UTILIZATION OF WASTES

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PRODUCTION OF FOAM GLASS WITH GRANITE SIFTINGS FROM THE MIKASHEVICHI DEPOSIT

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The possibility of using granite siftings from the Mikashevichi Deposit in the Republic of Belarus for production of porous heat-insulating materials was investigated. The initial glasses were synthesized with from 50 to 70% (by weight) granitoids and additional incorporation of quartz sand, chalk, and soda. The region of compositions with the necessary viscosity at foaming temperatures of 800 and 830°C was determined. Foam glass with a bulk density of 180 – 190 kg/m^3, compressive strength of 0.72 – 0.78 MPa, and heat conduction of 0.091 W/(m · K) was fabricated with these compositions. The possibility of manufacturing foam glass by adding up to 60% of inexpensive natural raw material to the batch was demonstrated.

The market for heat-insulating materials is now practically limited to four types: foam plastic (primarily polystyrene foam), gas concrete, mineral wool, and foam glass.

The use of foam plastics in construction not only causes serious problems related to the high fire hazard, environmental toxicity, and adhesive incompatibility with cement and ceramic structures, but also and especially due to the fact that safety structures will not ensure the required heat resistance after 7 – 10 years [1, 2].

Mineral wool articles create important environmental problems during production and have yet another important drawback — a short lifetime, especially in a humid atmosphere.

Gas concrete, widely used in construction, is the most reliable and lasting, but it also has some drawbacks such as low strength and moisture and cold resistance.

One of the most promising heat-insulating materials is foam glass, which has a number of advantages over other heat-insulating materials: it is durable, incombustible, impermeable to moisture and steam, chemically stable, and is characterized by the stability of the physical characteristics in time and low density, is environmentally safe, and is not subject to degradation [3].

In the mid-1950s, there were important process difficulties in fabricating quality industrial foam glass. To solve them, Gomel'sk Glass Works was selected in the USSR as the enterprise for introducing the latest scientific advances in foam glass production. A science and technology school on foam glass production problems was created in Belorussia. The well-known Belorussian scientist, Dr. B. K. Demidovich, who made important efforts to optimize chemical and physical processes in foam glass production, headed the school [4, 5]. Sector scientific sections were involved in solving these problems. This became one of the main factors that allowed such unique production of foam glass in Belarus to survive in the 1990s. At the end of the 20th century, Germany, the Czech Republic, and Poland lost their own production. At present, there are Pittsburgh-Corning foam glass works in Germany and the Czech Republic; Pittsburg-Corning is the largest manufacturer of foam glass in the world.

In most cases, foam glass production is based on the use of bottle (most common), container, or sheet glass cullet. Table 1 reports the compositions of container glass suitable for manufacturing foam glass [6].

The generalized compositions of glasses for production of foam glass can thus be represented as (%): 67 – 72 SiO_2, 1 – 6 Al_2O_3, 7 – 11 CaO, 1 – 7 MgO, 14 – 15 Na_2O.[2]

However, cullet is used to a significant degree in basic production as reusable, so that supplying foam glass shops with cullet significantly limits the production volumes. In organizing high-capacity foam glass production, the glass melt is cooked in special bath furnaces followed by granulation.

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[2] Here and below: mass content.

TABLE 1

Country	Mass content, %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	MnO
USA	71.36	0.79	0.12	8.89	0.32	15.38	0.62	0.51	–
Holland	70.92	2.26	0.27	11.41	1.50	12.78	1.04	–	–
Scotland	70.18	2.59	1.25	9.30	0.86	14.07	0.68	0.26	0.13
France	70.40	1.80	–	9.60	1.20	15.00	0.20	–	–
Japan	73.30	2.11	0.10	7.43	0.48	17.50	0.82	–	–
Czech Republic	73.80	0.27	0.03	4.41	3.10	18.06	–	0.40	0.77
Poland	72.75	1.38	0.06	8.75	0.24	14.35	1.72	0.55	–
Hungary	72.23	2.17	0.30	5.58	2.13	16.15	1.00	0.45	–
	73.41	1.79	0.52	7.23	2.31	14.07	0.38	–	0.03
	71.47	1.39	0.06	7.50	4.36	14.07	0.30	–	–
	69.80	2.72	0.68	6.77	3.37	14.07	–	0.35	0.20
Yugoslavia	70.01	1.99	0.86	7.38	3.23	14.06	0.43	–	0.10
Russia	67.15	6.28	2.89	7.62	0.63	13.95	1.03	–	–
Germany	69.90	1.15	1.29	10.47	1.04	15.01	0.37	0.53	–
Belarus	72.07	2.05	0.42	6.60	4.00	14.86	–	–	–

For this reason, there was such a furnace for cooking glass and obtaining glass granulate to supply the raw material for operation of the foam glass shop at Gomel' Glass Works. Traditional glass production materials were used as the raw material.

Since the granulate obtained was more expensive than cullet, the question of using cheaper raw materials in production of granulate always arose. One way of answering this question was to obtain initial glass granulate from cheap natural raw material or industrial wastes. The promise of using sludge from Achinsk Alumina Combine and other associated wastes was demonstrated in [7]. The authors proposed a batch composition containing 25% nepheline sludge, 55% sand, and 20% soda for production of heat-insulating material with closed pores and a uniform structure. A feature of nepheline sludge is a significant CaO content (up to 53%), which gives glass high chemical stability and is simultaneously a good flux.

RF Patent No. 21292397 proposes a method of obtaining porous glass materials from zinc production slags. The invention concerns the area of processing zinc production slags into porous heat-insulating materials for construction with associated production of zinc vapors. The method of obtaining porous glass materials from the slags consists of the following. Up to 3% carbon is added to slag of the composition (%): 42.0 – 47.0 SiO_2, 17.0 – 20.0 Al_2O_3, 6.0 – 8.0 Fe_2O_3, 24.0 – 30.0 CaO, 4.0 – 6.0 MgO, 2.0 – 3.0 ZnO, 1.0 – 1.8 Na_2O. Melting is conducted in a reducing medium, and the melt is cooled by pouring in water. Glass material with low thermal conduction is obtained with this method, and this allows using it as heat-insulating material, but such material contains hydrogen sulfide, which worsens its heat-insulating properties.

A method of obtaining porous glass materials from nonmetalliferous raw material is described in RF Patent No. 221181. The technical result of the invention is expansion of the range of foamed compositions from melts of nonmetalliferous raw material and fabrication of porous glass materials with a bulk density of 30 – 100 kg/m^3.

The use of natural raw materials for production of foam glass is of great interest. The use of readily sintering rocks with a high content of alkalis — trachyte, syenite, nepheline, obsidian, volcanic tuff, etc., is currently being widely studied. A composition of production of foam glass containing nepheline syenite, volcanic glass, and container glass cullet in the following ratio of components (%), is proposed in RF Patent No. 2164898: 5 – 15 nepheline syenite, 45 – 55 container glass cullet, 7 – 9 sodium oxide hydrate, remainder — volcanic glass. Addition of nepheline syenite to the batch complicates the composition and increases the thermal stability of the glass due to aluminum oxide. A heat-insulating material is obtained — foam glass with improved properties (structure and density).

Use of compositions with different ratios of tripoli and soluble sodium silicate is proposed in [8]. The proportion of tripoli is 25, 37.5, and 50%.

To reduce the volume mass and foaming temperature of foam glass, RF patent No. 1821452 reports the following batch composition (%): 99.2 – 99.5 zeolite-containing tuff, 0.5 – 0.8 silicon carbide. Tuff contains calcites as impurities, and in decomposing, they yield calcium oxide, a strong flux that reduces the melting point of the batch. CaO also decreases the viscosity of the aluminosilicate melt, which allows manufacturing light foam glass since the ability of the melt films to stretch increases. The pore structure of foam glass becomes more developed and the volume mass decreases. Foam glass with a bulk mass of 190 – 280 kg/m^3 and foaming temperature of 1115°C was obtained in this way.

Examples of production of foam glass based on technogenic products, concentration "tails" and sludges, are cited in [9, 10].

We selected so-called granite siftings (more precisely, a mixture of granitoids) — wastes from production of crushed paving stone from Mikashevichi Granit RUPP (Belarus) — as the feedstock for production of glass granulate. It is especially important that the granite siftings of defined fractional composition can be supplied by Granit Co.; for example, the fraction with a grain size less than 1 mm, so that no additional equipment is required for preparing this raw material for addition to the batch.

The initial glass for production of foam glass should have sufficiently constant chemical composition and a minimal tendency to crystallize in the region of the foaming temperatures. The analysis of the data on the chemical composition of different samples of granite siftings showed that it is within the following limits (%): 60.30 – 63.40 SiO_2, 15.20 – 15.25 Al_2O_3, 4.00 – 4.30 CaO, 2.75 – 3.00 MgO, 2.45 – 3.40 Na_2O, 3.40 – 4.40 K_2O, 5.80 – 8.60 (Fe_2O_3 + FeO), 0.19 MnO, 0.90 TiO_2, i.e. the variations in the oxide content are comparatively small.

The process of formation of granite siftings itself ensures additional averaging of their composition due to repeated intermediate crushing of the rock. As a result of the comparative analysis of the content of basic components in the granite siftings and container glass cullet composition, we found that the composition of initial glass required for foam glass can be ensured by insignificant charge adjustment with quartz sand, chalk, and soda. For this reason, the experimental glasses were synthesized with a content of an important quantity of granite siftings in the batch — from 50 to 70% (Fig. 1). All of the glasses were melted at 1400 – 1420°C in a gas furnace. The glass melts were granulated by pouring in water.

The viscosity characteristics or temperature interval of the pyroplastic state are especially important for foaming processes in production of foam glass; for this reason, the temperature curves of the viscosity were calculated and plotted for the synthesized glasses based on their chemical composition. The calculation was performed with the Okhotin method with correction for the iron oxide content according to the Gelhoff and Thomas method.

According to the calculations, for industrial bottle glass, the logarithm of the viscosity at optimum foaming temperatures of 800 – 830°C is 4.0 – 5.5. The experimental glasses have calculated values of the viscosity logarithm from 3.1 to 6.0 at 800°C and from 2.6 to 5.7 at 830°C. Such compositions are characterized by an initial softening point of 570 – 580°C and the presence of a weak exothermic effect on the DTA curves in the 870 – 880°C interval, i.e., the crystallization temperatures are much higher than the usual foaming temperatures (800 – 830°C) and crystallization of the glasses is not observed in the foaming zone.

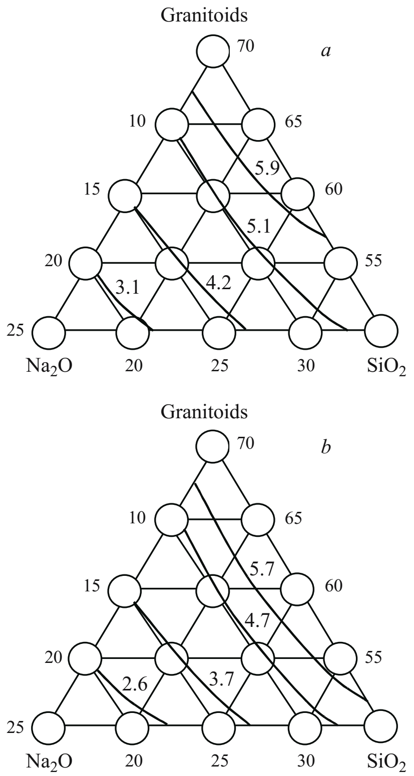

Fig. 1. Region of compositions of the investigated glasses and isocoms of the calculated viscosity at temperatures of 800°C (*a*) and 830°C (*b*). CaO content: 10%.

The calculations of the viscosity characteristics and crystallization properties thus confirm the possibility of using a number of compositions of these glasses for production of foam glass. Glasses with a viscosity logarithm within the limits of 4.0 – 5.5 at temperatures of 800 – 830°C were also used for foam glass production.

Ground coal (anthracite) was used in the amount of 1.7 – 2.0% as the foaming agent. The foaming mixture was prepared first by combined grinding of the glass granulate and coal to obtain a specific surface area of the powder of 5000 – 6000 cm^2/g.

Foaming of the synthesized glasses was investigated with the special setup shown in Fig. 2.

The foaming mixture was placed in a heat-resistant steel container, heated to the foaming temperature at the rate of 5 – 8 K/min, and held at this temperature until the foaming process ended. The mixture was then rapidly cooled to 600°C to stabilize the structure, annealed for 30 min, and then slowly cooled together with the furnace. The foaming process was monitored with a special optical instrument based on the rise height of the foamed glass melt. The duration of the process without final cooling was 3 h.

The curves of foaming of glasses with a different granitoid content but close values of the viscosity characteristics are shown in Fig. 3.

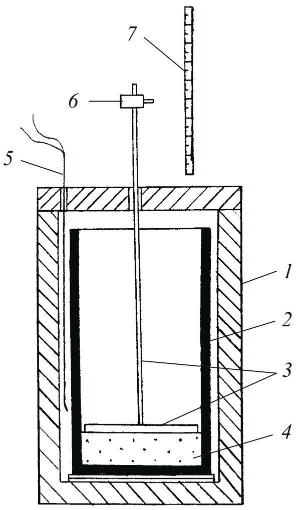

Fig. 2. Diagram of the glass-foaming unit: *1*) furnace; *2*) stainless steel cylinder; *3*) lid with rod connected to the optical instrument; *4*) initial mixture; *5*) thermocouple; *6*) optical instrument for measuring the height of the foamed mass; *7*) reference scale.

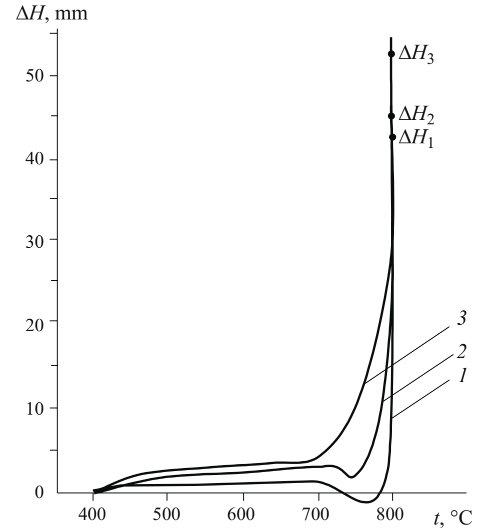

Fig. 3. Glass foaming curves at the maximum temperature of 800°C for compositions containing 50% (*1*), 55% (*2*), and 60% (*3*) granitoids.

The foaming capacity of all three compositions was assessed with the foaming factor, calculated with the equation:

$$K_{\mathrm{f}} = \frac{\Delta H + H_0}{H_0},$$

where K_{f} is the foaming factor; ΔH is the increase in the layer height as foaming ended, mm; H_0 is the initial powder layer height (10 mm).

For glasses with 50, 55, and 60% granitoids in the batch, K_{f} was 5.2, 5.5, and 6.2. At a 60% granitoid content in the glass, the initial foaming stage is observed at a lower temperature, but the foaming factor has the maximum value. It was found that all of the mixtures investigated foamed satisfactorily and formed a uniform pore structure.

The bulk density, thermal conduction, and mechanical compressive strength were eased for all of the samples of foam glass and their values varied within the following limits.

Bulk density, kg/m^3	180 – 190
Compressive strength, MPa	0.72 – 0.78
Heat conduction, W/(m · K), at:	
25°C	0.091
125°C	0.115

These data are in total agreement with the requirements of RB State Standard No. 1322–2002 for foam glass heat-insulating units.

Foam glass can thus be manufactured from granite siftings (granitoids) — wastes from crushed paving stone production from Mikashevichi Granit RUPP — by adding up to 60% cheap natural raw material to the glass batch.

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