High-Performance Thermal Insulation Material Based on Waste Glass

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Abstract. The article is devoted to the development technology of obtaining and properties of heat-insulating environmentally safe material production from waste glass. The subject of the study is a finely fraction of a mixture of window and container glass. Differential scanning calorimetry was used, the study of the gas release process was carried out on a specially designed and manufactured installation. Developed a foaming composition consisting of calcium carbonate and sodium nitrate, which allows you to combine the decomposition temperature of the main gas-forming agent (calcium carbonate) and the softening temperature of the glass, which is a necessary condition for obtaining a foam material with a minimum apparent density. The optimal mass ratio of sodium nitrate and calcium carbonate (100:35), the foaming temperature (700 °C) and particle sizes (less than 60 microns) were determined, allowing to obtain a material with a density of 80-100 kg/m³. The dependence of the apparent density of the obtained material on the time of foaming and the content of the gas-forming agent is obtained by mathematical modeling, which allows determining the optimal time of foaming at different temperatures. During the development of the technology, factors affecting the properties of the resulting foam material were identified, and the dependence of the main technological parameters on these factors was established. For the production of thermal insulation material, a continuous powder method is proposed, including the processes of preparing a foaming composition and producing foam blocks. The developed material has a lower coefficient of thermal conductivity, higher strength and low density compared to existing analogues and does not emit hydrogen sulfide during operation. According to the developed technology, a pilot batch of foam glass was produced, which was used by a number of construction companies in various areas of construction.

1. Introduction
Thermal insulation materials have to meet high, often conflicting requirements: they should be heat insulators and hydro bonders of high-quality, meet all sanitary and hygienic standards and be environmentally friendly, keep these indicators constant for a long time [1].

The modern insulation market is very diverse, but there are no materials fully meeting the requirements mentioned above. The main thermal insulation materials used at the present time are various kinds of mineral wool and expanded polystyrene [2–4]. Expanded polystyrene has high thermal insulation properties primarily due to its low density (20 – 40 kg/m³). But like all organic substances it is combustible (when burning it emits chemicals that are hazardous to human health) and
non-durable. Mineral wool insulation has a very high water absorption which causes a decrease in thermal insulation properties. In addition over time there is a gradual self-destruction of its fibers which also has an adverse impact on the thermal insulation ability and human health [1].

Currently foam glass, a unique material having undeniable advantages over all other heat insulators, appeared in the market of modern thermal insulation materials [5–8]. It is difficult to imagine other available heat-insulating material, excluding special-purpose products, which could withstand a direct torch with the temperature of more than 1000°C [9]. It retains its characteristics throughout the period of operation, and most importantly it belongs to the class of non-combustible materials.

For the first time foam glass as a building material was mentioned by academician I.I. Kitaygorodsky at the All-Union conference on standardization and production of new materials in Moscow in 1932 [10]. In the 1930s intensive research started and resulted in patents received for the manufacture of foam glass in many European countries (France, the Czech Republic, the UK and Germany) and the United States [6,7,11]. During the World War II the United States mastered large-capacity production of foam glass, mainly for the needs of the Navy, and then became a leader in the production and research in this technology for many years [12].

All properties of foam glass are determined by its structure, which is a molten glass bubbles filled with gases. Currently known varieties of foam glass determine the direction of application of the material: insulation and construction used for insulation of enclosing structures of buildings; insulation and installation used for thermal insulation of equipment and plants of moderate and deep cold, industrial plants, heat pipes with an operating temperature of up to 400°C; moisture protection, characterized by water absorption at most 1.8% by volume for 360 days; special purpose (alkali-free) and high-silica characterized by high strength, heat resistance, radio transparency (application temperature up to 600°C for alkaline porous glass and 1200°C for high-silica glass); acoustic (sound-absorbing); filtering, characterized by fine communicating porosity [13–15].

Differences in the types of foam glass are determined by such factors as the size of the cells, the composition of the glass, the presence of more or less free defects in the bridges between the cells. While the sound-absorbing and filtering cellular glass is to have an open continuous porosity, production of other species is aimed at obtaining a fine-porous structure with evenly distributed pores of a closed type.

The apparent density of foam glass almost definitely determines its thermal conductivity and strength [16]. Foam glass produced elsewhere has a significant disadvantage, i.e. high density (from 170 to 250 kg/m³) which does not allow achieving high thermal insulation capacity.

The nature of the porous structure of the glass foam is changed by changing the chemical composition of the raw material [17–19], the selection of the gas developing agent, its dispersion and flow rate, as well as by changing the sintering mode, affecting the intensity of gas decomposition and rheological parameters (viscosity) of the glass foam.

The average density of foam glass is usually controlled by changing the temperature and time of foaming, the selection of the gas developing agent, the degree of dispersion of glass powders [20,21].

Historically foam glass is produced with sulphate-containing glass. In his monograph B.K. Demidovich showed that when carbon is used as a gas developing agent in the reduction of Na₂SO₄, reaction with the release of H₂S occurs in the atmosphere of water vapour in the glass [21].

In all such cases in terms of chemistry the main fact is that the oxidized sulphur $S^\text{VI}$, the amount of which in conventional silicate glasses is not a problem for the end user, is converted into reduced sulphur $S^\text{II}$ in the production of foam glass. In this case sulphur is present in the structure of the finished foam either in the form of hydrogen sulphide gas or in the solid phase of the glass in the form of sulphide compounds. Moreover, sulphides in interaction with water vapour contained in the air undergo a hydrolysis reaction, in which the same hydrogen sulphide is released into the air as a gas [12]. Coupled with the high density it dramatically limits the use of foam glass in housing construction.
The aim of this work is to develop a technology for producing heat-insulating environmentally safe material from glass waste with apparent density of 80-100 kg/m$^3$.

2. Methods

Researchers used a finely milled (less than 100 microns) fraction of a window and container glass mixture chemically composed of: SiO$_2$ – 71.25%; Al$_2$O$_3$ – 1.87%; Fe$_2$O$_3$ – 0.29%; CaO – 7.3.0%; MgO – 3.25%; Na$_2$O – 15.64%, SO$_3$ – 0.4%.

The decomposition temperature of the gas developing agent was studied by differential scanning calorimetry with a synchronous thermal analysis device STA 449 F1 Jupiter® by NETZSCH (Germany).

The study of the process of gas release was carried out on a specially designed and manufactured plant. It was necessary as plants described in the literature [22] make it possible to study the decomposition of the gas developing agent at a maximum temperature of 200 – 250°C. In our case the decomposition temperature is in the range of 400 – 900 °C which requires a drastic change in the design of the plants mentioned above. Figure 1 shows the schematic diagram of such a plant.

A stainless steel capsule (2) having a 20 cm long fitting coming out of the furnace is placed in the muffle furnace with a maximum temperature of up to 1200°C (1). The capsule is installed in a special device ensuring its uniform heating. A heat-resistant silicone hose connected to a U-shaped glass tube (3) mounted on a tripod (4) is attached to the coming out fitting end. The heating rate (20 deg/min) is provided by an automatic voltage regulator (5), the temperature is controlled by a thermocouple (6). Since heating of the capsule is carried out by air, the temperature difference in the furnace and inside the capsule was investigated at the first stage. The thermocouple placed inside the capsule showed that at the temperature range of the muffle furnace 600 – 800 °C the temperature in the capsule was 95 degrees lower; and that was taken into account in the experiments.

Figure 1. Plant for determining the amount of the evolved gas

3. Results and Discussion

3.1. Development of a gas developing agent for low-density foam glass production

One of the main conditions for producing high-quality foam glass with low apparent density and low thermal conductivity without loss of mechanical strength is to obtain a material with a fine-cell uniform structure which is possible only if there is an opportunity to control the foaming process: foaming temperature control by the selection of the gas developing agent and its amount.

It is known [23] that the production of foam with a minimum apparent density is possible only in compliance of the decomposition temperature of the gas developing agent and the softening
temperature of the original glass, which can be provided with both selecting the appropriate gas developing agent and changing the softening temperature of the original glass.

Hence, calcium carbonate $\text{CaCO}_3$ was chosen as the main gas-forming component and sodium nitrate $\text{NaNO}_3$ as an additional gas developing agent which can change the crystal structure of the glass, thereby changing the softening temperature of the latter.

It was found with differential scanning calorimetry (DSC) (Figure 2) that the decomposition temperatures of $\text{CaCO}_3$ and $\text{NaNO}_3$ are 648.3°C and 307.6°C, respectively. At the same time the softening temperature of the glass is 588.2°C, that is, the difference between the softening temperature of the glass and the decomposition temperature of the gas is very significant.

In our opinion it can explain the high apparent density of foam glass when individual substances are used as a gas developing agent. When $\text{NaNO}_3$ is used as a gas developing agent its decomposition occurs much earlier than the softening of the glass, which leads to the loss of gas that cannot be retained in the non-softened glass, and the density of the material is 250 kg/m$^3$. In the case of using $\text{CaCO}_3$ as a gas developing agent, on the contrary, the decomposition of the gas developing agent occurs much later than the softening temperature of the glass. The viscosity of the latter in this case is insufficient to retain the formed gas in the melt and, as a result, the apparent density of the samples is 400 kg/m$^3$.

As shown by figure 2, with the introduction of $\text{NaNO}_3$ into the system softening temperature curve of the original glass shifted and was 644.9°C, which is very close to the decomposition temperature of the main gas developing agent. With the introduction of both gas developing agents into the system, it was no longer possible to separate the endothermic peaks of $\text{CaCO}_3$ decomposition and glass softening, which made it possible to obtain foam with a minimum apparent density.

The process of decomposition of the gas developing agent, namely the volume of the released gas and the kinetics of gas release, plays an important role in the formation of the structure of foam glass during foaming.

The plants described in the literature make it possible to study decomposition of the gas developing agent at a temperature not higher than 200 – 250°C. In our case the decomposition temperature is in
the range of 400 – 900°C which requires a fundamental change in the design of the plants mentioned above.

Table 1 presents data on the change in gas number at different temperatures and component ratios.

| Ratio NaNO₃ : CaCO₃ | Decomposition T (°C) | V (ml/gr) |
|-------------------|----------------------|-----------|
| 1 : 0.20          | 600                  | 79        |
|                   | 650                  | 86        |
|                   | 700                  | 89        |
| 1 : 0.37          | 600                  | 87        |
|                   | 650                  | 93        |
|                   | 700                  | 96        |
| 1 : 0.60          | 600                  | 88        |
|                   | 650                  | 94        |
|                   | 700                  | 97        |
| 1 : 0.80          | 600                  | 90        |
|                   | 650                  | 96        |
|                   | 700                  | 101       |

Therefore a system of gas developing agents consisting of calcium carbonate and sodium nitrate was developed to combine the decomposition temperature of the main gas developing agent and the softening temperature of the glass, which is a necessary condition for obtaining foam with a minimum apparent density.

3.2. Foam production technology
The results obtained were used to determine the main technological parameters of the process of foam glass production

![Figure 3](#)

**Figure 3.** The dependence of the density of the foamed material (ρ) on the ratio of the components of the gas developing agent at a constant concentration of the gas developing agent at a temperature, ° C: 500 (1), 550 (2), 600 (3), 650 (4), 700 (5).
Figure 3 shows the effect of the ratio of the used gas developing agents on the apparent density of the foam at different temperatures. It is found that these dependences have extreme character at all investigated temperatures. The favourable ratio of gas developing agents depends on the temperature. Thus, at a temperature of 500°C, the minimum density is observed at a ratio of NaNO$_3$:CaCO$_3$=100:66 and at a temperature of 700°C, the optimum ratio is 100:35 which provides means for obtaining foam with a density of less than 100 kg/m$^3$.

To determine the optimum amount of the injected gas developing agent to produce foam glass with a minimum apparent density the dependence of the apparent density on the amount of the gas developing agent was studied. As shown by figure 4, obtaining the minimum density depends on the foaming temperature and the amount of the gas developing agent. Within the temperature range of 600 – 700 °C, which is optimal for foaming, the minimum required amount of the gas developing agent is 2%, so in the future when developing a technology for producing foam the concentration of the gas developing agent mixture is 2.2%.

![Graph showing the dependence of the density of the foam (ρ) on the amount of gas developing agent mixture Cgm (NaNO$_3$:CaCO$_3$=100:37) at temperature, °C: 500 (1), 550 (2), 600 (3), 650 (4), 700 (5).](image)

Methods of mathematical modelling were used to identify the dependence of the apparent density of the obtained material on the foaming time at different contents of the gas developing agents studied (figure 5 a, b, c). As shown by figure 5 (b), the minimum density of the samples obtained using NaNO$_3$ gas developing agent was 160 kg/m$^3$, in turn, the use of CaCO$_3$ (figure 5(a)) makes it possible to obtain foam with a density of 190 kg/m$^3$.

The dependence of the apparent density of the foam material on the content of the complex gas developing agent at the ratio of components (NaNO$_3$:CaCO$_3$ = 1:0.37) and the foaming time presented in figure 5(C) makes it possible to determine the optimal foaming time at different temperatures.

Thus, at a temperature of 660°C, a foaming time of 20 minutes and a gas developing agent content of 1.5%, the minimum density of the material was 240 kg/m$^3$, while at a foaming time of 40 minutes – 120 kg/m$^3$. 
As is known [24], the quality of the resulting foam material is significantly influenced by the feedstock, primarily the particle size and composition of the glass. Used waste glass was subjected to crushing in a ball vibratory mill of MV-400 type with the method of dry crushing. The blow was carried out due to the interaction of glass particles with the walls of the working volume and grinding bodies at high-frequency vibrations of the case. Balls made of hard alloy steel were used as grinding bodies.

Based on the data presented in table 2, the optimal time for grinding the powder can be considered as 40 minutes with an average particle size of 60-70 microns after grinding.

With the increase in grinding time, the number of small particles increases, but along with this, energy costs, equipment wear and consequently the cost of the final product increase. For this reason further grinding is impractical and economically unprofitable.

Based on the previously mentioned, the dependence of the density of foam glass on the average size of glass particles (Figure 6) at different crushing times was revealed. So when the powder crushing time is 20 minutes, the average particle size of glass is 80 – 90 microns, and the average density of foam is 300 kg/m$^3$, while when crushing lasts for 40 minutes, the average particle size of glass is 60 – 70 microns, and the density of the finished foam is less than 200 kg/m$^3$.

Figure 5. The dependence of the apparent density of foam ($\rho$) on the content of the gas developing agent $C_{gm}$ (NaNO$_3$:CaCO$_3$ = 1:0.37) and on time ($\tau$) at temperatures, °C – 640(a), 660(b), 680(c).
| Particle size (µm) | Grinding time (min) | 0 (original) | 20 | 40 | 60 |
|-------------------|---------------------|---------------|----|----|----|
|                   | content (%)         |               |    |    |    |
| 120               | 8                   | 7             | 5  | 4  |
| 100               | 14                  | 8             | 6  | 5  |
| 90                | 40                  | 37            | 32 | 32 |
| 75                | 28                  | 38            | 46 | 48 |
| 60                | 10                  | 10            | 11 | 11 |

Thus, in the development of technology of foam production factors affecting the properties of the final material and the dependence of the main technological parameters on these factors were identified. Thanks to that we could develop a technology for producing foam of reduced density.

For the production of thermal insulation material by powder method a technological scheme consisting of two sections is proposed: area for the production of expandable compositions and area for production of foamed concrete blocks.

A continuous method of manufacturing foam glass using a continuously moving tape, which consistently passes the stage of loading, compaction, preheating, foaming, stabilization and cooling is developed. This method makes it possible to produce foam glass with a uniform fine-cell structure (pore size from 300 microns to 1.5 mm) and the shape of the cells mainly oriented perpendicular to the movement of the heat flow. This reduces the coefficient of thermal conductivity by 15 – 20% and increases the mechanical strength of foam glass.

Technological operations of heating, foaming of the prepared composition and annealing (cooling) of finished products are carried out in a two-stage way – in furnaces for foaming and annealing glass melt. The foaming furnace is a continuous furnace operating on electric heaters, the length of which is 14 meters, with the speed of the plate conveyor of 4 meters/hour. The walls of the working space and the arch of the foaming furnace are made of light kaolin plates and mats. This material is characterized by high heat resistance (1,100 – 1,250°C).
The prepared composition is loaded into a slit hopper-dispenser, which evenly distribute the layer of the composition with the set height on a continuously moving conveyor. Continuously moving conveyor in the foaming furnace provides making an endless sheet of foam glass tape with the same porosity, physical and mechanical properties and a given density.

When passing through the foaming furnace the molded layer of the composition passes the preheating stage. The operating temperature in the pre-heat treatment zone is 400 – 650°C. Further, a layer of glass which already started shaping enters the zone of temperature providing a porous structure of glass (foaming) with a maximum rise of foam to 220 mm. The hold-up time of the glass in the foaming furnace is 210 minutes. The temperature in the foaming zone is 760°C. At the exit from the foaming zone, a stabilization zone is provided – a shock cooling of the foamed glass melt at 100 – 110°C in order to increase the viscosity of the glass and stabilize the resulting porous structure.

When leaving the foaming furnace, the operation of separating the foamed glass from the plate conveyor with subsequent transverse sawing of the foam glass tape into blocks is provided. Further, with the help of a shifting device, the blocks enter the annealing furnace of the conveyor type, in which the foam is gradually cooled for 840 – 960 minutes according to the set mode. Annealing of foam glass blocks is a crucial stage which is carried out in order to remove residual internal stresses in the glass. The length of the furnace is 20 meters; the speed of the conveyor is 1.25 meters/hour. The operating temperature in the annealing furnace at the hot end is 650°C, the temperature drop rate is 0.7°C/min, to a temperature of 50°C at the cold end. The design of the furnace is a rail with a built-in mesh conveyor. When shifting the blocks are installed on a mesh conveyor "on the edge", which reduces the total length of the annealing furnace. To ensure a given annealing mode and averaging the temperature in the annealing furnace, forced circulation of the coolant is necessary, which is provided by the installation of circulation systems. After the exit, the finished foam enters the machining to bring the correct geometric shapes, is packed and sent to the warehouse of finished products.

The proposed technological scheme was implemented into production at OOO "Transpolimer", Kosterevo, Vladimir region.

The thermal insulation material is produced in industrial conditions, the main properties of which compared to the currently produced material are presented in table 3.

| Characteristics                  | Developed foam glass | Foam Glass "Foamglass" USA | Foam glass "Gomelsteklo" Belarus | Foam glass "Neoporm" Russia |
|----------------------------------|----------------------|---------------------------|---------------------------------|-----------------------------|
| Apparent density (kg/m³)         | 80 – 150             | 120 – 250                 | 170 – 190                        | 130 – 160                   |
| Thermal conductivity coefficient (W/m·K) | 0.035 – 0.050       | 0.04 – 0.10               | 0.048                           | 0.047 – 0.052               |
| Compression strength (MPa)       | 1.0 – 3.0            | 0.7 – 4.0                 | < 0.7                           | 1 – 2                       |
| Water absorption (% by volume) at most | 1 – 3               | 2                         | 5                               | <1                          |
| Vapour permeability coefficient (mg/(m·h·PA)) | 0.025               | -                         | 0.001                           | -                           |
| Upper temperature operating mode (°C) | 450 – 550           | 450 – 550                 | 450 – 550                        | 490                         |
| Flammability group               | non-combustible      | non-combustible           | non-combustible                  | non-combustible             |
| Operation period (years)         | 50                   | 50                        | 50                              | 50                          |
4. Conclusions
As shown by table 3, the developed material has a lower coefficient of thermal conductivity, higher strength and low density. In addition, it does not emit hydrogen sulphide during operation.

Additionally according to the data of OOO “Transpolimer” the proposed technological process made it possible to reduce production losses by almost 3 times in comparison with similar productions by reducing waste during mechanical processing of the product, and the productivity of this line was 4,600 m³ per year. 1,500 m³ of foam glass produced was used by a number of construction companies in various fields of construction.

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