The use of industrial waste and cullet for building foam glass

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Abstract. There is a huge raw material base for the production of foam glass. The aim of the work was to develop a technology for producing foam glass from cullet and industrial waste. Glass makes about 5% of municipal waste. Calcium carbonate which is the waste of ANP fertilizer production can be used as a foaming agent. The research task was to obtain effective heat-insulating and structural and heat insulating material with the corresponding physical and mechanical characteristics for low-rise and high-rise construction. The analysis of existing approaches to the production of foam glass was carried out in the course of the work, laboratory study of various mixtures composition was held and optimal mixtures of cullet and a foaming agent were proposed. Experiments showed that the density of foam glass made from different kinds of glass differs by up to 15%, which makes it possible to dispense with the expensive operation of sorting cullet.

1. Introduction

One of the rational ways to improve the energy efficiency of buildings under construction and renovation is wider use of heat insulating materials utilizing local resources. Foam glass is among such materials, which require further study and implementation.

At present, high requirements are imposed on heat insulating materials: firstly, to be high-quality heat and water insulators, which maintain their qualities constant for a long time; secondly, they must comply with all sanitary and hygienic standards and be environmentally friendly. Foam glass is one of the materials that meet these requirements. It is environmentally friendly, fireproof and does not emit toxic substances due to its inorganic composition.

The use of foam glass in construction is possible in two variants: as a heat-insulating or structural and heat-insulating material. The use of insulating foam glass with low heat conductivity (within 0.03 ... 0.07 W / m °C) can significantly increase the heat transfer resistance of the walls of the building. Structural and insulating foam glass combines both the heat engineering properties and strength required for wall material (at least 10 kgf / cm²).

The first in the world to mention about foam glass as a building material was academician Kitaygorodsky I.I. at the All-Union Conference on Standardization and Production of New Effective Materials, held in Moscow in 1932. Theoretical foundations of the technology for producing foam glass of various compositions and purposes are most fully considered in the work of Demidovich B.K. [1]. In recent years, there has been considerable interest in the research of foam glass [2]. Still, foam glass has not yet gained popularity in Russia due to the fact that even experienced builders do not know the technology of using foam glass as a heat insulator and few people consider foam glass as a construction material. It should be noted that the introduced technologies of foam glass use are...
focused, as a rule, on heat-insulating material with a low coefficient of heat conductivity. However, it is safe to say that foam glass with an efficient ratio of heat conductivity and strength would also find demand in the market as, for example, a wall material for low-rise constructions.

Large-scale introduction of foam glass in construction requires further research into optimization of compositions and improvement of production technology, taking into account the specifics of local resources.

Relevance of laboratory research work is determined by the need to improve the technology of production of foamed glass of the optimal pore structure using cullet with calcium carbonate as a foaming material which is production waste of Acron PJSC (Veliky Novgorod).

The pore structure of the foam glass is formed in accordance with general laws of foaming in pyroplastic silicate systems, similar to the heat-insulating materials obtained by bulking of silicate melts. However, the foaming mechanisms of aluminosilicate molten cullet with specified pore-forming components require extensive experimental research.

The issues of the relationship between the structure and properties of foamed glass with the chemical composition and characteristics of glass preparation, as well as technological modes of heating and foaming are to be studied.

Providing the required pore structure demands an integrated approach that takes into account the influence of various factors on the formation of foam glass from an aluminosilicate melt. For example, the choice of optimal temperature regimes allows to get a foam glass with a wide range of physical and mechanical properties. The formation of foam glass occurs as a result of the gradual accumulation of gaseous products when heated. The mechanism of foam glass structure formation is described by experimental curves of the foaming process. Experimental data and theory provide scientific explanations of the properties and structure of foam glass at various stages of its making. Control of the thermophysical state of the mixture and the dynamics of its change make it possible to obtain foaming curves.

2. The study of physical and mechanical parameters of raw materials

The structure, composition and properties of foam glass with improved structural properties are directly related to the quality of glass batch preparation, chemical and phase composition of the initial components, heating regime temperatures and foaming, etc. Thus, ensuring the optimal pore structure of the foam glass is a complex task of determining the influence of various factors on the process of forming the properties of foam glass as a material obtained by bulking at high temperatures.

Cullet can be of various origins: window and bottle glass, cathode ray tubes, lamps, etc. Preliminary experimental studies conducted in the laboratory of building materials of "Building Structures" Department of the Novgorod State University named after Yaroslav the Wise, showed the possibility of obtaining foam glass of the required quality from various raw materials. Similar results were obtained by Belokopytova A.S. [3]. The density of foam glass made from different types of glass varies by up to 15%, which eliminates the costly operation of sorting the cullet.

Calcium carbonate (CaCO₃, chalk) taken from Acron PJSC ammonium nitrate phosphate fertilizer waste dump was used as a blowing agent:

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \uparrow \]

where CaO is lime; CO₂ is carbon dioxide.

The study of phase changes of the batch structure was carried out by various methods that allowed solving specific questions posed.

Methods of preparation of cullet to be used as a filler in glass concrete were determined in the laboratory and it was established that the average particle size of cullet should not exceed 1 mm, and the maximum size should be 2 mm.

The analysis of the chemical composition of the used raw materials, performed in the chemical laboratory of PJSC Acron, gave the following results.

Bottle cullet contains the following amount of oxides in %: SiO₂ – 65.2; Al₂O₃ – 10.7; TiO₂ – 0.8; Fe₂O₃ – 1.2; CaO – 6.5; MgO – 0.7; Na₂O – 0.2; K₂O – 14.7; SO₃ – 0.
Chalk contains: SiO₂ – 1.3; Al₂O₃ – 0.7; TiO₂ – 0.1; Fe₂O₃ – 0.1; CaO – 54.7; MgO – 0.3; Na₂O – 0; K₂O – 0; SO₃ – 42.8.

The investigated batch was glass powder with an average specific surface area of \( S \approx 6000 \text{ cm}^2/\text{g} \), which corresponds to a typical technological process of foam glass production.

It was tried to bring in bound water in the form of silica gel into the raw mixture. During thermal decomposition of silica gel, water vapors are released that contribute to more intensive foaming due to the increase in the gas content, a significant decrease in viscosity, surface tension of the melt and make maximum foaming temperature lower, which will reduce the requirements for the raw glass composition.

Based on the analysis of literature [1], the following hypothesis is put forward. To improve the quality of foam glass made from cullet, it is necessary to artificially increase the content of bound water in the system at the stage of mixture preparation, which can be achieved either by hydration and hydrolysis of fine glass powder, or by directly adding an aqueous solution of sodium silicate to the system. During thermal decomposition of silica gel, as it was mentioned above, water vapors are released, which can contribute to more intensive foaming due to an increase in the gas content, a significant decrease in viscosity, melt surface tension and a decrease in the maximum foaming temperature, which obviously reduces the requirements for the composition of the raw glass.

3. Experimental studies of technological regimes

Optimal temperature regime is one of the most important stages in the rational production technology of foam glass, since, depending on the chosen mode, foam glass with a wide range of properties can be obtained. The work of R.V. Gorodova is devoted to the study of temperature conditions of sintering [4].

Laws of granules structure formation during heat treatment were considered in the work. Since foam glass is a heat-insulating material, it is necessary to strive to obtain granules with minimum coefficient of heat conductivity, which is achieved with a decrease in their average density. Strength of granules in this case is not a determining parameter, since during operation the material does not experience significant load, and in addition, strength of foam glass is several times greater than strength of other heat insulation materials of the same heat conductivity or average density.

Average density is controlled by changing the temperature, duration of foaming and humidity of the foaming mixture. Kinetics of granule foaming was studied to select optimal duration of the process.

The results of the experiment show that minimum values of density of the granules lies in the temperature range from 790 to 830 °C with a foaming time of 45–50 minutes.

The results obtained indicate that the heating regimes of the batch with linear increase in temperature at the initial stage and subsequent exposure at a constant temperature close to the sintering temperature can significantly improve the quality of heating, and, accordingly, the quality of the foam glass.

The effect of the moisture content of the initial mixture on the granules foaming is also of interest. It should be noted that optimal foaming temperature range from 790 to 830 °C is characteristic of all mixtures.

The smallest density foam glass – 286 kg / m³ was obtained from a mixture with a moisture content of 14.4% foamed at the temperature of 790 °C; the largest density – 461 kg / m³ was obtained from a mixture with a moisture content of 13.0% foamed at the temperature of 750 °C.

In addition, it should be mentioned that foam glass mixtures with the lowest moisture content are subject to the greatest fluctuations in the average density due to the change in the foaming temperature.

As a result of laboratory experiments, methods for preparing cullet as a filler in glass concrete were identified and it was established that the average size of cullet particles should not exceed 1 mm.

In the case when the glass is ground finely enough, the risk of destruction of glass concrete is significantly reduced.

It was also proved that the interrelation between the glass dispersity and carbon concentration affects on the bulk density of foam glass. Low bulk density of foam glass (160 kg / m³) is obtained from
highly dispersed mixtures; foam glass with a higher bulk density is obtained from low dispersed mixtures. It was also found that the amount of glass dispersion necessary to obtain a sample with a certain density and physical-and-mechanical properties depends on the carbon content in the mixture: in mixtures with 0.25–0.35% carbon content, a finer grinding of glass is necessary, whereas in mixtures, where the content of carbon is lower (0.15 – 0.20%) lower dispersion of the mixture is sufficient.

As a result of laboratory experiments, it was proved that the pretreatment of cullet with a solution of hydrochloric acid makes it possible to obtain reinforced foam glass concrete on its basis.

An important stage of the technology under discussion is bringing in the substances that promote hydrolysis of the glass granules surface.

When silicate glasses with a high SiO₂ content are dissolved in water, alkali metal oxides pass into the solution faster than SiO₂, as a result of which silica gel film forms on the glass surface. Chemical composition of silica gel is nSiO₂•mH₂O. It is inorganic polymer containing silanol groups (-Si-O-Si -) - O-H on the surface. Thus upon hydration and hydrolysis of glass particles, hydroxide groups appear on the surface.

It was concluded that silica gel containing chemically bound water in the batch for obtaining foam glass creates more favorable conditions for foaming. During thermal decomposition of silica gel, water vapors are released, which can contribute to more intensive foaming due to an increase in the gas phase content, a significant decrease in viscosity, melt surface tension and a decrease in the maximum foaming temperature, which obviously reduces the requirements for the composition of raw glass.

The use of aqueous solution of sodium hydroxide makes it possible to moisten and briquette the batch by pressing and also to foam the foam glass without bringing in additional gas forming agents.

Laboratory studies have also shown the possibility of using fly ash from the Novgorod CHP-20 which consists 40–60% of SiO₂ in raw mixture and does not require pre-crushing.

4. Obtaining foam glass samples with specified physical and mechanical parameters

The main way to reduce energy consumption for heating buildings is to increase heat transfer resistance of walling through the use of insulating materials. Since 2000, regulatory requirements for the design heat transfer resistance to walling in Russia have increased by an average of 3.5 times.

The main indicators characterizing physical-technical and operational properties of heat insulation materials are: density, heat conductivity and compressive strength. To be recommended for use as a heat insulating material it is necessary that the indicated parameters of the foam glass lie within the following limits: density – less than 300 kg / m³; compressive strength - not less than 5 kgf / cm²; heat conductivity coefficient – 0.04 ... 0.06 W / m • ° C.

The most important technical characteristic of thermal insulation materials is heat conductivity - the ability of material to transfer heat through its thickness, since the thermal resistance of the building envelope directly depends on it. In terms of quantity it is graded by the thermal conductivity coefficient λ, which shows the amount of heat passing through the sample of material 1 m thick and 1 m² size with temperature difference on opposing surfaces of 1 °C for 1 h. Density of material and its structure (type, size and location of pores) primarily affect thermal conductivity of heat insulation material. In production of insulating foam glass, it is necessary to strive to obtain material with minimum value of the volumetric density with the smallest possible diameter of closed pores.

Foam glass properties depend on the composition of the foaming mixture and foaming regimes.

For research, an unsorted cullet was used, consisting of sheet glass, dark bottle glass and light bottle glass in the ratio of ≈ 1: 1: 1. The blowing agent (calcium carbonate) was taken in the amount of 2% of cullet by weight. Moisture of the mixture was about 15%. The heat treatment process includes heating the foaming batch to the foaming temperature, holding at this temperature for complete foaming and cooling.

According to the results of laboratory studies, it was found out that the volumetric density of foam glass depends on the degree of dispersion of the foaming mixture consisting of crushed glass cullet
and calcium carbonate. So the increase in the specific surface area from 3000 cm² / g to 6000 cm² / g resulted in the decrease in the volumetric density from 225 kg / m³ to 50 kg / m³.

Dependence of volumetric density of foam glass of maximum foaming temperature and the foaming duration (exposure to maximum temperature) are established. It was revealed that with the decrease in the foaming temperature, the process of structure formation proceeds a longer period of time. With a "steep" foaming, the same values of volumetric density of the foam glass can be achieved in a shorter period of time. As the results of the experiment show, minimum values of granules density are in the temperature range from 790 to 830 °C with a foaming time of 45–50 minutes.

The results of laboratory studies allowed us to establish the dependence of compressive strength of the samples on volumetric density. So, in the density range from 150 to 250 kg / cm³ strength of the obtained foam glass samples was from 5 to 15 kgf / cm².

Study of the relationship between the heat conductivity coefficient of foam glass and the volumetric density showed that in the density range from 150 to 250 kg / cm³, the obtained samples of foam glass had heat conductivity range from 0.04 to 0.055 W / m • °C.

According to the results of research carried out as part of this work, obtained foam glass has the following (average) parameters: density – 200 kg / m³; compressive strength – 10 kgf / cm²; heat conductivity coefficient – 0.056 W / m • °C.

Foam glass having these physical and mechanical properties meets the requirements for insulating materials.

To be recommended for use as structural heat insulating material, it is necessary that the specified parameters of the foam glass lie within the following limits: compressive strength – at least 10 kgf / cm²; heat conductivity coefficient – 0.064 ... 0.10 W / m • °C.

Wall blocks made of structural heat-insulating foam glass with strength of 10 kg / cm² can be used as a self-supporting structural heat-insulating material in high-rise residential and industrial construction and wall blocks with strength of about 30 kg / cm² – as bearing structural heat-insulating material in low-rise (up to 3 floors) house building. This makes it possible to dispense with additional structural layers, which significantly cuts the cost (materials and labor) of construction, reduces the wall thickness, while increasing the useful area of the building.

As a result of laboratory experiments foam glass samples were obtained, combining the properties of both structural and insulating materials.

It was found that foam glass samples with average density of 631.8 – 681.2 kg / m³ and compressive strength of 4.6 – 5.6 MPa can be obtained from a batch containing 70% of cullet by way of changing the ratio of calcium carbonate (chalk) and fly ash.

Foam glass samples with average density of 598.5 – 645.2 kg / m³ and compressive strength of 3.4 – 4.7 MPa can be obtained from a batch containing 80% of cullet by way of changing the ratio of calcium carbonate and fly ash. When the blend contains 90% of cullet foam glass samples were obtained with an average density of 576.6 – 603.1 kg / m³ and a compressive strength of 3.3 – 3.6 MPa by changing the ratio of carbonate-calcium and fly ash.

The conditions for grinding the glass mixture components were determined, which made it possible to increase the physico mechanical properties of the foam glass of the formulations developed. It has been established that in order to increase the average density and strength of foamglass, it is advisable to grind cullet in a ball mill. At the same time, the optimal duration of mechanical activation of calcium carbonate was 2–5 minutes, fly ash – 10–15 minutes.

It was also proved the effectiveness of pre-heat treatment of foaming mixtures based on the developed compositions to improve the structural properties of foam glass. Increasing the strength of foamed glass is achieved at the temperature of heat treatment of these mixtures in the range of 550 – 700 °C.

As a result of preliminary heat treatment of a batch containing 70% of cullet the average density of the foam glass is 659.8 – 715.8 kg / m³ and compressive strength of 6.4 – 8.0 MPa. When the content of cullet is 80% the average density of foam glass drops to 634.4 – 684.6 kg / m³ and compressive
strength to 4.9 – 7.2 MPa. When the content of cullet is 90% the average density of foam glass samples reaches 620.4 – 658.7 kg / m³ and compressive strength of 4.7 – 5.3 MPa.

The decrease in the amount of calcium carbonate from 2% to 1.5% led to an increase in density and strength (1.2 – 1.4 times).

In all the samples obtained, the coefficient of heat conductivity met heat insulation requirements.

5. Conclusion
The authors carried out theoretical substantiation of the main directions of scientific work as well as the study of raw materials. Experimental studies of technological regimes were conducted.

The research work held at the Department of Building Structures of the Novgorod State University named after Yaroslav the Wise allowed to obtain samples of heat insulating and structural and heat insulating foam glass that meets the specified physical and mechanical parameters.

The results of the work on this topic (optimal compositions and technological parameters of production) can be handed over for implementation to enterprises engaged in the production of building materials and having the necessary equipment. Such enterprises are plants for the production of ceramic bricks or crockery.

In the future it is planned to study the physical and mechanical properties of foam glass samples. It is necessary to further examine the strength, frost resistance and water absorption of heat insulation and structural and heat insulation foam glass samples.

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