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A STUDY ON THE KAOLIN DEPOSITS OF BELARUS WITH A PURPOSE FOR THEIR USE FOR THE MANUFACTURE OF CERAMIC TILES OF VARIOUS FUNCTIONS

The article presents the results of the complex study of the physical, chemical and technological properties of the primary caolins from the «Sitnica» and «Dedovka» deposits enriched with the method of clarification. It has been stated that caolins having a particular degree of quality can be used for the production of ceramic tiles of various functions. The compositions of the masses for obtaining tiles for the internal lining of walls and for floors are recommended with partial replacement of the imported refractory clay and caolins for caolins from the «Sitnica» and «Dedovka» deposits with the correction of the quantity of quartz-containing raw material.

Introduction. Ceramic tile is one of the most effective facing materials derived from a mixture of clay, quartz sand and other natural raw materials by semi- dry pressing and burned at high temperatures. These products belong to the Group of stone and ceramic materials, their features being a high mechanical strength, high resistance to abrasion, fire resistance, resistance to atmospheric influences, etc. The above mentioned properties account for the durability of the material [1].

Despite the variety of properties of ceramic tiles, the main raw materials for their manufacture are clays. One of the most important components of the ceramic mass is kaolin, which provides improved rheological properties of slip in the production of tiles. It also widens ceramic masses sintering interval that increases their adaptability. The use of kaolin improves strength characteristics of finished products by forming mullite crystal phase during firing. Useful qualities of natural and enriched kaolin are due to its fire resistance, chemical inertness, whiteness, dispersity, low dielectric permeability and other valuable properties. Mineral admixtures can significantly affect the properties of kaolin. 60 % of kaolin is used for the production of ceramics as compared to the production of paper, refractory materials, etc.

Ceramic tiles must satisfy the requirements of the normative and technical documentation [2-4] and find their application primarily for flooring and wall facing in the objects of industrial and civil construction. Currently the manufacturers of ceramic tile in Belarus are: JSC «Keramin», JSC «Beryozabuildingmaterials», JSC «Brest KSM», who work exclusively on imported kaolin raw material of different brands. The annual demand for this raw material is about 40 thousand tons costing for about 2.5 million $ US.

In the Republic of Belarus there are considerable deposits of kaolin. The information concerning kaolin formation conditions and prospects for their development, specific chemical and mineralogical composition and their potential enrichment has been previously reported in [5, 6]. The use of kaolin from the Sitnitsa and Dedovka deposits in compositions of ceramic masses for manufacturing tiles instead of imported clay components will not only increase the raw material base of domestic ceramic industry, but also reduce the cost of production.

Main part. Experimental work on studying the possibility of using natural and enriched kaolin in ceramic masses was based on a comprehensive research of chemical-mineralogical composition, properties, and their behavior while heating and phase transformations during thermal processing [5]. Table 1 presents comparative characteristics of kaolin from the Sitnitsa and Dedovka deposits in their natural and enriched states.

Kaolin raw material plays a key role in the structure formation and phase formation of a ceramic body (potsherd) in the firing process due to a sufficiently high Al_2O_3 content (25–30 %) that meets the ceramic raw materials demands. The mineral composition of kaolin was calculated by us on the basis of x-ray and chemical analysis techniques [7]. The natural kaolin, used for the production of ceramic tiles can contain kaolinite minerals of 27–50 % by weight, 11–32 % of mica, montmorillonite – up to 4 % by weight, quartz – 7– 37 mas. %, feldspar – 5–8 % by weight, others –1–3 mas.%.

Table 1 demonstrates that the studied kaolin satisfy the above mentioned requirements.

We should also note the high sand content and, consequently, the insufficient plasticity of natural kaolin due to which silica content in the raw material composition must be reduced.

Table 1

Chemical and mineralogical composition of kaolin raw materials and technological parameters

Parameter	Kaolin «Sitnitsa»		Kaolin «Dedovka»	
	natural	enriched		natural
Content of oxides, mas. %*:				
SiO_2	61.7	46.1	70.3	50.7
Al_2O_3	25.1	34.6	19.0	33.4
Fe_2O_3	1.56	2.53	0.46	1.05
TiO_2	0.68	0.94	0.26	0.63
CaO	0.19	0.23	0.09	0.21
MgO	0.45	0.42	0.06	0.11
Na_2O	0.12	0.47	0.10	0.01
K_2O	3.85	2.00	6.02	3.24
Calcination losses	5.64	11.9	3.63	10.54
Mineral composition, mas. %:				
Quartz	25.65	0.73	38.97	6.51
Microline	9.86	4.46	17.07	9.15
Albite	1.00	3.98	0.83	0.08
Kaolinite	42.52	74.63	14.82	65.80
Montmorillonit	0.01	3.13	0.02	2.22
Muscovite	15.37	6.96	26.63	14.27
Biotite	4.77	5.17	1.40	1.34
Rutil	0.67	0.94	0.26	0.63
Fine dispersion fraction, %:				
<0,01 мм	27.6	81.4	55.1	17.0
<0,001 мм	11.7	48.9	26.0	7.5
Plasticity number	6.9	18.5	2.9	12.6
Drying sensitivity	0.13	0.29	0.10	0.16
Air shrinkage, %	4.1	5.7	3.9	4.8
Sand content, %	65.2	1.80	60.4	2.73
Elasticity index, kg/m^3	49	132	60	144
Structure formation threshold kg/m^3	1175	1120	1355	1300
adsorption, mg/g	9.5	14.3	6.4	9.0
pH	5.7	4.8	6.6	7.9
Fire resistance, ^{o}C	1620	1710	1750	1780

* – Here and hereinafter, unless otherwise is noted, the weight content is given. Therefore the aim of this study is to develop mass compositions using natural and enriched kaolin raw materials of deposits of the Republic of Belarus for ceramic tiles production for interior facing of walls and floors that meet the requirements of the current normative and technical documentation.

High-temperature dilatometric curves of natural and enriched kaolin from the Sitnitsa and Dedovka deposits in the temperature range of 100–1400 °C with a heating rate 50 °C/min are given in picture 1. They were obtained by means of optical microscope heating MISURA ODHTHSM 1600–80.In the range of temperatures up to 500 °C there is a slight change in sample sizes of both kaolins, since their thermal expansion is largely compensated by shrinkage associated with water adsorption removal and the beginning of kaolinite dehydration. At a temperature of 500 °C the expansion reaches its maximum values for samples of enriched kaolin and turns into shrinkage, which continues up to 735 °C for Sitnitsa kaolin and is 1.18 %. And up to 700 °C kaolin «Dedovka» shrinks 0,31 %, due to the removal of water of crystallization and the destruction of the kaolinite lattice. In this temperature range for natural kaolin from both deposits there is a small expansion of Sitnitsa kaolin samples – 0.75 % and 0.50 % of expansion for kaolin «Dedovka», which is probably due to polymorphic transformation of quartz. Up to 945 °C temperature sample size is practically unchanged: shrinkage is due to thermal expansion.

Non-enriched kaolin samples under these conditions change their dimensions with a slight expansion, which is likely due to the formation at 1060 °C modification phase of silica i.e. metastable cristobalite.

Substantial shrinkage in the temperature range of 950–1050 °C for samples of enriched kaolin (2.08 % – «Sitnitsa» and 1.44 %, «Dedovka») is caused by dissociation of carbonate impurities present in small amounts, as well as the beginning of a process of mullite formation, contributing to the compaction of the structure.A sharp increase in its volume is compensated by combining of structural units of meta-kaolinite. At a temperature above 1150 °C there is a sharp transition of dilatometric curves in the side of shrinkage, which testifies to intensification of kaolin sintering process from both deposits with the formation of mullite.

It is known [8], that even a negligible content of Montmorillonite (0.5–3.0 %) in kaolinite-type clays has a positive effect on their sintering.

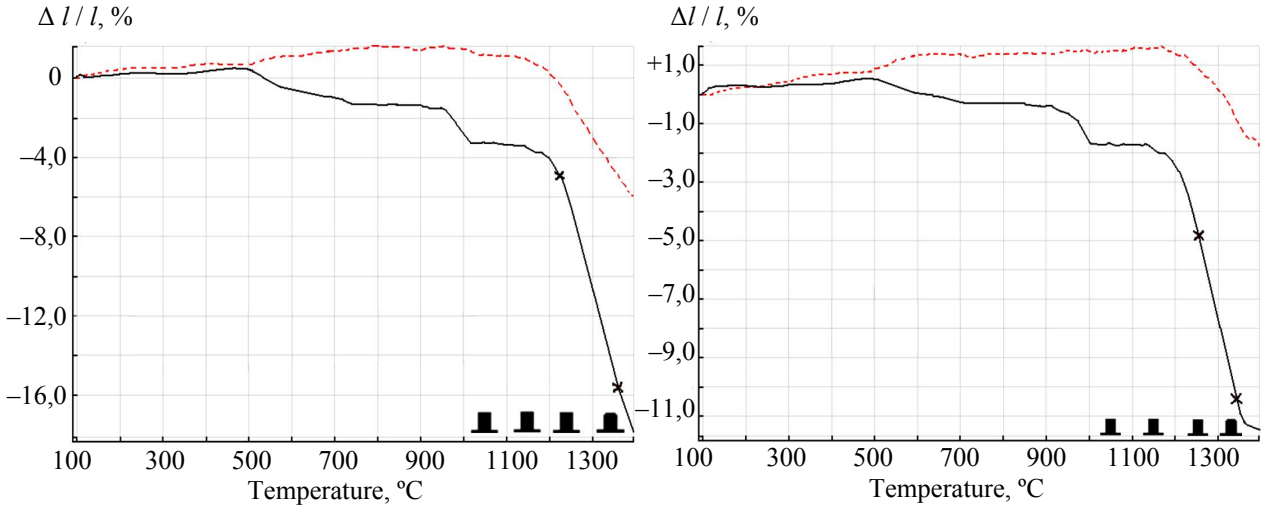
We should pay attention to the presence of the following characteristic points on the dilatometric curves of enriched kaolin (a modified form of the samples according to the method of research): 1) sintering, in which resizing is stated at 5 % level (temperatures are for the kaolin «Sitnitsa» – 1225 °C, for kaolin «Dedovka» – 1257 °C);

2) softening due to the formation of the liquid phase that causes rounding of corners and reduces surface roughness, which corresponds to a temperature of 1362 °C for kaolin «Sitnitsa» with the overall shrinkage of 15.70 % and T – 1343 °C for kaolin «Dedovka» with shrinkage of 10.45 % (fig. 1).

In contrast, curves of non-enriched kaolin in the studied temperature range do not detect any change in the sample, due to the greater sand content of natural difference of kaolin from investigated deposits, that preventing the baking. The kaolin «Dedovka» has a lower shrinkage compared with samples of the kaolin «Sitnitsa», which also can be explained by the greater number of quartz particles in this kaolin.

In the literature [9, 10] there described the results of research on the development of mass composition with primary and secondary kaolin for ceramic tiles with training of technological production parameters which indicate the appropriateness of their use in the manufacture of this type of products. A comprehensive study of natural and enriched kaolin deposits in Belarus shows that they meet the requirements for ceramic raw materials for the production of tiles.

Experimental compositions of masses for the manufacture of ceramic facing tiles are represented by the following raw materials: refractory clay DNPK (Ukraine) in the amount of 0–30 %, fusible clay «Gajdukovka» (Belarus) is 30 %, kaolin deposits of Glukhovets brand of KS-1 (Ukraine)–0– 3 %, natural primary kaolin of Belarusian deposits and enriched by washing on grid No. 0063 kaolin «Sitnitsa» – from 10 to 45 %, feldspar from Vishnevogorsk (Russia) – 11 %, dolomite «Ruba» (Belarus) – 14 %. The proportion of quartz sand of brand OVS-020-B (Belarus) was 12 %, in the experimental compositions it was declined almost by half (5 %), then this component was completely excluded from mass compositions.



a *b*

- - - - – natural kaolin; – enriched kaolin; – measure of shrinkage of enriched kaolin

Fig. 1. The dilatometric curves of natural and washed kaolin from deposits the «Sitnica» (a) and the «Dedovka» (b)

Table 2 shows the content of the used kaolin from – «Sitnitsa» and «Dedovka» in the studied compositions.

Ceramic mass has been prepared by joint wet grinding of raw components in laboratory ball mill, sodium tri-polyphosphate being used as electrolyte. Grinding of raw materials was made until the residue on sieve No. 0063 was not more than 3 %, followed by drying of the ready slip with humidity 36.5–39.0 % at a temperature of (100 ± 20 °C) and up to humidity of 3–4 %. The dried ceramic masses were subjected to grinding and then were wetted with rubbing through sieve No.1. The resulting press powders with relative humidity of 5.5–8.0 % were left undisturbed for 24 hours for their averaging. Tiles in the size of 50 × 50 mm and tablets of 20 mm in diameter were pressed at a pressure of (20 ± 5) MPA at the laboratory press. Samples were dried at a temperature of (100 ± 20) °C, and then were burnt in the electric muffle furnace at temperatures of 1000, 1100 and 1050 °C (for samples of wall facing tiles) and 1160, 1200 °C (for samples of floor tiles) with keeping them at a maximum temperature for 30 min.

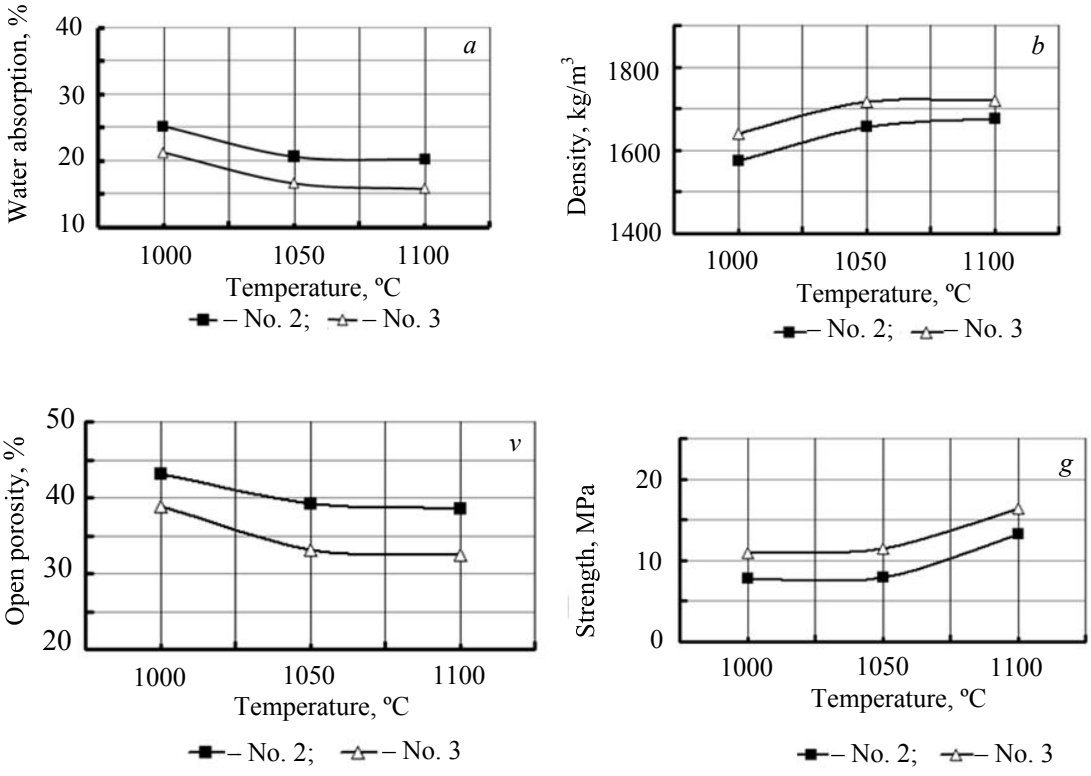
Study of basic performance properties (density, water absorption, mechanical strength) of designed compositions samples No.1-8 showed that the increased amount of natural kaolin «Dedovka» over 10 % can slow down the processes of sintering and worsen mentioned indicators. This allowed us to recommend 10 % of natural kaolin «Sitnitsa» and «Dedovka» as an optimum amount.

Figures 2 and 3 present dependence of physical and mechanical characteristics of samples of ceramic facing tiles made with the use of natural and enriched kaolin from deposits of the Republic of Belarus.

Table 2

Amount of imposed kaolin from «Sitnitsa» and «Dedovka» into the masses for ceramic facing tiles

The name of natural kaolin deposits	Composition number							
	1 production	2	3	4	5	6	7	8
«Sitnitsa»	–	–	10	15	–	–	–	–
«Dedovka»	–	10	–	–	15	25	35	45



No. 2 – composition with the natural kaolin «Dedovka»;
No. 3 – composition with enriched kaolin «Sitnitsa»

Fig. 2. The dependence of water absorption (a), density (b), open porosity (v) and strength (g) of ceramic tiles samples for internal facing of walls on the firing temperature

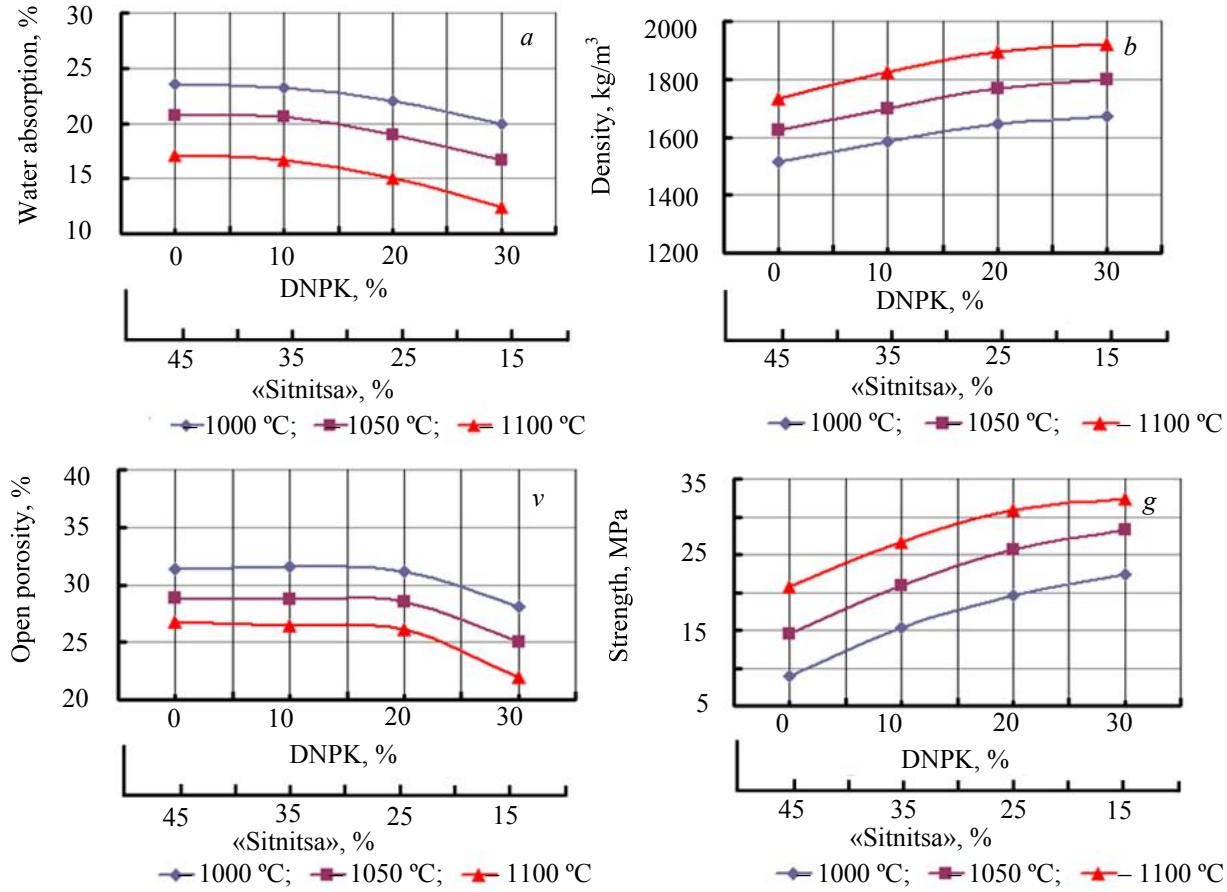


Fig. 3. Dependence of water absorption (a), density (b), open porosity (v) and strength (g) of samples of ceramic tiles for internal facing of walls on the firing temperature and content of kaolin «Sitnitsa»

Fig. 2 demonstrates that the properties of samples, burned at a temperature of 1100 °C have the following indicators: water absorption is 15.1–20.0 %, density–1680–1730 kg/m^3, porosity is 33–38 %, bending strength–14.5–17.0 MPa. The materials which include kaolin from deposits of the «Sitnitsa» due to its chemical-mineralogical and granular metric characteristics are considered to have the best properties.

The introduction of up to 5 % of quartz sand in experimental mass significantly degrades the performance characteristics of samples, so if you use natural kaolin, there is a need for adjustment of the mentioned component in the recipe of raw material compositions.

There was conducted a study on the influence of the replacement of refractory clay DNPK by enriched kaolin «Sitnitsa» in mass compositions upon the properties of ceramic tiles (fig. 3).

The carried out researches established that the use of enriched kaolin «Sitnitsa» in ceramic masses for manufacturing facing tiles as compared to tiles from natural kaolin promotes intensification of sintering material process. It happens due to removing the part of silica at kaolin enriching, it is confirmed by the graphical dependency of properties upon firing temperature in Fig.3. Thus, in the studied compositions 10–15 % of refractory clay can be substituted for enriched kaolin Sitnitsa, the performance properties of developed materials meeting the requirements of STB 1354–2002.

According to the XR analysis the qualitative composition of experimental samples of facing tiles with natural kaolin of Belarusian deposits and burned at a temperature of 1100 °C includes α-quartz, mullite, and feldspar, which mostly corresponding to the phase composition of industrial samples (tiles).

We have investigated the possibility of using natural kaolin in ceramic body compositions for the manufacture of floor tiles. It is known [3, 4] that the ceramic material of these products must meet higher requirements of its physical-mechanical properties, in particular of water absorption (up to 3.5 % at the firing temperature of 1160 °C and not more than 0.5 % at firing temperature of 1200 °C), bending strength (not less than 25 and 35 MPa). This is certainly linked to the quality of sintering, the strength of structure of the paste, the amount of glassy phase, etc. [1].

Batch(charge) composition of masses for manufacturing samples of ceramic tiles for floors is

based on the original (plant) recipe, replacing Ukrainian kaolin deposit Zhezhelevsky brand KZ-1, which was introduced in the amount of 6 %, by the primary kaolin deposits «Dedovka» and «Sitnitsa».

Refractory clay «Ceramic-Vesco» (Ukraine), its content ranged from 18.5 to 37.0 %; was partially removed. The enriched kaolin deposits of Glukhovets brand KS-1 (Ukraine) and quartz sand brand OBC-020-B (Belarus) were fully replaced by natural kaolin «Sitnitsa» and «Dedovka», the content of which has changed within 6–25 %.

Experimental set of samples with the content of domestic kaolin was investigated, see table 3. The technological process of manufacturing of prototypes is similar to the above described method of obtaining samples of facing tiles.

Table 4 presents the main properties of samples of ceramic tiles for floors, annealed at different temperatures.

Analysis of the obtained data allows us to state that the total shrinkage decreases if the content of natural kaolin from Belarusian deposits increases, water absorption slightly increasing, which is related to chemical-mineralogical features of kaolin, from «Sitnitsa» and «Dedovka». Then, as the content of kaolin decreases the water absorption falls significantly, approaching the production values.

Figure 4 shows the comparative strength indexes of samples containing different amounts of kaolin «Sitnitsa», «Dedovka» and production compositions.

Samples of ceramic tiles for floors with kaolin «Sitnitsa» compared with samples based on kaolin «Dedovka» are more durable due to the high content of Al_2O_3 (20.4 %–20.7). In addition, they have less amount of free quartz (41.8 % to 66.7 %), which positively affects the sintering process of such masses. However, due to the higher content of Fe_2O_3 in kaolin Sitnitsa (1.56 %) the samples with its use have a dark gray colour, and it should be taken into account when unglazed wares are produced. Using less ferrunginized kaolin «Dedovka» with water absorption of 7.3–8.2 % at 1160 °C requires additional fluxing components to activate the process of sintering such as fusible clay, feldspar and feldspar sand, ground glass, etc. The designed compositions of the masses using kaolin «Sitnitsa» may be recommended for the production of ceramic floor tiles of «Gres-type» with water absorption of less than 0.5 % when the firing temperature is up to 1200 °C.

According to laboratory tests the experimental samples of No.1 and 6 having 6 % of natural kaolin «Sitnitsa» and «Dedovka» possess nearly the same properties as production tile samples. An experimental manufacturing batch of ceramic tiles for floors in size 300 × 300 ×7 mm was manufactured at JSC «Keramin» using the following mass compositions:

– composition No.1 Zhezhelevsky raw kaolin was fully replaced by natural kaolin «Sitnitsa»,

– composition No. Zhezhelevsky raw kaolin was fully replaced by natural kaolin «Dedovka» with the addition of 1.5 % of «Gaidukovka» clay.

It was found that after the broader testing and further exploitation of Belarusian deposits of kaolin raw materials our developed ceramic compositions can be embedded in the production of floor tiles.

Table 3

Number of imposed kaolin «Sitnica» and «Dedovka» to the masses for ceramic tiles for floors

The name of depositis	Composition number										
	P (industrial)	1S	2S	3S	4S	5S	6D	7D	8D	9D	10D
«Sitnitsa»	–	6	18	24.5	17.1	9.7	–	–	–	–	–
«Dedovka»	–	–	–	–	–	–	6	18	24.5	17.1	9.7

Note: The index «S» corresponds to kaolin «Sitnitsa»; the index of «D» – to «Dedovka»

Table 4

Physical and technical properties of test samples of ceramic tiles for floors

Indexes	The number of compositions										
	P (industrial)	1S	2S	3S	4S	5S	6D	7D	8D	9D	10D
Firing temperature 1160 ºC											
Total shrinkage %	5.6	5.4	4.2	4.5	4.6	4.8	4.9	3.8	4.0	4.3	4.7
Water absorption, %	2.9	3.3	4.1	4.2	3.8	3.5	7.3	8.2	7.9	7.6	7.5
Firing temperature 1200 ºC											
Total shrinkage, %	6.7	6.6	4.9	5.3	5.5	5.8	6.4	5.7	5.9	6.1	6.3
Water absorption %	0.3	0.25	0.75	0.8	0.6	0.4	2.2	3.0	2.9	2.5	2.3

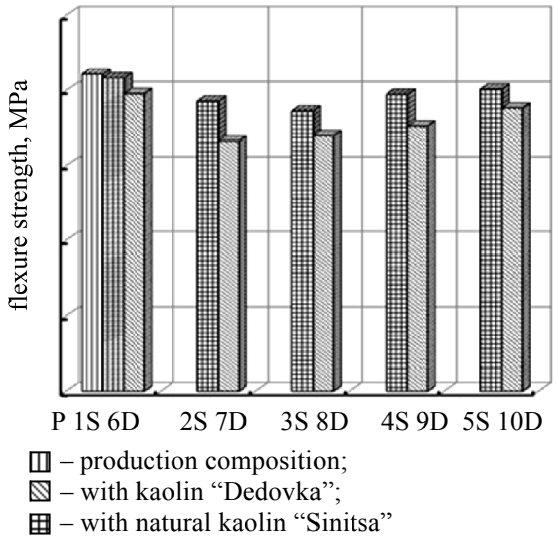


Fig. 4. Mechanical strength of tile sample for floors with studied compositions at bending, obtaine d at a firing temperature of 1200°C

Conclusion. Experimental results of our research work confirmed the possibility and reasonability to use kaolin of the two most significant Belarusian kaolin deposits «Sitnitsa» and «Dedovka» for the production of ceramic tiles for internal facing of walls and floors, as well as ceramic granite. The use of domestic kaolin can significantly reduce the import of expensive valuable clay raw materials and get the products with the required performance characteristics.

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