
INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Production of Foamed Materials from Synthesized Silicate Glasses

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Abstract—Possibility of obtaining materials with cellular structure directly in syntheses of silicate glasses was demonstrated. It was confirmed that water released in glass formation can serve as a gas-producing agent. The necessity for a deep extent of the topochemical glass-formation process was revealed. A resource-saving solution was suggested for synthesis of foamed glasses, based on the replacement of a part of glass being synthesized from hydrosilicates with a finished sodium-calcium glass.

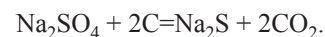
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Cellular silicate glasses, or foamed glass, are primarily known for their heat-insulating properties. However, this material is made unique by the set of properties, unreachable in combination for none of the known heat insulators. These are, in addition to the low heat conductivity and density, also full incombustibility, high strength, and absence of any corrosion or disintegration in the course of time.

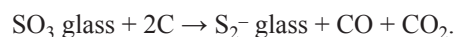
Unfortunately, Russia presently has no industrial manufacture of foamed glass, despite that the material had been produced before the early 1990s at several plants and thorough studies of the given technology were performed. At that time, foamed glass was predominantly fabricated from a specially melted sulfate glass, which markedly narrowed the range of raw material resources and raised the cost of finished products. The gas-formation process was based on the reduction of sulfur(IV) contained in the glass with carbon commonly added to the glass in the grinding stage. The above-mentioned monograph by B.K. Demidovich mostly presented results of studies concerned with just these glasses. The author confirms by thermodynamic calculations that “the reaction of Na_2SO_4 reduction by solid carbon ... in a silicate glass in the water vapor atmosphere has the following form:



It should be noted that, in accordance with the calculations presented by B.K. Demidovich, the most probable pathway for reduction of sulfates in the absence or at a small amount of water vapor, is via formation of sulfides:



Of a similar opinion is F. Shill [3], who gives the following scheme:



A fundamental circumstance in all of these cases is that the oxidized sulfur S_6^+ whose amount is subject to regulations in ordinary silicate glass and is no problem for a consumer is converted to a reduced sulfur S^{2-} in fabrication of a foamed glass. In this case, the latter is present in the structure of the finished material either as a gas, hydrogen sulfide, or as compounds, sulfides, in the solid phase of the material. When interacting with water vapor always contained in air, the sulfides are hydrolyzed with still the same hydrogen sulfide released

into air, with its amount organoleptically detected even in most of modern foamed glass samples upon a slight damage to the surface of the material. The possibility of a direct use of gases containing no sulfur for foaming of composites is presently under consideration [4].

Nevertheless, the authors mentioned above present experimental results on a prolonged hydration of dispersed glass, which led to substantial increase in the foam expansion ratio and, consequently, to an enhanced gas formation. In practice, this effect is used, for example, in manufacture of granulated foamed glass, when a prolonged grinding in an aqueous medium yields a suspension that can effectively release gases in the pyroplastic state [5]. However, the role played by water vapor in gas formation in a thermal treatment of preliminarily hydrated dispersed sodium-calcium silicate glasses and the possibility of purposeful application of the given effect are still insufficiently understood.

Ion exchange can serve as one way by which hydroxy groups are formed on the surface of a dispersed sodium-calcium glass. The exchange process $\text{Na}^+ \leftrightarrow \text{H}^+$ in an aqueous medium leads to formation of polysilicic acids on the surface of the dispersed glass [6]. These acids are decomposed at elevated temperatures with release of water vapor, which can, in turn, be used to obtain gas-filled composites.

The effect of dehydration in thermal treatment is characteristic of not only polysilicic acids, but also silicate formation processes. For example, the release of gases in syntheses of container or window sodium-calcium glass is due to the removal of carbon dioxide or sulfur dioxide gas in the course of silicate formation from carbonates or sulfates. Silicon dioxide in the form of α -quartz, commonly used to introduce silicon compounds into the system, reacts with alkaline and alkaline-earth components at temperatures above 1000 K. However, use of amorphous silicon dioxide makes it possible to perform silicate and glass formation processes at substantially lower temperatures. Moreover, it can be stated that the process of water vapor release is characteristic of systems containing amorphous silicon dioxide and sodium hydroxide and occurs to give glassy polysilicates at temperatures of 900–1100 K. For example, low-temperature synthesis of silicate sodium-calcium glasses similar in composition to container glass can be industrially implemented under these conditions [7].

Hydrated silicates can be obtained in systems with a dispersed glass by using an external, with respect to the starting glass, source of amorphous silicon. It is known that silicates can be formed from amorphous silicon oxide in alkaline media, with sol-gel processes occurring and silicates further converted to xerogels [8]. Therefore, it can be assumed that, under certain synthesis conditions, hydrated sodium polysilicates can form glasses under heating, with release of a water vapor.

In accordance with the concept of silicate glasses as polymeric composites [9], it can be assumed that water will be removed in rather wide temperature range. This circumstance can be used to foam a pyroplastic formulation [10].

Several variants can be suggested for producing composites from amorphous silicon oxide and alkaline compounds of Na^+ , which must form, when heated, anhydrous silicates in the glassy state, and the process itself must be accompanied by water vapor release. To employ dehydration combined with glass formation in a technological process, it is necessary to determine the amount of hydrosilicates in the system that would be sufficient for foaming of the composite. In addition to a direct synthesis of a gas-filled glass from a raw material in the form of amorphous silicon oxide and sodium compounds in an alkaline medium, it is also possible to add a dispersed sodium-calcium glass to the composite. On the one hand, an additive of this kind will diminish the energy expenditure due to the partial use of a finished glass, and on the other hand, use of a chemically inert, toward the process, filler in the form of a dispersed glass will preclude expenditure for the expensive main raw material.

The goal of our study was to confirm the possibility of using water vapor for foaming of sodium-calcium silicate glasses, find conditions in which this process can be performed, and solve the problem of directed synthesis of foamed glass from low-grade crushed glass.

EXPERIMENTAL

The following materials were used in the study: crushed glass [GOST (State Standard) R 52233–2004 “Glass containers, Crushed glass. General technical specifications”] dispersed until passing through a 0.1-mm mesh sieve, sodium hydroxide (GOST 2263–79 “Technical-grade sodium hydroxide”), tripoli for Potaninskoe deposit (Chelyabinsk oblast). The last

compound has the following composition in terms of oxides (wt %): SiO_2 76.16, Al_2O_3 9.33, Fe_2O_3 4.10, CaO 1.05, MgO 1.01, SO_3 0.31.

A mixture of amorphous silicon oxide with sodium hydroxide was prepared by impregnation of the moisture capacity of a silica gel ground until passing through a 0.1-mm mesh sieve with a sodium hydroxide solution of calculated concentration and drying at 363 K.

Thermogravimetric studies were carried out on a NETZSCH instrument. The solutions were analyzed to determine the Na^+ concentration with a PF-04 flame photometer. The silicate decomposition of samples was determined in conformity with GOST 8269.0–97.

To study the thermal stability of a cation-exchange-substituted dispersed glass, Na^+ ions were washed away in a 0.1 M hydrochloric acid until no Na^+ ions were photometrically detected in a sample. The powder was washed with distilled water to neutral reaction and dried at 363 K. The total amount of Na^+ ions washed away from the surface of dispersed glass under the given conditions was 2.26 mg per gram of the dispersed glass. An ion-modified glass with $\text{Na}^+ \leftrightarrow \text{H}^+$ replacement can be regarded as a composite material with a layer of active hydrated silicon oxide on its surface.

To determine the thermal dissociation of the resulting material, with removal of water vapor from its surface, we carried out thermogravimetric studies. The results obtained are presented in Fig. 1.

It was found that the ion-exchange-modified glass splits off water in the whole range of temperatures under study. Of particular interest is the temperature range 900–1100 K, because, just at these temperatures, the glass is in the pyroplastic state and has a viscosity

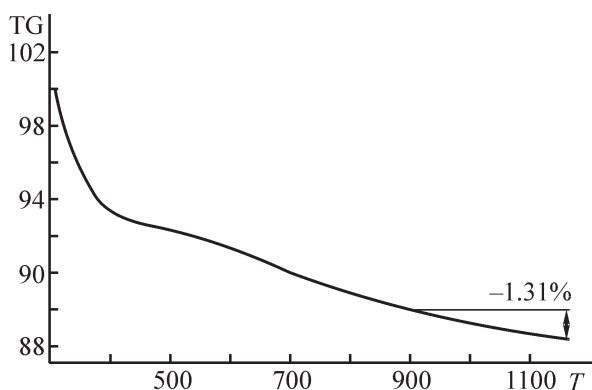


Fig. 1. Thermogravimetric analysis of an ion-modified sample of a dispersed sodium-calcium silicate glass.

suitable for synthesis of foamed glass. Analysis shows that the loss of mass in the given temperature range is 1.31 wt %. In terms of a kilogram of dispersed glass, it can be assumed that the amount of gaseous water released in the given temperature range will be no less than 50 L at atmospheric pressure. With the whole amount of the released gas used to foam the formulation, the specific mass of the latter will be 20 kg m^{-3} , which is an order of magnitude lower than that of the industrially manufactured foamed glass. Therefore, we can conclude that the permeability of the composite being formed, rather than the released amount of a gas, is the rate-determining factor in foaming of hydrated dispersed glasses. However, the ion-exchange-modified dispersed glass contains on the surface of its particles a layer of polysilicic acids, which are transformed under heating to silicon oxide precluding sintering of the powder because of the high melting point. Therefore, the released water vapor freely leaves the composite without foaming it.

A general technical solution of the problem of development of a gas-filled material that would make it possible to preclude free removal of gases from the formulation is to create in the preparation stage a gas-tight material that becomes plastic with increasing temperature. Just this way was taken in a synthesis of strained polystyrene in manufacture of foamed polystyrene [11]. In the case of silicate systems, hydrated sodium polysilicates can not only contain physically and chemically bound water in their composition, but also form pyroplastic glasses at elevated temperatures. This means that foamed-glass materials can be synthesized from hydrated polysilicates, with hydrated sodium polysilicates easily produced from amorphous silicon oxide and sodium hydroxide.

To determine whether gas release is possible in the above-specified temperature range in synthesis of foamed glass from hydrated mixtures of amorphous silicon oxide and sodium hydroxide, we subjected these formulations to a thermogravimetric analysis. The experimental results we obtained are presented in Fig. 2.

The silicate-formation process is not complete and, in the temperature range characteristic of the thermoplastic state of the substance, the amount of the gaseous product being formed is also sufficient for obtaining products with cellular structure of the type of foamed glass.

An ordinary solution for diminishing the water solubility of the sodium silicate glass is to add calcium

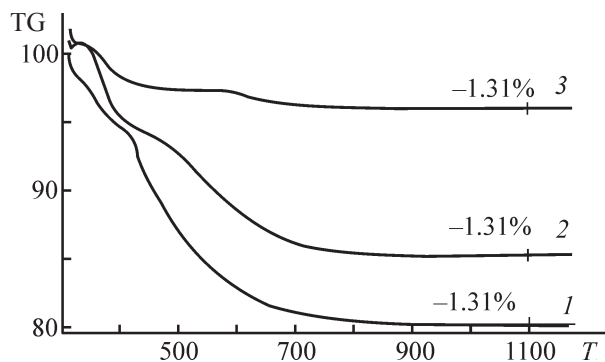


Fig. 2. Thermogravimetric analysis of formulations composed of silica gel and sodium hydroxide. Sodium hydroxide concentration (wt %): (1) 16.7, (2) 13.0, and (3) 9.1.

or aluminum compounds. Because the applied goal of the present study was to obtain a technical-grade product, the economically optimal solution is to use as a raw material natural amorphous silicon oxide already containing all these components in its composition. The natural minerals satisfying this condition are diatomite and tripoli. In the present study, we used tripoli from Potaninskoe deposit (Chelyabinsk oblast).

The formulations containing 15–20 wt % sodium hydroxide with Tripoli indeed demonstrated ability to form foamed structures similar to foamed glass [12]. Because the gas is released from a chemically homogeneous paste of polysilicates, the distribution of gaseous inclusions can be observed down to nanolevel linear dimensions. For example, Fig. 3 shows gas inclusions in primary silicate partitions.

It should be noted that the process of water removal at temperatures of 900–1100 K can be also simultaneously regarded as glass melting always accompanied by gas evolution. However, glass is commonly melted at temperatures higher by 300–500 K. Therefore, it is necessary to determine the extent to which the silicate-formation process occurred in the material obtained and find out whether it is similar in its physicochemical characteristics to the silicate glass produced by the conventional method. Because of the X-ray-amorphous structure of the material obtained, we determined the completeness of silicate formation in the standard way by analysis for the silicate decomposition in conformity with GOST 8269.0–97. The analysis was made with formulations containing 16.7 wt % sodium hydroxide mixed with tripoli. The size of raw material grains was 3–5 mm. The hydrated silicates were thermally treated

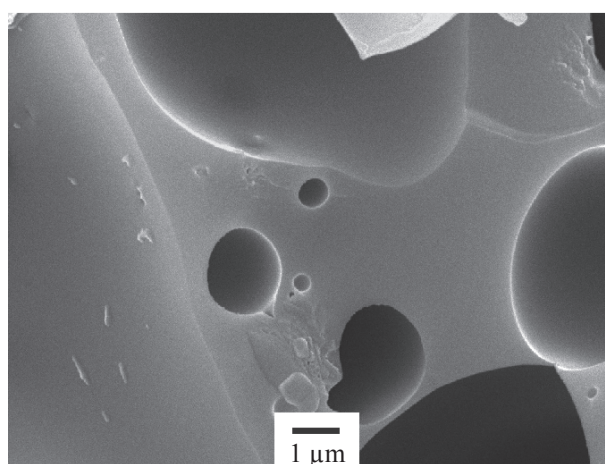
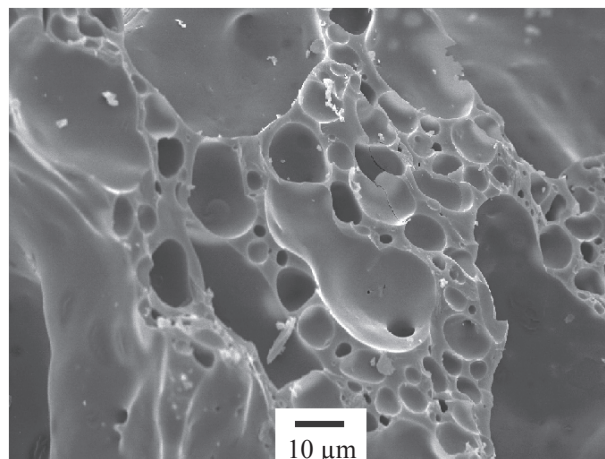


Fig. 3. Electron micrographs of a cleaved surface of the foam-silicate material.

at 1033 K in a rotating dead-end furnace. In parallel, the bulk density of the finished product was determined.

The results obtained are presented in Fig. 4. It can be seen that the process in which foamed glass is obtained has a complex nature. Despite that the finished product is seemingly obtained in a rather short interval of time, physicochemical processes of silicate formation actually continue to occur in the system. In fact, despite being seemingly similar to foamed glass, the product obtained during the first 10–20 min is a composite in which the glass-melting and silicate-formation processes occur. As a result, it becomes possible to simultaneously synthesize a glass and fill it with gases formed in glass melting. However, it is necessary to take into account that the silicate formation will be the rate-determining stage of the process of direct synthesis of foamed glass. Therefore, problems of using formulations of portland-cement concretes with granulated foamed glass produced

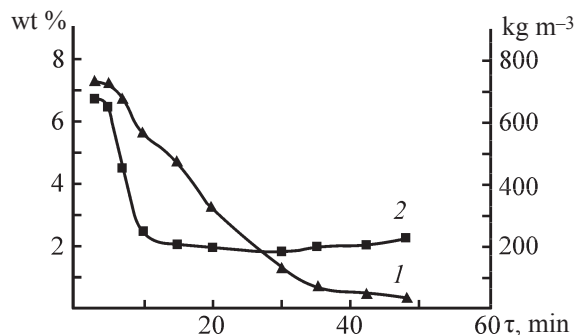


Fig. 4. (1) Silicate decomposition of a granulated foam-silicate material and (2) its bulk density vs. the thermal treatment duration.

by direct synthesis from hydrated polysilicates should be solved with consideration for the possible alkaline-silicate reaction [13].

It can be assumed that, with a part of a silicate formulation replaced with an already finished sodium-calcium silicate glass, the silicate formation process and synthesis of a finished product will be strongly accelerated. In addition, the revealed specific feature of glass synthesis from amorphous silicon oxide and sodium hydroxide at a sufficient gas evolution for a gas-filled material to be formed opens up prospects for secondary use of low-grade glass. Indeed, if the dispersed finished glass is regarded as filler in the matrix of hydrated polysilicates, then the process of gas formation under heating will depend to the minimum extent on the kind of filler and its thermal characteristics.

To verify this assumption, low-grade crushed glass was dispersed in a ball mill to a particle size less than 100 μm. The powdered glass and an aqueous paste of

polysilicates were used to prepare a paste. On being dried, this paste was thermally treated at 923 K, i.e., at a temperature at which an interaction between the amorphous silicon oxide and sodium hydroxide becomes possible. Micrographs of a sample before and after this thermal treatment are shown in Fig. 5.

It is clearly seen that a uniform melted layer enveloping primary grains of dispersed glass appears and gas bubbles are formed in this layer. A characteristic feature of the process is that the gas formation is independent of the nature of particles of the substrate, dispersed glass of various grades. The suggested approach based on the formation of hydrosilicates between dispersed glass particles makes it possible to use as filler the low-grade crushed glass by a technology independent of the composition of a glass being utilized [14].

CONCLUSIONS

(1) It was shown that the ion exchange of Na⁺ in an aqueous medium from the surface of a sodium-calcium glass can be used to provide gas evolution at temperatures of the thermoplastic state of the material.

(2) Synthesis of glassy polysilicates from the amorphous silicon oxide and sodium hydroxide occurs in the range in which polysilicates are in the thermoplastic state and can be used to obtain foamed glass materials, but it is necessary to control the extent of the process.

(3) Synthesis of glass from hydrated polysilicates in the intergrain space of dispersed glass can be used to obtain foamed-glass materials and secondary use of a low-grade sodium-calcium glass.

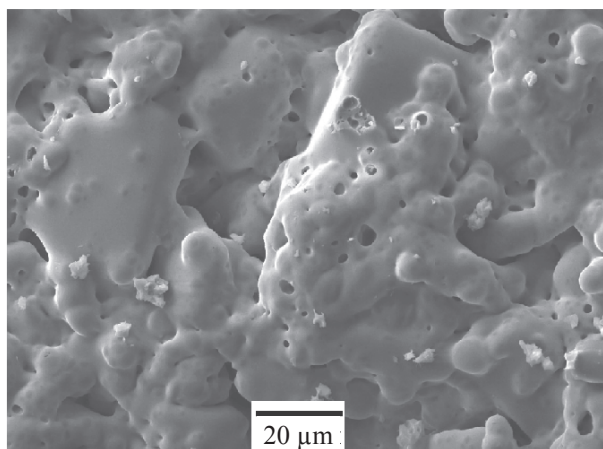
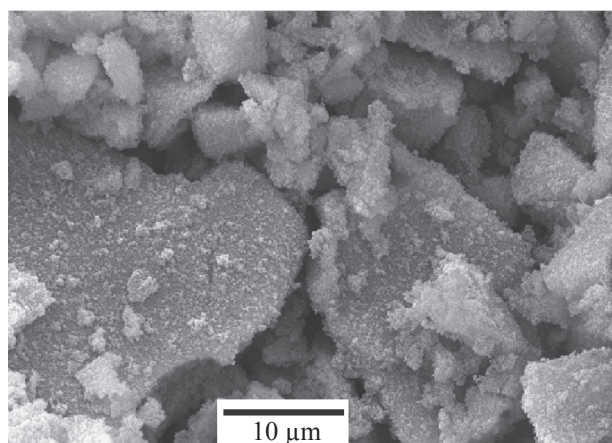


Fig. 5. Electron micrographs of dispersed glass coated with a layer of hydrosilicates before and after thermal treatment.

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