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BATCH PULPING ON THE BASIS OF NATURAL SUBSTANDARD SILICEOUS MATERIALS

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It is shown that using silica sand of Tugansk deposit (Tomsk region) and marshalite of Elbash deposit (Novosibirsk region) having more developed specific surface in comparison with silica sand of Tashlin deposit (Ulyanovsk region) in combination with their grain defective structure provides an increase of batch chemical activity at the stage of silica- and glass-formation. The effective method of preparing glass batch using substandard fine-dispersed siliceous materials in glass production is their compaction.

Glass production refers to material- and energy intensive technologies, where natural and man-made raw materials are widely used. The main constituent of the majority of industrial batches is natural siliceous materials (silica sand, quartzite, sandstone, vein silica) and synthetic alkali containing materials (soda ash, sodium sulphate, soda-potash mixture).

Recently enterprises of glass industry frequently face the problem of raw materials deficit stipulated by reserve depletion of imported conditional materials, by distance of raw materials bases from consumers, by lack of attention to the questions connected with modernization of operative deposits and mining of new ones.

One of the methods of solving this problem is using of new – nondeficient and medium-priced raw materials of natural and anthropogenic origin, which allow in some cases not only to decrease production price but to intensify a process of glass manufacturing [1].

In the given paper the influence of replacement of Tashlin deposit silica sand widely used in various types of glass manufacturing by substandard natural siliceous materials on process of pulping and glass quality was investigated. The subjects of inquiry are silica containing consistent of Tugansk deposite (Tomsk region) obtained while zircon-ilmenite ore concentrating and concentrated marshalite of Elbashin deposite (Novosibirsk region). The possibility in principle of using these materials in container glass manufacturing was determined by the authors earlier [2, 3].

Studying of influence of siliceous materials nature on the process of pulping was carried out on modeling batches representing three component mixture of sand, soda and dolomite in ratio 60:20:20 wt. % (respectively). Three sets of experiment were carried out, where as a siliceous component of a batch Tashlin sand, Tugansk sand and marshalite were used. Chemical composition of investigated raw materials is presented in table 1.

Table 1. *Chemical composition of siliceous materials*

Raw materials	Chemical composition, wt.%						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	п.п.п.
Tashlin sand	99,10	0,27	0,10	0,07	0,05	–	0,41
Tugansk sand	98,15	0,67	0,09	0,07	0,02	0,06	0,94
Marshalite	97,43	–	0,15	1,4	0,70	–	0,32

Glass manufacturing is a difficult physical-chemical process occurring at high temperatures in moving medium of variable composition, which depends on batch composition, conditions of heat exchange, temperature etc. By convention the process of glass manufacturing is divided into separate stages: silicate formation, glass formation, fining, homogenization, cooling. Every microvolume of a batch undergoes these stages in the process of its transformation into glass mass.

Different processes of physical and chemical nature such as components fusion, polymorphic transformations, solid-phase reactions, silicates formation etc. occur at the stage of silicate formation. Rate of silicate formation is determined by temperature conditions, nature, dispersion and chemical activity of batch components including siliceous one.

Solid-phase reactions occurring at the stage of silicate formation are presented in general terms by the following equations:

$$Na_2Mg(CO_3)_2+2SiO_2 \rightarrow Na_2SiO_3+MgSiO_3+2CO_2$$

$$Na_2Ca(CO_3)_2+2SiO_2 \rightarrow Na_2SiO_3+CaSiO_3+2CO_2$$

$$2CaCO_3+SiO_2 \rightarrow Ca_2SiO_4+2CO_2$$

$$Na_2CO_3+SiO_2 \rightarrow Na_2SiO_3+CO_2$$

Batches chemical activity was estimated according to the degree of their transformation, which is described with high accuracy by the value of mass loss, and in terms of calculation of energy activation [4].

The results of differential-thermal analysis obtained at a derivatograph (Q-1500 D Paulik-Paulik-Erdey) in a polythermal regime (20...1000 °C), with heating rate 10 °C/min, showed the presence of three groups of endoeffects. Endoeffects conneced with various forms of moisture removal are present in a low-temperature region (to 150 °C). The second group of effects at temperatures 538, 540, 560 and 751 °C conforms to the processes of dissociation of magnesium carbonate, polymorphic transformations of silica and beginning of solid-phase reactions with the formation of double salts and various silicates. The third group of endoeffects conforming to the fusion of eutectic silicates series Ca, Mg and Na was observed for the batch with Tashlin sand at temperature 830 °C, for the batches with Tugansk sand and marshalite at temperature 815, 812 °C respectively.

It is stated that at the stage of silicate formation, when using conventional sand, batch mass losses reach 9 %, while for batches with Tugansk sand and marshalite mass losses are 15 and 17 % respectively. Differences in mass losses are stipulated by fine-dispersed composition of Tugansk sand and marshalite (fig. 1), which 45 and 85 % (respectively) consist of fractions that are less than 0,16 mm. Specific surface value of Tashlin sand is 1037 sm^2/g for Tugansk sand and marshalite it is 2000 and 3000 sm^2/g respectively. Moreover, increase of batch chemical activity when using fine-dispersed siliceous materials is stipulated by structure imperfection of their grains (fig. 2).

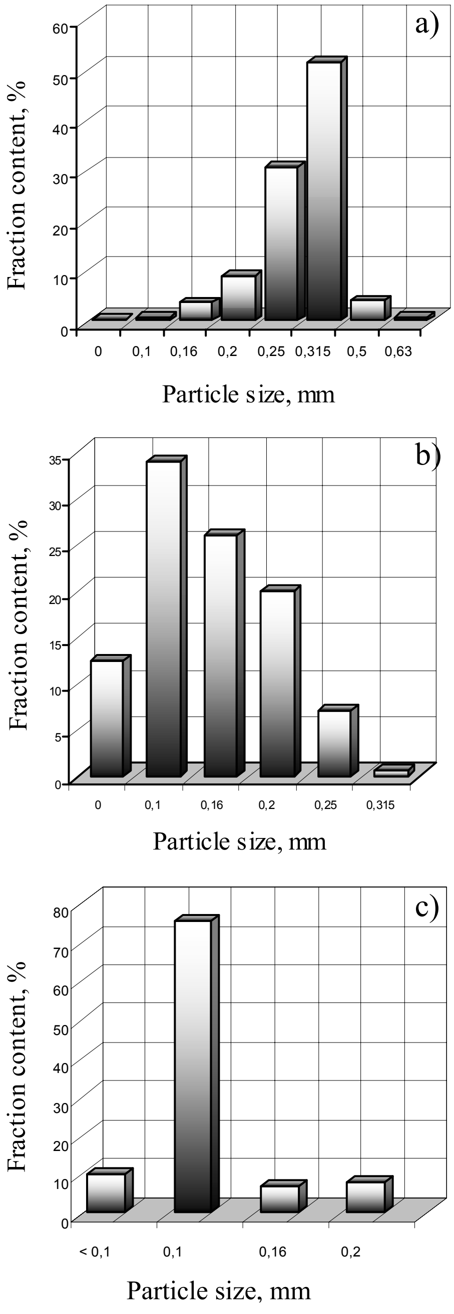

Fig. 1. *Granulometric composition of sand: a) Tashlin, b) Tugansk, c) marshalite*

Activation energy values were carried out by well-known procedure on which basis there is the Arrhenius equation.

$$K = A \cdot e^{-Ea/RT},$$

where K is the reaction rate constant; A is the coefficient of proportionality; E_a is the activation energy; R is the gas constant; T is the absolute temperature.

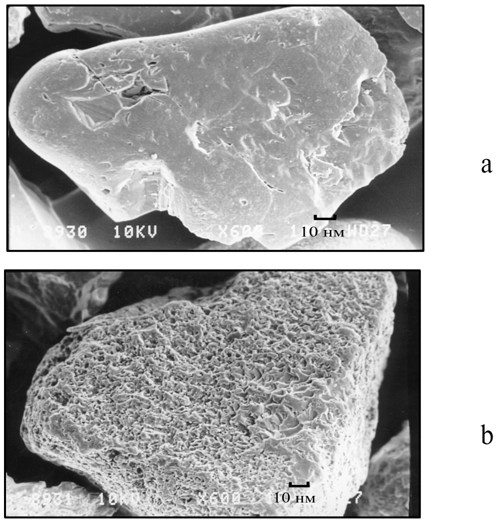

Fig. 2. *Electron microscope photographs: a) marshalite; b) Tugansk sand*

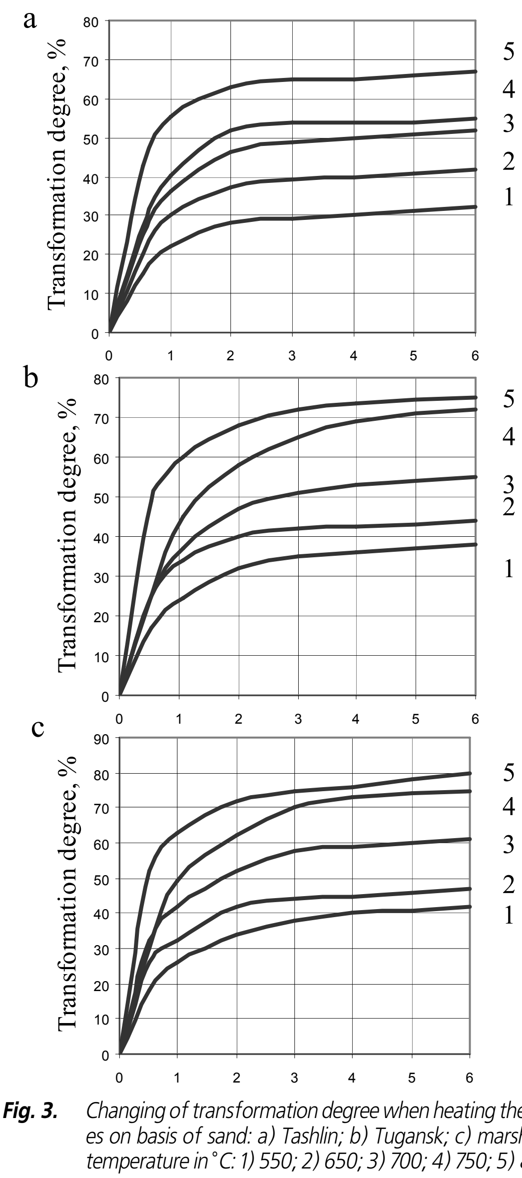

Fig. 3. *Changing of transformation degree when heating the batches on basis of sand: a) Tashlin; b) Tugansk; c) marshalite at temperature in °C: 1) 550; 2) 650; 3) 700; 4) 750; 5) 800*

Reaction rate constant was determined analytically from the Hinstling-Brownstein equation which describes rather accurately kinetics of solid-phase process in isothermal conditions.

$$F_{hb}= 1-2/3G-(1-G)^{2/3}=K\tau,$$

where F_{hb} is the Hinstling-Brownstein function; G is the part of a substance entered into reaction; K is the reaction rate constant; τ is the reaction time.

Activation energy was determined by the values of K for different temperatures:

$$\lg\frac{K_1}{K_2}=\frac{E_a}{2,3R}\cdot\left(\frac{1}{T_1}-\frac{1}{T_2}\right).$$

Curves of batches transformation degree when heating them in the rage 550...800 °C depending on process duration are presented on fig. 3. As it is seen, the batch on basis of silica sand of Tashlin deposit has the least degree of transformation (65...68 %) on the stage of silicate formation (fig. 3, *a*).

Calculated values of activation energy amounted 55,35 kJ/mole for a batch of Tashlin sand and 53,66 and 45,23 kJ/mole for batches on basis of Tugansk sand and marshalite respectively. Lower values of activation energy indicate increased rate of silicate formation reaction in batches on basis of substandard siliceous materials.

Limiting stage of glass manufacturing is glass formation in the duration of which silica grains dissolution in silicate melt and simultaneous silicates dissolution occur. For sodium- calcium- silicate glass this stage is usually completed at temperature of the order of 1200 °C when transparent glass mass is obtained. It is known that dissolution time of silica grain τ is connected with its size by r dependence [5].

$$\tau=Br^3,$$

where B is the coefficient depending on glass composition.

Probably the high degree of Tugansk sand and marshalite dispersion promotes the increase in reaction rate of glass formation. However the given materials do not conform to the requirements of State Standard (SS) 22551-77 for siliceous materials because of high (in 1, 5... 2 times) fines content (less than 0, 1 mm) that influences negatively the process of glass degassing and glass quality. It is known that sealing allows improving technological property of disperse materials and glass batches, therefore further research was carried out at sealed batches. The batch on basis of Tugansk sand was sealed by the method of compression at rolling press, the batch on marshalite was sealed by graining using the method of balling at plate granulator.

Laboratory melting of sealed glass batches for container glass manufacturing with the use of substandard siliceous materials was carried out in corundum crucibles with a capacity of 200 ml in a small-sized electric furnace with silite heaters and automatic control of temperature condition. Rate of temperature rising was 250 degrees/h.; maximal temperature was 1450±10 °C at 15 minute exposure. Glass formation rate was estimated according to the results of X-ray analysis of glass samples (diffractometer DRON-3M in copper radiation).

Sampling of glass obtained from the batches at investigated siliceous materials was carried out in the temperature range of 900...1200 °C. The rate of glass formation was considered by changing intensity of reflection maximums conforming to silica (4,23; 3,34; 1,815 A). As we see from fig. 4 there is no significant difference in intensity of silica reflection maximums for the batches with Tugansk and Tashlin sand in the temperature range 900...1000 °C. Further temperature rising to 1200 °C results in quantitative decrease of silica. The values of absolute intensities of silica reflection maximums decrease approximately in 1,5 times in glass samples, boiled from the batch on basis of Tugansk sand.

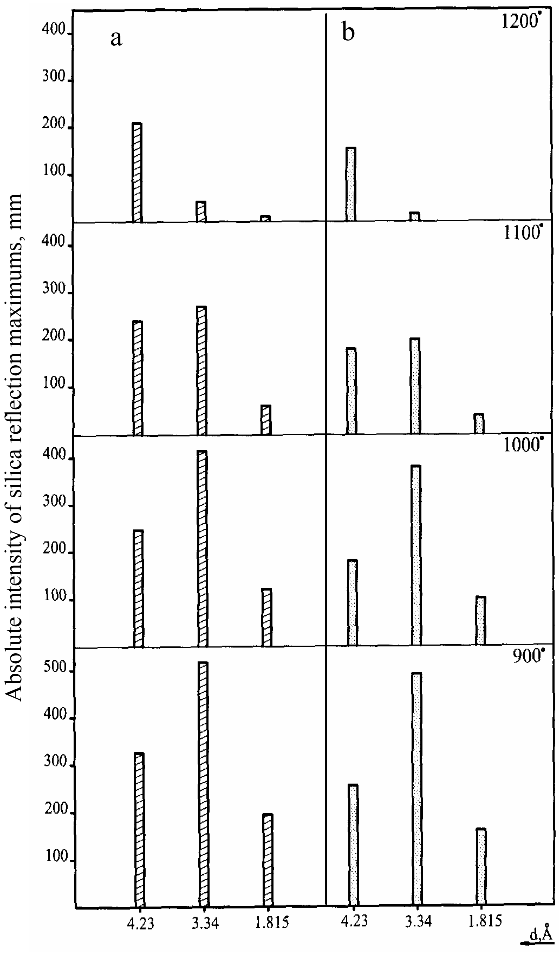

Fig. 4. *Changes in intensity of silica reflection maximums in batches on basis of sand: a) Tashlin; b) Tugansk*

The results of X-ray analysis (fig. 5) of glass samples from the batch on basis of marshalite selected at temperature 1200 °C showed that at simultaneous decrease in intensity reflection maximums conforming to silica the increase of amorphous halo area is observed, i. e. batch chemical activity rising.

Thus, the results of fulfilled laboratory melting show the increase of glass formation reaction rate in the case of substandard siliceous materials that is stipulated not only by their fine-dispersion and grains structure peculiarities, but also by reacting components intimate contact which is achieved at sealing.

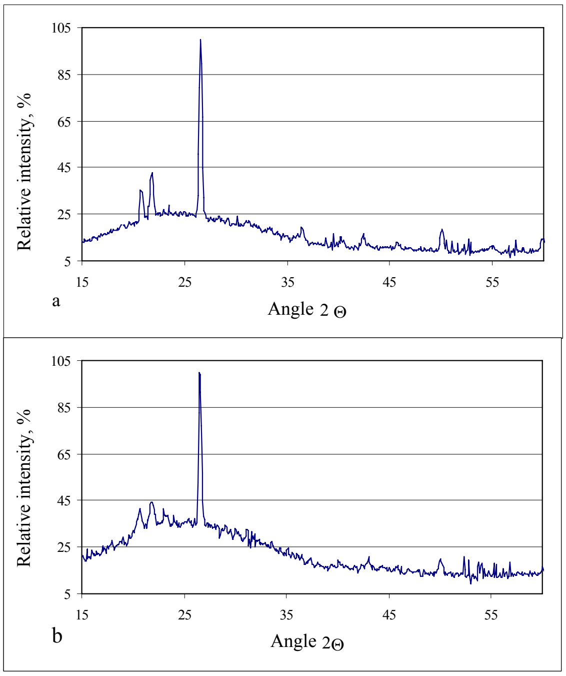

Fig. 5. *Changes in intensity of silica reflection maximums for batches on basis of: a) Tashlin sand; b) marshalite*

Standard samples, visual examination of which showed the presence of complete fusion and glass clearing, were prepared from obtained glass mass. According to the results of determination of physical-chemical properties of glass (table 2) it is seen that characteristics of the samples obtained from the batches on basis of substandard siliceous materials conform to the requirements of branch standards, formed for to container semiwhite glass. The analysis of transmission spectra carried out with the use of spectrophotometer SPh-26, for samples of 3 mm thick, in spectral region 400...700 nm, showed that glasses at the researched siliceous materials have the value of optical transmission on 1...3 % lower in comparison with the glass melted from the conventional sand of Tashlin deposit, that is not a matter of principle for container glass.

Table 2. *Glass samples properties*

Glass obtained on basis of	TCLTE $\times 10^7$, degree^{-1} in the range 20...400 °C	Density, g/sm^3	General optical transmission of the samples of 3mm thick in region 400...700 nm, %
Tashlin sand	90,0	2,50	87
Tugansk sand	91,0	2,52	85
Marshalite	91,5	2,51	84
The requirements of State Standard (SS)	92	2,48...2,52	65

TCLTE – thermal coefficient of linear thermal expansion

The results of carried out investigations showed that substitution of conventional silica sand on Tugansk sand or marshalite in batches composition for container glass manufacturing results in increase of reaction rate of silicate- and glass formation, stipulated by high chemical activity of batches and allows production of qualitative glass. The effective method of batches preparation using natural substandard fine-dispersed siliceous materials is their sealing.

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