Low Temperature Synthesis of Composition Poros Materials from Mortar Sands

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Abstract. It is established that the eliminations of construction sand with the content of SiO\(_2\) about 70 wt. % and particle size less than 60 \(\mu\)m are suitable for the production of a foamglass-crystal material on the basis of the low-temperature frit, which was synthesized at the temperature 900 °C. The obtained foamglass-crystal material exceeds foamglass (by 3.0 times) and clayite (by 1.5 times) by strength and is characterized by low value of water absorption (0.1 %).

Introduction

The production of lightweight and efficient building materials, in particular of lightweight granulated materials, is a constant and modern subject of scientific investigations. One of the high-efficient heat-insulating materials that meet the requirements of environmental safety is foam glass. Raw material for production of foamed glass can serve various types of waste. One of the wastes which contaminates territory as collecting sludge ponds are fine dispersive sand screenings which are formed as result of mining and processing of quartz sands \[1\].

The aim of work is to investigate the possibility of preparation of foam material similar to foam glass on the basis of frit synthesized from quartz sands screenings. Industrial technology of foam glass is based on the use of glass cullet or frit with composition of sheet and container glasses. High dispersiveness of quartz sand wastes allows to suppose the possibility of low temperature synthesis of frit. Therefore one of assigned tasks of this research was development of blend compositions suitable to obtain frits at temperatures not exceeding 900 °C, excluding traditional glass melting process.

When one selects chemical composition of low temperature frit, it is necessary to meet the following requirements. The first condition which defines the component composition of a blend is provision sufficient quantity of glass former (60 – 75 mas %) and the alkali metal oxides (13 – 22 mas %). At that it is necessary to take into account that foaming occurs at viscosity of \(10^5 - 10^7\) Pa\(\cdot\)s, therefore it is necessary to use the glasses which reach such viscosity at temperatures of 750 – 900 °C. It is possible to estimate preliminary viscosity properties of the glass by its composition using viscosity modulus, which value can be in range 1.6 – 1.8 \[2\]. The second selection condition is formation of not less than 70 % of melting at temperature not exceeding 900 °C, what has been stated by results of previous experiments \[3\]. The third condition is hydrolytic stability of glass (not below the 3rd class) and the presence of active oxidizing component in sufficient quantity to carry out foaming reactions, for example, presence of SO\(_3\) in quantity not less than 0.2 %. One of the main requirements to all blend components are their dispersiveness; particle size must not exceed 100 \(\mu\)m.

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Glass composition corresponding to the above mentioned requirements, selected by the state diagram of Na$_2$O–CaO–SiO$_2$, has the following content of components: Na$_2$O-14, CaO-13, SiO$_2$-73 mass %. The composition of sand under investigation according to results of chemical analysis is presented by relatively low quantity of main glass forming oxide (SiO$_2$) and sufficiently high quantity of the alkali metal oxides, aluminas, and iron oxides (Table 1). According to data of X-ray phase analysis sand contains together with quartz and illite, tiff, plagioclase, and feldspar in about equal proportions. High dispersiveness of sand is confirmed by results of screen analysis according which 50 % of sand is presented by fraction of particles less than 60 μm that meets necessary requirements.

Table 1. Characteristics of the surveyed Sands

| Chemical composition, content of oxides, mas % | SiO$_2$ | TiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | MnO | CaO+MgO | Na$_2$O+K$_2$O | P$_2$O$_5$ | SO$_3$ | opr. |
|---------------------------------------------|---------|---------|------------|-------------|-----|----------|---------------|-----------|-------|-----|
| 69,67                                       | 0,47    | 7,12    | 3,93       | 0,09        | 7,75| 2,66     | 0,15          | 0,03      | 0,16  |

| Mineralogical structure, mass %              | Quartz | Illite | Plagioclase | Potassium feldspar | Calcite | Rutile (anatase) | Ferric hydroxide | Organic |
|---------------------------------------------|--------|--------|-------------|--------------------|---------|------------------|-----------------|---------|
| 50                                          | 15     | 5 – 10 | 10          | 10 – 15            | 1       | 5                | < 1             |

| Granulometric structure, mas %               | < 2 μm | 2 – 63 μm | >63 μm |
|---------------------------------------------|-------|------------|--------|
| 6,8                                         | 49,7  | 43,5       |

To obtain frit of selected composition one prepared a blend containing sand under investigation and fluxing addition in form of calcined soda in quantity of 80 and 20 mas %, accordingly. Calculated composition of glass has following oxide content, mass. %: SiO$_2$ – 66.3; Na$_2$O – 13.4; CaO – 6.5; Al$_2$O$_3$ – 6.8; Fe$_2$O$_3$ – 3.7; K$_2$O – 1.8; MgO – 0.8; MnO – 0.1; TiO$_2$ – 0.5. Value of viscosity module, calculated according to the formula, is 1.8, that falls into the recommended interval.

$$M_v = \frac{(M_{SiO_2} + 2M_{Al_2O_3})}{(2M_{Fe_2O_3} + M_{CaO} + M_{MgO} + 2M_{K_2O} + 2M_{Na_2O})}$$  \hspace{1cm} (1)

where $M_v$ is viscosity module; $M_{tot}$ is quantity of the corresponding oxides, mass %.

Preparation of foam crystalline material has been carried out by two stage technology proposed in the paper [4]. The first stage includes synthesis of frit consisting of glass (not less than 70 %) and residual crystalline phase (not more than 30 %), that is provided by chemical composition of a blend. The second stage includes preparation of foam forming blend from frit powder with obtaining finished foam material.

Results of DTA showed that at heating of the blend of selected composition up to 1000 °C one observed endo-effects corresponding to removal of hygroscopic and crystallization water of the blend (82 and 245 °C), polymorphic transitions of quartz (571 °C), melting of forming double salts and eutectics (733 and 797 °C). The main mass losses occur at temperature range of 500 – 800 °C, corresponding to silication reactions. At temperature of 800 °C thermogravimetric curve comes out on horizontal that shows total binding of sodium carbonate and completion of silication reaction according to equation (2).

$$n SiO_2 + Na_2CO_3 \rightarrow Na_2O \cdot nSiO_2 + CO_2 \uparrow$$  \hspace{1cm} (2)

It is stated by data of thermal analysis that thermal treatment of the blend under investigation at temperatures of 800 – 900 °C secures total completion of silication processes. To confirm this supposition one carried out X-ray phase analysis of frit prepared at temperatures of 800 – 900 °C (with step of 25 °C). Results of quantitative X-ray phase analysis show that frit consists of glass phase in range from 66 to 72 %, remaining crystalline phase presented by residual quartz (d=3.342 nm; 2Θ = 26.76°), feldspar and silicate Na$_2$O•CaO•5SiO$_2$.

Differential – thermal analysis of frit showed no exothermic effects both at heating up to 1000 °C, and at cooling to 200 °C, that testifies absence of crystallization processes. DTA of foam forming
mixtures prepared on the basis of frits prepared at various temperatures (from 800 to 900 °C) with addition of soot (0.5 %) showed presence of exo- and endo-effects corresponding to processes of oxidation of gas forming agent and melting of glassy phase. Increase of frit preparation temperature biases exo-effect temperature in higher field, so for admixture from frit (800 °C) effect occurs at 463.7 °C, while for frit (900 °C) value is 498.6 °C, that is conditioned by differences of phase composition of frits. According to quantitative XFA results when sintering temperature of frit increased from 800, 825, 850 to 900 °C, content of crystalline phase decreased from 34, 32, 29 to 27 %.

Bias of oxidation temperature in higher field is favorable for foaming process since probability of early burning out of gas forming agent decreases. Total mass losses for frit (800 °C) is 5 times more in comparison with foam forming admixture prepared from frit (900 °C). In addition, thermograms of admixtures of low temperature frits (800 and 825 °C) show some endo-effects, thermograms of frits with temperatures 850 and 900 °C show one endo-effect that points on large inhomogeneity of low temperature frits and the presence of some phases differing with melting temperature.

Foaming of pellets (d=10 mm), prepared from foam forming admixtures (specific surface 6000 cm²/g), has been performed in temperature range 900 – 975 °C (with step 25 °C) with exposure at maximal temperature in 20 minutes. It is stated that foam material with relatively uniform fine porous structure is obtained at foaming temperature of 950 °C. While macrostructure of the samples obtained at 900 – 925 °C has dense crust with thickness more than 3 mm, and the samples obtained at 975 °C are deformed in consequence of vitrification and show random structure with the presence of large pores with size more than 5 mm. It is stated by XFA data that if foaming temperature increases from 900 to 975 °C quantity of crystalline phase in finished foam material decreases from 23 % to 8 %.

One traces connection of foam material macrostructure with temperature of preparation of frit, from which foam forming admixture is obtained. The foam material obtained from frit at 900 °C is the most optimal from point of view of pore size and uniformity of their distribution.

Values of the main physical – mechanical properties of samples prepared from frit synthesized at various temperatures (Fig. 1) allow to make a note of following laws in changes of properties. If temperature of frit synthesis increases from 800 to 900 °C, density of pellets decreased on an average in two times, strength – in four times, and water absorption – in 13 times.

![Fig. 1 – Properties of the foam material received from frit, synthesized at: a – 800; b – 825; c – 850; d – 900 °C](image)

Comparative characteristic of the samples prepared on the basis of mortar sand screenings with other heat insulating materials shows that the material occupies intermediate position between foam glass and expanded clay (Table 2). The value of strength coefficient of the foam crystalline material, which is ratio of strength to density, exceeds one of foam glass and expanded clay. Material differs with high strength, low water absorption and relatively low heat conduction coefficient that allows to recommend its as heat – insulating and construction material.
Table 2. The comparative characteristic properties of foams

| The granulated material          | Bulk density, kg/m³ | Strength at compression in the cylinder, MPa | Heat conduction coefficient, W/m.K | Water absorption volume, mass % | Strength coefficient |
|----------------------------------|---------------------|---------------------------------------------|-----------------------------------|--------------------------------|----------------------|
| Foamglass-crystal                | 300 – 450           | 4,5 – 5,5                                   | 0,09 – 0,10                       | 0,5 – 0,7                      | 1,3                  |
| Foamglass from a cullet          | 100 – 250           | 1 – 1,5                                     | 0,06 – 0,08                       | 5                              | 0,7                  |
| Clayite                          | 300 – 800           | 0,6 – 4,5                                   | 0,10 – 0,16                       | 8 – 20                          | 0,5                  |

Conclusions.
1. Screenings of mortar sands with content of SiO₂ about 70 mas % and size of particles less than 60 μm are suitable for preparation of foam crystalline material from low temperature frit synthesized at temperature of 900 °C. Glass phase of frit is not crystallized in range of foaming temperature, has sufficient viscosity and temperature of its pyroplastic state coincides with temperature of oxidation of gas forming agent.
2. If the synthesis temperature increases from 800 to 900 °C quantity of glass phase in frit increases from 66 to 73 %. The crystalline phase of frit is presented by residual quartz and feldspar as well as appearance of new phase in form of silicate Na₂O•CaO•3SiO₂. Content of crystalline phase in finished foam material decreases from 23 to 8 % in dependence on increase of foaming temperature from 900 to 975 °C.
3. Frit synthesized at 900 °C and foaming temperature 950 °C are optimal for preparation of foam material with improved properties. Prepared foam crystalline material has higher strength up to 5.5 MPa at bulk density 450 kg/m³ and low water absorption not exceeding 1 mas %.

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