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Improving the Quality of Porous Silica Ceramics by the Method of Plasticization of Slurries for their Application in Thermal Protection Structures

V. A. Beregovoi* and A. M. Beregovoi

Department Technology of Building Materials and Wood Processing, Penza State University of Architecture and Construction, Penza, Russia; vabereg@rambler.ru, ambereg@rambler.ru

Abstract

Objectives: The problem of producing a cellular ceramic from well-foamed slurries with low water content can be solved by introducing diluting additives – salts of sodium, potassium, lithium and organic plasticizers. **Methods/Statistical Analysis**: Suttard's viscometer was used to study the theology of silica slurries. The experimental data were processed by methods of mathematical statistics, using Student-Fisher criterion. It was established, that there are two different areas of concentration of diluents: effective (reducing the viscosity of suspension) and inefficient (increasing the viscosity of suspension). **Findings:** The experiments show, that in the case of concentrated siliceous suspensions siliceous inorganic diluents show the maximum water-reducing effect. This refers to salts based on lithium and sodium compounds ($Na_4P_2O_7$, NaOH, Na_2SiO_3, Li_2CO_3, Na_2CO_3), with their content not exceeding 0,5...0,75 %. The effect of the concentration of electrolytes on the viscosity index is described by complex processes associated with specific adsorption of ions (electrolytes are determined by the more complicated processes associated with the specific adsorption of ions). The purpose of this work is to determine the applications of the effective concentration of different types of diluents. **Application/Improvements:** Experiments and numerical calculations show that diluting effectiveness of the admixes in the suspensions of the gaize was achieved: for water-reducing effect 1.25…1.29; for reduction of water demand 20…22.6 %.

Keywords: Porous Silica Ceramics, Plasticization

1. Introduction

In the production of porous ceramics are widely used the raw slurries, based on plastic clays. Their high shrinkage results in the formation during drying and roasting of significant internal stresses in the structure of the cellular raw material that reduces the quality of the ceramics. An easy-to-implement method for obtaining of low-shrinkage ceramic slurries consists in replacing the clay component by the siliceous component, produced from opal-cristobalite rocks. Considering the wide distribution and lack of demand of natural gaize from the industry, were considered the technological aspects of the application of these opal-cristobalite rocks[1].

2. Materials and Methods of Research

The materials were produced according to the technology, consisting of the preparatory and main stages. The preparatory stage consisted in crushing up to 5000 … 6000 cm^2/g of pre-dried natural component – a siliceous gaize. The composition of the gaize (mass. %): chemical: SiO_2 (87); Al_2O_3 (2); Fe_2O_3 (1,9); CaO (1,3); MgO (0,6); loss on ignition ~ (7); mineralogical: quartz (15…20), montmorillonite (10…15), opal silicon dioxide (55…65).

Modifying additives (Li_2CO_3, Na_2CO_3, Na_2SO_4, Na_2SiO_3, $NaNO_3$, KNO_3, K_2CO_3 and CaO, $CaMg(CO_3)_2$) were entered into composition of the raw mix before

**Author for correspondence*

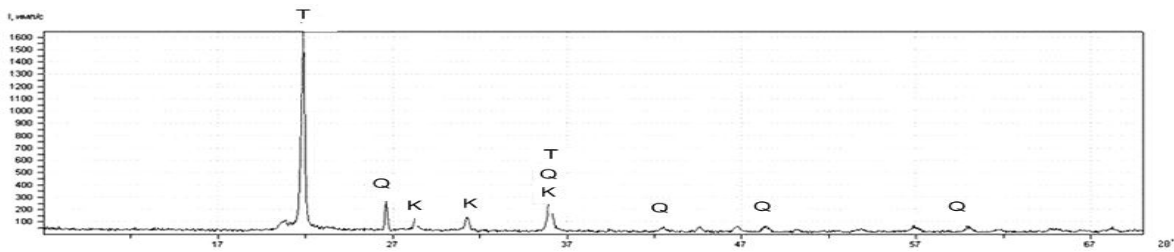

Figure 1. X-ray pattern of the gaize with an additive of Na_2CO_3 and Na_2SiO_3.

roasting. Roasting of the material (1 hour at a temperature of 800...820 °C) provided the activation process of sintering and formation of the phase composition[2]. According to x-ray phase analysis in Figure 1. It is represented by glass and a crystal phase in the form of residual quartz (Q) and its temperature modification – tridymite (T) and krystobalite (K).

Control of structure formation processes was carried out by varying the amount and chemical composition of additives-modifiers.

Suttard's viscometer was used to study the theology of silica slurries. The experimental data were processed by methods of mathematical statistics, using Student-Fisher criterion.

3. Results and Discussions

Improving the indicators of strength and shrinkage of a matrix was achieved by reduction of thickness of the water interlayers on the surface of the mineral particles due to reducing the water-solid ratio (W/S) in the raw mix.

Siliceous gaize and tripoli powder (which differ in the content of clay impurities) were used in the studies[2].

Influence of W/S on strength of the matrix substance, received by roasting of a gaize at a temperature of 900 °C, is given in Table 1.

The dependence of mechanical strength from W/S is expressed by the ratio[3]:

$$R_{matrix} = \frac{R^{/}}{m \cdot \left(\frac{W}{S}\right)^{n}}, \qquad (1)$$

Where R_{matrix}– mechanical strength of the ceramic matrix, when W/S =0,4; n and m – empirical coefficients, that take into account the negative effect of mixing water.

Table 1. The influence of W/S-ratio on the properties of the matrix substance

W/S-relations	Indicators of properties	
	Compressive strength, MPa	Average density, kg/m³
0,35	19,5…22,4	1280…1350
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

The production of mobile and well-foamed slurries with low water content is possible under the condition of using effective diluting agents. As diluents were chosen the salts of sodium, potassium and lithium. Their use activates the mechanism of viscosity decrease, based on the processes of ion exchange, as well as on the change in the electro kinetic potential of particles of the solid phase.

The dependence of the fluidity of the slurries from the type and amount of injected Na-containing additives (W/S=const), is shown in Figure 2.

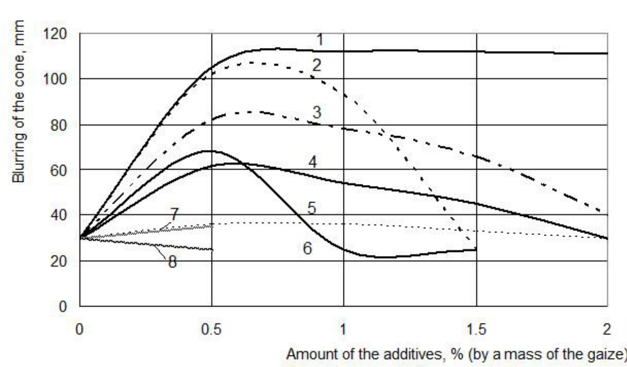

Figure 2. Influence of Na-containing additive on the viscosity of the slurry 1– $Na_4P_2O_7$; 2 – NaOH; 3 – Na_2SiO_3; 4 – Na_2CO_3; 5 – NaF; 6 – $Na_2B_4O_7$; 7– $Na_2C_4H_4O_6$; 8 – NaCl.

Figure 2 shown that the increasing content of additives $Na_4P_2O_7$, NaOH, Na_2SiO_3, Na_2CO_3 and $Na_2B_4O_7$ to 1% significantly enhances the fluidity of the water suspensions of the gaize. The mechanism of the liquefaction process takes the form of deflocculation with micelles by an exchange of divalent captions, their salvation layer (Ca^{2+}, Mg^{2+}) on monovalent (Na^+), accompanied by an increase of electrokinetic potential and the release of bound water.

The anionic part of the electrolyte, binding bivalent cations in slightly soluble salts, forms the main driving force of the process of fluidifying (this is indicated by the absence of the thinning effect of adding sodium chloride)[4].

The introduction of additives in excess of the optimum content (0,5…1,5 %), leads to the opposite effect – viscosity of the suspension increases. The mechanism of fluidifying is limited by the contents in the gaize of the impurities, which are capable to hydrate with the formation of specific multicharged cations. After removal of the majority of exchangeable cations, further increase in concentration of ions of Na^+ leads to the raise of viscosity of the slurry by lowering Zeta-potential and the rapprochement of particles (descending branch of the diagrams in Figure 2.

The dependence of the diffusion layer thickness on the electrolyte concentration in the solution can be expressed by the Debye-Huckel equation

$$\lambda = \sqrt{\frac{\varepsilon \cdot \varepsilon_{\hat{i}} \cdot R \cdot T}{2 \cdot F^2 \cdot I}}, \quad (2)$$

where F is the Faraday number; ε – the dielectric constant of the liquid phase; ε_0 – the universal electric constant; I – the ionic strength of the solution, determined by the Lewis formula

$$I = \frac{1}{2} \cdot \sum_{i=1}^{n} C_i \cdot z_i^2, \quad (3)$$

where C_i – molar concentrations of ions (mol/l), z_i – ion charges.

From the equation (2) follows, that the thickness of the diffuse layer on the particles of the gaize is inversely proportional to the square root of the concentration of the diluent additive. This dependence is valid for the case of nonspecific adsorption of ions, introduced into the system, which presupposes the predominance of electrostatic interactions.

In most technological processes the dependence of Zeta-potential from the concentration of electrolytes is determined by a more complicated process, associated with the specific adsorption of ions. This is indicated by data, obtained during the study of the influence of the type of cation of the diluent on the plasticization of gaize suspension in Figure 3.

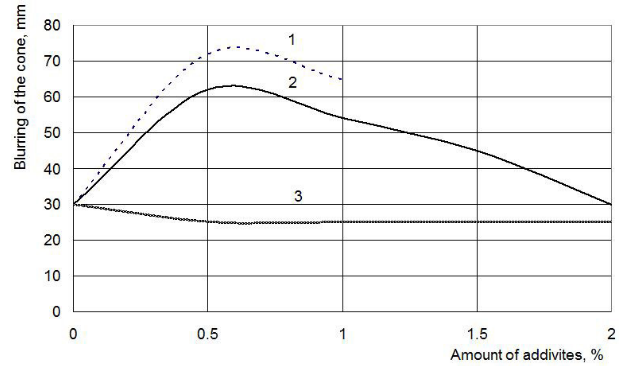

Figure 3. The viscosity of the slurry: influence of type of the cation of additives 1 – Li_2CO_3; 2 – Na_2CO_3; 3 – K_2CO_3.

Figure 3 shows that for gaize suspensions the increase of the diluting effect from the use of additives with monovalent ions is consistent with a number, that takes into account the size of their hydration shell: Li^{2+}(0,340 nm); Na^+(0,240 nm); K^+(0,170 nm). The cations, having the minimum size in the hydrated state (K^+), are capable of high concentration in the 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 the solid particles, as well as the width of the diffusion part and the fluidity of the system.

The effectiveness of the use of additives was evaluated according to the magnitude of the water relations

unplasticized $\left(\frac{W}{S}\right)_{base}$ and plasticized $\left(\frac{W}{S}\right)_{plast.}$

slurries, having the same mobility. The comparison was carried out by the variables:

water-reducing effect

$$W_{eff} = \frac{\left(\frac{W}{S}\right)_{base}}{\left(\frac{W}{S}\right)_{plast.}} \quad (4)$$

reduction of water demand

$$\Delta W_{eff} = \frac{\left(\frac{W}{S}\right)_{base} - \left(\frac{W}{S}\right)_{past.}}{\left(\frac{W}{S}\right)_{base}} \cdot 100 \qquad (5)$$

The results of calculations of rheological indicators of the effectiveness of Na-containing additives in the suspensions of the gaize are presented in Table 2.

Table 2. The diluting effectiveness of the admixes in the suspensions of the gaize

Type of the diluent	W_{eff}	ΔW_{eff}, %
$Na_4P_2O_7$	1,29	22,6
NaOH	1,25	20
Na_2SiO_3	1,1	13
$Na_2B_4O_7$	1,05	5
Na_2CO_3	1,047	4,55
NaF	1,04	4

Further studies were related to the development of methods to enhance the effect of plasticization of gaize slurry.

Method No 1. Based on the ability of some synthetic plasticizers, used in concrete technology, to show activity in siliceous slurries. As a synthetic plasticizer, organic substances were tested on the basis of: sulfonated melamine-formaldehyde polycondensates (MF: «Melment F15C»); Sodium naphthalene sulfonate (NF: «C-3»); Sodium lignosulfonate (LST); Polycarboxylates and polyacrylates («Melflux 2651; 5581»).

It was found, that for base mixtures, the greatest plasticizing effect is achieved with the addition of Melflux 5581 (the increase in fluidity of the slurries up to 42 ... 46 %). The mechanism of action is ensured by the presence of a significant steric component. This circumstance is indicated by the intensification of the plasticizing effect from Melflux 2651 to Melflux 5581 from 12 to 46% (the numbers in the marking indicate the relative length of the side hydrophobic polyester chains forming the steric plasticization effect).

The plasticizing effect of the synthetic plasticizers, in the mechanism of action of which the main role belongs to the effect of electrostatic repulsion (type of NF, MF or LST), is absent. This is due to the predominance of negatively charged active centers on the surface of the gaize particles that leads to a decrease in the adsorption of anion-active substances.

The effect of synthetic plasticizers on the fluidity of gaize mixtures is shown in Figure 4.

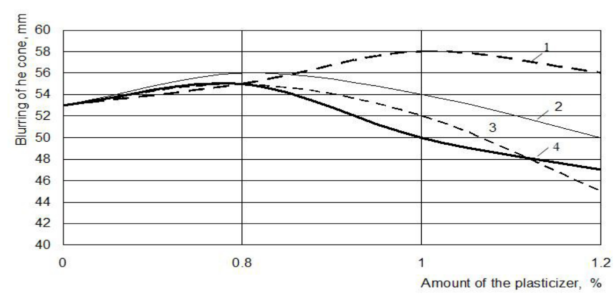

Figure 4. Individual and combined influence (with the addition of Na_2CO_3) of plasticizers on the fluidity of the slurry: 1 – «C-3» + additive (1%); 2 – LST; 3 – «C-3»; 4 – LST + additive (1%).

The manifestation of a positive effect when using additives «C-3» and LST, having negatively charged functional groups, is due to the mosaic of the surface of the gaize particles. This is reflected in the presence on it of positively charged defects and impurities, forming the adsorption centers.

The observed difference in the nature and extent of the effect of individual synthetic plasticizers on the rheological properties of the slurry is related to the solubility of complex compounds. These compounds are formed by interaction of Ca^{2+} ions, derived from the solvation layers with polyanions of dissociated molecules of synthetic plasticizers.

Method No 2. The introduction of an organic plasticizer in the composition of agaize slurry with a

Table 3. Physical and mechanical properties of porous silica ceramics

Components of the raw mix	**r_m [kg/m³]**	**K_{wr}**	**R_c [MPa]**	**l [W/(m×K)]**	**Heat resist.[Cycl]**	**T_{max} [°C]**
Gaize+Na_2CO_3+ blowing agent(H_2O_2) + coal powder	500	0,9	2,1	0,105	20	900
Slag cement + gaize+ plasticizers +foaming agent	400	0,85	1,7	0,085	15	1000

hydrophobizing type of action. As such was used a finely divided powder of activated carbon.

The experimental data for the case of use as diluents Na_2SiO_3 are shown in Figure 5.

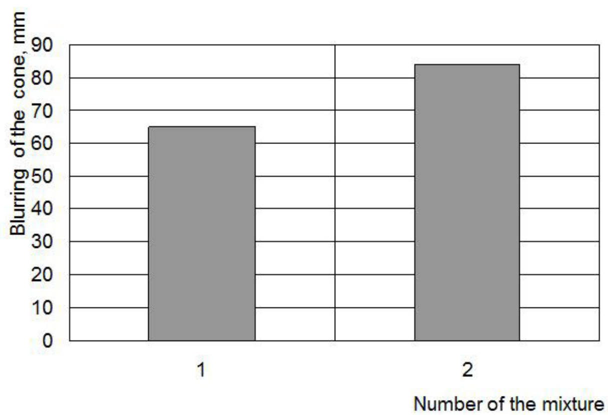

Figure 5. The influence of coal powder on the fluidity of the gaize slurry: 1 – control; 2 – with the addition of Na_2SiO_3 (1,5% of the mass of the gaize).

The formation of a cellular structure was carried out, using hydrogen peroxide as a blowing agent in combination with a diluting Na_2CO_3 additive. The use of H_2O_2 made it possible to obtain samples of a structural and heat-insulating material with a density of 650 kg/m^3 and a strength of 2.0 MPa (Table 3).

To obtain the heat-insulating ceramics the basic mixture was supplemented with a Portland cement as a technological bundle for fixing the cellular structures of the raw[5]. The addition of cement positively affects the plasticizing ability of most of the tested plasticizers. This occurs as a result of partial neutralization of acidic surface centers of siliceous particles due to the adsorption of positively charged cement hydration products.

Figure 6 and 7 show the combined effect of a diluent (NaF) of plasticizers («C-3», «Melment F15C») and a foaming agent (PB-2000) on the viscosity of a gaize slurry with the addition of 15% Portland cement.

The results of experiments indicate, that when a complex additive, consisting of «C-3» (or «Melment F15C», LST) and NaF (or Na_3PO_4) is introduced, a significant increase in the plasticization effect is observed. The presence of a foaming agent in the slurry reduces the plasticizing effect from the introduction of a complex plasticizing additives.

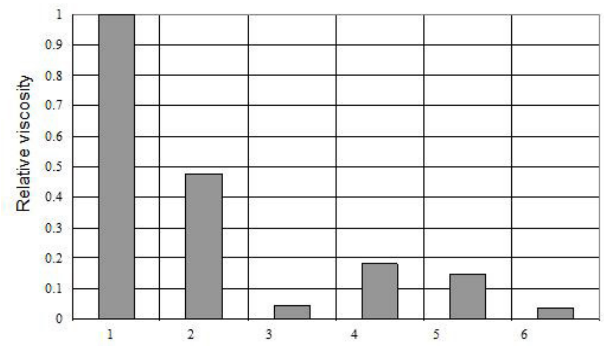

Figure 6. Effect of additives on the viscosity of a cement-gaize slurry: 1 – control (no additives); 2 – «C-3» (0,08%); 3 – «C-3» (0,08%) + NaF (2%); 4 – «C-3» (0,08%) + NaF (2%) + «PB-2000» (0,075%); 5 – «C-3» (0,16%) + NaF (2%) + «PB-2000» (0,075%); 6 – «C-3» (0,16%) + NaF (3%) + «PB-2000» (0,075%).

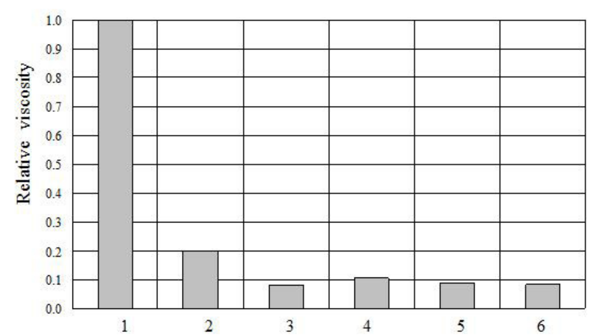

Figure 7. Effect of additives on the viscosity of a cement-gaize slurry: 1 – without additives; 2 –«Melment F15C» (0,08%); 3 – NaF (2%)+«Melment F15C» (0,08%); 4 – NaF (2%)+«Melment F15C» (0,16%); 5 – NaF (3%)+«Melment F15C» (0,16%); 6 – NaF (3%) + «Melment F15C» (0,16%)+«PB-2000» (0,075%).

4. Results:

In the group of inorganic diluents additives, the greatest effect has the Li-containing compound, impact of which is based on a combination of electrostatic and spherical effects; in the group of Na-containing additives the maximum water-reducing effect is shown by $Na_4P_2O_7$, NaOH, Na_2SiO_3 and Na_2CO_3.

Substances with molecules, containing sodium sulfonates (C-3, LST), show a positive activity among synthetic plasticizers.

The effect of the combined introduction of a synthetic plasticizer and an inorganic diluent is characterized by additivity - the amount of viscosity reduction is composed of the sum of the effects of each component;

When the amount of additives of diluents is more than 1.5%, the introduction of ground coal is accompanied by an additional positive effect

5. Conclusion

Considering, that in the process of heat treatment of porous raw material, coal powder acts as a burn-out and heat-releasing additive, it can be recommended as a constant component of raw mixtures for production of porous ceramics from natural gaize.

The physico-mechanical and thermal values of received porous silica ceramics make it possible to consider them as effective thermal insulation materials, recommended for use as thermal insulation of outer enclosures in individual, low-rise houses, buildings of frame construction in form of single-layer enclosure structure and as insulating layer.

6. References

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