NONCONVENTIONAL TECHNIQUE TO MAKE BOROSILICATE GLASS FROTH

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ABSTRACT: The article shows testing outcomes of preparing a froth from residual borosilicate bottle utilizing lignite coal powder as an expanding agent in association with water glass to avoid premature pre-oxidation of carbon before reaching the sintering temperature of the glass powder. The resulted froth had excellent heat-insulating properties, the apparent denseness and heat conductivity having low values (0.35 $g \cdot cm^{-3}$ and 0.061 $W \cdot m^{-1} \cdot K^{-1}$, respectively). The compression resistance corresponding to the optimal version reached 2.6 MPa and the pore size interval was between 0.7-1.5 mm. In this experiment, the non-conventional electromagnetic wave heating technique was adopted and as an originality, a mixed heating method (partly direct and partly indirect) was chosen to keep safe the inner structure of the froth. The effectiveness of the method was demonstrated by the economic value of the energy consumption of the process (0.73 $kWh \cdot kg^{-1}$).
KEYWORDS: froth, borosilicate glass, microwave heating, lignite coal, water glass.

1. INTRODUCTION

Borosilicate glass is a glass type with silica and boron as the main components. This material type has very low coefficients of heat expansion (about $3 \cdot 10^{-6}$ K^{-1} at 20 °C), being more thermal shock resistant compared to any other ordinary glass. According to [1], the world borosilicate bottle market was estimated to USD 1142 million in 2023 and it is anticipated to reach USD 1142 million by 2030. Several international companies including Yaohui Group and Linuo Group (China), Borosil (India), Shott Group (Germany), Corning (the United States), etc. constitute the main world borosilicate glass key players. China represents the largest market (over 50 %), Europe and India being the following global suppliers.

Due to its chemical and heat resistance, borosilicate glass is commonly used as laboratory vessels in chemistry and in the industrial environment as well as kitchen vessels and premium wine glasses. In accordance with the work [2], borosilicate glass is often used to limit the high radioactive level of some wastes by forming a passivating gel layer. The boron contained in borosilicate glass represents an adequate model for avoiding its corrosion and protecting the environment for a long time.

The content of boron oxide (B_2O_3) of borosilicate glass is over 8 %, while the content of silica (SiO_2) is between 70-80 %, having the role of network formers. Bottle containing 7-13 % B_2O_3 is recognized as low-borate borosilicate bottle, being utilized for the manufacture of lamps, devices for chemistry, and tube covers. The bottles containing 15-25 % B_2O_3 are recognized as high-borate borosilicate bottle and is made for producing bottle pores glass largely applied as a specific medium in chromatography [3].

The interest in recycling the borosilicate glass waste and its valorisation in the form of other products with newly created value has significantly increased in the last decades, aiming at the manufacture of porous materials with special chemical and heat properties.

The manufacture of a glass with porous structure as a result of the heat treatment leads to the formation of two interconnected phases: one rich in silica and one borate rich in alkali [4]. The thermal treatment and filtration parameters can be adapted depending on the required dimension and volume of pores. Thus, porous bottle based on sodium borosilicate can be produced according to requirements, ensuring good flexibility for different applications.

Borosilicate glass coming from laboratory chemical equipment and components of process installations have several important beneficials such as: optical clarity, cleanability, corrosion resistance, heat resistance, low heat expansion, affordability, inert behaviour [5].

An experiment regarding making the expanded bottle from residual borosilicate bottle using variable amounts of antimony oxide (Sb_2O_3) is presented in [6[. The effect of this oxide introduction on the porosity and compression resistance of the froth is a favourable one. The weight proportion of 0.9 wt. %

Sb_2O_3 added to the borosilicate glass powder and sintering at 775 ℃ were the principal optimal frameworks of the making technique. The microstructure of the expanded product is uniform, with large pore size and relatively smooth cell walls. Its characteristics indicate a lower bulk density, relatively high compression resistance, and reduced water absorption. Increasing the proportion of Sb_2O_3, the pore dimension initially leads to growing followed by decreasing. Higher quantities of Sb_2O_3 increase the vitrification of the froth.

An almost similar way of capitalizing the residual borosilicate glass by its sintering and expanding is shown in the paper [7]. Except for recycled glass waste, quartz and borax were utilized as raw materials. The chosen expanding agent was calcium carbonate ($CaCO_3$) and the fluxing agent was sodium carbonate (Na_2CO_3). By investigation, it was observed that by decreasing the quartz proportion between 30.0 and 17.5 % and increasing the borax ratio between 5.0-17.5 %, pore size, porosity, and thermal insulation capacity of the obtained froth significantly increased, while the compression resistance easily decreased. The optimal proportions of quartz and borax content were determined to be 17.5 %, contributing to obtaining the best performance of the product: average pore size of 1.9 mm, their uniform distribution, porosity of 83.4 %, thermal conductance of 0.071 $W \cdot m^{-1} \cdot K^{-1}$, and compressive strength of 2.4 MPa.

Preparing a glass-ceramic froth by the sinterization of residual borosilicate bottle with organic binder as an expanding product was presented in the work [8]. According to the measurement results, softening the material was initiated at 800 ℃ and crystallizing process at 845 ℃, being finished at 900 ℃, with an expanding of about 40 % in the range of 850-900 ℃. The products had porosity of around 78.5 % and apparent denseness of around 0.5 $g \cdot cm^{-3}$, corresponding to the features of ordinary closed-cell porous bottle froth utilized for heat-insulating. Porosity and pore size varied with the sintering temperature leading to different microstructure versions. The pores obtained by expanding initially have a spherical shape and low dimensions, changing by increasing the temperature to polyhedral shapes.

Lv et al. [9] tested making borosilicate bottle froth using carbon black as an expanding agent. The analyzes showed that a pre-oxidation of carbon from the carbon black occurs before the thermal expansion temperature is reached. Experimentally, determinations were carried out in the case of several heating rates of residual bottle. It was discovered that growing the warming speed contributes to decreasing of the early oxidizing degree, thus avoiding the formation of inhomogeneous structure of the froth. In the case of carbon black having particle size of 150 μm, the optimal heating rate during the sintering process was identified at 8 $℃ \cdot min^{-1}$.

The experiments mentioned above [6-9] aiming at the expansion by sintering of borosilicate glass waste utilized traditional conventional heating methods.

The Romanian writers of the present work recently adopted the non-conventional technique of microwave heating. Discovered more than 80 years ago, microwaves were mainly applied in telecommunications and radars and too little in solid heating processes, despite their energetic efficiency recognized by some specialists [10].

The article [11] presented outcomes of making a bottle froth from residual borosilicate ware (laboratory ware) by applying the energy generated by microwaves. Several versions of expanding agent (SiC, $CaCO_3$, and activated carbon) and addition materials (fly ash and disodium phosphate) were successively tried in the Daily Sourcing & Research Company (Romania). The froths had similar features to products produced from borosilicate bottle through by the traditional warming method. Thus, apparent density had low values (0.34-0.47 $g \cdot cm^{-3}$), but superior to that of residual soda-lime bottle, while compression resistance between 1.5-2.5 MPa is higher than those of soda-lime glass. The conclusion of the test was that the froths recycled from residual borosilicate bottle are adequate to be utilized as insulation materials in building.

A bottle froth produced through the sinterization at 790 ºC utilizing residual borosilicate bottle, carbon black (1 %) as an expanding product, Na_2HPO_4 (5.9 %) as a preserving product, Sb_2O_3 (0.8 %) as an oxygen supplier, and add of water (10 %) as a binder was made by electromagnetic wave radiation [12]. Bottle froth features were: denseness of 0.34 $g \cdot cm^{-3}$, porousness of 84.5 %, heat conductance of 0.06 $W \cdot m^{-1} \cdot K^{-1}$, and compression resistance of 2.2 MPa. The pore dimension was within the limits of 0.4-0.7 mm. The energy expenditure had very low value (0.68 $kWh \cdot kg^{-1}$) under the range of bottle froth expenditure manufactured at industrial scale by traditional procedures.

The current article presented below has adopted a new solution for preparing the borosilicate glass waste foam, using lignite coal powder as an expanding agent, water glass (sodium silicate)

having the preserving role of coal particles by covering to avoid their premature oxidizing before reaching the glass sintering temperature value. As in other previous experimental processes of expanding silicate waste, the authors adopted the very little application technique of non-conventional electromagnetic wave warming.

2. MATERIALS AND METHODS

2.1 Materials

Preparing the porous material based on expanding by sintering required the use of recycled residual borosilicate glass, lignite coal powder, water glass, and supplementary water addition.

The recycled residual glass came from chemical laboratory ware. The glass was processed in a low-capacity grinding device, the grain dimension being less than 70 μm. The composition of borosilicate glass utilized in this experiment contained 80.9 % SiO_2, 13.2 % B_2O_3, 2.0 % Al_2O_3, and 3.9 % Na_2O.

Lignite coal powder having in composition 66.9 % C, 4.8 % H, 0.6 % N, 27 % (O+S), and 0.8 % ash [13], was mechanical processed by grinding mill and then, selected after sieving the dimensions below 75 μm.

Water glass (Na_2SiO_3) is accessible on the market as water-soluble solid lumps or powders as well as a slightly viscous liquid [14]. The liquid version (with a concentration of 38 %) was chosen for use in the experiment.

Four testing versions were chosen including the mass ratios of the material components, that are shown in Table 1.

Table 1. Testing variants components (wt. %)

Component	Variant 1	Variant 2	Variant 3	Variant 4
Residual borosilicate glass	92.9	92.6	92.1	91.7
Lignite coal	1.0	1.0	1.1	1.1
Water glass	6.1	6.4	6.8	7.2
Water addition	12.0	12.0	12.0	12.0

In accordance with Table 1, the main variable of composition values was that of water glass from 6.1-7.2 %. The proportion of lignite coal was almost constant, with a very small variation between 1.0-1.1 %. Normally, the wide variation of water glass content also determined an important variation of residual borosilicate glass (91.7-92.9 %).

2.2 Methods

The basic method of manufacturing glass foam using residual borosilicate glass was based on the sintering of the powder mixture of component materials. The expanding agent (lignite coal powder), used in association with water glass, was chosen in such a way that the thermal softening of the glass powder takes place at a temperature slightly lower than the temperature at which carbon from the lignite begins to oxidize and carbon dioxide is released, forming bubbles. Including the water glass has the role of avoiding premature oxidation of carbon particles at a temperature lower than that of the glass sintering process.

On the other hand, the heating method for sintering the mix was the non-conventional method of microwave heating, adopted as a heat-efficient procedure in the last 6-7 years in the Romanian company Daily Sourcing & Research. The testing facility was an electromagnetic wave furnace usually used in household activities, but constructively and operationally adapted for applications at high thermal requirement of above 1000 ℃ (Figure 1a). Since the direct heating of the glass powder proved too intense, causing destruction of the internal structure of the expanded specimens, the mixed heating technique (partly direct, partly indirect) was adopted by placing a SiC and Si_3N_4-microwave susceptible crucible. The optimal dimension of the crucible wall was 2.5 mm (Figure 1b), which tempered the electromagnetic waves effect on the heated material.

a b

Figure 1. Testing facility
a – the adapted furnace; b – the crucible.

2.3 Investigation methods to identify the specimen features

Investigating the physio-mechanical, heat, and microstructural peculiarities of bottle samples was made utilizing known common procedures. Archimedes' method was chosen for determining the denseness and porousness (ASTM D792-20), in accordance with the literature recommendation [15]. The thermal conductance was determined using "the heat-flow" procedure (ASTM E1225-04), while the

compressive resistance was identified with "TA.XTplus Texture" analyzer in accordance with ASTM C552-17 standard. Volumetric amount of water-uptake was determined through the H_2O-submersion procedure (ASTM D570). The appearance of glass specimen microstructures was investigated with ASONA type Smartphone Digital Microscope.

3. RESULTS AND DISCUSSION

3.1 Results

The principal operational frameworks of the technological process are shown in Table 2. The amount of materials constituting the feedstock was kept to the constant value of 520 g.

Table 2. Operational frameworks of the making process

Framework	Variant 1	Variant 2	Variant 3	Variant 4
Feedstock amount (g)	520	520	520	520
Process temperature (°C)	785	790	796	803
Heating time (min)	31	32	34	36
Heating rate (°C·min^{-1})	24.7	24.1	22.8	21.8
Cooling rate (°C·min^{-1})	5.3	5.2	5.0	5.2
Volume growing indicator	1.79	1.93	2.12	2.29
Bottle froth quantity (g)	452	454	453	453
Specific consumption of energy (kWh·kg^{-1})	0.71	0.73	0.78	0.83

According to Table 2, the thermal interval at which the sintering/expanding process of borosilicate glass takes place is relatively small (785-803 °C). Because the effectiveness of the non-conventional warming technique allows great heating rates (between 21.8-24.7 °C·min^{-1}), the sintering process was quite short (between 31-36 min) and the energy consumption was below 0.83 kWh·kg^{-1}.

The physical appearance of borosilicate bottle froth products performed by the four testing variants mentioned above is shown in Figure 2.

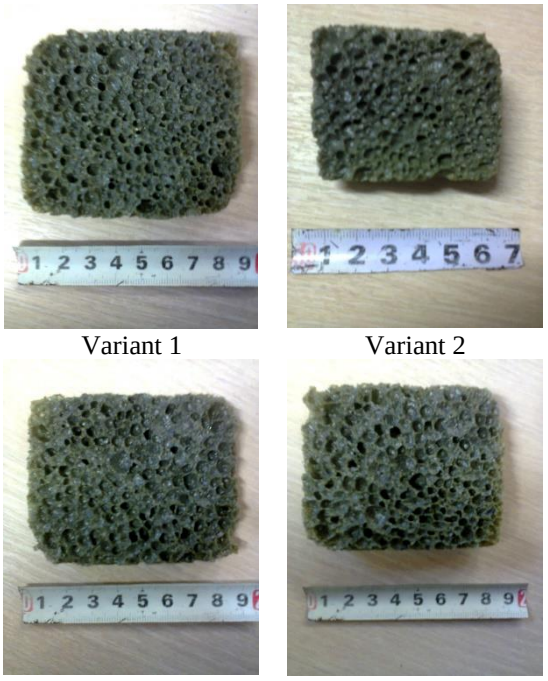

Figure 2. Physical appearance of products prepared in the four testing variants

In accordance with these pictures, the porous aspect of the surface of products is continuously increasing, beginning with the specimen performed in version 1 and finishing with the specimen that corresponds to version 4.

The application of the previously mentioned investigation methods led to the identification of the physio-mechanical, heat, and morphological features of each borosilicate bottle froth specimen presented in Table 3.

Table 3. Physio-mechanical, heat, and morphological features of borosilicate bottle froth specimens

Feature	Variant 1	Variant 2	Variant 3	Variant 4
Denseness (g·cm^{-3})	0.37	0.35	0.34	0.32
Porousness (%)	83.4	84.3	85.0	86.2
Thermal conductance (W·m^{-1}·K^{-1})	0.064	0.061	0.058	0.055
Compression resistance (MPa)	2.8	2.6	2.5	2.3
Water-uptake (%)	2.5	2.5	2.6	2.6
Cell dimension (mm)	0.5-1.0	0.7-1.5	1.4-2.7	1.5-2.9

Features included in Table 3 highlight the excellent heat insulation properties of all specimens of borosilicate glass froth obtained by the sintering/expanding procedure. Thus, the apparent

density of the glass foams has low values within the limits of 0.32-0.37 $g \cdot cm^{-3}$ and the thermal conductance also falls in very low limits (0.055-0.064 $W \cdot m^{-1} \cdot K^{-1}$). From this point of view, the experimental version 4, benefiting from the highest values of the content of water glass and lignite coal as an expanding agent, could be considered the most favourable. Porousness of the expanded samples also falls within an advantageous value range for a heat insulation product (83.4-86.2 %). Analyzing the value level of the compression resistance of specimens, it falls within the normal limits [11, 12] of this type of expanded material (2.3-2.8 MPa), the highest values being reached in the case of the samples with the lowest porousness. The water-uptake determined through the immersion method under water of specimens showed constancy of values (2.5-2.6 %) in all cases, representing a normal level of this type of material. In microstructural terms, the examination of expanded samples appearance revealed that specimens 3 and 4 with the best insulating performances have relatively inhomogeneous microstructure (quite large differences between the dimension of cells that make up the structure), which can adversely influence the circulation of the heat flow caused by the non-uniformity of its intensity. The images in Figure 3 support the idea presented above.

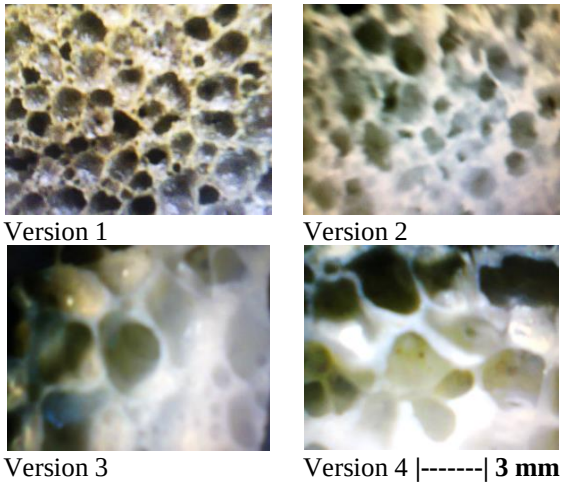

Figure 3. Microstructural aspect of products prepared in versions 1-4

3.2 Discussion

Taking into account observations with microscopic character, confirmed also in Table 3 with reference to the pore size, the testing version 2 was adopted as the optimal version.

The optimal version characteristics include adequate heat-insulating properties (i.e. 0.35 $g \cdot cm^{-3}$ the denseness, 0.061 $W \cdot m^{-1} \cdot K^{-1}$ the heat conductivity, and 84.3 % the porousness). Also, the compression resistance has a good value (2.6 MPa). The microstructural appearance of this specimen is homogeneous, the pore size falling within narrow limits (0.7-1.5 mm).

The sintering process temperature, at which the expansion of the heat softened mixture takes place, was relatively low (790 °C) and the average heating rate used in this experiment was 24.1 $°C \cdot min^{-1}$. The utilization of the microwave warming procedure allowed to achieve very economical energy expenditure of only 0.73 $kWh \cdot kg^{-1}$.

The testing production of the froth from borosilicate bottle by use of lignite coal powder as an expanding agent in association with water glass with avoiding role of premature pre-oxidation of carbon has confirmed the possibility to obtain a material with adequate properties for applying in construction as a heat-insulating product.

4. CONCLUSION

A new testing version of froth manufacturing by sintering residual borosilicate glass, made in the same original conditions designed by the authors for non-conventional mixed heating (direct and indirect simultaneously) with electromagnetic waves, is described in this article. In the premiere, the process of expanding borosilicate glass was obtained with lignite coal powder as an expanding agent, in association with water glass to avoid the premature oxidation of the carbon in the coal particles before reaching the sintering temperature of the glass. The obtained froth, in its optimal version (version 2) had excellent heat-insulating properties (0.35 $g \cdot cm^{-3}$ for apparent denseness, 0.061 $W \cdot m^{-1} \cdot K^{-1}$ for the heat conductance, and 84.3 % for the porousness). On the other hand, the resistance to compression was acceptable (2.6 MPa) and the microstructural appearance of the specimen made in optimal version is homogeneous, the pore size having values in

narrow limits (0.7-1.5 mm). The necessary thermal requirement of the sinterization procedure was determined by the experiment at 790 °C, under the conditions in which the warming speed was 24.1 °C·min^{-1}. The use of non-conventional heating technique has confirmed its remarkable energy efficiency compared to the conventional methods. The energy expenditure was thus extremely economical (0.73 kWh·kg^{-1}).

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