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## Effects of the Basaltic Tuff Additions on the Properties, Structure and Phase Composition of the Ceramic Tiles for Interior Wall Facing

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### Abstract

Basaltic tuffs are indispensable associated rocks during extraction of basalts, which are formed from igneous basalt fragments, cemented and compacted by volcanic glass and ash. The chemical and mineralogical composition, behaviour during heating and particle size of tuffs compared with basalts are studied. Physical and chemical properties, the structure and phase composition of the samples of tiles using tuffs are defined. The possibility of sharing basalts and tuffs in the composition of masses for the tiles of interior wall facing in order to improve the mechanical strength of finished products and reduce their material capacity is established.

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*Keywords:* basaltic tuff; physical and chemical properties of ceramic tiles; the structure; phase composition.

### 1. Introduction

The literature contains extensive information about the practical application of the rocks of volcanic origin in the compositions of ceramic masses for obtaining of various products for construction purposes with high physical-chemical properties, including tiles for interior wall facing. Practical interest in these rocks is caused by their manufacturability, singularities of mineralogical composition and high mechanical characteristics of pure rocks [1].

Researches carried out by the authors established that decrease of ceramic tiles thickness is achieved by increasing their mechanical strength in the air-dried and fired state. Effective in achieving the latter is the introduction of basalt in the amount of 15 wt. % instead of granitoid screenings of the raw composition for producing tiles by single-firing technology, which leads to higher mechanical strength at 35–37% over the tiles, made according to a recipe of the enterprise.

Due to the fact that the tuff is an indispensable concomitant rock of basalt during its extraction and occur at a weight ratio of "tuff : basalt" near 1:2, it is appropriate to study the effect of the joint presence of the two rocks on the physical and chemical properties of tiles, their structure and phase composition.

In order to establish the possibility of practical sharing of basalt and tuff as a components for the manufacture of tiles of reduction material capacity for interior wall facing, is of interest to conduct a comparative study of the chemical and mineralogical composition of the basalt and tuff, as well as their technological properties.

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## 2. Study area

The object of study is averaged samples of sub alkaline basalt and associated basaltic tuff, deposits of which are being explored on the territory of the Republic of Belarus. Tuffs are aluminosilicate volcanic rock formed of solid products of volcanic eruptions such as volcanic ash, sand, lapilli, bombs, fragments of rocks, then compacted and cemented. A characteristic feature of tuffs is the angular of its fragments. Cement of tuffs is volcanic ash, clay and siliceous raw material mixed with the ashes of the decomposition products. In addition, tuff contains a small amount of secondary (chlorite) and ore minerals (magnetite, ilmenite). Volcanic material of tuff was formed by fragmentation and destruction of products of basic magma: volcanic glass and poorly-crystallized lava and to varying degrees of crystallized basalt.

In its structure, tuffs are coarse-grained and characterized by high porosity and low density.

## 3. Experimental methods

The behavior of the studied basalt and tuff by heating was evaluated visually in character of sinters produced by multi-site thermal treatment of rocks in an electric furnace in corundum crucibles at temperature exposures of 900, 1000, 1050, 1100, 1170, 1200 and 1300 °C with a heating rate of 600 °C/h and exposure at the maximum temperature for 20 minutes.

Thermal analysis of rock samples was carried out on the device of combined thermogravimetric analysis and differential scanning calorimetry TGA/DSC1 by company METTLER TOLEDO (Switzerland) in the temperature range 20–1100 °C at a climb rate – 10 °C/min, equipped by the software STAR.

Size distribution of rock samples was determined by laser diffraction particle microanalyzer “Analizette–22” by firm Fritsch (Germany).

Preparing the samples of ceramic tiles is carried out by dry pressing. Getting of the press powder was carried out by thermal dehydration of the slurry after the joint wet milling of mass components in a ball mill brand SPEEDY-1 (Italy). The two-step molding tiles made with the maximum specific pressure (20±2) MPa, and then molded semi-finished product fed to the drying and then was fired at the maximum temperature (1110 ± 5) °C in the flow-conveyor line RKK 250/63 in a production environment of enterprise “Berezastroymaterialy”.

Physical and chemical properties of the samples of ceramic tiles (water absorption, mechanical strength and temperature coefficient of linear expansion (TCLE)) were determined according to the GOST 27180–2001, humid expansion – by STB EN ISO 10545–11–2006 by measuring the proportional change of length of fired ceramic tiles.

The study of the microstructure of ceramic tiles was carried out using a scanning electron microscope JSM 5610 LV JEOL (Japan).

Phase composition of the product samples was studied in X-ray diffractometer D8 ADVANCE by company «Bruker» (Germany). The recording was made in the angular range 2° – 10–80° in steps of 0,1–0,2° and the accumulation of pulses for 2 s. To identify the crystalline phases used by the International Card Index Join Comities on Powder Diffraction Standarts 2003 and soft-ware DIFFRAC PLUS by company “Bruker”.

## 4. Comparative study of basalts and tuffs

The analysis of the chemical and mineralogical composition of the rocks, their dispersion and behaviour during heating was studied in order to establish the possibility of sharing basalts and tuffs in the compositions of ceramic masses for tiles of interior wall facing.

The chemical composition of tuffs is almost complete analogue of effusion of basalt according to the Geological Institute of Belarus. However, the conducted researches note some variations in the chemistry of the rock samples, which is, apparently, connected with the presence of impurities in tuffs of terrigenous feldspar-quartz material (up to 5–15 wt.%), weathered of fine-clastic tuff and by process of its epigenesis.

Tables 1 and 2, respectively, show the average chemical and mineralogical composition of the samples studied rocks.

Table 1. The average chemical composition of the basalt and tuff

	Oxide content, wt. %									
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO
Tuff	46.85–	14.55–	0.40–	3.30 –	8.28 –	0.10 –	2.03 –	12.78–	1.67 –	0.02 –
	48.04	15.34	1.05	4.15	8.32	0.15	2.49	14.14	2.00	0.05
Basalt	48.25–	14.66–	7.75 –	2.87 –	1.94 –	2.05 –	1.85 –	9.49–	4.85–	0.02 –
	50.79	15.64	10.35	3.47	2.43	2.64	2.49	9.85	5.15	0.04

Table 2. The average mineralogical composition of the basalt and tuff

Minerals	The content of minerals, vol. %	
	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	1.0 – 3.0
Ore minerals (magnetite, ilmenite)	5.0 – 15.0	8.0 – 10.0
Hlorofeit	–	5.0 – 10.0
Obsidian	20.0 – 80.0	1.0 – 2.0
Analcime	2.0 – 10.0	1.0 – 2.5
Litoklastes of basalt lava (amorphous litogel)	5.0 – 60.0	–
Chlorite	5.0 – 20.0	–
Clay minerals (montmorillonite, saponite, kaolinite)	10.0 – 40.0	–
Quartz	0 – 10.0	–

Regular deviations of contents of some oxides in tuffs from their average values in basalts speak by chemical instability of volcanic products of the basic structure in exogenous conditions. Intensive processes of devitrification and decomposition of volcanic glass, secondary changes of femic minerals and plagioclase led to a significant redistribution (concentration and removal) of some oxides and, above all, easy mobile alkali and alkaline earth metals, silica and iron oxides in different oxidation states. The average content of silica in tuffs is average on 3–4% less than in the basalts that connected with the removal of amorphous silica in postsedimental stage in the process of sedimentation. Differences in the content of silica are also explained by the structural features of tuffs. Fine-clastic tuff, as a rule, contains a minimum amount of silica.

According to the content of titanium, aluminum and total of the iron tuffs are almost indistinguishable from basalts. An essential difference observed for iron oxide (+ III) and Fe (+ II). Tuffs, usually contains more  $\text{Fe}_2\text{O}_3$  than FeO. A decrease and sometimes complete disappearance of iron (+ II) is caused by the easy oxidizability of finely divided of volcanic material.

Significant differences of chemistry of tuffs and basaltes are observed in the content and ratio of oxides of alkali and alkaline earth metals. The average content of MgO in tuffs is on 2–4% higher than in the basalts. The opposite picture is observed with CaO: the number of its in tuffs sharply reduced. Magnesium is part of chlorite and clay minerals of montmorillonite group such as saponite, which are rich in tuffs, during the decomposition of pyroclastic material and secondary mineral formation. Backordered calcium is basically taken out of the rock, forming sometimes disseminated of secondary carbonates, as evidenced by the total value of carbonate tuff, which is 0.5–2%.

It was established that the distribution of alkali metal oxide has the following characteristics: total their content in tuffs is approximately 2 times higher than in the basalts.

Most increased content of  $\text{K}_2\text{O}$ , reverse pattern is observed in sodium content. Such anomalies in the content of alkali metal oxides are the result of secondary alteration of pyroclastic material of basic composition and authigenic mineralization that occurred during sedimentation, diagenesis and epigenesis under the influence of sedimentation basin water, and residual circulating solutions. Widespread high content of potassium connected, apparently, with the sorption of its cations from sea water and residual solutions of authigenic clay minerals. Sodium, the released during the decomposition of plagioclase and volcanic glass and the absence of new phases of sodium containing minerals, like calcium was leached. Most of the iron hydroxide is in the fragments of lava volcanic rock and glass.

The mineralogical composition of the rocks listed in the table 2, is consistent with their chemical composition.

Thus, tuffs are characterized by significantly content of clay minerals, which are absent in the basalt. In addition, the tuffs are characterized by the almost complete absence of plagioclase, which is subject to degradation in the process of epigenesis, and low content of clinopyroxene, which is submitted only with fragments of basalt.

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

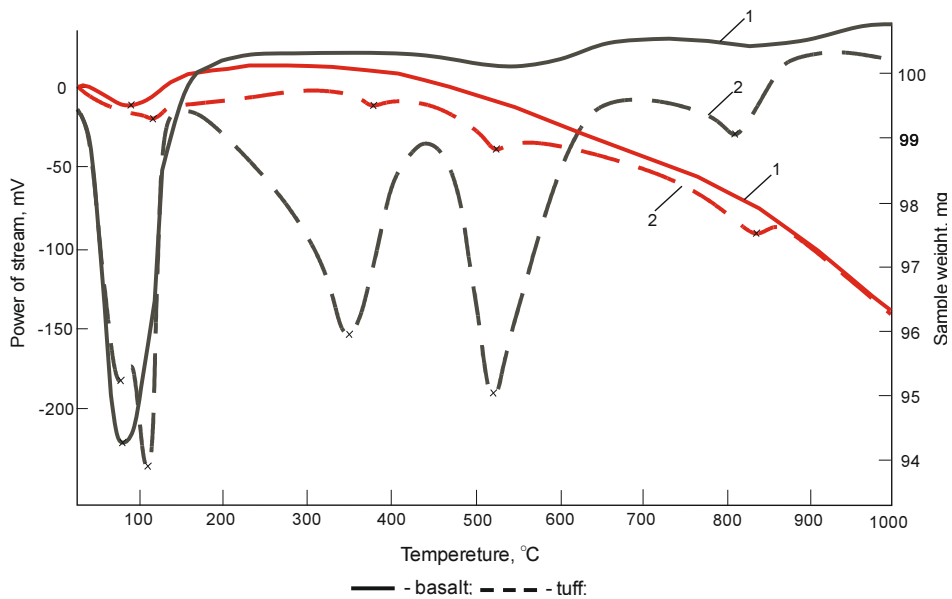


Fig. 1. Differential scanning calorimetric (1) and thermogravimetric (2) curves of rocks samples

The results of thermal analysis give the possibility to establish that heating of basalt accompanied by one endothermic effect with a minimum at 85–90°C, corresponding to the removal of physically bound water from the rock, which is absorbed by the surface tension forces. General weight loss of basalt by heating is 3.0–3.1%.

Heating of tuffs is characterized by five endothermic effects, all of which are accompanied by decrease in the weight of the sample that can be traced on DTG curve. It should be noted the two-stage low-temperature effect with a minimum at 75 and 120 °C, corresponds to the presence in the rocks of minerals of the montmorillonite group. The temperature minimum at 75 °C is associated with the removal of water in the interlayer area. As the packets in the minerals of the montmorillonite group formed been left out for each other like-charged tetrahedral layers, the water in the interlayer area is held by weak van-der-Waals forces, which are easily broken even at low temperature. The minerals of the montmorillonite group have a wide range of isomorphic transformations, which is why the amount of water in the interlayer area depends on the type of cation involved in the substitution. This causes the second minimum at low temperatures on DTG curve.

In the temperature range 300–400 °C removes the chemical and electrostatic bound water from montmorillonite.

Endothermic effect in the temperature interval 500–550 °C indicates the presence in the mineralogical composition of the rocks of significant amount of chlorite.

Endothermic effect corresponding to the decomposition of clay minerals is observed in the temperature range 800–850 °C. Some researchers have thought that in this area is removed chemically bound water, formed by the reactions of the hydroxyl groups between two structural motives such as micaceous and brucite layers [2].

General weight loss by heating of tuff is much higher than that of basalt and is 6.8–7.1%.

The results of multi-site heat-processing of samples of basaltic tuffs and their comparison with basalts revealed that initial melting point of tuff is  $1080 \pm 5$  °C, which is 60–80 °C lower than that of basalts. The above is caused by a high content of low-melting oxides of iron, calcium and alkali metals in tuffs. In addition, structure of tuff is more subtle and loose compared to the dense texture of basalt, as the data of size distribution of the studied rocks, shown in Figure 2 a, b.

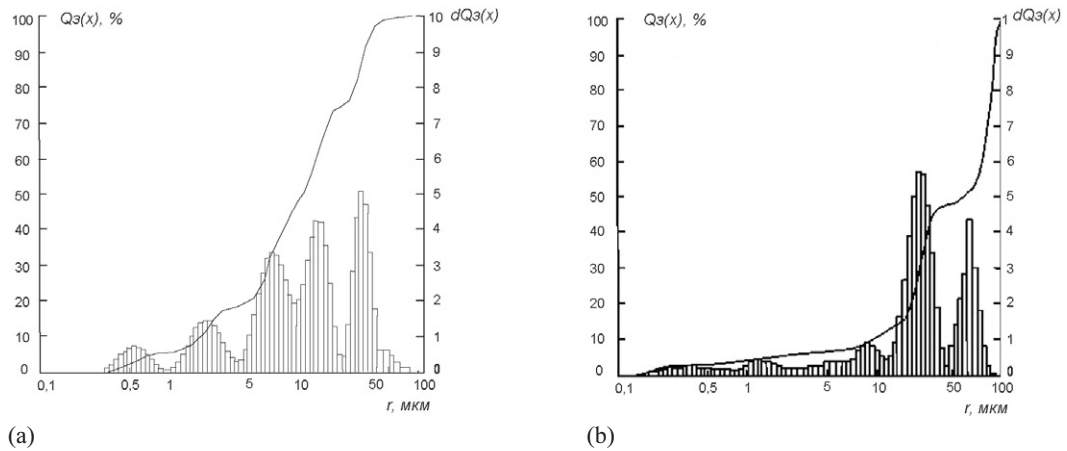


Fig.2. Particle size distribution of basalt (a) and tuff (b)

Data given in Figure 2 shows that the tuff is characterized by large quantities of fines, due to which fine particles of tuff have greater surface area, which results in its ability to intensify the sintering of the masses.

Thus, a comparative study of the tuffs and basalts found that, due to the nature of its formation tuff is several different in chemical and mineralogical composition from the basalts. Due to the greater content of oxides of alkali and alkaline earth metals, as well as the presence of clay minerals that are more finely dispersed and thus more reactive, tuffs are characterized by comparatively low temperature of the melting, which determines its ability to use in ceramic materials as a component intensification of sintering process.

### 5. 3. The study of physical and chemical properties, structure and phase composition of the ceramic tiles

Based on the preliminary findings of the expediency of application of tuff in ceramic masses for tiles of interior wall facing, were designed compositions of masses, in which tuff and basalt were entered in various weight ratios ranging from 1:5 to 5:1, respectively. Physical and chemical properties of samples of tiles of designed ceramic masses were studied.

Dependences of the physical and chemical properties of the samples of tiles on the ratio of "tuff: basalt" are shown in Figure 3.

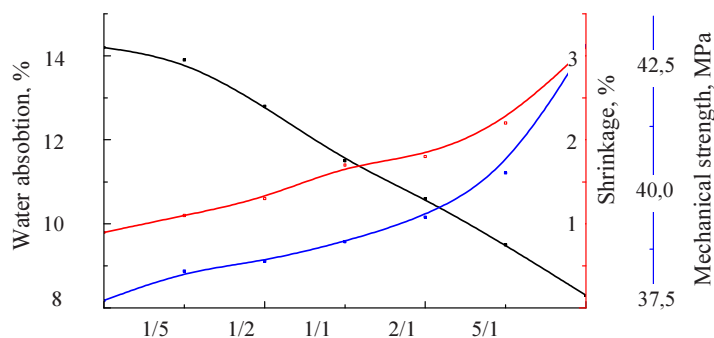


Fig. 3. Dependences of the physical and chemical properties of the samples of tiles on the ratio of "tuff: basalt"

The data shown in Figure 3, revealed that the effective of introduction of tuff to the mass is in the range of ratio "tuff: basalt" from 1:5 to 1:1. In this case, there is a slight increase of mechanical strength of fired tiles, connected both with the additional formation of a liquid phase that fills the pore area (Sanchez, 2006), and the presence of clinopyroxene in the two

rocks, which is diagnosed by X-ray phase analysis. On the formation of an additional amount of liquid phase evidenced by the reduction of water absorption and increased firing shrinkage.

Determination of moisture expansion of ceramic tiles has shown that with the introduction of tuff instead of basalt to the ceramic mass, values of this indicator increase and is 0.035–0.042%. It is known that the moisture expansion depends on the phase and chemical composition of the material. Swelling of ceramics in a wet environment made up of expansion of the crystalline and glassy phases, with the largest influence the liquid phase. To reduce of moisture expansion helps reduce of the content of glassy phase, as well as oxides of alkali metals. Formation of a significant amount of the liquid phase during the heat treatment of tuff, and the high content of oxides of alkali metals in its structure resulting in higher moisture expansion of fired material. Since practical experience is recommended to apply the criterion upper limit of moisture expansion of 0.06%, introduction of the tuff will not result in a reduction of the use of finished products.

In conducting a comparative analysis of the chemical composition of raw materials is noted that tuff is characterized by large amount of iron oxide content than basalt. Since  $\text{Fe}_2\text{O}_3$  refers to oxides of transition d-elements, and causes coloring products in a dark brown color, color characteristics of the samples of ceramic tiles were determined. The results of researches showed that the increasing of quantity of introduced tuff leads to a change in the color samples from creamy orange to the color of coffee with milk. Replacing tuff over mass ratio "tuff: basalt," is 2:1, is impractical because a ceramic potsherd becomes dark that is why using a light-colored glazed which will lead to raised expense engobe and glaze for her disguise.

Studying of samples of ceramic tiles by the method of X-ray diffraction allowed pointing out some features of the phase formation in the samples of tiles based on the tuff containing masses. The phase composition of the samples is quartz, plagioclase, clinopyroxene and hematite. However, the composition of plagioclase changes with an increase in the content of tuff. It was noted the increase of the share of K-feldspar, and, accordingly, decrease of the anorthite component, due to the change in the chemical composition of the ceramic material.

Due to the fact that the pyroxene phase represents a continuous series of solid solutions are prone to isomorphic substitution between one-, two- and trivalent cations, there is change in the composition of clinopyroxene. Composition of clinopyroxene is varied from augite (Ca, Na) (Mg, Fe, Al, Ti)  $(\text{Si, Al})_2\text{O}_6$  and to omphacite (Ca, Na) (Mg, Fe, Al)  $\text{Si}_2\text{O}_6$ , with the introduction of tuff to the composition. This can be explained by differences in the chemical composition of the rocks and, therefore, the raw masses with different contents of tuff and basalt.

Figure 4 shows the electron microscopic image of the surface of the sample of ceramic tiles in mass ratio "tuff: basalt" is 1:1.



Fig.4. Electron microscopic image of the surface of the sample of ceramic tiles

Analysis of the structure shown in Figure 4, shows that the introduction of tuff promotes to formation of dense structure with high degree of crystallinity and uniform distribution of the glassy and crystalline phases.

The rational combination of the above phases not only provides a dense, homogeneous texture and microstructure of the samples, but also causing high strength characteristics, along with the required water absorption, density, porosity and shrinkage.

## 6. Conclusions

Comparative studies of basalts and tuffs have established expediency of using the latter as a component of ceramic masses intensifying of sintering process due to the high content of alkali metal oxides and iron, as well as by its (tuffs) finely dispersed.

The optimal mass relation of “tuff: basalt” is 1:5 to 1:1, which ensures the required physical and chemical properties and dense and homogeneous structure of tiles. It should be noted that this relation is often corresponds to that of the natural occurrence of basalts and their effusions.

Increase the mechanical strength of the tiles with the introduction of tuff contribute to solving the problem of reducing material capacity, as it provides an additional supply of samples for strength, preventing their destruction during production.

It was found that the use of basalt and tuff in ceramic masses for tiles of interior wall facing do not need to selective extraction of basalt, which facilitates large-scale application of these rocks in the ceramics industry.

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