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THE USE OF BASALTS AND TUFFS AS CERAMIC MATERIALS FOR INTERIOR WALL FACING TILES

The results of study of chemical and mineralogical composition and technological properties of basalts and tuffs, explored on the territory of the Republic of Belarus are presented, and the possibility of their use as components of ceramic materials for interior wall facing tiles is established. The criterion of intensification of the sintering process of raw compositions, expressed by ratio of oxides ($SiO_2 + Al_2O_3$) / (Fe_2O_3 + FeO + Na_2O + K_2O), is defined and the limits of its values is set, at which open porosity of the tiles reduce to 16.0–21.5%, mechanical flexural strength up to 35.0–36.5 MPa, water absorption value is 13.2–9.8%, shrinkage – 1.2–1.3%, thermal coefficient of linear expansion (TCLE) – $(6.87–7.05) \cdot 10^{-6}$ K^{-1}

Introduction. The improvement of the quality of building materials and ensurence of their high performance require the solution of problems related to the development of the most effective ways to intensify the process of raw material compositions sintering in the preparation of ceramic tiles for interior wall facing. Sintering refers to one of the most important processes for the synthesis of various silicate and other refractory materials, which forms their structure and provides the desired physical and chemical properties. With increasing degree of sintering increases the density, strength, volume stability at high temperatures, chemical resistance and resistance against various corrosive environments. The process of obtaining a solid body of powders at high temperatures due to spontaneous reduction of free energy of the material at its heat treatment is understood as sintering. Factors accelerating the sintering process are mechanical, thermal and chemical, but the most widespread in practice was the last, which is the selection and introduction of additives in the raw materials mixture, that contribute to the formation of increased amounts of the liquid phase of the reaction. In most cases, the choice of additives is reduced to an empirical selection of initiator sintering composition, however, this approach does not provide optimization of the adopted technical solutions. Furthermore, there are no criteria for evaluating the effects of various additives in the interaction with the components of raw materials composition which inhibits their widespread use in the ceramic industry. As shown in works [1–2], the positive effect of additives is determined not only by the accelerated formation of the liquid phase in the ceramic dispersed systems, but also the rheological properties of the melt (viscosity, structure, etc.).

In the literature there are reports [3–4] on the possibility of practical application of rocks of volcanic origin in the ceramic mass for the intensification of the sintering process in the preparation of various products for construction application with high rates of physical and chemical properties. It is found that at temperatures of 1100–1150°C in these rocks there formed materials with almost zero water absorption and structure close to the glass-ceramic [5].

The above allowed to predict the effectiveness of the use of such species as components, intensifying sintering of ceramic materials for interior wall facing tiles. Moreover, at the present time the involvement in the production of local raw materials instead of imported, better utilization of raw materials of exploited fields, as well as the development of non-waste technology are actual.

In Belarus, within Brest region there explored deposits of basalt, which belong to the Vendian (Neoproterozoic) age and occupy an area of about 28 thousand km^2. Formationaly these rocks belong to the Trapp Volyn-Brest magmatic province (VBMP), which is widespread in the south-western outskirts of the East European platform and is located on the territory of Poland, Belarus, Ukraine and Moldova.

The depth of the basalt deposits within the province varies considerably. In Belarus Vendian basalts occur at a depth of 40 to 600 m. Trapps of VBMP are presented by interbedded basalts flows and basaltic tuffs packs and have homogeneous mineral and chemical composition on the area. In nature, rocks occur together with different weight ratio.

In this regard, the aim of this work is to study the possibility of using the basalts and tuffs, explored on the territory of the Republic of Belarus, as components of ceramic materials for interior wall facing tiles and the establishment of criteria to intensify the sintering processes of raw material compositions.

Main part. Selected bulk samples of basalts and tuffs occurring within Malaryta district, Brest region, derived from ten point samples taken from different depths within the deposit are the object of the investigation.

The change of the state of aggregation of rocks in the process of heating was estimated visually by sinter obtained by multiposition heat treatment of samples in an electric furnace of brands LH 15/14 of Nabertherm firm (Germany) in corundum crucibles at temperature exposures of 900, 1000, 1050, 1100, 1150, 1170, 1200 and 1300°C at a heating rate of 600°C/hr and 20 min exposure.

The production of ceramic tiles samples was carried out by semi-dry pressing. The preparation of molding powder was carried out by thermal dehydration of the slurry after wet grinding of the joint components in a ball mill of brand SPEEDY-1 (Italy). The two-stage compression of tiles was made with the maximum surface pressure (20 ± 2) MPa, after which the shaped intermediate product was fed to drying at a temperature of (150 ± 5)°C and then calcined at a maximum temperature (1110 ± 5)°C in the flow-conveying line RKK 250/63 under production conditions of OSC "Beryozastroymaterialy", as the mode of firing operating in the enterprise is difficult to reproduce in the laboratory.

Basalt is a rock of normal alkaline series formed by the eruption of magma, with porphyritic or pore structure, which depends on the crystallization process and rock formation time. In appearance they are dark, dark gray or black, dense and fine-grained rocks having a high density (3000–3300 kg/m^3) and the strength (compressive strength is 400–450 MPa). Tuffs are volcanic aluminosilicate rocks formed from the solid products of volcanic eruptions – ash, sand, lapilli, bombs, rock fragments, subsequently compacted and cemented. Rocks are distinguished by angular fragments with different sizes due to what their structure is characterized by a high porosity and low density compared with basalts. Binder components of mineral constituents of tuffs are volcanic ash, clay and siliceous raw materials, secondary (chlorite with thin scales) and ore minerals (magnetite, ilmenite) are present in small amounts. Volcanic material in tuffs is formed due to fragmentation and destruction of the products of basic magma, volcanic glass, poorly crystallized lava and in varying degrees of crystallized basalts.

Tables 1 and 2, respectively, show the chemical and mineralogical composition of samples of basalt and tuff of the Republic of Belarus, used in experimental studies.

Systematic deviations of the content of some oxides in tuffs from their average values in the basalts are explained by chemical unstability of volcanic products of the basic composition in exogenous conditions.

Intensive processes of devitrification and decomposition of volcanic glass, secondary changes of femic minerals and plagioclases resulted in a significant redistribution (concentration and removal) of some oxides and, above all, easy mobility of alkali and alkaline earth metals, as well as silica and iron oxides in various oxidation states [6].

Table 1

The chemical composition of basalt and tuff

Raw material	Content of oxides, wt. %								
	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	Fe_2O_3	FeO
Basaltic tuff	46.8–48.0	14.5–15.3	0.4–1.0	3.3–4.1	8.8–8.2	0.1–0.2	2.0–2.4	12.8–14.4	1.7–2.0
Basalt	48.2–50.7	14.6–15.6	7.7–10.3	2.8–3.4	1.9–2.4	2.0–2.6	1.8–2.4	9.4–9.8	4.8–5.1

Table 2

The mineralogical composition of basalt and tuff

Minerals name	minerals content in rocks, %	
	Basalt tuff	Basalt
Plagioclase	10.0–30.0	40.0–45.0
Clinopyroxene (augite, pigeonite)	0–20.0	30.0–35.0
Feldspar	0–10.0	2.5–3.0
Ore minerals (magnetite, ilmenite)	5.0–15.0	8.0–10.0
Chlorofeit	–	5.0–10.0
Volcanic glass, basalt lava lithoclasts	20.0–80.0	4.0–6.0
Analcime	2.0–10.0	1.0–2.5
Chlorite	5.0–20.0	–
Clay minerals (montmorillonite, saponite, kaolinite)	10.0–40.0	–
Quartz	0–10.0	–

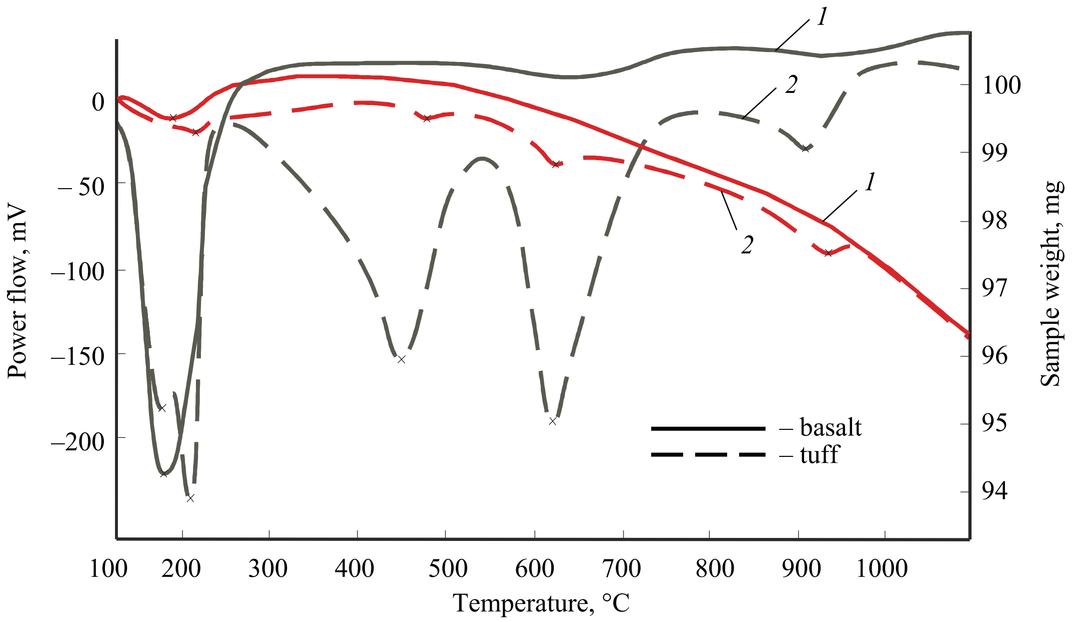


Fig. 1. The curve of differential scanning calorimetry (*1*) and thermogravimetric curve (*2*) of the test samples

Thus, the silica content in tuffs is in average of 3–4 wt. % less than in the basalts, which is associated with the possible removal of amorphous silica in postsedimentary stage. Differences are observed in the amount of iron oxides (III) and iron (II), and in tuffs usually Fe_2O_3 content substantially predominates over FeO. Reducing and sometimes complete disappearance of iron oxide (II), is due to easy oxidizability of finely divided volcanic material. Differences of the chemical composition of basalts and tuffs occur in the content and ratio of oxides of alkali and alkaline earth metals. The average content of MgO in the tuffs is 2–4 wt. % higher than in basalts. Reverse pattern is observed for CaO, the amount of which in the tuffs dramatically reduced.

The distribution of the alkali metal oxides, has the following features: their total content in tuffs is about 2 times higher than in basalts; the amount of K_2O is increased and Na_2O content is reduced. Such anomalies are the result of secondary changes of pyroclastic material of the basic composition and authigenic mineral formation that occurred in the process of sedimentation diagenesis and epigenesist influenced by sedimentation basin water, and residual circulating solutions. Ubiquitous high potassium content is due, apparently, to the sorption of its cations from seawater and residual solutions by authigenic clay minerals. Sodium, released during the decomposition of plagioclase and volcanic glass and the absence of sodium-containing newformed minerals leached similarly calcium. The bulk of the iron hydroxide is in the composition of fragments of lava, volcanic rock and glass [6].

Rooks mineralogical composition in Table 2 shows that the basaltic tuffs are characterized by a considerable content of volcanic glass and clay minerals, and almost complete lack of plagioclase which undergoes decomposition during epigenetic.

Fig. 1 shows the results of thermal analysis of samples of basalt and tuff.

It has been established that heating of basalt is accompanied by one endothermic effect with a minimum at 85–90°C, corresponding to removal of water from the formation. Total mass loss when basalt is heated makes up to 3.0–3.1%.

Heating of the tuffs is characterized by 5 endothermic effects on thermogravimetric curve, accompanied by a decrease in mass of the sample. It is necessary to note the two-step nature of the low-temperature effect with a minimum at 75°C and 120°C, corresponding to the presence of the montmorillonite group in the composition of rock minerals.

Packages in the minerals of the montmorillonite group are faced to each other by like-charged tetrahedral layers; the water in the interlayer space is retained due to weak van der Waals forces, which are easily broken even at low temperature. Due to the fact that for montmorillonite group of minerals a wide range of isomorphic transformations is typical, the amount of water in the interlayer space is different and depends on the type of cation involved in the substitution, and this explains the second minimum in the low-temperature region. Effect of endoreaction at 300–400°C is explained by the removal of water from the hydrated clay minerals. Endothermal effect in the temperature range 500–550°C indicates the presence in the mineralogical rock composition of significant amounts of chlorite and in the temperature range 800–850°C corresponds to the decomposition of clay minerals. Total mass loss upon heating of tuffs is significantly higher than that of basalt and constitutes 6.8–7.1%.

Results of multiposition heat treatment of studied basalt and tuff allowed to determine the temperature of the beginning of the tuff component sintering of 1080–1090°C, and basalt – 1160–1180°C, which is associated with an increased content of low-melting iron oxides and alkali metal oxides in the tuffs. Moreover, by its structure tuff is looser compared with dense basalt. The results of the granulometric composition of the rock after wet milling for 20 minutes show that tuff is characterized by larger amounts of fines (0.1–120.0 μm), thereby the surface area of the particles increases and the sintering temperature decreases.

Comparative study of tuff and basalt allowed to establish the possibility of their use in the compositions of ceramic materials as components intensifying the process of sintering. The above is explained by the features of the chemical composition of the rocks that are in the presence of low-melting iron oxides and alkali metal oxides and the mineralogical composition – in the presence of significant amounts of volcanic glass. The sintering temperature of rocks is lower than the maximum firing temperature of tiles, which also promotes the formation of a solid ceramic substrate.

The object of the investigation contained raw material composition comprising, by weight. %: fusible clay deposit of "Lukoml" – 13, granitoid screenings of Mikashevichy RUPP "Granit" – 29, dolomite deposit of "Rube" – 14, quartz sand of Gomel GOK – 7, waste production – pieces of tiles – 5, as well as imported from Ukraine refractory clay of brand DNPK – 32 (Basic).

Clay of deposit "Lukoml" is a low-melting (1225–1230°C fire resistance); by Al_2O_3 content it refers to a semi-acid clay (Al_2O_3 content is of 13.7–16.2 wt.%); by Fe_2O_3 and TiO_2 content to clay with a rich content of mentioned above oxides. By the number of plasticity clay is medium plastic (the number of plasticity is 17–19), it contains 52–55 wt % of particles with the size less than 0.001 mm. The mineralogical composition of clay is represented by quartz, feldspar, carbonate, mica and ore minerals.

Clay of brand DNPK (Donetsk region, Ukraine) is classified as a semi-acid (Al_2O_3 content is 20–38 wt. %),with low content of Fe_2O_3 (1.5–2.7 wt. %). The number of fraction particles of less than 0.001 mm is 27.6–62.0 wt. %, medium plastic (plasticity is 14–16), fire resistant (fire resistance is 1450–1750°C). According to a mineralogical composition clay refers to hydromica kaolinite, small amounts of inclusions of quartz, feldspar, calcite, and rutile are present.

Granitoid siftings are substandard siftings fraction with a particle size of 3–5 mm, resulting from the production of small road stones Mikashevichy RUPP "Granite". The main rock-forming minerals are plagioclase, microcline, quartz and biotite, secondary minerals are epidote, chlorite and sericite.

Ceramic tiles obtained based on the above basic system by a single firing at a temperature of (1110 ± 5)°C, have a mechanical strength of 19.0–20.3 MPa; water absorption is 16.2–16.5%. To increase its mechanical strength and to ensure the operational reliability of the products the possibility of intensifying sintering of the ceramic material was investigated.

Basalts and tuffs were introduced into the raw material compositions instead of granitoid siftings, both individually and jointly in various weight ratios. Analysis of physical and chemical properties of the samples of tiles allowed to determine the optimal number of basalt, which provides more active sintering of ceramic materials which is 15 wt. %. This is confirmed by a decrease in the open porosity of the tiles up to 17.4–20.0% and water absorption value constituting 12.5–13.2%, with marked increase in strength up to 30–33 MPa. By increasing the content of basalt (17.5 wt.% or more) there is a sharp increase in shrinkage of samples caused by the action of surface tension of the liquid phase, which is a negative factor in the production of tiles, because it requires changes in the size of the molds and leads to distortion of finished products decor.

Based on the mass compositions comprising tuff there produced tiles whose properties at a single firing temperature (1105 ± 5)°C, are within the following ranges: water absorption is 7.5–13.8%, apparent density – 1858–2500 kg/m^3, open porosity – 6.2–11.8%, mechanical strength in bending is 34.5–42.5 MPa, TCLE – (6.79–7.19) · 10^{-6} K^{-1} , the shrinkage – 1.1–3.5%, humid expansion – 0,041–0,052%. At joint introduction of basalt with tuff the intensification of sintering increases, which is associated with a considerable content of volcanic glass in the composition of the tuff. It was established that the optimum ratio of rocks is 1:1 in their total content of 15 wt. %.

The mechanism of sintering of studied ceramic materials is predominantly liquid phase. The liquid phase which is formed by the interaction of fine clay components, fusible impurities present in granitoid dropout, and dolomite dissolves volcanic glass present in the tuffs and basalts, while enriching with the mobile cations of alkali metals and iron oxides, which helps speed up the diffusion of the melt and its free movement over the surface of the solid particles. The reactive liquid phase during firing partially dissolves silica sand and granitoid rocks, enriched with more refractory oxides of calcium, magnesium, aluminum and silicon, it becomes more viscous and better resists deformation.

It is determined that the introduction of basalt and tuff promotes increase of the amount of liquid phase during sintering of compositions, thus its rheological characteristics vary. The results of X-ray phase analysis allowed to judge the increasing content of amorphous component, as evidenced by an increase in the profile of diffractometric curve above the background level with increasing content of basalt and tuff in the structure of the raw compositions and the dependence of the integral intensity of the halo on the composition of the ceramic mass, shown in Fig. 2.

The increase of the amorphous component content during firing of compositions is confirmed by infrared spectroscopy results.

The broad absorption band in the spectra in the frequency range of 950–1200 cm^{-1} with a minimum at 1080 cm^{-1} indicates the presence of silicates of different structure (frame, chain, and layer). It should be noted that the maximum of the band is diffuse, indicating an increase in the content of the vitreous component, and its amount is increased with increase in the content of basalt in the structure of the raw material compositions. Changes in the composition of the liquid phase during sequential introduction of basalt and then tuff were recorded by electron microprobe analysis, the results of which are shown in Table 3. It was revealed that at the introduction of basalt and especially tuff melt formed during firing of raw material compositions was enriched with iron oxides and alkali metals, with a marked decrease of the amount of silica and alumina materials. This is consistent with the above described liquid phase mechanism of sintering of the ceramic materials.

On the basis of the data obtained for the studied ceramic materials there is a criterion of intensification of raw material compositions sintering, expressed by the attitude of oxides ($SiO_2 + Al_2O_3$) / ($FeO + Fe_2O_3 + Na_2O + K_2O$), that is at values of 8.6–9.1 and constant total content of ($CaO +$ $+ MgO$), constitutes 7.5–8.4 wt.%. It provides the formation of melt with rheological characteristics increasing the degree of sintering and determining the open porosity parameters of the ceramic crock up to 16.5–20.0% (Fig. 3).

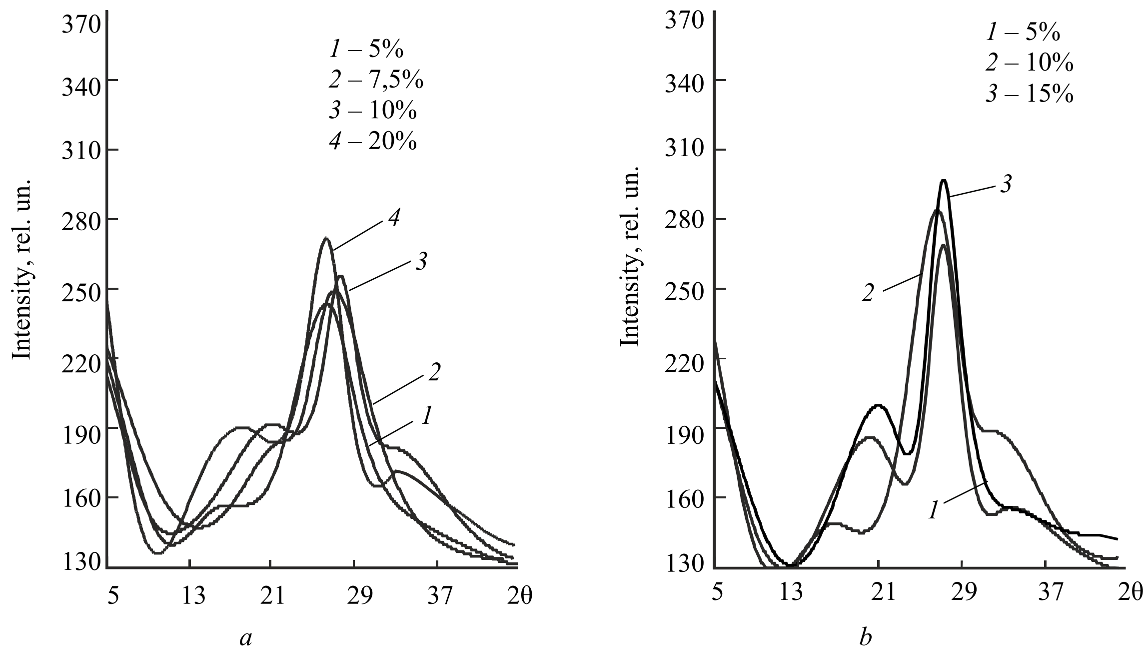
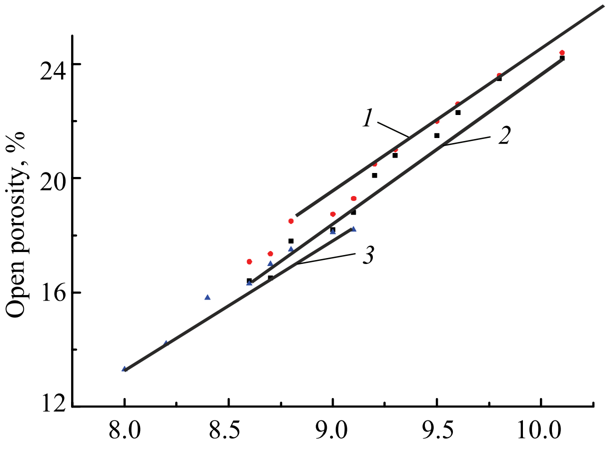


Fig. 2. Dependence of the integral intensity of the halo field of samples of tiles on the content of basalt (*a*) and tuff (*b*) in the raw compositions

Table 3

Average composition of the liquid phase formed during the firing of raw compositions with different content of basalt and tuff

The content of raw material components, %		Contents of oxide in the resultant melt, %							
Basalt	Tuff	SiO_2	TiO_2	Al_2O_3	Fe_2O_3+ FeO	CaO	MgO	K_2O	Na_2O
–	–	52.5	1.2	22.5	5.0	10.6	6.7	0.8	0.7
10	–	51.6	1.6	21.4	6.9	9.8	6.2	1.3	1.2
15	–	50.5	1.3	21.9	6.5	10.6	6.3	1.7	1.2
10	5	49.4	1.6	19.5	9.6	10.4	5.7	2.5	1.3
7.5	7.5	47.5	1.9	18.9	11.8	10.3	5.2	2.9	1.5



Ceramic compositions:
1 – basic system; *2* – with basalt content;
3 – with basalt and tuff content

Fig. 3. Dependence of the open porosity of the samples on (SiO_2 + Al_2O_3) / (FeO + Fe_2O_3 + Na_2O + K_2O)

It is revealed that the growth of values of above mentioned relationship leads to higher open porosity of the samples of tiles, which is connected with the peculiarities of the formation of the liquid phase, which has a decisive influence on the sintering of raw material compositions and the value of open porosity of the material.

Besides the increase in the amount of liquid phase and the reducing of the temperature of its formation a certain influence on the rheological characteristics of the melt has its composition.

It is known that the increase in the concentration of silicon oxide inevitably leads to an increase in viscosity, indicating the crucial role of groups Si–O in mutual displacement of the melt layers. Cations of iron in molten basalt and tuff is present in two oxidation states – in the form of di- and trivalent ions, performing the role of glass former and modifier. Iron oxide FeO reduces melt viscosity and Fe_2O_3, conversely, increases.

Thus, with introduction of basalt and tuff melt viscosity is reduced, its mobility and wetting capacity increase, which intensifies the sintering raw material compositions due to the diffusion of the active-flowing alkali metal cations Na^+ and K^+.

Conclusion. Given comparative studies of basalts and tuffs, explored on the territory of the Republic of Belarus, allowed to reveal differences of chemical and mineralogical composition of tuffs and basalts, which resulted in a lower sintering temperature of the tuff (1080–1090°C) compared to the basalt (1160–1170°C). It has been established that the intensification of the sintering process and improvement of the mechanical strength of the ceramic tiles when introducing basalt and its combination with tuff is achieved by increasing the number and changing the composition of the liquid phase formed during firing. The considerable amount of low-melting iron oxide (12.8–14.8%) and oxides of alkali metals (8.1–9.0%) results in the formation of low-viscosity melt at lower temperatures. It fills the pore space, and at rational combination of crystalline phases increases the mechanical flexural strength of the ceramic crock at 35.0–36.5% compared with samples of the production composition.

It is revealed that formed during the heat treatment, the liquid phase is enriched in alkali metal oxides and iron oxides, and the content of the refractory oxides of silicon and aluminum is reduced. It is found that the most significant effect on the sintering of ceramic materials containing basalt and tuff, has a ratio (SiO_2 + Al_2O_3) / (Fe_2O_3 + + FeO + Na_2O + K_2O) at a total mass of CaO and MgO, constituting 7.5–8.4 wt.%. Low levels of open porosity (16.5–20.0%), leading to high strength of ceramic tiles are marked with the values of the above ratio 8.6–9.1.

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