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UTILIZATION OF RECYCLED SULPHIDIC MOLYBDENUM ORES FOR PRODUCTION OF LOW-FIRED PORCELAIN

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ABSTRACT
This article presents a description of one of the promising applications of overburden pegmatites and quartzofeldspathic tailings from molybdenum ore at Sorsky GOK copper and molybdenum mining complex in the production of low-fired porcelain. The proposal is to move away from exploiting natural fluxes which are becoming scarce, replacing them with secondary material resources. Presence of potassium and sodium in the chemical composition of pegmatites and quartzofeldspathic sand in feldspar may produce a viscous mass in a reasonably low temperature melt, contributing to the dissolution of quartz and clay matter. The research work presented below offers a solution to the challenge of replacing the classic porcelain mass (kaolin-quartz-fluxing agent) with industrial products by implementing a porcelain molding process. If the quartzofeldspathic tailings mass percent in porcelain ceramics is 45, a minimum water absorption of 0.84 percent is reached for the sintered ceramics. This optimizes the porcelain material composition and the mass percent (kaolin clay 60-50, quartzofeldspathic sand 35-45, cullet 5), as well as the sintering process parameters (firing temperature is 1,175 °C, isothermal exposure is two hours). A flow chart has been developed for achieving semi porcelain products with the water absorption of 0.8-5 mass percent.

Keywords: quartzofeldspathic tailings, fluxing agent, low-fired porcelain, water absorption, shrinkage, albite, mullite.

INTRODUCTION
One of the high-priority tasks for the Siberian region's mining industry is processing industrial waste, including tailings left over after molybdenum ore beneficiation at Sorsky GOK copper and molybdenum mining complex [1]. Overburden and enclosing pegmatites are industrial waste, tailings left over after mining the ore, as well as quartzofeldspathic tailings, which are obtained after the consecutive implementation of four-stage crushing processes, wet single-passage grinding, bulk and differential flotation, recovery of copper and molybdenum concentrates, dewatering, drying and blending [2]. Solving the priority task of tackling the complexity of processing sulphide molybdenum ores would help to reduce anthropogenic impact on the region, and also allow the region to profit from selling the products produced by industrially processing raw materials. The ceramic material industry is one of the most resource-demanding branches of the national economy. Sustainable use of fuel, raw materials and other natural resources is becoming a decisive factor for successful industry development. A future-orientated way to put tailings to good use at Sorsky GOK copper and molybdenum mining complex is in the production of fine ceramics.

In the ceramics industry, feldspathic and quartzofeldspathic materials are used as a fluxing agent (flux) for the production of fine ceramics (porcelain, faience). The possibility of substituting the exhausted deposits of natural fluxing components with the alternative of industrial tailings is of particular significance. Processing operations for sulphidic molybdenum ores in porcelain and faience production is significantly simplified due to partial exclusion of the primary crushing and milling stages.

THEORETICAL ASPECTS
Two kinds of feldspathic tailings from Sorsky GOK copper and molybdenum mining complex have been explored as possible replacement materials for natural feldspars: overburden pegmatites as well as quartzofeldspathic sand as waste products left over after the beneficiation of copper and molybdenum ores at Sorsky GOK copper and molybdenum mining complex. Table-1 shows the chemical composition of tailings as well as that of other ceramic masses for the production of porcelain.

Table-1. Chemical composition of raw materials being studied, mass percent.

Raw material name	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Loss on ignition
Overburden pegmatite	69.86	17.12	0.17	0.71	0.94	0.32	4.84	5.62	0.41
Quartzofeldspathic sand	62.05	15.94	0.58	4.18	4.72	2.01	4.27	3.85	2.39
Cullet	67.40	5.81	-	1.76	7.21	3.38	12.73	2.0	-
Chamotte fireclay (Kantat Deposit)	61.79	23.20	-	0.34	0.27	0.15	1.24	1.43	11.57

The pegmatites contain significant amounts of low-melting potassium and sodium oxides (10.46 mass percent). The minimum content of ferrous oxide has been fixed (0.71 mass percent). Accumulated quantity of Na_2O and K_2O in quartzofeldspathic sand is slightly lower than in pegmatites. According to GOST 23034-78 quartzofeldspathic gangue belongs to a group of raw materials with a ratio of alkali metal oxides (K_2O:Na_2O) lower than two. With regard to well-known fact that the most important parameter proving quality of feldspathic raw material is correlation of K2O mass fraction to Na2O we have identified an advantage of pegmatite effectiveness as fluxing agent that has potassium module 1.2 against that equal to 0.9 in quartzofeldspathic sand.

Pegmatites in a spoil tip infractions are sized 5-50 mm and need to undergo two-stage crushing followed by fine grinding in ball mills. Table-2 shows the granulometric composition of quartzofeldspathic sand.

Table-2. Granulometric composition of quartzofeldspathic sand, mass percent.

Material	Content of particles, size measured in mm						
Quartzofeldspathic sand	-1.4+1	-1+0.8	-0.8+0.5	-0.5+0.315	-0.315+0.08	-0.08+0.056	-0.056
	0.14	0.36	2.07	11.21	60.31	20.42	5.49

The elementary and phase composition of pegmatites and quartzofeldspathic sand has been determined respectively, by means of X-ray spectrum analysis using the Lab Center XRF-1800 Shimadzu (Japan) spectrometer and X-ray phase analysis using the XRD-6000 Shinadzu diffractometer. The mineral composition of pegmatites is represented with orthoclase $KAlSi_3O_8$, albite $NaAlSi_3O_8$ and anorthite $CaAl_2Si_2O_8$, a solid solution of albite and anorthite (plagioclase), quartz crystals (SiO_2) intergrown through feldspars. There are small amounts of calcite $CaCO_3$ impurities. The plagioclase minerals in pegmatites may partially replace orthoclase minerals in porcelain, although they may reduce the sintering temperature range and make the mass susceptible to loosing form during firing. In its phase composition, quartzofeldspathic sand is characterized as having a significantly lower albite and orthoclase content, predominantly feldspathic component of anorthite and plagioclase, with a high quartz and haematite content. The presence of pegmatites and quarzofeldspathic sand made of complex potassium and sodium feldspars may ensure more viscous mass during melting, which may help to maintain the form of a product during firing, and facilitate the formation of the product using lower temperatures and maintaining a sufficiently wide sintering range, while at the same time ensuring intense dissolution of quartz and clay matter. In terms of their mineral composition (see GOST 23034-78), both studied tailings belong to a group of quartzofeldspathic sand with a crystalline quartz content of over 10 mass percent. Materials containing feldspar are preferable for industrial use where the sum of K_2O + Na_2O alkaline oxides is over seven percent, the mass weight of Al_2O_3 is over 11 percent, and the mass weight of SiO_2 is 63-80 percent. Tailings from Sorsky GOK copper and molybdenum mining complex conform to the given practical recommendations as investigated replacements of natural feldspars. Given that quartz and feldspar are traditional components in ceramic masses, overburden pegmatites and quartzofeldspathic sand from Sorsky GOK copper and molybdenum mining complex may be considered as replacements for feldspars and quartz. The alternative of clay matter from the Kantat Clay Deposit instead of kaolin for obtaining low-fired porcelain has been made on the basis of its mineral composition, as it has a significant kaolinite mineral content.

Using efficient fluxing agents is one of priorities for achieving lower porcelain firing temperatures; these fluxing agents melt under the maximum temperatures for the sintering process, and they form silicate melts separately or with other materials, therefore making these materials more durable [3-6]. The fluxing effect of feldspars in the ceramic mass takes place at 900°C. Further raising the temperature would lead to the kaolinite and quartz melting and the formation of a glass phase melt in the ceramic mass quantity required to sinter an article. A melt with moderate activity reacts with filler. The glassy phase joints the mass particles, fills in pores and increases the density of the article. If the glassy phase consists of up to 45-50%, the products durability is increased, although when this figure is increased the articles become fragile, and heat resistance is reduced. A high diffusion rate of melt components leads to an accelerated volumetric solidification due to a more intense mass transfer.

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Replacing kaolin with fireclay and high-melting clays should also be considered as an alternative to decrease the firing temperature of certain kinds of porcelain [7-10].

Increased flux content in low-fired porcelain mass allows an article to be fired within a temperature range of 1, 160-1, 250°C. The addition of potassium feldspar to the ceramic mass is recommended for forming a more viscous melt and to help the product to become more rigid. The presence of small quantity of albite in potassium feldspar lowers the melting temperature, while it does not affect viscosity of the melt in any way. Sodium feldspar is characteristically less viscous under high temperatures in comparison to potassium, with a lower melting temperature and shorter temperature interval for the ductile phase; at the same time, this material melts quartz and clay matter more intensively in comparison to orthoclase [11-17].

One of known methods of creating the low-fired porcelain is the use of two kinds of feldspars of the K_2O - Na_2O system. This way of obtaining the low-fired porcelain has been highlighted in this article as being preferential.

LABORATORY STUDIES

Based on analysis of the chemical composition of tailings and the state diagrams of Na_2O –Al_2O_3 –SiO_2 and K_2O - Al_2O_3 - SiO_2, intense pegmatite melting has been estimated to begin at a temperature of 1,050°C. During heat treatment of pegmatite-based ceramic masses, the most probable crystalline phases would be albite and orthoclase, which allow for liquid-phase sintering of ceramics and mullite, which delivers high performance characteristics. The melting of quartzofeldspathic sand is characterized by the intense formation of the melt in lower temperature ranges in comparison to pegmatite (from 1,000°C). Nevertheless, it ought to be noted that presence of potassium feldspars may lead to some increase in the melt formation temperature. Albite, orthoclase, anorthite and mullite are likely to form during heat treatment of quartzospathic sand, promoting the sintering process and the improvement of ceramics properties.

In the research work presented below a solution to the challenge of replacing the classic porcelain mass (kaolin-quartz-fluxing agent) with industrial products by implementing a plastic porcelain molding process under a relative molding-moisture content of 22 mass percent is given. Raw materials underwent milling in a ring mill until 1-2 mass percent was left on screen no. 0054. Initial evaluation was performed to determine how the quantity of quarzofeldspathic raw material effects the sintering process for ceramic mass, based on calculations of water absorption and general linear shrinkage parameters for sintered samples at an isothermal exposure temperature of 1, 150°C. The results are shown in Figure 1 (*a, b, c*).

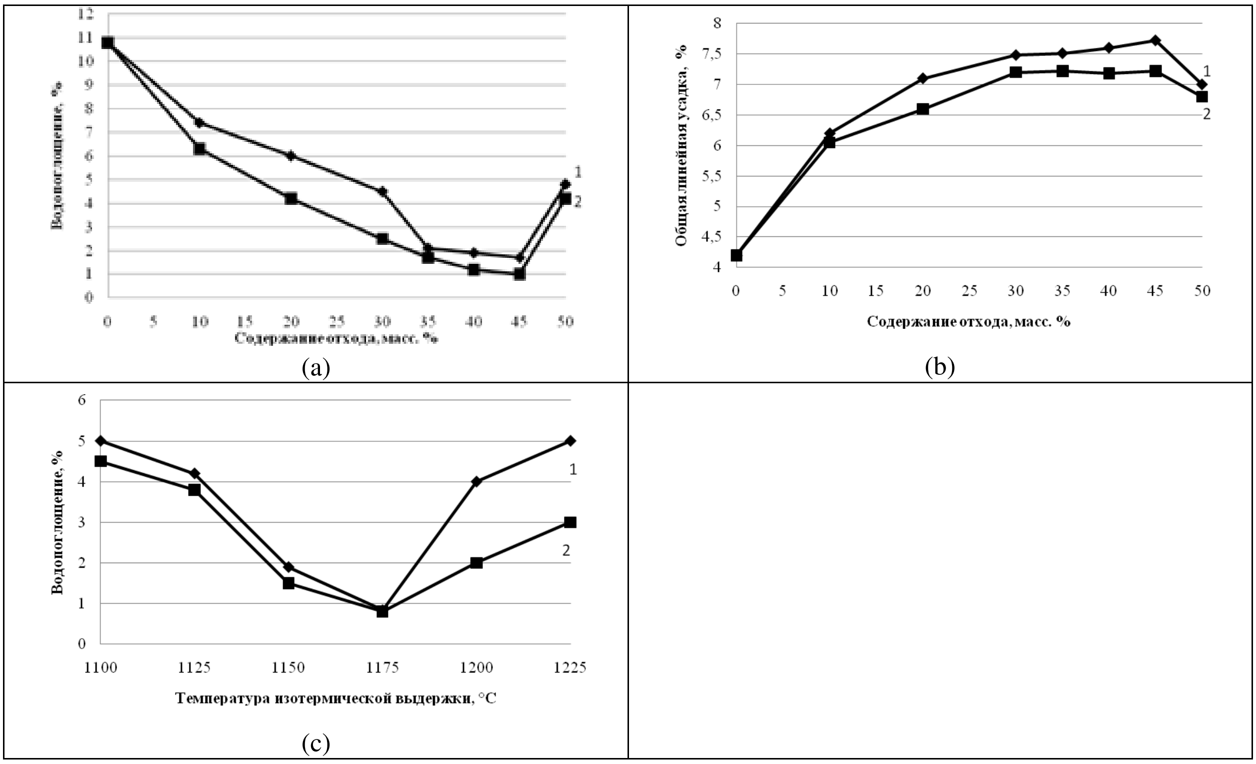

Figure-1. Change in water absorption (a) and general linear shrinkage (b) from waste content, water absorption (c) from temperature of isothermal exposure:
1 - quarzofeldspathic sand content, 2 - pegmatite content

When quarzofeldspathic raw material content is increased by up to 45 mass percent, general linear shrinkage increases and reaches a maximum value of 7.2 and 7.6 percent for ceramic mass containing both quarzofeldspathic sand and pegmatites (Figure-1, *b*). The minimal values of effective porosity determine that maximum shrinkage has been reached during the period of vitrification, which is established as an objective law (Figure-1, *a*). It should be noted that where there is 45 mass percent of quarzofeldspathic waste, the minimum water absorption reached is 0.8-0.84 percent for sintered ceramics containing both quarzofeldspathic sand and pegmatites. On the graphs (Figure-1, *a* and *b*), the effect of increased water absorption and reduced shrinkage of sintered samples is visible when the content of feldspathic raw material is raised by up to 50 mass percent. This is clearly related to the significant increase in the length of the liquid phase, and is confirmed by the visible deformation and partial buckling of samples. In view of this, any further increase in waste content in excess of 40-45 mass percent has been found to be counterproductive, despite the possible additional effect of reducing the firing temperature. The correlation between the water absorption of the experimental masses displayed in Figure-1, c, indicates the possibility of obtaining minimal water absorption for ceramic masses containing pegmatites and quartzofeldspathic sand at the isothermal exposure temperature of 1, 175°C. Moreover, a sufficiently wide interval is achieved for the sintered state.

Figure-2 is a micrograph, demonstrating the fine matrix structure of low-fired porcelain in a form of mullite and anorthite crystals, and a glassy phase, which retains quartz grains. X-ray analysis (Figure-2, *b*) confirms the presence of these crystalline phases in the samples of sintered porcelain ceramics.

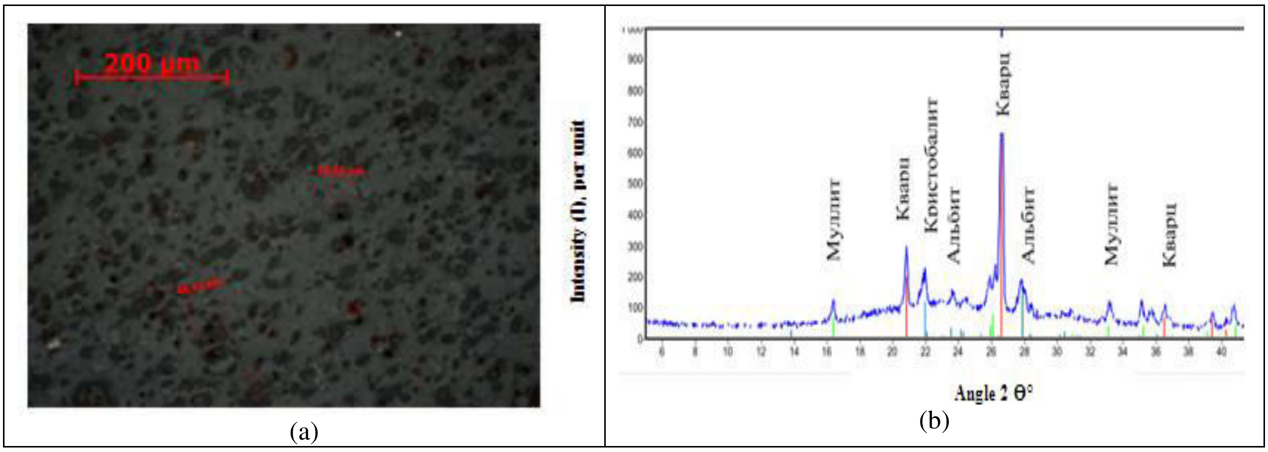

Figure-2. Microstructure (*a*) and X-ray diffraction pattern (*b*) of sintered ceramics with content no. 2 at an optimal temperature of 1,175 °C

Taking initial research on ceramic mass sintering processes into account, quarzofeldspathic sand has been selected as the raw material best suited to practical use, which constitutes flotation tailings from copper-molybdenum ores, which do not require multiple stages of milling and grinding.

Optimizing the process parameters for the production of low-fired porcelain was carried out by completing a full factorial experiment 2^3. Water absorption of sintered masses, their general linear shrinkage and density were chosen as the optimization variables. The firing temperature, isothermal exposure and quantity of quarzofeldspathic sand have been identifie as influencing factors. Table-3 provides the levels and intervals of factor variation.

Table-3. Levels and intervals of factor variation impacting the production process of low-fired porcelain.

Factors	Factor levels			Variation interval
	-1	0	+1	
X_1 : content quarzofeldspathic sand, mass percent	35	40	45	5
X_2: firing temperature, °C	1,125	1,150	1,175	25
X_3: isothermal exposure, hours	1	1.5	2	0.5

The following process parameters remained constant during the production of low-fired porcelain (semi-porcelain), which were established during the initial stages of the study:

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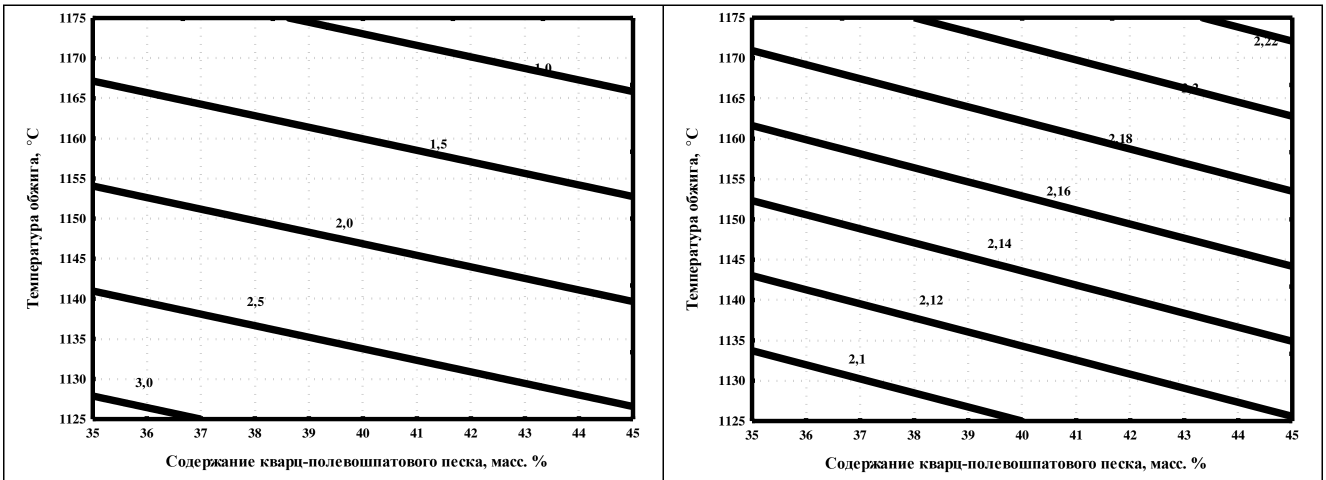
- relative molding-moisture content: 22 mass percent;
- molding pressure: 2 MPa;
- size of solid ground particles of raw mixture relative to the remainder 2 mass percent on screen no. 0054:
- cullet content 5 mass percent.

The optimization results have been worked out using the Statistica software, and are represented in Figure-3.



(a) (b)

Figure-3. The change in water absorption (*a*) and apparent density (*b*) resulting from firing temperature and quarzofeldspathic sand content

The correlations visible in Figure-3 prove that it is possible to achieve a high sintering effect using the ceramic masses in question, and it is possible to produce semi-porcelain melts in accordance with GOST R 54396-2011 for household crockery using the low-fired porcelain. It should also be noted that it is possible to produce low-fired porcelain with water absorption of less than 5 percent with quartzofeldspathic raw material added as a blending component within a considerably wide range from 35 to 45 mass percent, for the production of sanitary stoneware for hygienic and household applications in accordance with GOST 15167-93. The coloured melt as a finished product may also be used for the production of crockery for multiple applications as well as for art and decorative purposes. The physical and technical parameters of sintered ceramic masses with optimal material composition are given in Table-4.

Table-4. Physical and technical properties of porcelain.

Material composition, mass percent	Firing temperature, °C	Water absorption, %	Apparent density, g/cu.cm	Flexural strength, MPa	Compressiv e strength, MPa
Clay 50, quartzofeldspathic sand 45, cullet 5	1,175	0.84	2.23	28a	76

The process flow diagram which has been developed for the production of low-fired porcelain articles is shown in Figure-4.

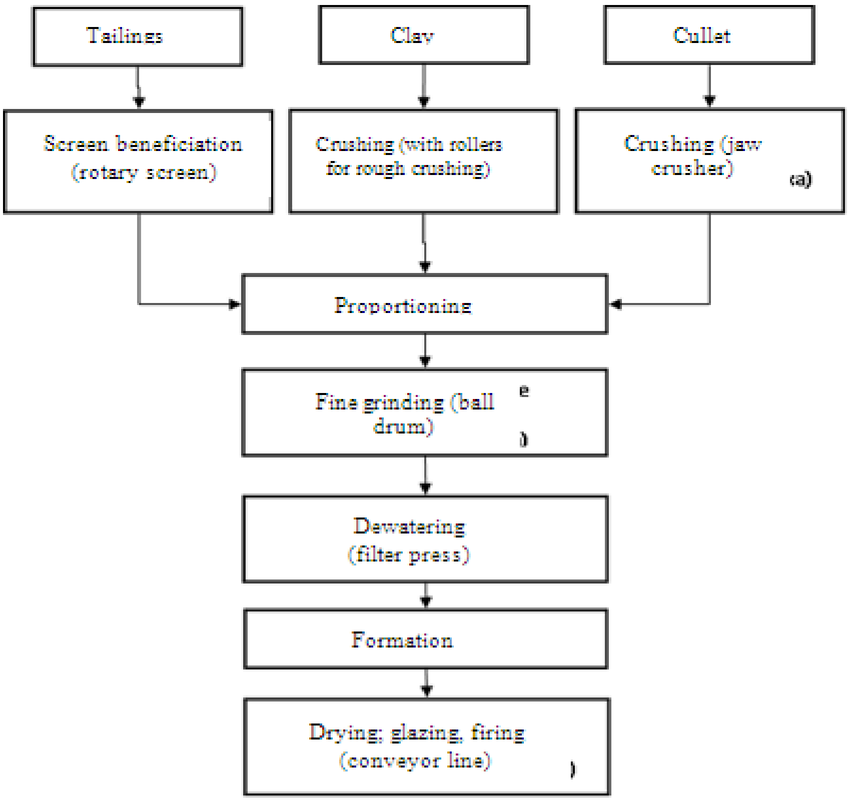


Figure-4. Production flow diagram for semi-porcelain products using molybdenum ore beneficiation tailings from Sorsky GOK copper and molybdenum mining complex

CONCLUSIONS

The flow diagram which has been developed for the technological production of low-fired porcelain using quartzofeldspathic sand supports the production of household crockery, ceramic sanitary stoneware, as well as art and decorative articles with a water absorption range of 0.9-5 percent, flexural strength 28 MPa, compressive strength 76 MPa, apparent density 2.23 g/cm^3 under optimal isothermal exposure temperature of 1, 175°C with a quarzofeldspathic sand content in the ceramic porcelain mass of 40-45 mass percent.

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