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Forecasting Properties of Facing Construction Ceramics on the Base of Industrial Wastes

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The work contains the results of study on improving the grain distribution of high-silica technogenic products for obtaining facing ceramic materials with forecastable operating properties. The study presents a model of facing composite material on the base of quartz grain fill. The optimal grain distribution of high-silica wastes was detected with the purpose of adjusting the packing density of ceramic materials at the stage of feed preparation, moulding and baking.

Keywords: ceramics, burnt moulding sand, concentration tails, molybdenum ore, fraction, improvement, simplex

Introduction

The increasing deficit of conventional raw materials, primarily clay materials, considerable amount of various industrial wastes accumulated annually, as well as the possibility to intensify process flow sheets, increase operating properties of materials produced with use of recycled wastes, causes the growing interest of ceramics industry towards resource saving issues. At the same time there is no systematic approach to processes of producing facing materials on the base of natural and industrial waste materials that would rely on setting the criteria for forming the structure, forecasting and directed adjusting of ceramic material composition and process flow sheets of their production.

Perspective industrial wastes that could be efficiently used as the main component of facing ceramic material include huge dumps of high-silica burnt moulding sand – wastes of casting departments within machine-building plants, as well as molybdenum ore concentration tails from Sorsk molybdenum mining and concentration complex.

Burnt moulding sand is primarily a quartz product of reaction between case metal (steel, cast iron or non-ferrous allow) with a casting mould. Mineralogical composition of molybdenum concentrate flotation tails beside silica includes feldspar minerals: orthoclase, albite and anorthite that provides fluxing effect at baking temperature of 1050 °C and over.

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Materials and experimental technique

Mineralogical composition of raw material and sintered masses was defined basing on the results of X-ray structural analysis conducted by means of DRON-3 diffractometer in the mode with a copper anticathode at 20 kV voltage and 20 mA current. Thermographic analysis was conducted by means of Netzch derivatograph. Preparation of initial raw materials was done by ShchD-6 jaw crusher and ROCKLABS ring mill. Microstructure of grain distribution in waste uniform particles was studied with use of MBS-9 microscope, microstructure of facing ceramics – with use of Axio observer A1m microscope. Fractionation of raw material was performed at VPT 220 testing sifter**.** Experimental investigation was carried out on samples of high-melting clay of Kompanovski deposit (Krasnoyarsk Territory) represented mostly by clayey components, namely, kaolinite and hydromica.

Chemical composition and grain size distribution of wastes and other investigated components of facing ceramic body are stated in Tables 1 and 2.

Model structure

In general, the model of facing composite material on the base of high-silica raw material can be outlined as follows. Free silicon oxide can act as a composite fill. Sources of free silicon oxide include technogenic products: quartz-feldspar Sorsk sand and burnt moulding sand, as well as coarse-grained high-silica admixtures of clayey component. Coarse grains of quartz make up a skeleton or a fill that is practically unchangeable and is rarely involved in physical and chemical processes. Skeleton made of coarse grains of quartz that prevails in ceramic materials provides the possibility to produce facing materials subject to insignificant changes during baking within temperature range of 950-1000 °C, as well as minor internal stress and deformations caused by these changes. Fluxes of quartz-feldspar Sorsk sand, glass waste and clayey material act as a binding matrix.

Table 1. Chemical composition of initial components, wt %

Material	$SiO_{2\,св}$	Al_2O_3 + TiO_2	Fe_2O_3+ FeO	CaO + MgO	K_2O + Na_2O	SO_3	$SiO_{2\,общ.}$
Burnt moulding sand	79.17	4.86	11.14	4.56	2.47	0.16	79.17
Sorsk tails	62.05	16.52	4.18	6.73	8.12	-	-
Glass waste	-	2.34	0.18	10.26	29.28	0.19	71.45
Kompanovsky clay	4.64	18.03	3.53	2.45	1.55	0.03	62.16

Table 2. Grain size distribution of high-silica wastes

Material	Content of certain fractions (in mm), wt %							
	+1,4	-1,4+1,0	-1,0+0,8	-0,8+0,5	-0,5+ +0,315	-0,315+ +0,08	-0,08+ +0,056	-0,056
Sorsk tails	–	2,14	2,36	14,49	31,42	44,31	3.21	2,07
Burnt moulding sand	–	6,03	2,03	5,41	14,03	67,12	3,63	1,75

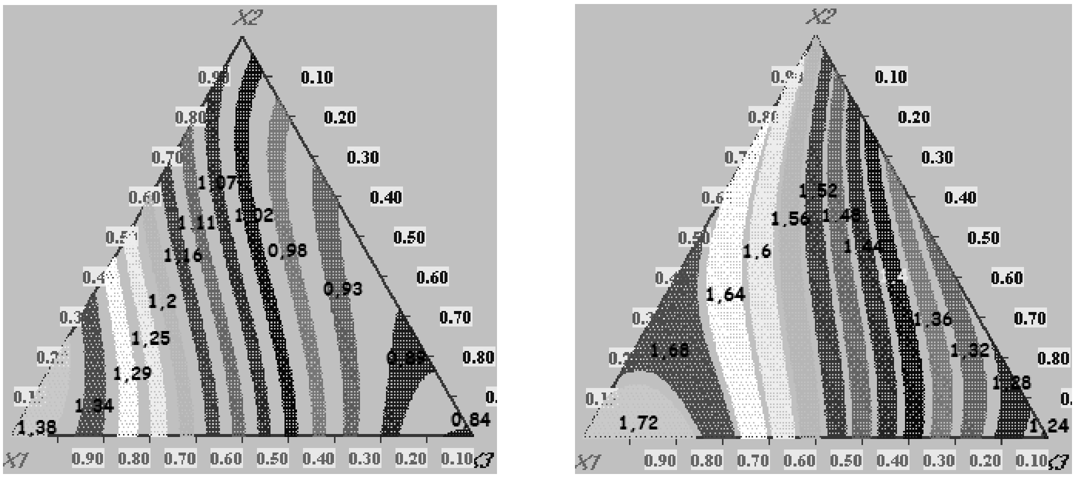
Presented experimental investigation was aimed at reaching the highest density of fractions (grains) packing in a press form and in a finished product. Investigation [1, 2] on packing grains of similar size with shape similar to spherical resulted in actual volume of 58-63 % to be occupied by grains. Due to the fact that powders being used are not of spherical shape, it appears impossible to do theoretical calculations in respect of conditions required to reach the highest density of packing, therefore, the number of specific fractions and grain sizes with the view of oriented adjusting of packing density was selected on an experimental basis. The principle of reaching the highest density of high-silica facing materials was based on obtaining precise ratios of specific fractions and initial grain sizes. The work was based on a principle of selecting the so-called «non-continuous» arrangement that does not imply any grains of intermediate sizes between grains of preset fractions. According to results [1, 2], grains of the coarsest fraction form a skeleton, voids of which are filled with grains of the next fraction. New voids can be filled with the third fraction etc. The increase of semi-finished product density provides favourable conditions for sintering to obtain a high-density material. Non-continuous arrangement was selected basing on known concepts claiming that this type of arrangement provides the highest packing density [1]. The «non-continuous» arrangement option proved non-efficient in case of high-silica facing materials due to failure to obtain the required ratio of fractions that would provide maximum powder packing density without sieving and fractional dosing.

Experimental results

In order to improve the fraction distribution of high-silica wastes, a third order simplex-lattice design was implemented for a three-component mixture. Fraction distribution was improved using samples of a blend with fixed composition (clay – 20 %, quartz-containing wastes – 55 %, glass waste – 25 %). Improvement investigation covered technogenic high-silica products of -0.315+0.08 mm fraction (x_1), -0.08+0.056 mm fraction (x_2), and – 0.056 mm fraction (x_3). The investigation included monitoring the fixed values of clay and glass waste fractions (-0.056 mm), molding pressure (43 MPa), duration of isothermal curing at the maximum baking temperature (60 min), relative molding-moisture content of the blend (10 %). The selection of fraction sizes of high-silica skeleton of designed composite material at the stage of looking for non-continuous arrangement options with highest density was based on the assumption that the coarsest fraction shall be at least 5 times bigger than the finest fraction. The results of waste fraction distribution improvement aimed at obtaining the maximum density of high-silica skeleton and the blend formed at its base with adding clay and glass waste, as well as obtaining the minimum water absorption and maximum density of baked samples are shown in Fig. 1, 3, 4.

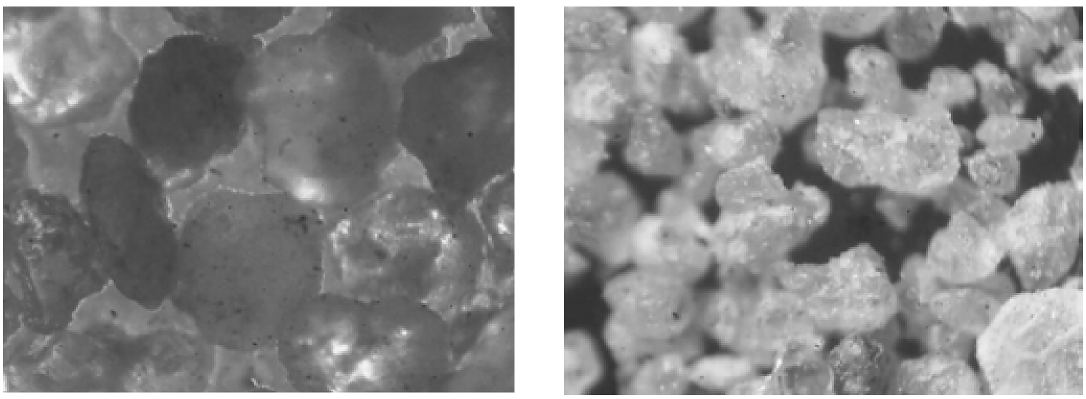
Analysis of results represented in Fig. 1 proves that the range of obtained tap density of grain skeleton formed of Sorsk tails is 1.25 – 1.72 g/cm^3, which corresponds to void ratio density from 34 to 19 %.

It should be noted that obtained results of void ratio of multi-fraction system of Sorsk tails that primarily consists of isometric grains of irregular shape significantly differ from void ratio resulting from tapping grains of the same size and having the shape close to spherical (37-42 %). Maximum tap density can be reached by using coarse monofraction Sorsk tails (-0.315+0.08mm – 100 wt %), as well as two-fraction system containing -0.315+0.08 mm fraction (85-90 wt %) and -0.08+0.056 mm fraction (10-15 wt %).

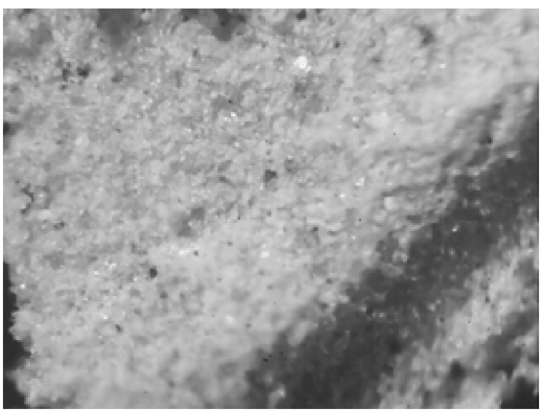


a *b*

Fig. 1. Projections of lines of equal bulk density (*a*) and tap density (*b*) of Sorsk tails on a three-component simplex



a *b*



c

Fig. 2. Micro images of monofraction particles of burnt moulding sand *a*- -0.315+0.08 mm fraction (× 48); *b* – -0.08+0.056 mm fraction (× 48); *c*- -0.056 fraction (× 48)

The fact of reaching the maximum packing density of nonplastic high-silica facing materials on the base of prevailing coarse fraction of Sorsk tails and burnt moulding sand proves the existing concepts on reaching high density of packing in clayey systems. Considerable increase of bulk density and tap density of coarse monofraction powders is caused by large weight of each quartz particle with small amount of contacts between them within a unit of volume (Fig.2) [1,2]. Micro images of monofraction particles of burnt moulding sand are shown in Fig. 2.

When selecting an optimal fraction distribution, one should take into consideration the difficulties in precise dosing of medium fraction and homogeneous mixing it with coarse and fine fractions due to limited need of this fraction for dense packing. Increasing the amount of medium fraction (+0.08-0.056 mm) over the limits set within the framework of investigation can cause spreading of coarse grains, whereas its decreasing can lead to crossflow of fine fractions from one pore to another, which also causes loosening of the packing. Medium grains (Fig.2 b) represented in sufficient amount in polydisperse medium and located at necks of pores formed by coarse grains act as a plug and prevent the crossflow of fine fractions [1, 2].

The situation is slightly different in case of reaching the maximum possible tap density for a blend that alongside with Sorsk tails contains fine (- 0.056 mm) fraction of clay and glass waste, their total amount being 45 wt. %. Considerable increase in fine fraction content in the blend leads to drastic decrease of the blend tap density (density varies from 1.05 to 1.45 g/cm^3, void ratio of their packing – from 22 to 57 %). The observed trends (Fig.3) are caused by small particles forming loose irregular lattices that prevent even distribution of particles within volume and their compact packing [1]. This leads to increase in the amount of arch formations in powders [1], whereas the bulk weight, i.e. packing density decreases. Analysis of experimental data proves that as the content of finely dispersed fractions in the blend increases, the difference between the blend bulk density and its tap density increases up to 1.3 times. Maximum tap density of the blend can be reached in case of using monofraction of Sorsk tails (+0.315-0.08 mm – 100 wt %), as well

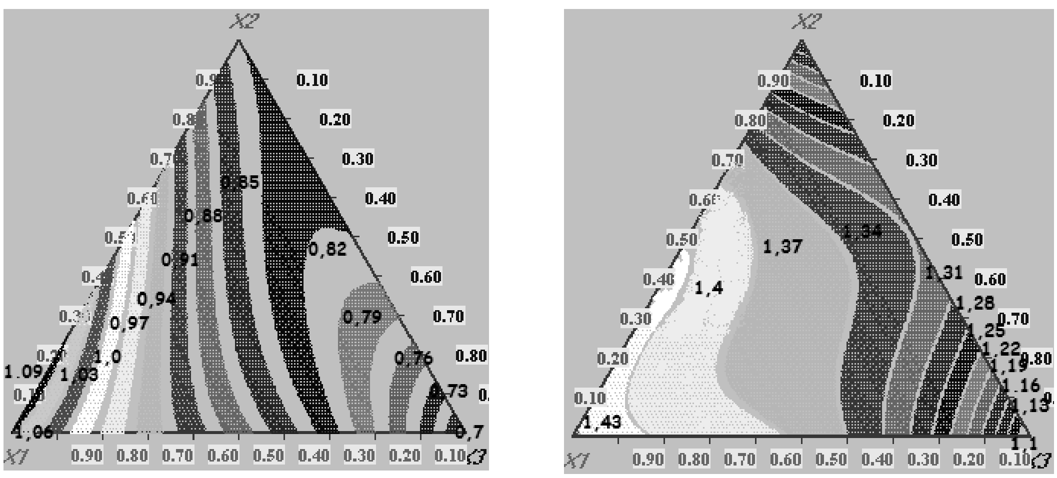


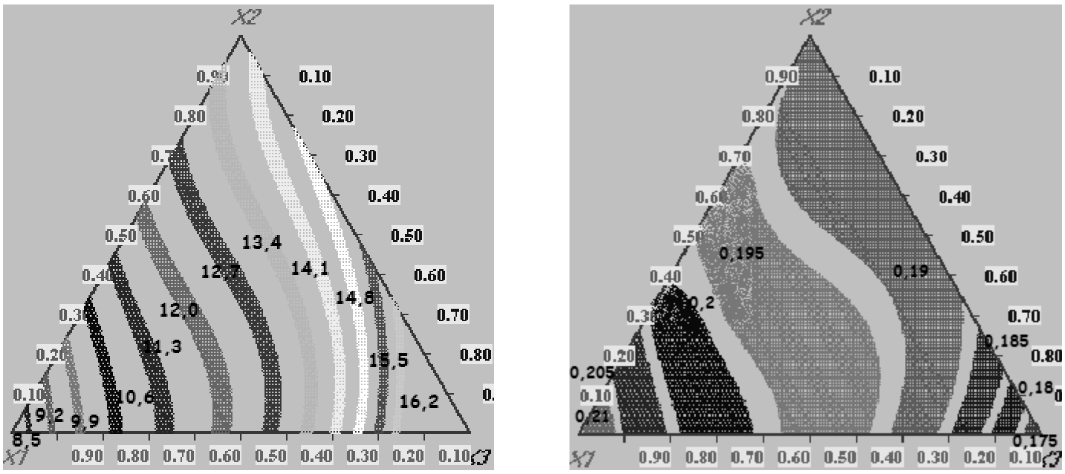
Fig. 3. Projections of lines of equal bulk density (*a*) and tap density (*b*) of blend (Sorsk tails – 55, glass waste -25, Kompanovsky clay – 20 wt. %) on a three-component simplex

as a two-fraction system (+0.315-0.08 mm fraction – 70 wt % and +0.08-0.056 mm fraction – 30 wt %).

Packing density increase caused by using adjustable fraction distribution of high-silica technogenic product contributes to production of sintered facing material samples with low water absorption and improved parameters of apparent density (Fig. 4).

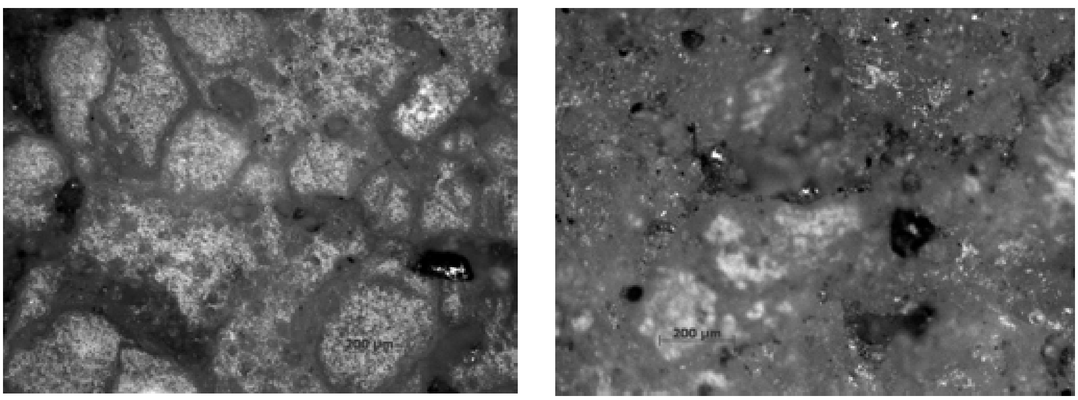
Microstructure of facing ceramic bodies on the base of burnt moulding sand is shown in Fig. 5, 6.

Microstructure analysis of facing ceramics on the base of quartz skeleton made of burnt moulding sand proves the feasibility of creating dense low-porosity structures on the base of monofraction +0.315-0.08 mm – 100 % (Fig.5,*a*) and two-fraction system (+0.315-0.08 mm fraction 70 wt % and



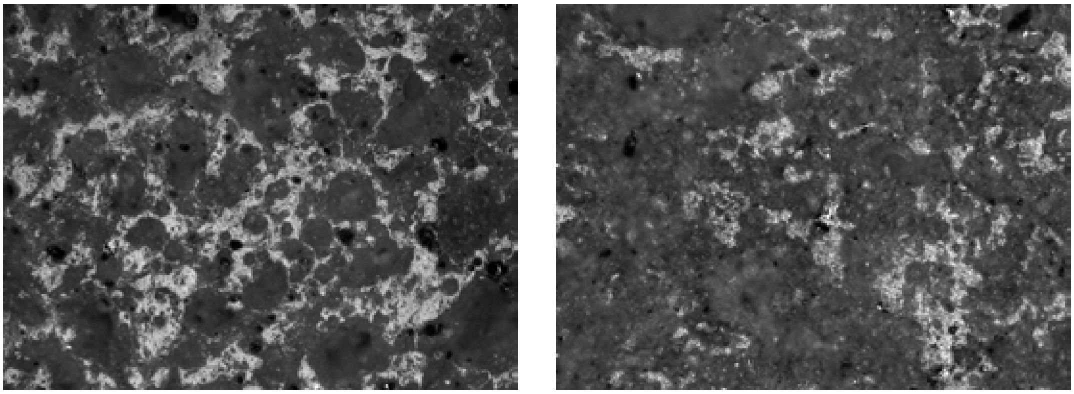
a *b*

Fig. 4. Projections of lines of equal water absorption by sintered facing materials (%) (a) and equal apparent density g/cm³ (b) of the mixture (Sorsk tails – 55 wt %, glass waste -25 wt %, Kompanovsky clay -20 wt %) on a three-component simplex (baking temperature 1000 °C)



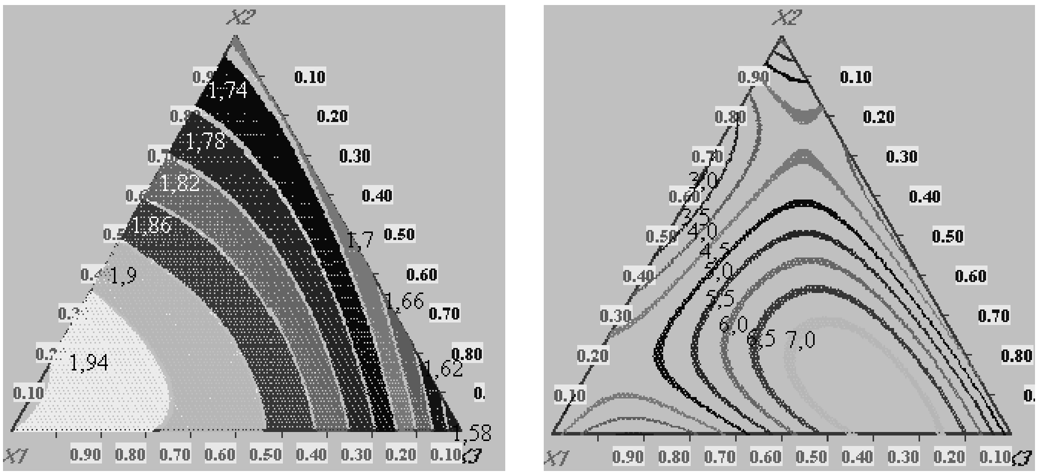
a *b*

Fig. 5. Microstructure of facing ceramics on the base of burnt moulding sand of optimal grain composition (× 160): (*a*) – on the base of monofraction +0,315–0,08 мм – 100 %, (*б*) – on the base of befraction system (фр. +0,315-0,08 мм-70 и фр. +0,08-0,056 мм -30 масс. %)



a *b*

Fig. 6. Microstructure of facing ceramics on the base of burnt moulding sand of unreasonable grain composition (× 160): (*a*) – on the base of monofraction +0,08-0,056 мм, (*b*) – on the base of monofraction -0,056 мм



a *b*

Fig. 7. Projections of lines of equal water absorption of sintered facing materials (%) (*a*) and equal apparent density g/cm^3 (*b*) of the mixture (Sorsk tails – 55 wt %, glass waste –25 wt %, Kompanovsky clay –20 wt %) on a three-component simplex (baking temperature –950 °C)

+0.08-0.056 mm fraction-30 wt %) (Fig. 5 *b*). Use of monofractions +0.08-0.056 mm and -0.056 mm proved unfeasible due to relatively high values of water absorption (Fig. 7, *a*) and low density values (Fig.7, b), which is quite natural due to considerable amount of pores (Fig 6 a, b).

The detected correlation between fraction distribution of Sorsk tails and burnt moulding sand and water absorption values (W, %) and apparent density of sintered samples (ρ, g/cm^3) is represented in the corresponding regression equations (abbreviated form):

for Sorsk tails (baking temperature– 1000 °C) :

$W=7.8750X_1+13.722X_2+20.4080X_3$

$\rho=0.2080X_1+0.1870X_2+0.1680X_3$

for burnt moulding sand (baking temperature – 950 °C)

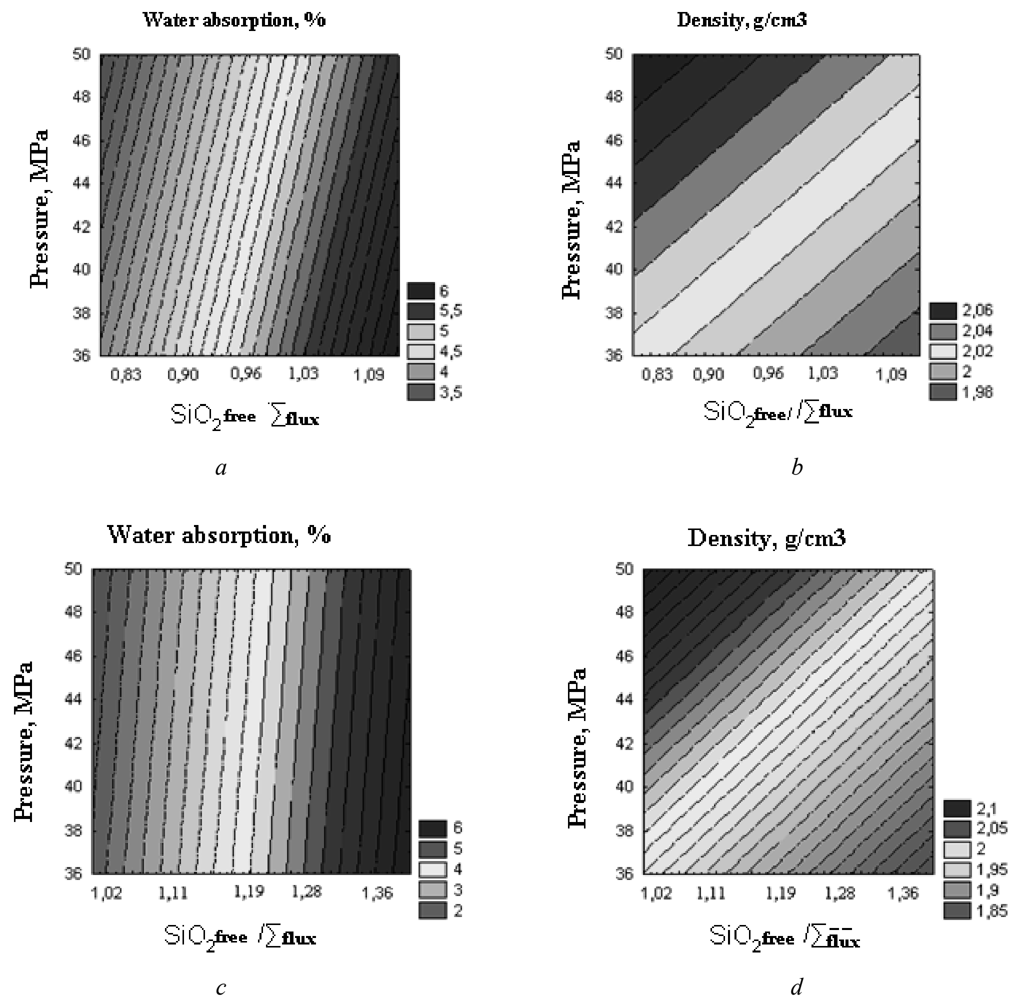


Fig. 8. Projections of lines of equal apparent density and water absorption by samples on the base of Sorsk tails and Kompanovsky clay at baking temperature 1050 ºC (*a*, *b*), burnt moulding sand and Kompanovsky clay at baking temperature 1000 ºC (*c*, *d*)

$W = 1.9610X_1 + 1.7130X_2 + 1.5620X_3$

$\rho = 4.8390X_1 + 6.2710X_2 + 4.6560X_3$

The threshold of maximum water absorption of facing materials on the base of burnt moulding sand was selected to be its value corresponding to 5 % (standard requirements). This value can be reached within quite extensive ranges represented by experimental simplex. The best option would be to use quartz skeleton of two-fraction composition with the following ratio: fraction x_1 – 10-80 wt % and x_2 -20-90 wt %. The selection of optimal ranges was also based on the possibility to use burnt moulding sand without considerable costs required for its further grinding (Table 2). The threshold of apparent density of sintered ceramics was selected to be its value 1.9 g/cm^3 and over. The stated experimental data proves that the required density values can be reached in case of using monofraction x_1, as well as in case of combining fractions x_1 and x_2 with 70:30 ratio.

The presented dependencies prove that the total content of particles within the blend on the base of high-silica technogenic product, glass waste and clay corresponds to the content of particles with maximum size of +0.315-0.08 mm within 39-46 %, particles +0.08-0.056 mm – 9-16 %, particles below 0.056 mm – 45 %.

In order to improve process parameters for production of facing ceramic materials on the base of technogenic quartz products, investigation has been conducted to define the optimal value of free quartz content in relation to total content of fluxes ($SiO_{2free}/\sum_{flux.}$) by planning using the method of complete factorial experiment. The main factors influencing the processes of high-quartz material structure formation include the change rate of ratio $SiO_{2free}/\sum_{flux}$ – X_1 (0.83-1.09), compacting pressure X_2 (1.0- 3.0 MPa), baking temperature X_3 (950 – 1100 °C). During the investigation, previously detected optimal fraction distribution of granular quartz skeleton and blend in general was maintained at the preset level. The investigation results proved that in case of kaolinite and kaolinite-hydromica clay, there is a certain dependency of sintering capacity on ratio $SiO_{2free}/\sum_{flux.}$.The results of improvement of process parameters of obtaining composite material on the base of high-quartz facing ceramic materials are given in Statistics program (Fig. 8). It was established that as $SiO_{2free}/\sum_{flux}$ ratio decreases, the density increases, whereas water absorption value decreases. Improvement of ceramic material properties alongside with $SiO_{2free}/\sum_{flux}$ ratio decrease is due to increase in the amount of liquid phase amount and intensification of sintering process.

As the moulding pressure increases, apparent density of the material also increases. This is caused by higher density of grain packing at a higher pressure. Resulting dense compacting packing at the stage of moulding, provides for obtaining less porous structures after baking, which is proven by decrease in water absorption. As the baking temperature increases, density increases and water absorption decreases. Higher temperature causes formation of larger amount of liquid phase that fills pores and thus leads to material compacting.

Conclusions

Thus, the suggested model of composite facing material with quartz skeleton and method of increasing the density of packing within the material, enables us to detect some trends in correlation between the apparent density value and tap density of quartz skeleton and ceramic blend in general depending on the ratio of fractions of different sizes within optimal ranges. The optimum of free quartz content in relation to the total content of fluxes ($SiO_{2free}/\sum_{flux}$) was also defined that provides for reaching a high level of sintering facing ceramic materials.

References

1. Yu.E.Pivinsky. Ceramic and refractory materials [Text] Yu.T.Pivinsky – St.Petersburg, Stroiizdat 2003 T1 686 p.

2. V.A.Kondratenko. Ceramic wall materials: improvement of their physical and technical properties and process parameters of production [Text] V.A.Kondratenko – Moscow: Composite-508p.

3. Patent 2412129 Russian Federation, IPC C 04 B 33/132 (2006.1). Raw material feed for production of ceramic facing tiles. / E.M.Nikiforova, R.G.Eromasov, A.I.Nikiforov – No.2009127913/03; application 20.07.2009; published 20.02.2011 Bulletin No.5.

4. Patent 2422399 Russian Federation, IPC C 04 B 33/132 (2006.1). Ceramic body. / E.M.Nikiforova, R.G.Eromasov – No.2010104057/03; application 05.02.2010; published 27.06.2011 Bulletin No.18.

5. Patent decision for Application No. 2010104058/03, IPC C04B33/132 dd 2011.04.01 Mixture for heat insulation production. / E.M.Nikiforova, R.G.Eromasov

6. Patent decision for Application No. 2010116442/03, IPC C04B33/132 dd 23.05.2011 Method of facing tiles production. / E.M.Nikiforova, R.G.Eromasov

Прогнозирование свойств облицовочной строительной керамики на базе промышленных отходов

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Приведены результаты исследований по оптимизации зернового состава кремнеземистых техногенных продуктов для получения облицовочных керамических материалов с прогнозируемыми эксплуатационными свойствами. Представлена модель облицовочного композиционного материала на базе наполнителя из зерен кварца. Выявлен оптимальный зерновой состав кремнеземистых отходов с целью регулирования плотности упаковки керамических масс на стадии подготовки сырья, формования и обжига.

Ключевые слова: керамика, горелая земля, «хвосты» обогащения, молибденовые руды, фракция, оптимизация, симплекс.