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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Oxidation of Carbon by Water Vapor in Hydrate Gas-Formation Mechanism in Manufacture of Cellular Glass

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Abstract—Gas formation in production of a cellular glass is considered for the case when the hydrate mechanism is operative and water vapor is used as oxidizing agent. It is shown that the presence of carbon in the system leads to a steam conversion and larger volume of released gases. Differences in the structure of materials obtained with different carbon reducing agents and formation depth of polysilicates in the raw material are discussed. It is shown that a light cellular glass can be obtained.

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Porous glasses with closed cell structure and densities lower than 250–300 kg m^{-3} are rather attractive as functional heat-insulating materials, especially in the case when waste glass is used as a raw material. Commonly, the gas formation in the thermoplastic state is provided by melting a special glass with addition of special reagents. Conventionally, a sulfate-containing glass and a powder technique of its thermal treatment are used [1]. However, the procedure for melting of special glasses entails higher energy expenditure for obtaining the final product and providing carbon dioxide emission.

To obtain a cellular glass, it is necessary to select the conditions in which the gas-formation process occurs at temperatures higher than the softening and sintering points of the glass powder, which corresponds in the case of a sodium-calcium glass to temperatures above 923–973 K. It is possible in this case not only to use a glass containing a component of a redox pair, but also to add a compound that undergoes a thermal dissociation, e.g., manganese oxide MnO_2 as suggested by the authors of [2]. The authors could secondarily use, together with the sodium-calcium glass, fiberglass. The thermal treatment temperatures of the formulation were in the range 1173–1323 K.

However, the conventional sodium-calcium glass exhibits a hydrothermal activity, especially at a high dispersity of the material. This property can be used to process waste glass into functional materials [3, 4]. Hydration of silicates in the glass at high pressure or temperature makes it possible to obtain composites capable of releasing water vapor at high temperatures, thereby expanding the silicate composite, which is in the thermoplastic state under these conditions. The composition-dependent thermal plasticity of a composite determines the water release and composite expansion temperatures. The authors of [5, 6] demonstrated the possibility of expanding the material produced from a sodium-calcium silicate glass under a hydrothermal treatment at temperatures of about 923 K.

There is a technical opportunity for at all excluding the hydrothermal treatment of a dispersed glass if this glass is used as filler in a composite material and the intergranular space is filled with synthetically hydrated sodium polysilicates [7]. In this case, synthesis of glass in the intergranular space at temperatures close to that in the case described above also lead to release of water vapor and expansion of the composite without hydrothermal treatment of the dispersed glass.

Because polysilicate structures are formed in hydration and dehydration processes of composites that are not described by the Gibbs rule of phases and formally are nonstoichiometric, water vapor is released in

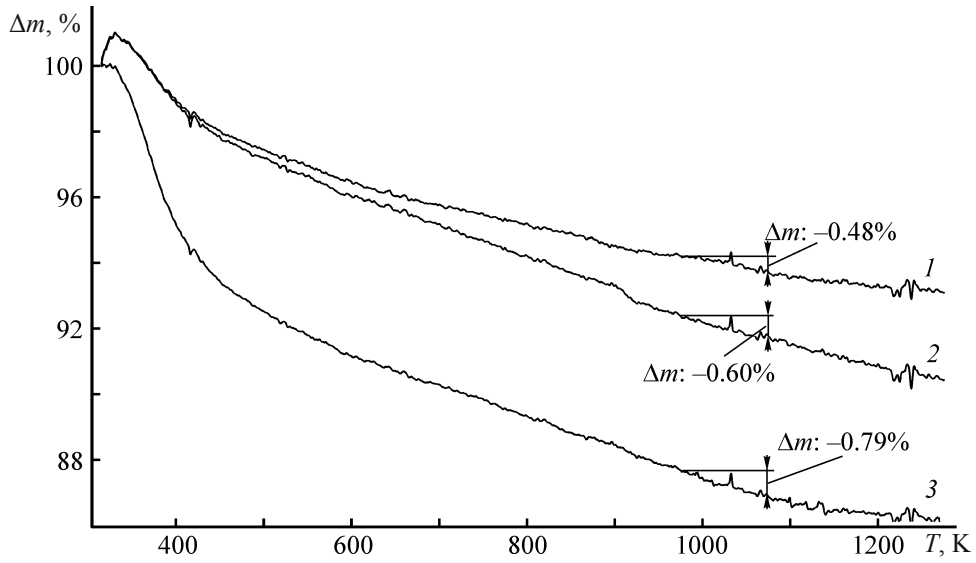

Fig. 1. Thermogravimetric curves for formulations with silica gel, sodium hydroxide, and reducing agent. (Δ*m*) Loss of mass and (*T*) temperature. (*1*) Silica gel and 3.5 wt % sodium hydroxide; (*2*) silica gel, 3.5 wt % sodium hydroxide, and 3.5 wt % activated carbon; (*3*) silica gel, 3.5 wt % sodium hydroxide, 3.5 wt % activated carbon, and 3.5 wt % sodium silicate.

a rather wide temperature range and it becomes possible to reduce the synthesis temperature of cellular glass. This can be done with glasses that are more thermoplastic than the conventional sodium-calcium glass, e.g., SiO_2–Na_2O–B_2O_3 glass [8]. A hydrothermal treatment of the glass under pressure made it possible to obtain a cellular material at comparatively low temperatures. For example, a noticeable gas evolution occurs already at 423 K, and above 473 K the process is so vigorous that a sharp decrease in the apparent density of the cellular material to below 400 kg m^{-3} is observed.

In practice, the effect of using water vapor to expand a thermoplastic composite is used in manufacture of granulated expanded glass [9]. In this case, the silicate glass in the disperse state is hydrated because of the mechanochemical treatment of the material in the course of prolonged grinding.

It has been shown that it is, in principle, technically possible to produce cellular materials by the hydrate mechanism [7]. The method in which a glass is synthesized in the intergranular space of a dispersed glass can be used to obtain expanded-glass materials and secondary use of ungraded sodium-calcium glass. However, the density of the thus obtained materials was found to be higher than that of analogs produced by the conventional sulfate technology.

Therefore, it was suggested that the gas evolution from the silicate composite can be enhanced by the redox reaction between water vapor and carbon. Compared with the conventional technique in which carbon is oxidized by sulfate ions from the glass, water vapor have a substantially lower oxidizing capacity, but the suggested solution is supported by the fact that the reaction becomes nontopochemical and the oxidizing agent comes from the gas phase.

It should be suggested on this basis that the apparent density of the resulting cellular silicate materials will decrease due to the more vigorous gas formation accompanying the redox reactions of carbon oxidation by water vapor.

The goal of our study was to confirm the possibility of obtaining low-density cellular silicate materials by the hydrate mechanism due to the stronger gas evolution in the course of the redox reaction between water vapor and carbon.

EXPERIMENTAL

We used the following materials: scrap glass defined in GOST (State Standard) “Glass Packing. Scrap glass. General technical specification,” dispersed to pass through a 0.1-m mesh sieve, and sodium hydroxide defined in GOST 2263–79 “Sodium hydroxide of technical grade.”

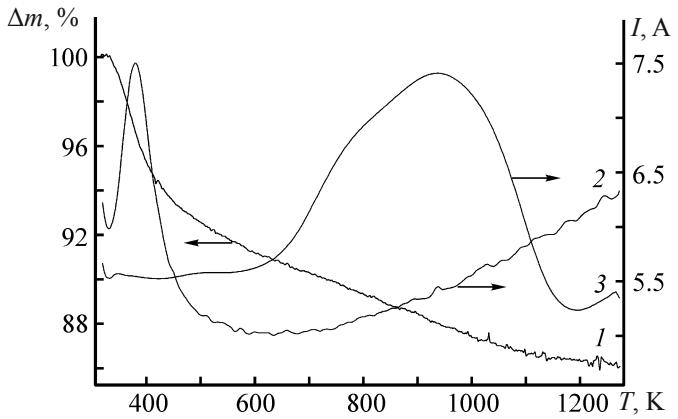

Fig. 2. (*1*) Thermogravimetric curves for a formulation with silica gel, 3.5 wt % activated carbon, and 3.5 wt % silicate, combined with mass spectra of (*2*) water and (*3*) carbon dioxide.

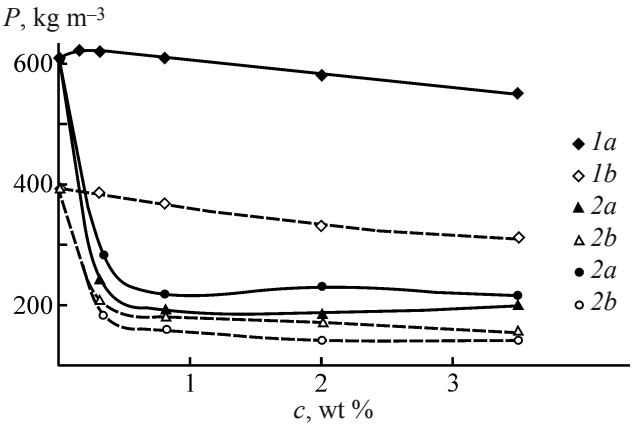

Fig. 3. Density ρ of the resulting cellular material vs. the concentration c of the reducing agent in the starting mixture. Reducing agent: (*1*) activated carbon, (*2*) saccharose, and (*3*) glycerol. Temperature (K): (*a*) 1033 and (*b*) 1093.

A thermogravimetric analysis was made with a Netzsch STA 449 F1 synchronous thermal analyzer (Germany), which enables a thermal study of a sample and simultaneously records its thermogravimetric and calorimetric characteristics. Gaseous products were analyzed with an Aeolos QMS 303 CF mass spectrometer (Germany). The results obtained were processed with the software packages of the instruments.

To determine the possibility in principle of the reaction of carbon with water vapor formed when a glass is synthesized from a mixture of silica gel and sodium hydroxide, we prepared appropriate samples and made their thermogravimetric analysis (Fig. 1). In the context of the purposeful synthesis of a cellular silicate material in the thermal plasticity region of the silicate melt, we determined how the mass of the samples varies within the temperature range 973–1073 K.

It was found that, in the given temperature range, synthesis of a double-component glass leads to a loss of mass by 0.48 wt %. Addition of carbon to the formulation results in that the mass decreases by 0.60 wt %. Apparently, such a sharp increase in the evolution of water vapor in the given temperature range can be only attributed to intensive removal of water from the melt due to the redox reaction with carbon. This is additionally confirmed by the increase in the loss of mass in the given temperature range to 0.79 wt % upon addition of liquid glass.

A mass-spectrometric analysis combined with thermogravimetry confirmed the oxidation of carbon by water vapor (Fig. 2). The release of water vapor is observed in the whole temperature range, with a maximum near the removal of free physical water and gradual removal of water from the silicate melt upon an increase in temperature, whereas the presence of carbon(IV) oxide is predominantly observed at elevated temperature, 700–1200 K, with a maximum at 950 K.

Therefore, presence of carbon in the raw silicate formulation favors removal of water vapor from the formulation at the synthesis temperatures of cellular materials due to the redox reactions between water vapor and carbon. This effect can be used to synthesize cellular silicate materials with low apparent density.

To verify this assumption, we prepared formulations composed of dispersed glass with addition of 20 wt % liquid glass and 2 wt % silica gel. Various amounts of activated carbon or organic compounds that form pyrolytic carbon on being heated and are commonly used in syntheses of expanded glass were added to the resulting formulation. The dependences of the apparent density of the resulting cellular materials at 1033 and 1093 K on the concentration of the reducing agent are shown in Fig. 3.

It was found that the density of the material obtained decreases least in the case of free carbon, despite that its amount in fact exceeds that of pyrolytic carbon in organic compounds, because a considerable mass of the substance is lost with pyrolysis products. Probably, this effect can be attributed to the high activity of the pyrolytic carbon obtained in initial stages of heating of the composite at 573–823 K. In addition, the sizes of activated carbon particles are determined by the grinding and fall within the micrometer range, whereas pyrocarbon particles

formed in the course of thermal decomposition of organic compounds are two to three orders of magnitude smaller.

As a result, the oxidation of pyrocarbon in organic compounds is more vigorous and easier than that of free carbon, a substantially larger volume of gases is formed, and the apparent density of the materials obtained is lower and comparable with the density of cellular materials produced by the conventional sulfate synthesis method.

CONCLUSIONS

(1) Raising the number of Na^+ ions in the raw silicate formulation leads to an increase in the amount of bound water removed at thermal plasticity temperatures of sodium-calcium glasses (973–1073 K).

(2) The presence of carbon in the raw silicate formulation favors removal of water vapor from the formulation at the synthesis temperatures of cellular materials due to the redox reactions between water vapor and carbon.

(3) The redox reactions between water vapor and carbon in synthesis of a cellular silicate material favor an increase in the gas evolution and a decrease in the density of the articles obtained. It is preferable to use pyrocarbon formed in thermal decomposition of soluble organic compounds.

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