Analysis of Influence of Foaming Mixture Components on Structure and Properties of Foam Glass

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Analysis of Influence of Foaming Mixture Components on Structure and Properties of Foam Glass

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Abstract. It is recommended to use high-quality thermal insulation materials to increase the energy efficiency of buildings. One of the best thermal insulation materials is foam glass - durable, porous material that is resistant to almost any effect of substance. Glass foaming is a complex process depending on the foaming mode and the initial mixture composition. This paper discusses the influence of all components of the mixture – glass powder, foaming agent, enveloping material and water - on the foam glass structure. It was determined that glass powder is the basis of the future material. A foaming agent forms a gas phase in the process of thermal decomposition. This aforementioned gas foams the viscous glass mass. The unreacted residue thus changes a colour of the material. The enveloping agent slows the foaming agent decomposition preventing its premature burning out and, in addition, helps to accelerate the sintering of glass particles. The introduction of water reduces the viscosity of the foaming mixture making it evenly distributed and also promotes the formation of water gas that additionally foams the glass mass. The optimal composition for producing the foam glass with the density of 150 kg/m^3 is defined according to the results of the research.

1. Introduction

1.1. Foam glass - advantages and disadvantages

At present, the problem of ensuring the energy efficiency of new and reconstructed buildings in Russia has become very relevant. One of the directions for solving this problem is the development and production of effective heat-insulating materials, the most promising of which is foam glass – cellular glass with the structure of foam.

Foam glass – durable, ultra-light, moisture-proof material with atmospheric and chemical stability. Foam glass has high thermal insulation properties. Foam glass can be used as a thermal insulation, construction and insulation, soundproof, decorative, floating, electrical insulation material depending on its chemical composition, density and texture. Foam glass is produced in the forms of building blocks and heat insulating fillers – crushed stone and granulate. Foam glass of the world's leading manufacturers have high strength (0.6-1.0 MPa), low density (120-160 kg/m^3), low thermal conductivity (0.04-0.07 W/(m·K)) and low water absorption (≤ 5-6 kg/m^2 after 28 days).

At present, there are examples of obtaining heat insulation foam glass using a variety of raw materials. The most popular raw material nowadays is glass waste [1-5], as well as its mixtures with organic materials [6-8], metallurgical waste [9-11], coal combustion products [12-20], etc. The reasons

that foam glass is still underestimated and not widely used in construction practice are not its operational characteristics, but the price associated with the technology of its production.

Thus, improving the technology of foam glass production using the optimal compositions and techniques has the highest priority. Taking into account the fact that existing foam glass technologies were directed, first of all, to the production of thermal insulation materials, extensive studies were carried out with regard to foam glass with a low coefficient of thermal conductivity. It is very important in this case to ensure the conditions for creating the optimal pore structure of foam glass, which determines the quality of the material synthesized.

1.2. Peculiarities of the foam glass structure formation using various foaming agents

In modern foam glass technology, there are two approaches to the formation of foam glass: the use of oxidation-reduction carbonaceous blowing agents (starch, glycerol, soot, anthracite, graphite, etc.) or neutralization inorganic foaming agents in the form of carbonates, boron and phosphorus oxides. In the first case, it can be obtained the so-called "black" foam glass, in the second - "white".

1.2.1. Neutralization foaming agents. It is a group of foaming agents, whose action is the result of a neutralization reaction. This group is no longer used in industry with a small exception. Some components of glass, especially SiO_2, B_2O_3 and P_2O_5, are the acidic component in the neutralization reaction, and the foaming agent, which is usually an alkaline-earth metal carbonate, is the alkaline component. The gas discharge at the moment when the glass is already sufficiently liquid to form a foam can be expressed with a simple reaction (1), for example, for limestone:

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2 \quad (1)$$

The actual reaction mechanism between glass and calcium carbonate is more complex. In addition to the neutralization reaction, the thermal decomposition of limestone simultaneously takes place, depending not only on the temperature, but also on the partial pressure of carbon dioxide in the foam glass cells. Foam glass in a pure white color is produced using colorless glass. Colored glass can produce foam glass of various colors. However, in the glass manufactured using neutralization foaming agents, the individual cells are uneven in both their size and shape, and many channels associated with each other can be observed with a naked eye. The water absorption of such products is very high, on average about 70% by volume, so this technology is practically not used in modern industry.

1.2.2. Oxidation-reduction foaming agents. At present, almost all foam glass in the world is produced using this technology. The method is based on the reaction by which a certain glass component is reduced by a foaming agent to form gases. The reduction component of the glass is usually SO_3, the reducing foaming agent is carbon or an organic substance containing it. The reaction of the foam glass formation can be represented by the following scheme (2):

$$\text{glass-}SO_3 + 2C \rightarrow \text{glass-}S^{2-} + CO + CO_2 \quad (2)$$

The reaction described this way is literally only a scheme. Regardless of the reaction mechanism between the foaming agent and some components of the foaming mixture, one thing is clear: due to these reactions, the necessary amount of gases is formed at the most favorable moment, when the glass has already sintered and is able to form a glass foam.

Due to the great influence of the carbon dispersion on the porous structure uniformity, a promising foaming agent is carbon, distributed in some inert material, such as solutions of an organic readily decomposable substance, for example, sugar or glycerol producing fine-dispersed carbon during thermal processing. Compared with the use of pure soot, foam glass of better quality is obtained, since carbon is better distributed in the foaming mixture and, therefore, can be used in smaller quantities.

Additionally, it is important to take into consideration that carbon in fine-grained forms is highly inclined to oxidation. Since the use of dense forms or foaming in a furnace with non-oxidizing

atmosphere in real production is difficult, the primary way of preventing premature burnout of carbon is introduction of materials that envelop the carbon particles and prevent its premature oxidation. Thus, the aim of the research is to study the influence of the main components of the foaming mixture – carbon foaming agent, enveloping material and water – on the structure and properties of foam glass. Glycerol $C_3H_5(OH)_3$ was used as carbon foaming agent, and sodium waterglass $Na_2O{\cdot}SiO_2{\cdot}nH_2O$ – as enveloping material.

2. Methods

Production of foam glass was performed by standard powder technology. The colorless (white) glass powder was dried at 120 °C and milled into particles with sizes of up to 420 μm (sieve No. 40). The chemical composition of the glass was detected using the energy dispersive X-ray fluorescence spectrometer ARLQUANT'X and is presented in the Table 1.

Table 1. Chemical composition of white glass, wt. %.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3
72.0	2.40	0.1	9.0	2.0	0.1	14.3	0.2

The foaming mixture was prepared in a separate vessel by mixing the components (waterglass, glycerol, water) in predefined proportions. The prepared raw materials were mixed for 30 minutes in a drum mill. Further, samples in cubical form were made from the resulting batch. The samples had the edge length of 20 mm and a mass of 10 g (volume $8{\cdot}10^{-6}$ m^3, density 1250 kg/m^3). The samples were loaded into furnace for heat treatment according to the Figure 1.

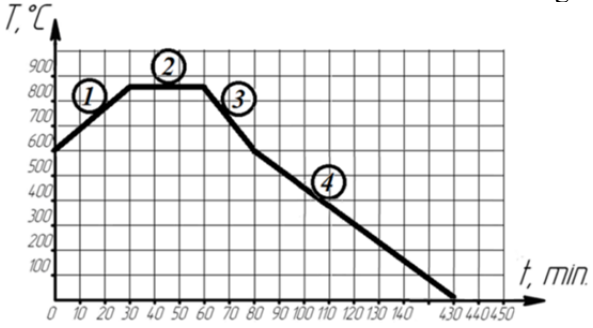

Figure 1. Foam glass synthesis mode: 1 – heating, 2 – foaming, 3 – rapid cooling with structure stabilization, 4 – slow cooling (annealing).

When the air inside the furnace cooled to room temperature, the samples were removed from the furnace and subjected to mechanical treatment (filing) for obtaining the regular shape. Next, the mass of the samples was determined and calculations of the volume and apparent density were made according to formulas (3)-(4).

$$Volume,\ cm^3 : V = a{\cdot}b{\cdot}c \tag{3}$$

$$Apparent\ density,\ kg/m^3 : D_a^T = m/V \cdot 1000 \tag{4}$$

where a – sample length, cm; b – sample width, cm; c – sample height, cm; V – sample volume, cm^3; m – sample mass, g.

Each recorded value is the average result of 5 measurements.

3. Results and discussion

To study the influence of the foaming mixture main components (glycerol and waterglass) on the formation of porous structure, a number of compositions of "A" series was developed, including the raw materials in the following proportions: colorless glass powder – 90, mixture "waterglass + glycerol" – 10. The ratio of components in mixtures is represented in Table 2.

Table 2. Compositions of "A" series.

Component	Component content, wt.%, in composition, #								
	A1	A2	A3	A4	A5	A6	A7	A8	A9
Glycerol	1	2	3	4	5	6	7	8	9
Waterglass	9	8	7	6	5	4	3	2	1

Samples of the "A" series were pre-dried at a temperature of 110 °C and then subjected to heat treatment according to Figure 1 at the temperatures of stage 2 (foaming) 800, 825, 850 °C. The internal structure of the obtained samples is represented in Figure 2, the samples density is shown in the Table 3.

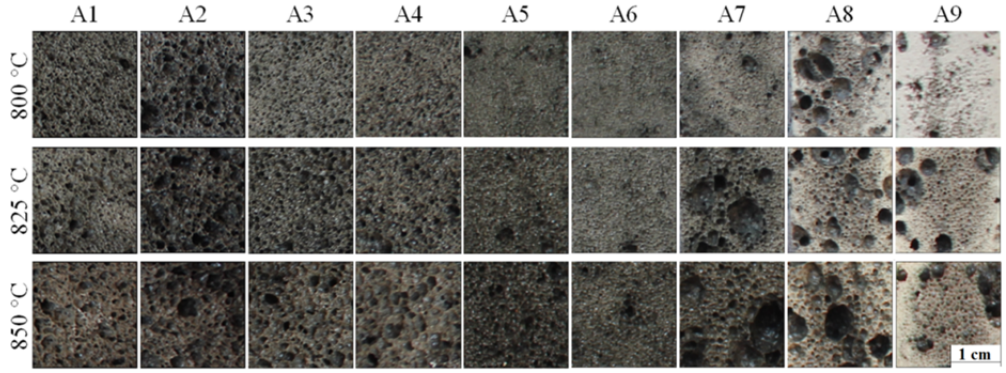

Figure 2. Internal structure of the "A" series samples.

Table 3. The density of samples in the "A" series.

T, °C	Apparent density D_a, kg/m^3								
	A1	A2	A3	A4	A5	A6	A7	A8	A9
800	199	251	246	227	261	327	336	394	526
825	196	234	206	197	205	223	231	287	339
850	208	181	175	147	149	185	188	197	280

It should be noted that in this paper two characteristics were used to describe the samples: the density and the character of the porous structure. This approach is justified by the fact that the density of porous materials is the main parameter that determines other operational properties: total porosity, strength, thermal conductivity, etc. However, as can be seen from Figure 2 and Table 3, the size and distribution of pores at close density values can differ substantially. The following tendency is obvious: with the displacement of the ratio "waterglass: glycerol" towards glycerol, it can be observed, first, a decrease in the uniformity of the porous structure due to the formation of large defective pores, and, second, a change in the color of the material from dark to light.

It is necessary to consider the role of the each batch component during the foaming process to explain these effects. The glass powder is the basis of the future material. At the foaming temperature, the glass is in a highly viscous state, and the process of interaction between the individual particles of the glass powder leads to the formation of a silicate frame responsible for the material strength characteristics.

Glycerol is a foaming agent decomposing in the oxidizing atmosphere of an electric furnace. Due to the decomposition, a spectrum of compounds from carbon dioxide to pure carbon and hydroxyl compounds is formed, creating an overpressure and allows foaming in three directions. Carbon

particles also cause black color of the foam glass. When the glass mass is foamed, the gases form closed pores of predominantly spherical shape.

As mentioned above, the enveloping material, sodium waterglass, was introduced into the batch composition in order to avoid premature burning out of carbon. This component is required to ensure the safety of the carbon component around each glass particle up to a certain temperature range. In addition, due to the proximity of the chemical composition, the waterglass contributes to a more complete contact between the glass powder particles and accelerates the silicate frame formation.

The composition A4, corresponding to the ratio "waterglass : glycerol" = 6 : 4, was selected as the optimum based on the obtained results. Using the mentioned ratio, a number of "B" series compositions were developed, including raw materials in the following ratio: colorless glass powder – 90, mixture "composition A4 + water" – 10. The ratio of the components in the mixture is presented in the Table 4.

Table 4. Compositions of "B" series.

Component	Component content, wt.%, in composition, №				
	B1	B2	B3	B4	B5
Composition A4	9	7	5	3	1
Water	1	3	5	7	9

Samples of the "B" series were heat-treated in accordance with Figure 1 at the temperatures of stage 2 (foaming) of 800, 825, 850 ° C. The internal structure of the obtained samples is represented in Figure 3, the density of the samples is shown in the Table 5.

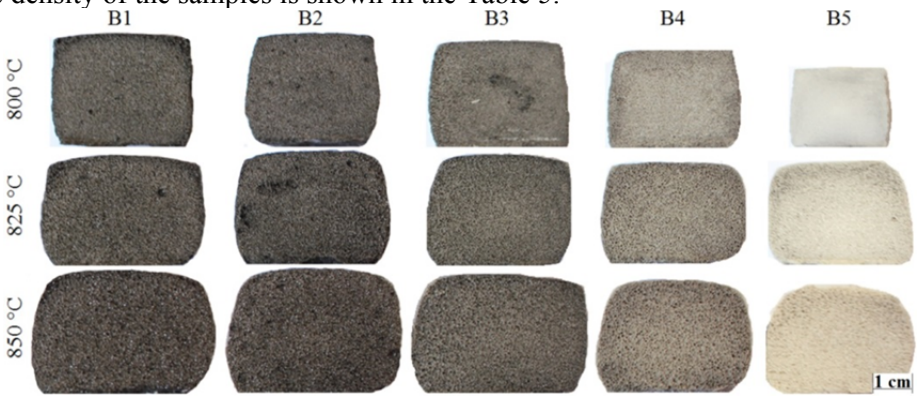

Figure 3. Internal structure of the "B" series samples.

Table 5. The density of samples in the "B" series.

T, °C	Density of series "B" samples D_a, kg/m^3				
	B1	B2	B3	B4	B5
800	218	231	322	327	634
825	181	176	214	249	372
850	150	149	186	188	330

As can be seen in the Figure 3 and the Table 5 above, the introduction of even a small amount of water into the foaming mixture leads to a significant increase in the porous structure uniformity. This is due to two factors. At first, the introduction of water leads to a decrease in the viscosity of the mixture and its better distribution in the batch. Secondly, the excess water in the presence of carbon leads, at the temperature of about 800 °C, to the formation of so-called water gas (H_2 + CO), which

creating an additional volume of gases foaming the glass. The by-product of this reaction is hydrogen sulphide, which is not only distinctly felt by smell when scraping pores, but can also be detected chemically. Color change of the samples in the line B1 → B5 is explained by a decrease in the amount of glycerol and a corresponding decrease in residual carbon on the pore surface. Based on the data in Table 5, the composition B2, corresponding to the ratio "composition A4 : water" = 7:3, was chosen as the optimum. Using this ratio, it is possible to obtain a uniform porous structure with the pore size of 300 μm.

4. Conclusion

Foaming of glass is a complex physical-chemical process, influenced both by the conditions of foaming and the composition and ratio of the batch components. This research has allowed to determine a role of each component on formation of porous structure. Glass powder is the basis of the future material. Glycerol forms a gas phase in the process of thermal decomposition which foamsthe viscous glass mass. The unreacted carbon residue provides a dark color of the material. The waterglass slows the glycerol decomposition, preventing its premature burning out, and, in addition, helps to accelerate the sintering of glass particles. The introduction of water reduces the viscosity of the foaming mixture, making it evenly distributed, and also promotes the formation of a water gas that additionally foams the glass mass. According to the results of the research, the optimal composition of the batch for the foam glass production was formulated, wt. %: glass powder – 90; glycerol – 4; waterglass – 3; water – 3.

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