

## Siliceous Ceramics for Fire Engineering and Heat Insulation Constructions

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**Abstract:** The compositions of porous heat-resistant materials having a density  $250,400 \text{ kg m}^{-3}$ , for protection of structures ( $T_{\text{max}} = 1000^\circ\text{C}$ ) were developed. The silica clay (gaize) which presently are not used for the production of ceramics was choosed as a principal structure formation substance in the creation of materials. The formation of the cellular structure of raw was carried out with the use of gas developing agent ( $\text{H}_2\text{O}_2$ ). Fixing of structure was provided due to effect of thixotropic hardening (without the addition of binders). Increasing the strength and temperature resistance of the siliceous ceramics was achieved by introducing Na-containing substances into mixture. It was established that additives like  $\text{Na}_2\text{O}$ ,  $\text{SiO}_3$  and  $\text{Na}_2\text{CO}_3$  combine the properties of the plasticizer gaize suspensions (slurries), a catalyst of the decomposition process of  $\text{H}_2\text{O}_2$  as well as the corrector of the the phase.

**Key words:** Porous siliceous ceramics, gaize siliceous microporous sedimentary rock, heat-resistant and heat insulation building structure, modifying additive, Russia

### INTRODUCTION

The increase of the cost of power resources promotes the rise of efficiency of industrial heat equipments and thermal protection of the buildings through their appropriate use in the construction of buildings and by improving the composition and structure of the thermal protective materials. It is known that in the technology of fabrication of lightweight and heat-resistant ceramics, having porous fillers are commonly used diatomite or modified refractory clay. Significant researches and developments on heat-resistant and insulation ceramics were carried out by Beregovoi *et al.* (2008).

Direct usage of such siliceous microporous sedimentary rock as gaize in the compositions of high-porous ceramics, made by technology of gas generation is associated with the following problems: the gaize has a high water absorption; the considerable moisture content of raw increases thermal deformations and reduces the mechanical durability of ceramics; binding ability of gaize suspension is insufficient to ensure the raw mechanical durability; the inertness of the majority of gas developing agents to solution of gaize; temperature gradient across the section of the calcining material because of low thermal conductivity (Xue *et al.*, 2011; Guo and Zhang, 2008; Geng, 2010).

This study, reports the results of scientific investigation, the purpose of which is to develop the compositions and research of basic processes,

accompanying the formation of a microstructure of porous siliceous ceramics (density from 250 up to  $400 \text{ kg m}^{-3}$ ), the maximum operating temperature of which amounts up to  $1000^\circ\text{C}$ . The solution of a problem of designing of structures of heat-resistant siliceous ceramics compositions on the basis of gaize was found by the addition of sodium substance. Mineralogical composition of the used gaize includes polymineral connections with predominance of minerals of siliceous grouping; it is characterized by a different degree of content of kaolinite-montmorillonite clays (Distanov, 1987). To improve the material mechanical durability the fine-ground carbon fillers as well as other correction additives were used.

### MATERIALS AND METHODS

#### Mix design and modification of structure

**Mix design of structure:** High mechanical durability of a ceramic matrix is a necessary condition to obtain high-quality cellular materials. Influence of the relationship "Water-Gaize" (W/G) on the mechanical durability (R) and density of the ceramic matrix, received by heating at a temperature of  $900^\circ\text{C}$  is shown in the Table 1. After the data Table 1 was obtained the dependence of the mechanical durability of the base material from water-solid ratio:

$$R = \frac{R'}{m \left( \frac{W}{G} \right)^n} \quad (1)$$

Table 1: The influence of water-gaize ratio on the properties of the ceramic matrix

The relationship W/G	Indicators of properties	
	R (MPa)	Average density (kg m <sup>-3</sup> )
0.4	14.0-16.0	1200-1220
0.5	10.0-10.5	1100-1140
0.55	6.1-6.5	1000-1060
0.75	1.4-1.6	900-915
0.9	1.1-1.3	815-830

Where:

R' = The mechanical durability of the ceramic matrix  
 (W/G = 0.4); = The coefficients equal, respectively 3.63 and 26.3

Taking into account the influence of macroporosity on mechanical durability of the cellular ceramic (R<sub>cell</sub>), dependence Eq. 1 takes the form:

$$R_{cell} = 0.7 \frac{R'}{m \left( \frac{W}{G} \right)^n} \left( 1 - V_{cell}^{\frac{2}{3}} \right) \quad (2)$$

where, V<sub>cell</sub> the macroporosity, created by the process of gas generation. The analysis of the data, obtained during tests showed that the maximum values of mechanical durability of the siliceous ceramic matrix don't exceed 18 MPa. Samples of cellular ceramics with a density of 350-450 kg m<sup>-3</sup>, made by porization of this matrix, had the mechanical durability of no >0.35 MPa.

Essential increase of mechanical durability of siliceous cellular ceramics was achieved through additives which form in structure of the calcined material vitreous melt in an amount of 10-20%. The strengthening effect of introduction of the additives is combined with the improvement of heat-insulating indicators of ceramics due to low thermal conductivity and hygroscopicity of a vitreous phase. Influence of studied additives on properties of the modified matrix is shown in Fig. 1.

R(k) and R(i) the mechanical durability of the control mix and the composition with the additive; D(k) and D(i) the density of the control mix and the composition with additives: 1 without additives (control); test mix with additives: 2-3% NaF; 3-6% Na<sub>2</sub>SiF<sub>6</sub>; 4-2%Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O; 5-4% Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O; 6-4% Na<sub>2</sub>SiO<sub>3</sub>; 7-8% Na<sub>2</sub>SiO<sub>3</sub>; 8-5, 4% BaF<sub>2</sub>; 9-3% NaF+3% dolomite.

The data in Fig. 1 show that the maximum increase in mechanical durability is achieved by using compounds of sodium, consisting of ions F<sup>-</sup> (NaF, Na<sub>2</sub>SiF<sub>6</sub>). Increasing the density of the samples confirms the formation in the structure of the material a certain amount of a vitreous melt. Phase composition of ceramics and raw

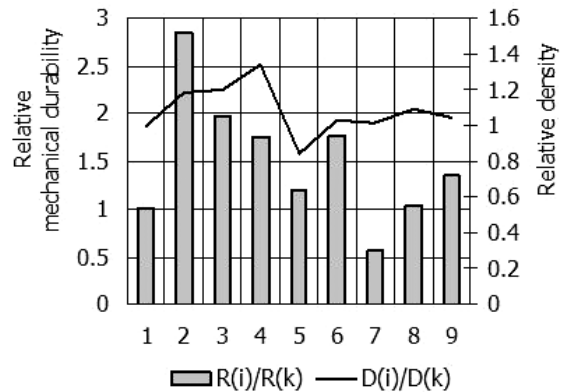


Fig. 1: The influence of additives on the properties of the ceramic matrix

materials was studied by the method of the X-ray analysis. Conducted research revealed the following: The main X-ray-identified components of the gaize are the silicon-containing (siliceous) minerals presented by quartz, tridymite and krystobalite and impurities of clay (sepiolite).

The introduction of additives (Na<sub>2</sub>SiF<sub>6</sub>) is accompanied by intensive development phase of a plagioclase in the course of roasting. The X-ray pattern demonstrates that the decomposition products of minerals of the gaize almost completely dissolved in the melt. Also the quartz phase has undergone partial melt. Vitreous material is noted as X-ray amorphous substances in the field of corners 20-26°C (Fig. 2). Results of the conducted researches were taken into account in the further development of the compositions of siliceous ceramics.

## RESULTS AND DISCUSSION

**Study of the influence of the plasticizer on the viscosity of the slurry:** As the plasticizers were selected the various inorganic salts (Fig. 3). Their use activates the mechanism of lowering the viscosity, based on processes of ion exchange but also on the change of electrokinetic potential of the solid phase.

As is seen in Fig. 1, the increase in the content of additives Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, NaOH, Na<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> in an amount up to 1% improves the fluidity of the aqueous suspension. The mechanism of the liquefaction process is realized through deflocculation of gaize's micelles by exchanging bivalent cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>) of their solvate layer on monovalent cations (Na<sup>+</sup>). This process is accompanied by the increase of electrokinetic's (Zeta) potential and the release of bound water. Anionic part of additives must bind Ca<sup>2+</sup> in poorly soluble salts. This is indicated by the absence of effect of liquefaction, when adding NaCl.

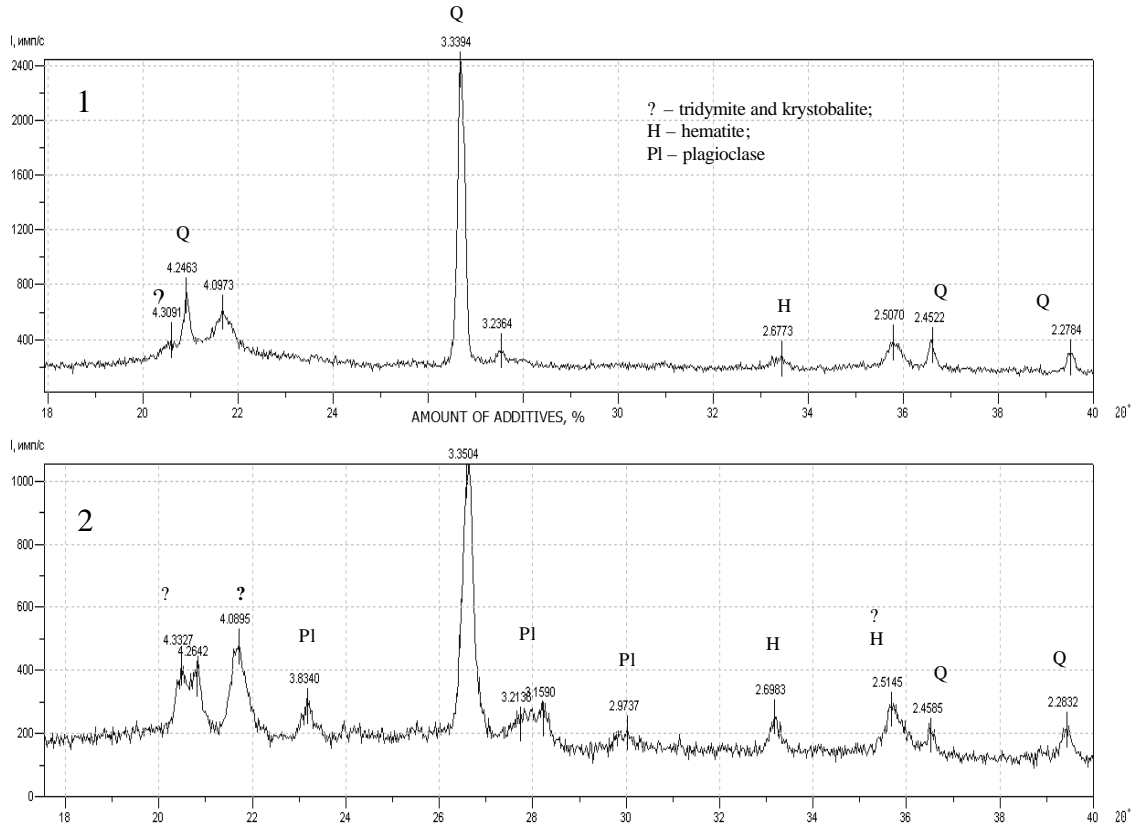


Fig. 2: X-ray pattern of the siliceous ceramics: 1-gaize (100%); 2-with additive  $\text{Na}_2\text{SiF}_6$  (20%)

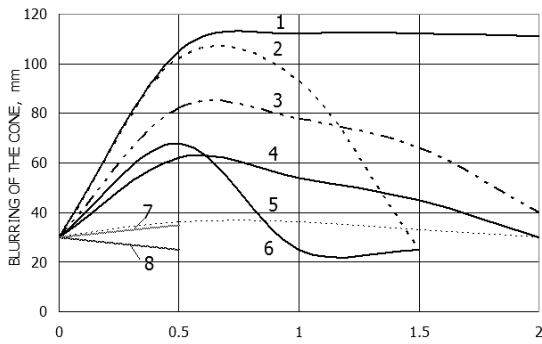


Fig. 3: The influence of Na-containing additives on the viscosity of the slurry: 1- $\text{Na}_4\text{P}_2\text{O}_7$ ; 2- $\text{NaOH}$ ; 3- $\text{Na}_2\text{SiO}_3$ ; 4- $\text{Na}_2\text{CO}_3$ ; 5- $\text{NaF}$ ; 6- $\text{Na}_2\text{B}_4\text{O}_7$ ; 7- $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ ; 8- $\text{NaCl}$

The introduction of additives in excess of the optimum content (0.5-1.5%), leads to the opposite effect the suspension viscosity increases. The mechanism of liquefaction is limited by the content in the gaize of impurities, capable to hydrate with the formation of multiply charged cations. The increase of amount of

sodium salts after removing of exchangeable cations according result in can lead to the raise of viscosity of the slurry by lowering electrokinetic's Zeta-potential and the rapprochement of the particles (descending branch of the diagrams in Fig. 3).

In most technological processes the dependence of electrokinetic's potential on the electrolyte concentration is determined by a more complicated process, associated with a specific adsorption of ions. This is indicated by data obtained during the study of the influence of the type of cations of the diluent on the plasticizing of gaize suspension (Fig. 4).

From the Fig. 2 it is seen, that for the gaize suspensions the increase of effect of diluting, when using additives with monovalent ions, is consistent with a number, considering the sizes of their hydrate cover:  $\text{Li}^{2+}$ (0.340 nm);  $\text{Na}^+$ (0.240 nm);  $\text{K}^+$ (0.170 nm). The cations, having the minimum size in the hydrated state ( $\text{K}^+$ ), are capable to increasing of concentration in Stern's layer.

In turn, a more complete shielding of potential determining ions on the surface of the gaize reduces the magnitude of the electrokinetic potential of solid particles, the width of the diffusion part and the mobility of system. The efficiency of the use of additives was estimated by

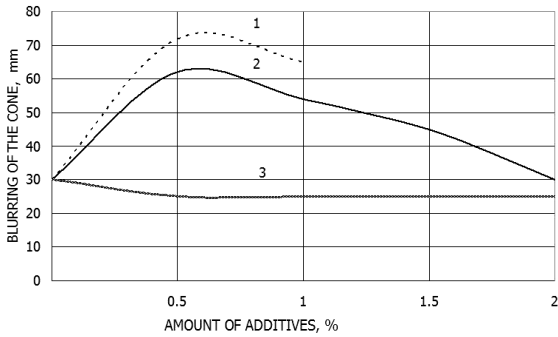


Fig. 4: The influence of type of the cations of additives on the viscosity of the slurry: 1-Li<sub>2</sub>CO<sub>3</sub>; 2-Na<sub>2</sub>CO<sub>3</sub>; 3-K<sub>2</sub>CO<sub>3</sub>

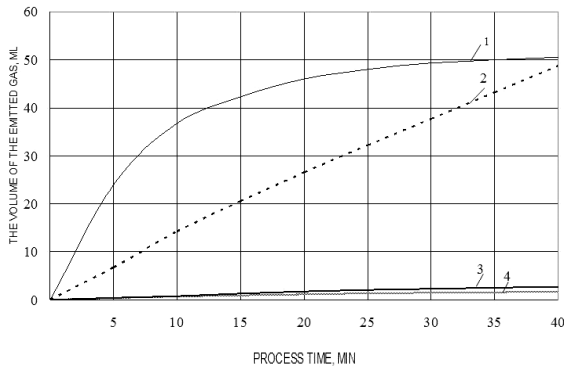


Fig. 5: The generation of gas at decomposition of H<sub>2</sub>O<sub>2</sub> in the presence of the catalyst: 1-powdered coal; 2-Na<sub>2</sub>CO<sub>3</sub>; 3-Na<sub>2</sub>SiO<sub>3</sub>; 4-Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>

the value of reducing the water demand of gaize suspension. On this indicator the studied substances are placed in the following sequence: Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (22,6%); NaOH (20%); Na<sub>2</sub>SiO<sub>3</sub> (13%); Na<sub>2</sub>CO<sub>3</sub> (5%); Na<sub>2</sub>CO<sub>3</sub> (4,55%); NaF (4%).

**Study of the influence of the plasticizer on the process of gas generation:** High technological properties, displayed by hydrogen peroxide at the stage of preliminary samples making, resulted in the selection of H<sub>2</sub>O<sub>2</sub> as gas-forming substance.

The influence of the catalyst on the parameters of the decomposition process of hydrogen peroxide was determined on model systems, consisting of 5 mL of hydrogen peroxide of 3% concentration and 1.7% of the additive.

In this quality have used homogeneous catalysts in the form of the Na-containing salts and the organic plasticizers as well as heterogeneous catalyst powdered coal. A constant additive in mix was K<sub>2</sub>MnO<sub>4</sub>

Table 2: The values of the parameters

The type of solution	Parameters	
	V <sub>max</sub>	Mp <sub>a</sub>
Without any additives	205.8	0.227
With adding of S-3	192.1	0.281
With adding of LST	189	0.104

Table 3: Cemetics properties description

Parameters	Values
Density (kg m <sup>-3</sup> )	250-450
Mechanical durability, Mpa	1.5-2.0
Maximum operation temperature (°C)	950-1000
Coefficient of heat conductivity (W m <sup>-1</sup> , K)	0,07-0.10
Maximum sorption moistening (%)	3-4

(~50 mg L<sup>-1</sup>). In graphing the experimental curves the volume of the oxygen, emitted at decomposition of H<sub>2</sub>O<sub>2</sub> was determined by a gas-metric way (Fig. 5).

The influence of organic plasticizers on oxygen generation was studied on the additives naphthalenesulfonates of Sodium (S-3) and Lignosulfonate of Sodium (LST) (1.35%). These additives show a positive effect of decrease of viscosity in gaize suspension. In the process of running the experiment was made a basic solution, consisting of 20 mL of hydrogen peroxide of 3% concentration also Na<sub>2</sub>CO<sub>3</sub> (2.5%) and K<sub>2</sub>MnO<sub>4</sub> (0.05%). The amount of the emitted gas during the decomposition of H<sub>2</sub>O<sub>2</sub> to a certain point of time is expressed by relation:

$$V = V_{max} (1 - \exp^{-bt}) \quad (3)$$

Where:

- V<sub>max</sub> = The maximum volume of the emitted gas (mL)
- τ = Time (min)
- b = The parameter of the process, depending on the type of plasticizer (Table 2)

After manufacturing and heating up to temperatures 900-950°C the obtained ceramics have got the properties are shown in Table 3 (Beregovoi *et al.*, 2011).

## CONCLUSION

The achieved results allowed to develop a list of the corrective additives to compositions of lightweight silica ceramics, obtained by the method of gas generation (agent H<sub>2</sub>O<sub>2</sub>):

- Plasticizers; Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, NaOH, Na<sub>2</sub>SiO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>
- The catalyst of the process of gas generation Na<sub>2</sub>CO<sub>3</sub>

- The multipurpose additive powdered coal increases the effect of diluting and is the catalyst of decomposition  $H_2O_2$ , as well as burnable and heat generating component in the course of roasting
- The glass-forming additives, improving the mechanical durability and heat-insulating properties  $Na_2CO_3$ ,  $Na_2SiO_3$ ,  $Na_2B_4O_7 \cdot 10H_2O$ ,  $Na_3PO_4$ ,  $Na_2SO_4$ , NaF

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