product type cannot be made worldwide because the information is missing in the literature. However, data are presented in [9] on specific energy consumption obtained by the same team of authors in the experimental manufacture of foam glass gravel by microwave irradiation, but using a different type of liquid foaming agent (glycerol). The data (0.81-1.07 kWh/kg) are close in value, with a low advantage of energy efficiency (0.72-0.73 kWh/kg) in favor of the process described in the current paper.

4. CONCLUSION

The paper aimed to manufacture a high-strength porous glass foam using a liquid foaming agent (sodium silicate aqueous solution) and a fluxing agent (sodium borate).

The work originality was the use of the nonconventional microwave heating technique, unlike the conventional techniques commonly applied worldwide in similar manufacturing processes.

The main physical, thermal, mechanical and microstructural characteristics of the optimal glass foam samples manufactured by sintering the glass waste at 842-847 ºC were: apparent density between 0.23-0.27 g/cm^3, porosity between 87.7-89.5%, thermal conductivity in the range 0.063-0.070 W/m·K, compressive strength between 6.4-6.8 MPa and pore size between 0.2-0.6 mm.

In qualitative terms, the optimal samples were almost similar with the products previously made in the world and could be assimilated with foam glass gravels.

The energy efficiency of the experimental process of manufacturing glass foam using the microwave heating was excellent allowing to obtain low specific energy consumption (0.72-0.73 kWh/kg), slightly below the most economical values of energy consumption previously obtained also using the nonconventional technique.

The type of porous product with high mechanical strength experimentally obtained can be used as foam glass gravels, i.e. as a thermal insulating material for application fields that require mechanical, chemical and thermal shock resistance.

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