ISSN 1087-6596, Glass Physics and Chemistry, 2015, Vol. 41, No. 2, pp. 157–162. © Pleiades Publishing, Ltd., 2015.
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The Scientific and Technological Aspects of Foam Glass Production[1]

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Received December 10, 2014

Abstract—Cellular silicate glass and foam glass-ceramic materials are of considerable interest from scientific and practical perspectives due to their unique performance properties. It is shown that the previous powder technology was based on the sulfate mechanism of gas formation which had inherent disadvantages. Reasons are given for an opportunity to use quite a different, i.e., hydrated, mechanism of gas formation. The data concerning the peculiarities of the obtained cellular material are given. The peculiarities of hydrated technology are discussed.

Keywords: foam glass, foam glass-ceramic material, sulfate and hydrated mechanisms of gas formation, low-temperature glass phase synthesis, silicate binding properties, technology

DOI: 10.1134/S1087659615020133

INTRODUCTION

Cellular silicate glass, or foam glass, is famous for its heat-insulating properties. However, the unique nature of this material is provided by the composition of properties that none of the other known heat insulators have: complete incombustibility, high strength, and absence of corrosion and destruction over time, in addition to its low conductivity and density.

Unfortunately, there is no industrial production of foam glass in Russia at the moment, although the material was produced at several factories until the beginning of the 1990s, and deep investigations of this technology were carried out [1, 2]. During that period, specially melted sulfate glass was mainly used to produce foam glass, which considerably increased the cost of finished products. The process of gas formation was based on the process of recovery of sulfur(IV) contained in glass and the addition of carbon to glass, usually at the grinding stage. The above-mentioned monograph by B.K. Demidovich [1] provides mainly the results of research dealing with such glass. Using the thermodynamic calculations, the author argues that the reaction of Na_2SO_4 reduction by solid carbon in silicate glass in water vapor atmosphere is as follows:

$$Na_2SO_4 + 2C + SiO_2 + H_2O = Na_2SiO_3 + 2CO_2 + H_2S. \quad (1)$$

It should be noted that, in accordance with the calculations given by B.K. Demidovich, in the event of the absence or the presence of a small volume of water vapors, the formation of sulfides is the most probable way to recover sulfates

$$Na_2SO_4 + 2C = Na_2S + 2CO_2. \quad (2)$$

The author adheres to a similar opinion [3], giving the following scheme,

$$\text{glass}SO_3 + 2C \rightarrow \text{glass}S_2^- + CO + CO_2, \quad (3)$$

where "glass SO_3" is understood by the author as a glass option containing sulfur (VI), which corresponds to SO_3 oxide, and "glass S_2^-" is understood as the glass option in the event when sulfur included in glass is recovered to sulfide.

In all these cases, it is particularly important that oxygenized sulfur S^{+6}, the amount of which is regulated in ordinary silicate glass without creating any problems for consumers, is transformed into recovered sulfur S^{-2} in the event when foam glass is obtained. In this case, the latter is present in the structure of the finished material or in gaseous form, i.e., in hydrogen sulfide, or in the solid phase, i.e., sulfide. Moreover, when interacting with water vapors, which are always contained in the air, sulfides are subjected to a hydrolysis reaction in which the same hydrogen sulfide is emitted in the air.

In addition to the inevitable involvement of sulfur compounds(VI) in the process of gas formation according to the above-described scheme, the traditional technology also has a significant disadvantage from the economic point of view. In fact, the production of special glass in glass-melting furnaces at temperatures of more than 1500°C to use it as raw material requires high energy consumption, even though there is additional cullet charging.

[1] Published according to the proceedings of the conference "Glass: Science and Practice," which was held in St. Petersburg on November 6–8, 2013.

The possibility to reduce energy consumption for the preparation of raw glass is discussed in [4], where the potential use of amorphous silica as silicate raw material is described, and it is also noted that rocks are used as raw silicate materials containing amorphous silicon oxide of more than 60 wt %, which makes it possible to omit the glass melting stage [5]. However, in our view, such a solution does not allow one to avoid the main disadvantages of the present technology, i.e., the preparation of special raw glass and the presence of sulfides in the finished product, since it is still proposed to process quenched cullet obtained using the low-temperature method into glass according to the classical powder method.

Nonetheless, we know not only of low-temperature glass synthesis options but also of gas formation during glass melting not only based on sulfates and carbonates, but also based on hydroxides. "Kanazit" glass melting is an example of this technology, when low-temperature glass melting is based on the reaction of silicate- and glass formation from amorphous silica and sodium hydroxide [6].

It should be noted that the temperature interval for melting glass from amorphous silica and sodium hydroxide (720–850°C) actually coincides with the temperature interval of foam glass synthesis, i.e., with such temperatures when sodium-calcium silicate glass is in the pyroplastic state and is capable of plastic deformation, but, at the same time, glass viscosity is not sufficient for the free discharge of gases from fluid glass. This peculiarity of silicate glass synthesis was used by us to combine glass synthesis processes with glass foaming; however, gases formed during synthesis, which are mainly water vapors, simultaneously foam the composition and form gas-filled structures [7]. The process of silicate formation also continues outside the temperature interval, which is characteristic of the thermoplastic state of the substance, and requires the additional heat treatment of the obtained material; however, that is another task that is implemented by selecting the operational mode. However, the significant amount of emitted water vapors and the need for high heat flow density to remove the water allows the direct solution of the task to obtain silicate cellular materials only for granulated material. In addition, the problem of using unsorted cullet (as a cheap material and, at the same time, one that requires secondary use) is not solved in the above-described solution in terms of ecology.

The issue on the possibility of obtaining modular foam-glass objects based on hydrated gas formation is more complicated, which can be solved not only in theoretical terms but also at the level of industrial production. For this purpose, it is sufficient to use the process of silicate- and glass formation according to the hydrated mechanism in the intergranular space of silicate glass powder particles rather than throughout the work piece. In this case, the chemical and even disperse composition of glass powder have an insignificant impact on the properties of the obtained product. The experience of the successful operation of the factory producing foam glass plates according to the first option of this technology has shown a high level of consistency and the economic feasibility of the proposed technical solutions [8, 9].

EXPERIMENTAL PROCEDURE

The thermogravimetric analysis was carried out on NETZSCH equipment. A high-resolution scanning electron microscope was used to study the structure of the materials. The study of the phase composition was carried out on an XRD-7000 X-ray diffractometer produced by the Japan firm Shimadzu.

DISCUSSION OF RESULTS

The issue on the creation of the relevant compositions to combine the processes of gas emission and glass formation can be solved in different ways; two of them are of primary importance in practical terms. First, it is possible to create polysilicic acids on the surface of dispersive glass by means of the ion-exchange modification of the surface according to the $Na^+ \rightleftarrows H^+$ scheme (implemented as a technical solution [10]). Second, amorphous silicon oxide of natural origin can be used to achieve the set result, such as tripoli, diatomites, and other rocks similar to the structure, as described earlier [11] (implemented as a technical solution [12]). The addition of finished glass powder to glass-forming composition does not materially change the processes and makes it possible to consider the additional glass powder as an inert aggregate.

Based on the knowledge of silicate glass as polymer compounds [13], it can be assumed that real hydrated polysilicates consist of a mixture of polymers with a varying chain length. However, the thermal dehydration of different compounds takes place at different temperatures; therefore, one may suggest that the removal of water during the heating of a polysilicate mixture will be carried out in a rather wide temperature interval. This can be used for the foaming of composition at temperatures when water vapors are still emitted, but the material is already in the pyroplastic state, i.e., at 650–780°C [14]. Indeed, the thermogravimetric data confirm the emission of water vapors from the composition of amorphous silicon oxide and sodium hydroxide up to a temperature of 850°C (Fig. 1). The sample loses 0.09 ± 0.01 wt % in the temperature interval from 700 to 850°C, i.e., in the temperature range of thermoplasticity of silicate sodium-calcium glass.

Such a change of weight is sufficient for the formation of the volume of gas that could foam the composition to the level of density corresponding to the density of foam glass materials. It is not difficult to calculate the density of the obtained cellular material, if we

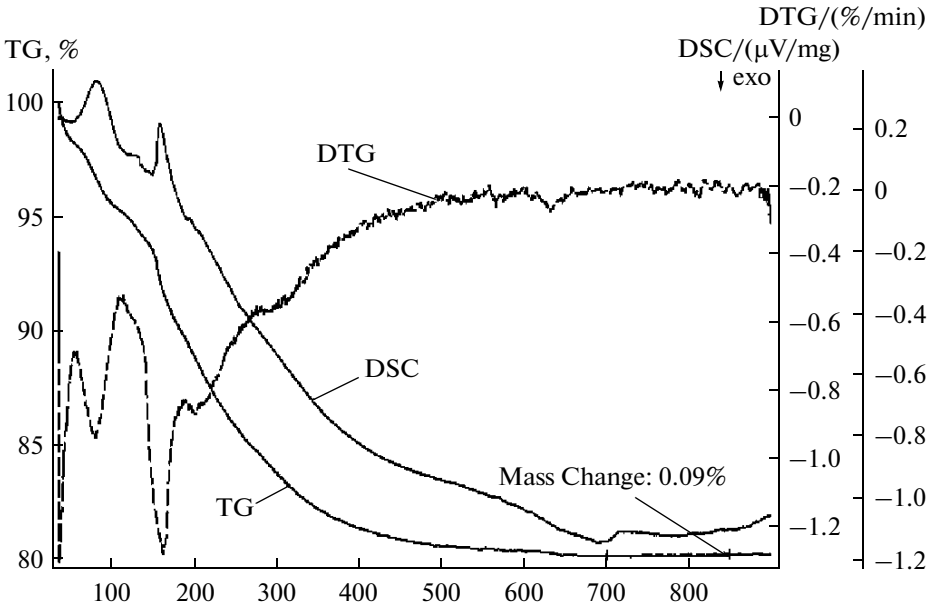

Fig. 1. Thermogravimetric analysis of the mixture of silicagel and sodium hydroxide water solution.

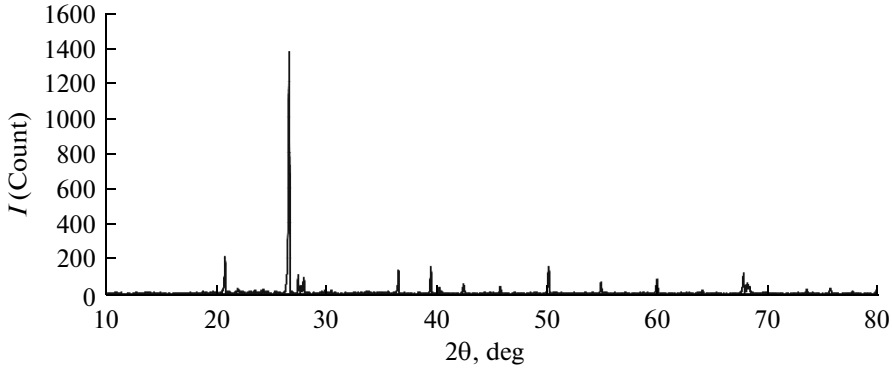

Fig. 2. X-ray phase analysis of a sample of synthesized foam silicate material.

assume that water vapors behave as an ideal gas. Let us assume that 100 g of raw composition are extracted in the thermoplastic state of water with a weight of 0.09 g, as defined experimentally above. The volume of vapors of this amount of water at 740°C and normal atmospheric pressure will be 0.416 L. If we neglect the volume of solid substance and assume that the entire generated gas has remained inside the composition, then the density of the obtained cellular material will be 240 kg/m^3.

The experiment shows that, in practice, the density of the material obtained by this method is 420–480 kg/m^3. The higher value of density, compared to the theoretical one, can be explained by the diffusion of the portion of water vapors from the material; nonetheless, silicate composition foaming may possibly take place when using only water vapors as a gas-forming agent.

By its chemical composition, the initial sample is actually a hydrated sodium polysilicate, and, in terms of glass processing, it represents a mixture for low-temperature glass melting.

As a result, there is an opportunity to create foam glass materials on a quite new chemical and technological basis, when the process of glass synthesis followed by the emission of water vapors is used for gas formation. The high silicate module of composition suggests that there is high resistance both to the alkali-silicate interaction in case of the use of the obtained material in compositions with Portland cement and to silicate decomposition in water environments. The high content of silicon oxide in the obtained material results in the formation of the α-quartz phase in it, which is confirmed by the X-ray phase analysis data (Fig. 2).

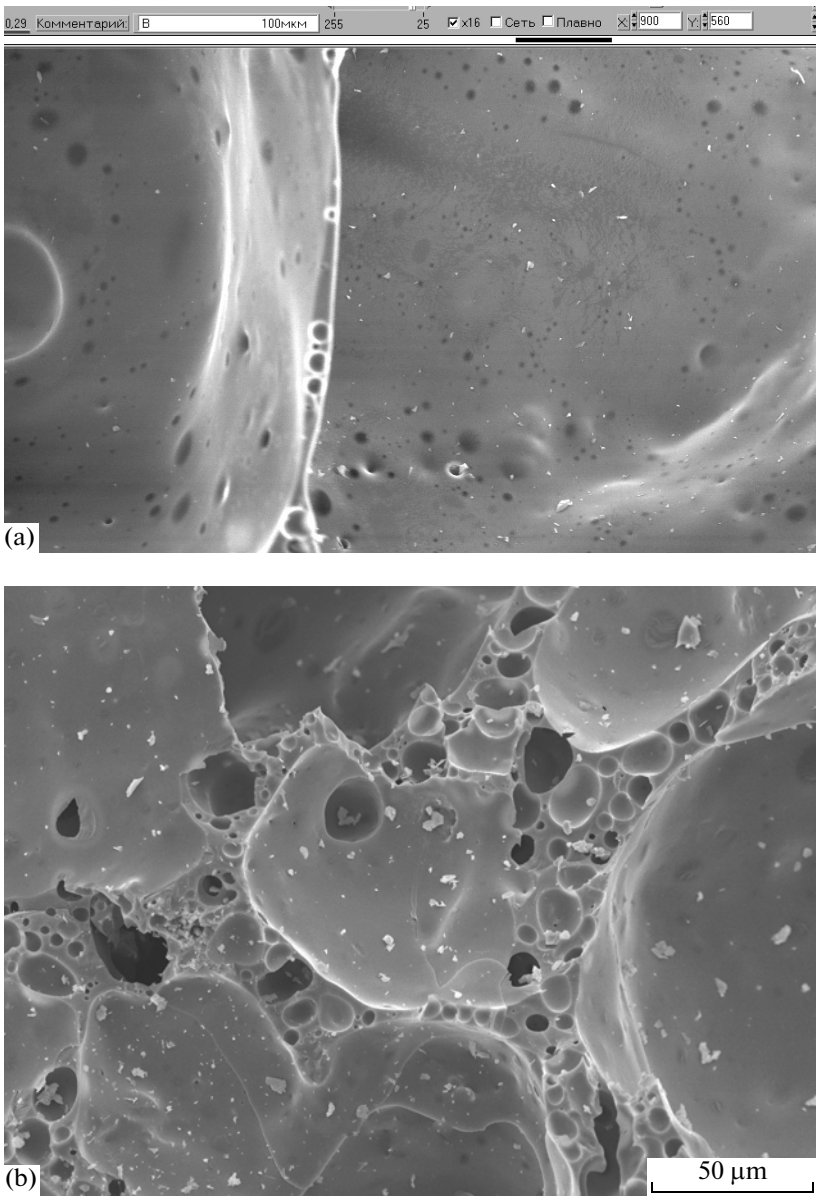

Fig. 3a. SEM photographs of a sample of foam glass obtained according to sulfate-powder technology (a) and according to hydrated technology (b).

Fig. 3b. Dependence of composition strength from time in case of exposure at 80°C. Composition formulation 20 wt% of hydrated sodium polysilicate and dispersive container glass (fractions < 100 microns).

The main peaks on the X-ray diagram of the sample correspond to SiO_2 substance (quartz mineral, *P*3221 spatial group from ICDD PDF-4+ 2012 database).

Due to a change of the mechanism of gas formation during the production of foam glass, the structure of the obtained material also changes. Figure 3 presents the scanning electron microscopy photographs of foam glass obtained according to the standard powder (sulfite) technology, and those of foam glass obtained according to the hydrated method. The bulkheads of foam glass obtained according to the standard technology are characterized by low porosity. This is in line with the knowledge of the formation of the structure of finished material from coked mass from the centers of gas formation, i.e., carbon particles. The pyroplastic mass is extended in this case, depending on the amount of carbon in the composition.

The picture is different for bulkheads in the material obtained according to the hydrated technology. In this case, bulkheads are porous formations. It is obvious that the process of gas formation in the given case takes place throughout the material, since the bound water is completely emitted.

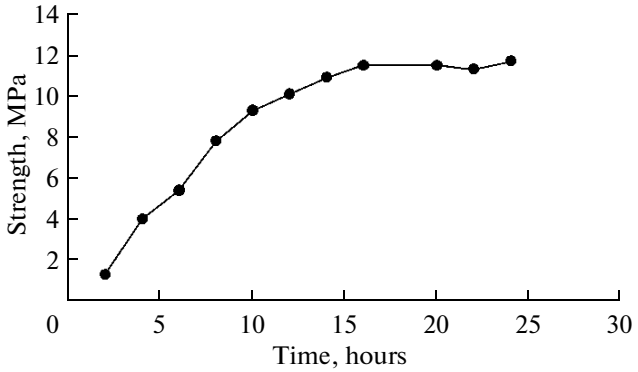

Fig. 4. Dependence of composition strength from time in case of exposure at 80°C. Composition formulation 20 wt % of hydrated sodium polysilicate and dispersive container glass (fractions < 100 microns)

Using the hydrated mechanism has made it possible to solve the problem of applying unsorted silicate cullet as a raw material to produce foam glass materials. Indeed, if the process of gas formation in the proposed technical solution occurs based on glass synthesis, then the composition can be filled with a material that is inert toward the primary reaction of gas formation, for instance, with unsorted glass. In this case, the composition and properties of glass play an insignificant role with respect to the process of gas formation, and the transition into the pyroplastic state at operating process temperatures of 700–850°C is the only requirement for this filling.

On the other hand, hydrated sodium polysilicate which is the basis for the synthesis of new glass according to the hydrated technology is prone to sol-gel transitions, in particular when the silicate module is high. This allows one to obtain binding compositions based on hydrated sodium polysilicate and dispersive sodium-calcium silicate glass. Thus, Fig. 4 shows the dependence of the strength of composition on hydrated sodium polysilicate and dispersive container glass. Strength enhancement is stabilized in the interval from 10 to 12 MPa, which is sufficient both for technological process stages of raw composition and for its transportation.

It is important to note that hydrated sodium polysilicate included in composition retains the capability for gas formation, which can be concluded from the results of scanning electron microscopy (Fig. 5).

The photograph of the initial composite material (Fig. 5a) shows the particles of dispersive glass, which are covered by the layer of the bond from hydrated sodium polysilicate. We can see the shapes of glass particles on the photo of the material after heat treatment (Fig. 5b) under the layer of the bond that initiates foaming. It is evident that dispersive glass in the given case functions as a filler and does not participate in the process of gas formation.

In practice, the proposed approach to the production of foam glass products, based on the hydrated mechanism of gas formation, did not only allow one to suggest a number of new products with improved consumer performance and high economic indicators but also to develop the industrial manufacturing of foam glass materials. Its further improvement allowed the transition to a separate manufacturing of raw materials to produce foam glass and foam glass materials themselves, which was also suggested before [15], but the practical opportunity appeared only after the validation of the new mechanism of gas formation.

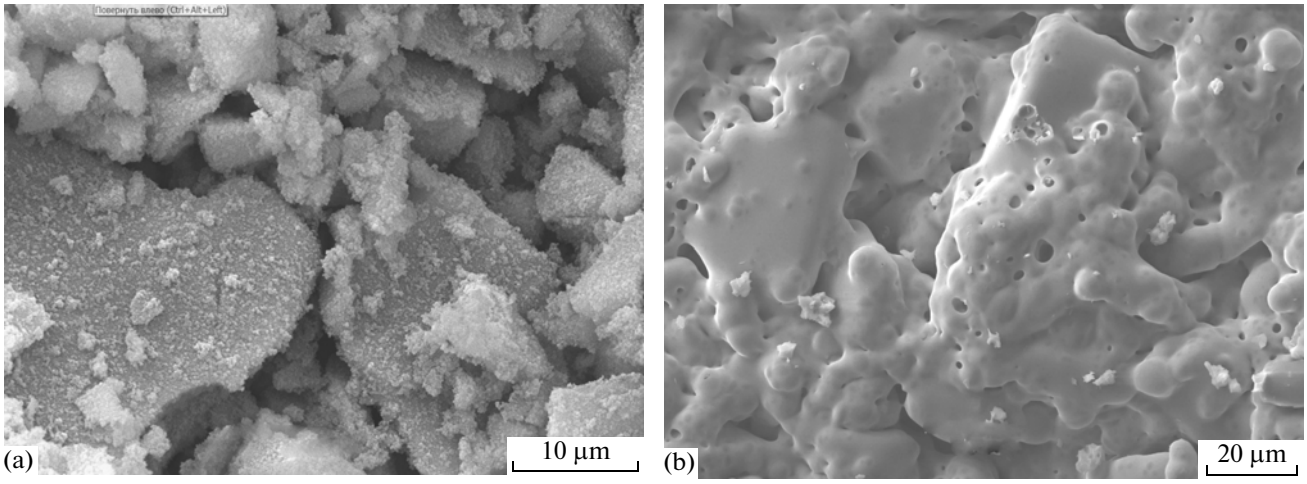

Fig. 5a. SEM photographs of a sample of composite material from hydrated sodium polysilicate and dispersive container glass before heat treatment (a) and after short-term treatment at 700°C (b).

Fig. 5b. SEM photographs of a sample of composite material from hydrated sodium polysilicate and dispersive container glass before heat treatment (a) and after short-term heat treatment at 700°C (b).

CONCLUSIONS

As a result of the conducted research, it is shown that the previous powder technology was found on the sulfate mechanism of gas formation, which has inherent disadvantages. Reasons are given for an opportunity to use quite a different, i.e., the hydrated, mechanism of gas formation.

It is shown that the amount of water vapors emitted during glass synthesis according to the hydrated mechanism at temperatures ranging from 700 to 800°C is sufficient for the formation of foam silicate material.

The possibility to obtain high-modulus gas-filled silicates directly from raw material in the form of hydrated sodium polysilicates is established, with the high content of silicon oxide leading to the crystallization of the α-quartz phase in the finished product.

It is determined that hydrated sodium polysilicate can serve as a matrix for filling with dispersive glass from unsorted cullet, and the latter in this case does not play any role in the process of gas formation. The binding properties at room temperatures and gas formation in the pyroplastic state are a characteristic feature of material from hydrated sodium polysilicate.

As a result, the technology allowing one to obtain foam silicate materials with the use of unsorted cullet and a bond from hydrated sodium polysilicate is substantiated and implemented in practice.

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Translated by D. Zabolotny

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