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## Getting Fired Material with Vitreous Binder Using Frame Technology

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### Abstract

There is no chance to expand kiln materials properties and scope as such materials do not have any coarse aggregate in their composition. In this regard, we decided to develop a fired material with coarse aggregate. It is only possible to add coarse aggregate in a material composition when we get unshrinkable binder that has strong adhesion to the aggregate grains. In this article, we describe a method for producing such a binder of waterglass and sodium-lime-silica glass powder during firing semifinished product. We propose to use frame technology for molding the semifinished product – the binder components are used sequentially with the gluing the frame of the coarse aggregate in the form of waterglass and impregnation of the extracted hardened frame with the glass powder suspension. The frame technology provides a large pore structure of the material and reduces the amount of binder. The impregnation of the hardened frame and the firing of the semifinished product performed at 740 - 780 ° C without molds. By using the proposed technology, we obtained the fired material with coarse aggregate on unshrinkable porous vitreous binder. Physical and mechanical characteristics of the material allow to use it for manufacturing of insulating or structural-insulating products for building purposes in the form of blocks or slabs.

**Keywords:** coarse aggregate, waterglass, soda-lime-silicate glass, roasting

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### 1. Introduction

Ceramics is attractive as a building material because of its durability and eco-friendliness. The most available and massive raw material for ceramic building products is natural clay which has a heterogeneous composition. To correct the molding, drying and roasting properties of clay raw materials, they use different corrective additives, including fine aggregates, but coarse ones are used in a very limited way. Unlike the production of roasting-free binder materials, in which coarse aggregates are widely used as controllers of material properties and to reduce binder consumption. The reason for this lies primarily in increased shrinkage of the ceramic mass during the firing, preventing the formation of defect-free contact zone between a ceramic crock and a coarse aggregate. Studies related to the use of coarse aggregates in roasting materials follow the path of replacing the clay component with other eco-friendly fired binders, allowing us to create defect-free contact zone between binder and coarse aggregate [1-3].

Thereupon, as described in this paper, the results of research are very important as they aimed at developing technology for getting a fired material with a coarse heat-resistant aggregate and eco-friendly, vitreous and porous binder.

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## 2. Objective and Methods

The objective is to develop the fired porous vitreous binder and the technology for the production a material with a coarse heat-resistant filler based on this binder.

The methods for the research included: selection of the aggregate type and materials for fired porous vitreous binder, establishment of basic technological parameters of producing finished products using the frame molding technology.

We used expanded clay gravel as the filler.

For fired porous vitreous binder, we selected glass powder obtained by grinding utilized container and building glass and liquid sodium glass.

The choice of glass powder is due to the chemical activity and ion exchange properties of dispersed glass. These properties allow us to use it under certain conditions as a binder [4]. It is important to note that glass becomes pyroplastic when heated and is able to act as a high-temperature (calcining) binder.

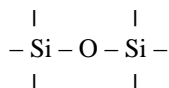
Liquid sodium glass was selected as a source of alkali silicate solution as it is able to provide the flow of leaching and supplying with water of the glass powder initial structure [5, 6] during the semifinished product molding and drying. Liquid glass also performs the function of an adhesive for bonding the filler granules at a two-stage molding of semifinished product using the frame technology.

The two-stage molding of non-calcined materials with fillers includes preliminary bonding frame of the aggregate grains and then filling the voids of hardened frame with the binder (matrix composition) [7]. The difference between the proposed technology and the one described above is that after filling the voids of the hardened frame with the matrix composition, the binder is synthesized during the following drying and calcining the semifinished product. The frame molding technology was chosen to speed up the drying process of the semifinished product before firing. The degree of filling of the intergranular voids volume with the calcining binder leads to the obtaining solid or macroporous structure of the material. It should be noted that the possibility of obtaining large-pore material structure is an advantage of the frame molding technology compared to the concrete molding technology.

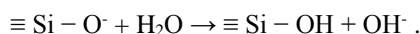
Theoretical justification of the synthesis mechanism of a two-component composition porous glassy binder is conducted on the analysis of modern conceptions about structure and properties of alkaline silicate solutions described in [5] and physico-chemical behaviour of alkali silicate glasses in contact with water, given in [6].

When drying liquid sodium glass, which sticks together frame, there are supersaturated metastable solution with the subsequent transition into the vitreous state of sodium silicate hydrate forms during moisture evaporation.

Solidification is accompanied by polymerizing silicon-containing chemical bonds when removing the hydroxyl-hydrogen groups and forming the three-dimensional polysilicon frame structure with cells of this type:



The cured adhesive bond has a strong adhesion to the surface of the porous filler and high strength, but it is not water-resistant. During subsequent drying of the frame impregnated with an aqueous suspension of glass powder, there is a dissolution of vitreous liquid-glass bonds as the process of interaction with a layer of a glass suspension. The process of the hydrated sodium glass dissolution is accompanied by a transition to a solution of sodium cations due to solvation interaction. The kinetics of silicate dissolution is determined by the glass module and the temperature. Towards the sodium cations, water molecules diffuse in the glass phase, some of which enter the hydrolysis reaction with the anionic glass frame:



Having high mobility, the formed hydroxyl ions leave the reaction zone at the interface and go into the solution. Released monomeric and polymeric anions (existing in the glass) can also go into solution. Cations have a higher transition speed in the solution than anions do. The consequence of this is the creation of conditions to increase the hydrated silica concentration at the interface. As the temperature rises during the processes of material drying and the pH lowering, there is polymerization of hydrated silica and the formation of the silica gel film. At a certain stage of drying, the formed viscous gel layers slow down the process of vitreous liquid-glass bonds dissolution of the frame, and it helps the frame to save certain strength and allows us drying the impregnated frame without molds. Simultaneously with the process of interaction between the glass mortar slurry and liquid-glass frame adhesive, there are processes of leaching and watering of the original structure of the glass particle suspension, which mechanism is based on the interaction between aqueous alkali solutions and alkali-silica. The glass watering goes together with hydration and hydrolysis and is accompanied by the adsorption of alkaline metals hydrated cations on the silica surface active areas that develop when grinding the glass. Further there is the depolymerization of silica due to the hydrolysis of bonds:  $\equiv \text{Si} - \text{O} - \text{Si} \equiv$  along with the formation of silanolate groups  $\equiv \text{Si} - \text{OH}$ .

Hydrated silica when dried is transferred to the surface of glass particles. With an increase in its concentration in the drying process, the silicic acid polymerization takes place to form dense elastic gel film having astringent properties. As the removal of free water from the drying material, sodium hydrosilicates develop from the destruction products of the adhesive bond of the frame and the glass particles suspension. After drying, the remaining free water forms hydrogen bonds with the silanol water. Subsequent heating of the raw product in the kiln to 400 °C is accompanied by removal of water from sodium hydrosilicates. With further temperature increase to 740-780 °C silica bonds are destroyed, silicon-oxygen tetrahedra polymerized and the water is released while the dehydration of the hydroxyl glass cover. In the same temperature range, the eutectic mixture of Na<sub>2</sub>O-CaO-SiO<sub>2</sub> system forms from the components of the complex binder and during melting, it provides the accumulation of significant amounts of melt with the necessary pyroplastic mobility and the closed pores formation in the calcining bond volume. In case of coincidence of the gassing and the closed pores formation processes, there are the conditions for the swelling of the binder with a sharp increase of vapor pressure in the pores.

### 3. Process description

The technology of obtaining material with the proposed calcining binder includes the following operations:

1. Mixing of the aggregate with liquid glass and the prepared mixture placing into molds.
2. Curing of vitreous binder frame in the molds during the drying process at temperatures of 60-80 °C and obtaining the frame.
3. Removing the hardened frame from the mold and impregnating it with an aqueous suspension of glass powder.
4. Drying impregnated frame at a temperature of 60-80 °C.
5. Calcining of the impregnated and dried frame at 740-780 °C.
6. Cooling of the calcined product inside the kiln.

The rheological characteristics of the binder at the calcining operating temperatures provide products resistance to deformation and preservation of regular geometric shape with some increase in volume, and it allows us to calcine products without special tooling, using a heat-resistant trays with a smooth surface.

The binder has a strong adhesion to the aggregate grain surface.

Obtained material can have a coarse or a monolithic structure depending on the degree of the frame pores filling with the binder during the products molding (see Fig. 1):

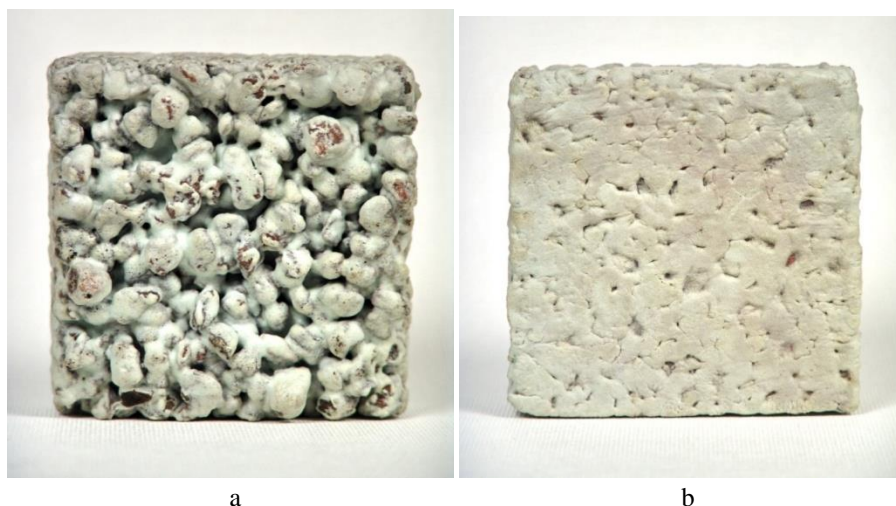


Fig 1. Macroporous (a) and monolithic (b) structure material with expanded clay fraction 5-10 mm.

Physico-mechanical properties of the obtained samples of the large-pore structure are changed depending on the characteristics of the filler, on the degree of filling voids between the grains with the calcining binder and are characterized by the following indicators: density of 600-846 kg / m<sup>3</sup>; water absorption determined after boiling the samples in water for 30 minutes is 10,6-24,2%; the thermal conductivity of the sample (density of 730 kg / m<sup>3</sup>) - 0.17 W / (m·°C); the compressive strength is 1.5 to 2.5 MPa.

The diameter of the pores of the calcined glassy bundle defined by microscopic examination is 0.02 to 0.50 mm.

#### 4. Results and Analysis

The results showed that the swelling of the binder compensates its shrinkage during firing, which prevents the formation of shrinkage cracks during the interaction of the binder with the filler grains frame, leading to a sharp reduction of the material strength. The effect of eliminating shrinkage cracks during glassy binder swelling shown in Fig. 2.

To confirm the assumption that the vitreous binder intumescent agent is water vapor in pyroplastic state during calcination, we performed the infrared spectroscopic studies. In the IR binder absorption spectrum after drying the impregnated frame, we recorded a broad absorption band in the range of  $3\,300 - 3\,600\text{ cm}^{-1}$  associated with O – H bond stretching vibrations in oxyhydriyl groups  $\text{O}_m\text{H}_n$  [8], and the absorption band at  $1446\text{ cm}^{-1}$  associated with the presence of carbonate ions. After firing the semi-finished product, the intensity of the absorption band of the calcining bundles (associated with stretching vibrations of the O – H bond) decreases and the carbonate ions absorption band is completely disappear. Thus, the presence of absorption in the  $3300 - 3600\text{ cm}^{-1}$  in the calcining bundle indicates that the expanding agent is water vapor.

To establish the mechanism of pore development in the calcining binder we used thermogravimetric analysis with the TGA/DSC1 derivatograph. The binder samples for analysis were chosen from impregnated and dried at a temperature of  $60\text{--}80\text{ }^{\circ}\text{C}$  frame. Three parameters were automatically recorded: temperature rise (T), thermogravimetry ('TT' - weight loss of the sample), the rate of weight change ('DTT' - intensity of destruction), see Fig. 3. After the appropriate preparation, the sample was heated from  $25$  to  $750\text{ }^{\circ}\text{C}$  at a rate of  $8\text{ }^{\circ}\text{C}/\text{min}$ .

On the vitreous binder sample derivatogram (see Fig. 3a) in the temperature range from  $625$  to  $720$ , at which the binder swelling occurs, we noted changes on 'TT' and 'DTT' curves that can be explained by the water removal from the watered structure of vitreous binder in the observed temperature range.

On liquid sodium glass sample derivatogram of (see Fig.3b) in the temperature range corresponding to the swelling of the binder, we did not observe any significant processes of degradation and decomposition of the sample (no steps on the 'TT' curve and peaks on the 'DTT' curve) associated with the evolution of gaseous reaction products. Analysis of the sodium-lime-silicate glass sample derivatogram showed similar results.

The results show that new formations are the source of the gaseous phase during the binder swelling. These new formations come from the interaction of water glass binder with particles of the impregnating glass suspension in the process of the material heat treatment.



Fig. 2. Contact zone of the calcining bundle without swelling (a) and with swelling (b) of the vitreous binder.

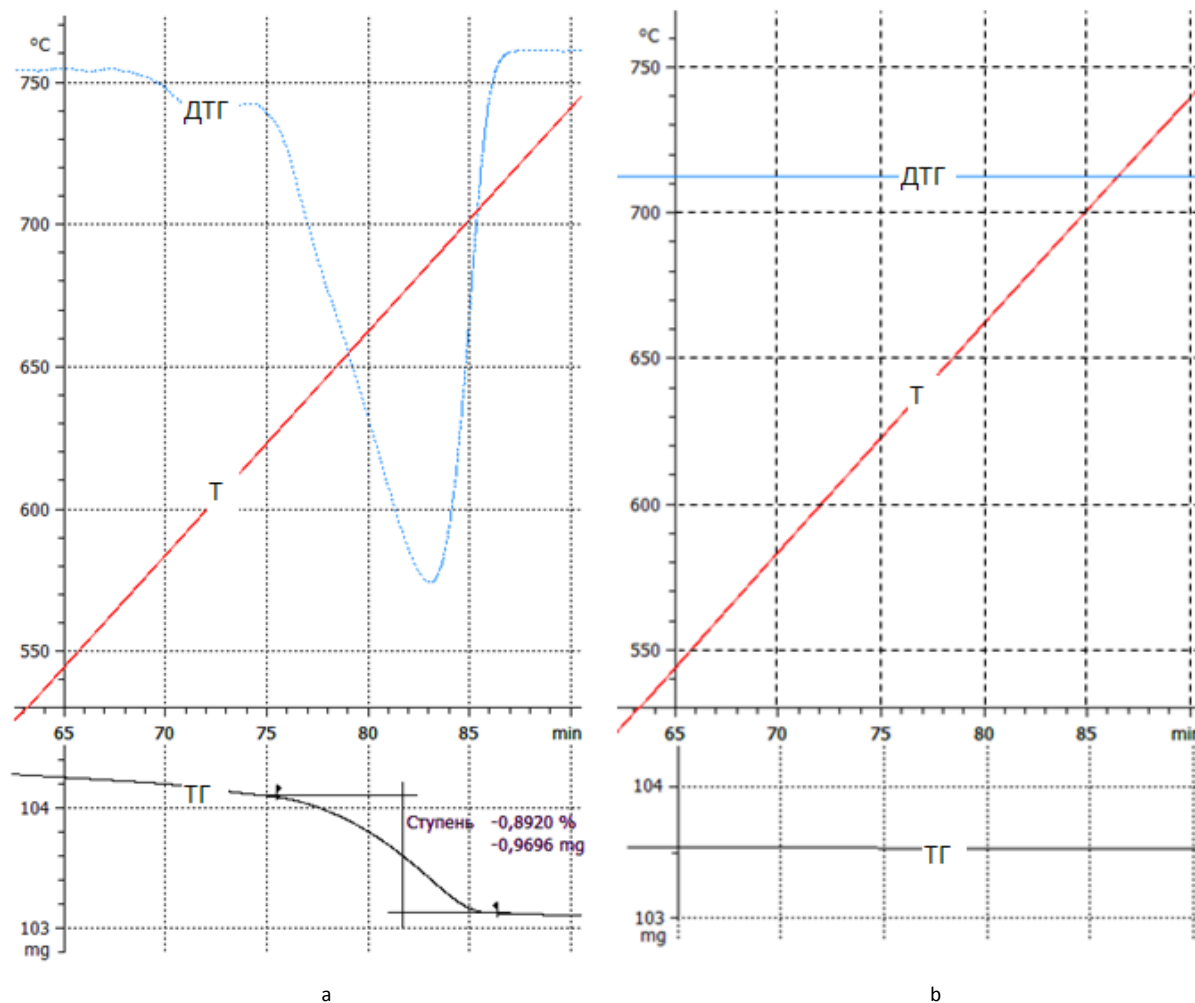


Fig. 3. Derivatograms of: vitreous binder (a), liquid sodium glass (b)

## 5. Conclusions

The results of these studies, having searching nature, prove the possibility of obtaining a calcined material with coarse aggregate on a calcining porous vitreous binder using frame technology. Swelling of the binder compensates its shrinkage during firing, it prevents the formation of shrinkage cracks during the interaction of the binder with a coarse aggregate rigid frame.

Rheological characteristics of the calcining binder of the developed material make it possible to calcine products without special molds, using only heat-resistant trays with smooth surface.

The obtained material has a water resistance, fire safety, environmental cleanliness. Physical and technical characteristics of the material make it possible to use it in construction as an insulating or structural-insulating construction material in the form of blocks or slabs.

The results obtained can be used for the development of industrial production of the developed material with in brick factories with the addition of supplementary process equipment.

## References

- [1] Mizyuryaev S.A., Mamonov A.N., Gorin V.M. i dr. The structured high-porous soda-silicate material raised warm and thermal stability. Stroitel'nye materialy [Construction materials]. 2011. No.7, pp. 7–9 (In Russian).
- [2] Pichugin A.P., Denisov A.S., Khritankov V.F. i dr. The progressive concept of formation of wall blocks from light concrete on an roasting binder. Stroitel'nye materialy. [Construction materials]. 2011. No.12, pp. 22–24 (In Russian).
- [3] Erofeev V.T., Korotaev S.A. Structurization of waterglass binder macroporous ceramic material. Stroitel'nye materialy. [Construction materials]. 2006. No.7, pp. 64–65 (In Russian).
- [4] Ketov A.A., Puzanov S. Nanotechnologies by production the foamglass of materials of new generation. Stroitel'stvo: novye tekhnologii – novoe oborudovanie. 2010. No.1, pp. 15–19 (In Russian).
- [5] Korneev V.I., Danilov V.V. Proizvodstvo i primeneniye rastvorimogo stekla: Zhidkoe steklo [Production and use of soluble glass: Waterglass]. L.: Stroizdat. Leningradskoe otdelenie, 1991. 176 p. (In Russian).

- [6] Shelkovnikova T.I., Baranov E.V., Petukhova N.S., Tishchenko I.V. The main physical and chemical regularities of receiving porous materials from the technogenic glasses flooded in various conditions. Nauchnyi vestnik Voronezhskogo gosudarstvennogo arkhitekturno-stroitel'nogo universiteta. Seriya: Fiziko-khimicheskie problemy i vysokie tekhnologii stroitel'nogo materialovedeniya. 2012. No. 5, pp. 50-56 (In Russian).
- [7] Bobryshev A.N., Erofeev V.T., Kozomazov V.N. Fizika i sinergetika dispersno-neuporyadochennykh kondensirovannykh kompozitnykh sistem [Physics and synergetics of the disperse and disorder condensed composite systems]. SPb.: Nauka, 2012. 476 p. (In Russian).
- [8] Yukhnovich G.V. Infrazrasnaya spektroskopiya vody [Infrared spectroscopy of water]. M.: Nauka, 1973. 208 p. (In Russian).