УДК 666.189.3

I. M. Tereschenko, O. B. Dormeshkin, A. P. Kravchuk, B. P. Zhih
Belarusian State Technological University

PRODUCING OF THERMAL INSULATING MATERIALS ON THE BASIS OF SILICA GEL BY ONE-STAGE PROCESSING TECHNOLOGY

The one-stage processing technique for producing of thermal insulation materials based on silica gel has been developed. Silica gel is AlF_3, waste products including following main stages: hydrothermal synthesis polysilicate, granulation, classification and foaming. As compared with well-known analogs, it differs significantly in lower power consumption, does not require complex and expensive equipment, provides the possibility of varying boundary-granulometric composition of the foam product (0.5 to 30 mm). The main influence on the stability of the product quality is caused by the processes of depolymerization and condensation occurring on the stage of hydrosilicates synthesis from the silica gel because of NaOH addition. It was found out that a final foamed product with a bulk density less than 200 kg/m^3 can be produced only if depolymerization and polycondensation of the silica gel stages are separated at the time.

The values of process parameters (silica module, suspension temperature, the intensity of her mixing, foaming temperature, the quantity and type of modifiers) synthesis of heat-insulating materials have been defined. The required concentration of dissolved silica in the suspension is provided by its intensive mixing for 15–30 min. The temperature of the mixture should not exceed 35–40°C. The most effective technique for the speed polycondensation control is to additive a carbon. Its amount should not be more than 0.2–0.3%. Fast transition gel suspension is achieved when it is heated to 70–80°C for 10–15 min. After aging and foaming of gels at a temperature of 450–500°C the proposed processing technique allows one to produce the thermal insulation materials possessing the characteristics which are not inferior to those of the foreign ones.

Key words: foamed glass, suspension of silica gel, gelation, foaming, carbon, thermal conductivity, density bulk, water resistance.

Introduction. Combination of high level of heat isolation properties with operating life and ecological purity put foamglass beyond competition with other similar materials (organic and nonorganic) for a long time. However, foamglass that is manufactured according to powder technology did not become a material of wide use because of the following factors:

– usage of specialy synthesized granulate or sorted out broken glass;

– working mass of high milling (power inputs to 110 kVt · h/m^3);

– thermoprocessing of working mass and fritting that are very unprofitable operations (energy consumption to 600 kW · h/m^3)

Technology of granulated foamglass turned out to be cheaper, though there are some application restriction, first of all, on vapor resistance and availability of hydrogen sulphide in the structure. It is produced from floured mixture of broken glass and gas-forming agent by means of granulation and following foaming. In this case technological process is considerably simplified in comparison with block-structured: energy consumption on thermoprocessing of products is 240–270 kW · h/m^3, requirements to the composition of the raw material and equipment are reduced. Although, according to technological properties it is a little inferior to block-structured it is considerably cheaper and in demand for production of lightweight concrete, thermos- and soundisolated backfill. The largest drawback of this product is the usage of glass because it is not cheap to produce it.

In connection with the above mentioned there were attempts of producing heat-insulating materials similar to foamglass according to their propertis but on the base of other kind of raw material. For example, materials with cell structure on the basis of different nature cilicates: plastic clay, perlite, zeolite tuff, tripolite and diatomite [1–3]. Obtaining articles have a wide range of apparent density and thermal conductivity. Method of forming of a cell structure due to gas release in silicate matrix, in pyroplastic state, is common for them. Apart from glass- and gas phase similar materials can contain a considerable part of crystalline. As glass is not an initial raw material in this case it is more logical to call such materials not foamglass but material of hot foaming. Due to this approach, it is possible to not only single out existing similar technologies into a separate group but also create conditions for synthesis of functional new material. At present, it is possible to declare that synthesis of foaming material from the preliminary obtaining glass is irrational as requires a double thermoprocessing. It is known that at the period of glass melting a large volume of gas phase is removed, then the melting is cooled, dispergated, gas-forming agents are introduced into the obtained powder and are heated again. At the same time it is known, that silicate and glass-forming can be achieved at the temperatures not lower than 800°C, that is considerably lower than the temperature of glass melting (1,450–1,500°C). This is just a temperature zone of foamglass synthesis. Thus, there is a technical possibility of combination of two different process: glass synthesis and forming of its cell structure into one stage, i. e. transfer to the technology of one stage synthesis of foamglass materials. According to external and internal experience at one stage technology of obtaining foamglass the temperature of synthesis can be considerably lower than (200–600°C), that is profitable.

It is important that in this case a raw material base is widen, local silicate rock with high disparsion ability as of nature origin (clay, opoka, tripoli, diatomites and etc.) and also of technogenic origin (mine wastes, smelter slag and etc.). Actually, application of cheap silicate raw material at the process of one stage synthesis of foaming material is becoming the main tendency at present.

Suggested approach makes it possible not only decrease energy consumption but also simplify technological process reducing the number of its stages. It is known that glass milling is a rather expensive operation: apart from high specific energy consumption (95–110 kW · h), high abrasive wear and power density of equipment are to be taken into account as quality of the obtaining foammaterial primarily depends on dispersiviness of working mass. According to this, there is one of the most important principals of the new technology: the following foammaterials will have the minimal density: those ones with size of initial components close to molecular, i. e. powders should never be prepared, synthesis should be carried out from solutions or gels. In this case it is possible to achieve cell walls thickness in the material smaller than 1 μm and, correspondingly, poured density about 70–80 kg/m^3. During the application of powder technology milling and usage of nature dispersed raw material abandoning is a wise decision.

Main part. The purpose of the present article is studying of possibility of obtaining foaming thermoisolation materials with properties of foamglass by means of low-temperature synthesis from silicate hydrogels preliminary obtaining from silica gel – production waste of AlF_3.

Process of desalination of amorphous silica from the initial raw material by caustic soda is taken as a main part of obtaining raw material method. Earlier this method was used for obtaining liquid glass, however, it has not become popular because of the formation of unsoluble sediment and difficulty of its separation [3].

At presen situation its application is considered to be very effective due to the following:

– searching material is obtained by means of foaming of non-mechanic mixture of compounds, but synthesizing chemical product (hydragel), comprising of all necessary ingredients as for glass forming and also for gas release;

– thermal synthesis of glass from hydrasilicates is carried out at the same time as its foaming (one stage process);

– foaming of the material is carried out during its transformation into pyroplastic condition by water vapor that is evaporated at thermaprocessing.

It should be noted, the present technology is based on the well-developed industrial operations, complex expensive equipment as well as fuel and electricity expenses are not required. The following should be regarded as its merits:

– low temperature of foaming (within the bound of 400–600°C);

– variability of grain composition of the finished product (from 0.5 to 30.0 mm) with the possibility of its narrow fractionation;

– possibility of overcoming of common drawback of the known foammaterials: low chemical water resistence, especialy hot water resistance.

Low parameters of density are achieved by preliminary obtained foaming during hydrothermal synthesis of sodium polysilicate, sodium hydroxide was chosen as a reagent actively interacting with amorphous SiO_2 forming a glass-like product. Polysilicates are formed in accordance with the following scheme:

$$n\mathrm{SiO_2} + 2m\mathrm{NaOH} \rightarrow (\mathrm{Na_2O})_m \cdot (\mathrm{SiO_2})_n \cdot m\mathrm{H_2O},$$

as a hydrogel including bound (silanol and intermolecular) and free water. In this case, during the foaming process, water vapor is a gasformator. Steady distribution of gasforming throughout gel with fine texture forming is a distinctive characteristic of the process. It should be mentioned that almost at the same time with the reaction of silicateforming there are processes of polycondensation and coagulation. As a result, increase of viscosity of suspensions with lose of plasticity and transformation into fragile condition are observed. At the next stages a fragile mass is exposed to granulation classification and foaming. Quality unstability of the foamed product at the initial stages of the research was connected with the stage of synthesis of hydrasilicates. It has been found out, that early hardness of hydrogel results to increased density and sometimes to the absence of foaming of the finished product. According the completed experiments during the introduction of NaOH into suspension of silica gel, process of dissolution of silica is observed, which should be considered from the side of the reaction of hydrolytic abruption of silicate connections at surface layer of the particles:

–Si–O–Si– + NaOH–Si–O–Na + OH–Si–.

The present process is accompanied by aeration and disparsion of silica particles, forming of double electric layer (from the side of solid phase) and hydratation of the surface. In the process of depolymerization in the reaction zone local decrease of pH of suspension to the parameters close to 9.5 together with increase of active forms content of the dissolved silica is observed. Decrease of ion concentration OH^- is nondurable (1–2 min after introduction of NaOH) then pH increases together with viscosity of suspension. Suspension is quickly exposed to jelling and then solidity which is connected with quickly developing processes resulting to coagulation. Obtaining product has a heterogeneous granular structure and is not exposed to foaming during thermaprocessing. Process of coagulation of silica suspension can be initiated by interaction between SiO_2 particles according to the scheme :

(particle 1) (particle 2)
$$\equiv SiO– + HO–Si\equiv \rightleftarrows \equiv Si–O–Si\equiv + OH^-.$$

During the experiment it has been revealed that foamed finished product with poured density less than 200 kg/m^3 can be produced only under the condition of the division of the depolymerization and polycondensation stages on time, i. e. a rather big amount of active dissolved SiO_2 is to be formed in the system till the beginning of a quick coagulation.

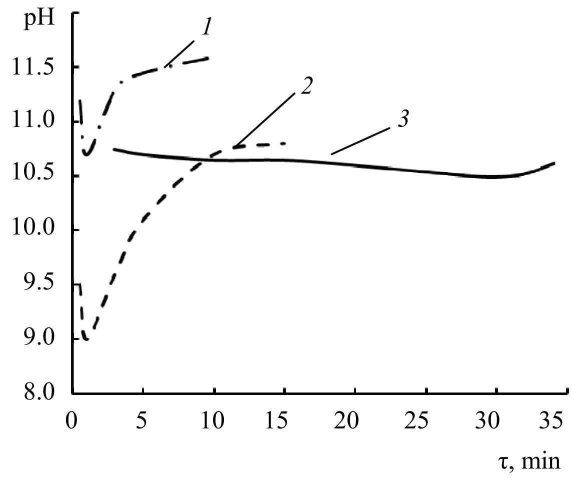
That is why, determining of the conditions providing complete fulfilment of the first stage is the main task which is solved during hydrasilicates synthesis.

The following important factors have been studied: temperature of the system; stirring intensity; introduction of supplements, regulating the process of suspension hardness.

It has been established that temperature rise (to 90°C) is always resulted to the increase of polycondensation speed at variation of silica module from 4.0 to 5.2 and content of a hard phase in suspension from 42 to 53%. As a result obtaining gel has a weak foaming properties and has a high density (ρ > 400 kg/m^3). Thus, heating of suspension at the initial stages is not rational.

Influence of stirring on the dynamic of the process taking place during the synthesis of polysilicates can be seen in the Figure.

According to the presented data intensive and non-stop stirring during the synthesis makes it possible to obtain suspensions, preserving movability within 35–40 min scince the beginning of the synthesis, while its absence or small intensivity lead to quick coagulation with the increase of concentration of OH ions. Foamed product obtained according to regime 3 had ρ_{sat} = 148 kg/m^3, other mixtures failed to foam.



Stirring regime influence on suspension pH:
1 – stirring within 3 min after introduction of NaOH, no more stirring afterwards;
2 – stirring within 15 min after the beginning of the synthesis, no more stirring afterwards;
3 – non-stop stirring during the synthesis

According to the completed studies optimal regim of polysilicate synthesis has been developed including 15–30 min of intensive stirring of reaction mixture heated to the temperature not higher than 35–40°C. Thus, necessary concentration of the active dissolved silica in suspension is provided. The following heating to 70–80°C within 10–15 min leads to quick transformation of suspension into gel.

As for supplements introduction of graphite with specific surface of 0.2–0.3% into the initial suspension appeared to be the most effective. In this case, polycondensation speed decrease is explained by steric motive. Hardening product of synthesis including carbon characterized by high elasticity and by good foaming properties.

Obtained gels, in accordance with the offered technology, after aging and foaming at the temperature of 450–500°C make it possible to get materials with properties described in the Table Comparison of properties of synthesized materials with the known industrial analogues "Poraver" (Germany) and "Penostek" (Russia) shows the perspectiveness of the organization of industrial production of foamed materials based on silica gel.

Conclusion. Thus, based on anthropogenic product being out of demand for a long period, granulated thermal-insulating materials on one-stage technology providing considerable decrease of power consumption, have been obtained. Synthesized materials can find a wide application in building.

Comparison properties of synthesized on one-stage technology materials on base of silica gel and known analogues

Properties of foamed materials	Silica gel		"Poraver" (Germany)	"Penostek" (RF)
	fraction (4–8 mm)	fraction (1–2 mm)	fraction 1–2 mm	
Packing density, kg/m^3	80–120	210–320	270	230
Heat conductivity coefficient, Vt/(m · K)	0.045–0.055	0.07–0.08	0.07	0.07
Water absorption, %	20–25	1.5	5–7	18
Crushing strength, MPa	0.5–1.4	3.2	1.1	1.6

References

1. Demidovich B. K. *Penosteklo* [Foamglass]. Moscow, Gizlegprom Publ., 1957. 235 p.

2. Malyavskiy N. I. Alkali silicate insulation. Properties and chemical production bases. *Zhurnal Ros. khim. ob-va im. D. I. Mendeleeva* [Journal of Russian chemical society], 2003, vol. 47, no. 4, pp. 39–45 (in Russian).

3. Eyne I. A., Khvastukhin Yu. I. Kremnesit – new energy- and resource-saving building material. *Ekotekhnologii i resursosberezhenie* [Ecotechnology and resource-saving], 2000, no. 5, pp. 13–18 (in Russian).

Information about the authors

Tereschenko Igor Mikhaylovich – Ph. D. Engineering, associate professor, Department of Glass and Ceramics Technology. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: tereschenko@belstu.by

Dormeshkin Oleg Borisovich – D. Sc. of Engineering, vice-rector on science. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: dormeshkin@yandex.ru

Kravchuk Aliaxander Petrovich – Ph. D. Engineering, senior lecturer, Department of Glass and Ceramics Technology. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: kravchuk@belstu.by

Zhih Bozhena Petrovna – undergraduate student, Department of Glass and Ceramics Technology. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: bozhena@belstu.by

Received 20.02.2015