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Peculiar Features of Formation of the Phase Composition of Black Clinker Ceramics

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Abstract

This paper examines the peculiarities of the phase composition of black clinker bricks based on the ceramic masses of Kerameya enterprise (Sumy, Ukraine). The principles of charge choice are given considering the ratio of coloring oxides Fe_2O_3, CoO, MnO_2, Mn_3O_4 and CuO. We found that the phase composition of black clinker bricks after firing at 1100 °C is mainly represented by quartz, microcline, mullite, residues of biotite, as well as hematite and hausmannite as the coloring phases, and also small amounts of cuprite. To produce black ceramic bricks on the basis of clay composition, we need to take 13.5 wt% elements with the ratio of Mn: Fe: Ti: Cu equal to 4.2: 7.7: 0.5: 1.1. Such ceramic mass is already used to produce ceramic clinker bricks with water absorption of 5%, mechanical compressive strength of more than 35 MPa and frost resistance of more than 150 freezing and thawing cycles.

Keywords

ceramic clinker brick, sintering, hausmannite, hematite, ceramic charge, plastic forming, water absorption,
X-ray phase analysis of ceramics

1 Introduction

Ceramic clinker bricks are the extremely popular construction material in the European countries due to their impressive physical and mechanical, as well as aesthetic properties [1, 2]. Recently, special attention has been paid to decorative properties of ceramic bricks. The most common methods of construction products decoration are engobe coatings [3] and volumetric coloring [4].

Engobe coatings allow to significantly diversify the color range of ceramic bricks. However, their production at a typical ceramic enterprise requires the additional equipment, which may appear economically impractical [5].

Therefore, volumetric coloring of ceramic masses is more frequently used. During the process of raw material mixing, careful averaging of the chemical and mineralogical charge compositions is an essential condition for obtaining clinker ceramics [6].

The work [7] demonstrates the outcome of volumetric coloring by adding manganese, iron ore and metal slags, as well as slags of galvanic production to ceramic masses. Low-melting clays are preliminarily whitened with chalk, fireclay or kaolin, and satiated with metal salt solutions with variable valences in order to obtain products of various colors. The use of natural raw materials and soluble salts significantly expands the raw material base, making ceramic products cheaper due to substitution of expensive materials. It also combines the synthesis of pigments and firing of products in one technological operation.

Low-temperature synthesis [8] involves the production of bricks by the method of plastic molding from high-siliceous clays, black sand and scrap glass. Grey-black low-porous and high-porous ceramic is obtained by sintering in conditions of oxygen deficiency. To increase the plasticity of the mixtures, montmorillonite is added to the charge, and low-melting glass additives with melting temperatures of 750 to 800 °C are used to ensure low-temperature sintering. The sintering of the mixtures with iron

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oxide content of about 5 wt% is carried out in reducing conditions at T = 800 °C for 8 h and leads to the formation of glass ceramics comprising quartz, feldspars and glass phase. The formation of anions of $[Fe^{3+}O_4]^{4-}$ and $[Fe^{3+}O_6]^{9-}$ in the composition of the glass phase and feldspars is the main source of black coloring.

Researchers found a possibility of clarification of ceramic bricks on the basis of low-melting colored clays [9]. Remarkable decorative and technical properties of ceramic bricks are achieved by introducing $CaCO_3$ into the ceramic mass using fine-grained sugar production waste.

The study demonstrates [10] that the color of a ceramic shard depends on its mineralogical composition. Mixtures of low-melting clay from the Girininkai deposit (Lithuania) with glauconite rock are fired at 600, 800, 1000, and 1025 °C. When the temperature changes from 600 to 1025 °C and the duration of isothermal holding varies from 0.5 to 4 h, the amount of iron in hematite increases by 5 times, whereas the amount of Fe^{3+} in the crystal lattices of other compounds in 3–4 times less, compared to the natural clay. That is why the ceramic object darkens, acquiring a reddish-brown color.

Karaman et al. [11] assert that the color of the ceramic shard correlates with the product strength.

Thus, the aforesaid data demonstrate that the product volumetric coloring is determined by chemical and mineralogical composition of the ceramic mass. However, the scientific and technical literature shows no systematized results of the correlation between the black color of ceramic shard and the elemental composition of the charge. These data could significantly improve the determination and reproduction of ceramic brick color characteristics.

2 Research objective and methods

The purpose of this work was to obtain volume-colored black clinker brick and to establish a correlation between the elemental composition of ceramic charge, main operational properties, and the phase composition of sintered material.

To achieve this purpose, the following tasks were set: to obtain samples of black-brown clinker ceramics by adding metal oxides of variable valence into the charge; to analyze the correlation between phase composition of sintered brick and elemental composition of ceramic charge; to measure the performance characteristics of resulting products.

Raw materials for the preparation of ceramic masses were crushed to fractions of less than 0.8 mm. Ceramic masses of a given composition were prepared by thorough blending of raw mixtures and then moistened. Normal operating humidity was 21%. Ceramic samples for research were made of plastic masses, dried at temperatures of 70–90 °C and sintered at 1100 °C. Pilot batches of ceramic bricks were also tested with the use of flash-firing in gas environment in conditions of oxygen deficiency at the last stages.

The elemental composition of clays was determined by energy dispersive analysis using SEO-SEM Inspect S50-B scanning electron microscope.

Sintered materials phase composition was determined by X-ray phase analysis on a DRON-3 diffractometer.

Water absorption was determined by the amount of absorbed water in the ceramic sample pores after 1 hour vacuuming; frost resistance was determined by the volume freezing method; ultimate compressive strength was determined by the magnitude of the destructive load per unit of the surface.

Color characteristics were determined by the express method using Color Grab 3.9.2 for Android.

3 Experimental procedure

"Kerameya" enterprise uses light-sintered clay from the Druzhkivka deposit and red clay from the Verkhnya Syrovatka deposit as the principal components for the process of production. The elemental composition of the clays was determined by energy dispersive analysis through comparison of five spectra. Summarized data of the elemental analysis are given in Table 1.

As a general rule, the black color is quite difficult to obtain even using chemically pure pigments [12]. It can be explained by the complex physical and chemical processes in ceramic charge components, which occur due to high-temperature reactions. The charge should be supplemented with the oxides of metals with variable valences,

Table 1 Elemental composition of the experimental clay (wt%)

Clay	O	Al	Si	K	Cu	C	Ti
1 (light)	29.9–45.2	10.0–11.8	23.2–28.7	2.1–3.4	0.2–10.1	12.8–17.4	1.3–2.0
2 (red)	25.7–39.3	2.9–7.5	29.2–47.1	0.6–1.1	2.7–4.1	13.9–17.7	0.2–0.4
Clay	**Fe**	**Ca**	**Mg**	**Na**	**W**	**Cl**	**Total**
1 (light)	0.5–1.5	0–0.4	0–0.1	0–0.3	0–0.3	0–0.4	100
2 (red)	2.9–4.4	0–0.3	0–0.6	–	–	–	100

that jointly form the given phase composition during sintering due to thermal transformations. Such oxides may include Fe_2O_3, CoO, MnO_2, Mn_3O_4, CuO, etc.

To obtain black ceramic bricks, ceramic charges were made on the basis of basic clays with the addition of the indicated oxides (Table 2).

Ceramic charge was carefully averaged. The samples were prepared by plastic forming, dried in laboratory conditions and sintered at 1100 °C. Visual assessment of the color and shade of samples is given in Table 2. The main properties of ceramic bricks samples are demonstrated in Fig. 1.

From the given data, we conclude that samples 1 to 4 have all the necessary properties for clinker bricks: water absorption of 4–5% and mechanical compressive strength more than 30 MPa. The strength index for these samples is 40–48 MPa, which is achieved because of the presence of refractory clay, which support the expansion of the ceramic shard sintering interval. At the same time, sintering is enhanced by metal oxides – iron and manganese. Samples based on fusible clay at the given sintering temperature show signs of melting, because of which the mechanical strength is low.

Rich black color was obtained by adding 5 wt% of oxides CoO: Fe_2O_3: Mn_3O_4 in the ratio of 1: 1: 1 (composition 1). However, practical application of this composition causes difficulties because of the high cost of cobalt oxide.

Table 2 Experimental compositions of colored ceramic masses and color of samples after sintering

The component	1	2	3	4	5	6	7	8
Clay 1	75	75	75	75	25	25	25	25
Clay 2	25	25	25	25	75	75	75	75
Above 100%								
CoO (China)	1.66	–	–	–	–	–	–	–
Fe_2O_3 (Germany)	1.67	3.33	3.33	3.33	3.33	5	5	3.33
Mn_3O_4 (France)	1.67	–	6.67	–	6.67	5	–	–
Mn_3O_4 (South Africa)	–	–	–	6.67	–	–	5	6.67
MnO_2 (China)	–	6.67	–	–	–	–	–	–
Color and shade after firing at 1100 °C, presence of melting	Black with mother-of-pearl	Brown	Brown	Deep black	Brown, signs of melting	Brown, significant melting	Brown, significant melting	Brown, signs of melting

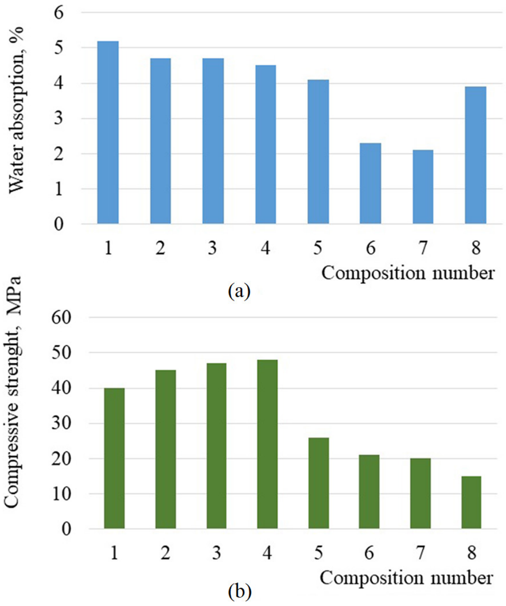

Fig. 1 Main properties of ceramic bricks samples; (a) water absorption; (b) compressive strength

Therefore, the search for an optimal ratio of raw materials and available coloring oxides was continued.

Compositions with prevailing red clay (5–8) are distinct because of their rich chocolate color and clear signs of melting; thus the further variation of coloring components was impractical.

Black color of ceramic samples (composition 4) was obtained due to the introduction of 3.33 wt% of Fe_2O_3 and 6.67 wt% of Mn_3O_4. Among the various Mn-containing pigments, Mn_3O_4 by Brickmax CR (South Africa) turned out to be the most reactive one.

To determine the elemental composition of ceramic mass 4, energy dispersive analysis was performed. This allowed to determine the most optimal ratio of oxides in the ceramic charge for obtaining black-colored clinker bricks (Figs. 2 and 3, Table 3).

The results of X-ray phase analysis of black clinker ceramics after sintering at 1100 °C are shown in Fig. 4, Table 4.

These ceramic masses are already used in the production of ceramic clinker bricks at "Kerameya" enterprise (Sumy, Ukraine). The main operational characteristics of the products are given in Table 5.

The samples of "Kerameya" ceramic clinker brick are shown in Fig. 5.

The properties of products made from designed black ceramic mass comply with DSTU B V.2.7-245:2010 "Ceramic clinker products. Specifications".

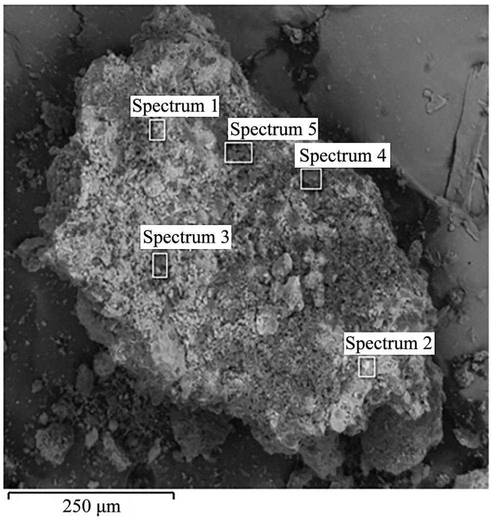

Fig. 2 Initial data for energy dispersive analysis

4 Results and discussion

Obtaining of necessary color characteristics for the volume-colored ceramic bricks is an extremely difficult task since natural clays have variable chemical compositions. Therefore, it is quite difficult to predict the color of the final product after sintering, even using raw materials from one deposit.

For example, for single light clay sample (Table 1) the set of elements significantly differs. The content of Si fluctuates the most – from 23.2 to 28.7 wt%, and Cu – from 0.2 to 10.1 wt%. Cuprum has no effect on the clay color (and therefore light clay does not have the dark gray shade typical for CuO), but the reactions described below occur when it is heated with the participation of oxygen.

$$4Cu + O_2 \xrightarrow{400\text{–}500\ ^\circ C} 2Cu_2O$$
$$(\text{with a lack of oxygen in a gas furnace}, \alpha < 1)$$

$$2Cu + O_2 \xrightarrow{400\text{–}500\ ^\circ C} 2CuO$$
$$(\text{with an excess of oxygen in a gas furnace}, \ \alpha = 2.5)$$

At higher temperatures, cuprite (Cu_2O) featuring red is formed:

$$4CuO \xrightarrow{1026\text{–}1000\ ^\circ C} 2Cu_2O + O_2.$$

Probably this thermal reaction takes part in the formation of the total ceramic brick color.

The chemical composition of the red charge is more consistent and predictable. However, it was impossible to obtain the black clinker on the basis of this clay due to its high fusibility and deformation capacity. Clay contains high amounts of ferrum (2.9–4.4 wt%, Table 1) and low content of aluminum (2.9–7.5 wt%), whereas Al_2O_3 usually increases the fire resistance of the clay.

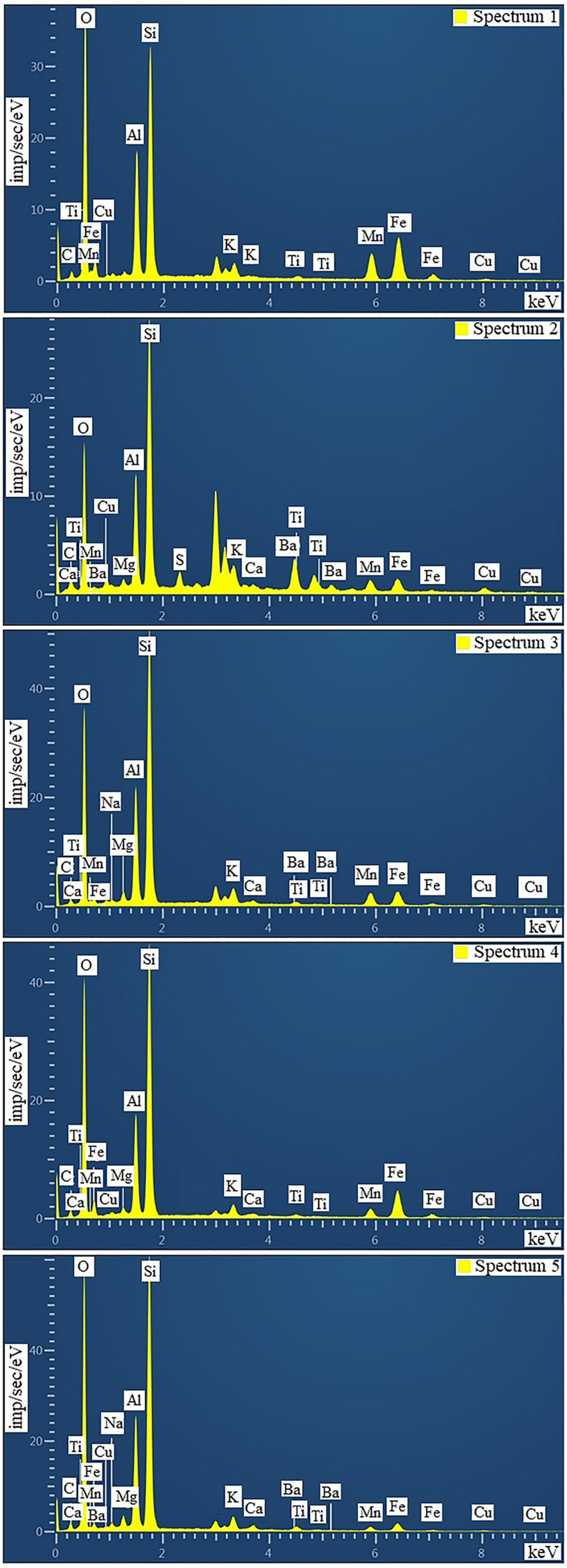

Fig. 3 Results of energy dispersive analysis of the charge for obtaining black ceramic bricks

Table 3 Elemental composition of the charge for obtaining black bricks (wt%)

O	Al	Si	K	Ca	Mg	Na	Ba
42.2	9.1	22.0	1.5	0.4	0.6	0.2	3.2
C	Mn	Fe	Ti	Cu	Other elements		Total
6.2	4.2	7.7	0.5	1.1	1.3		100

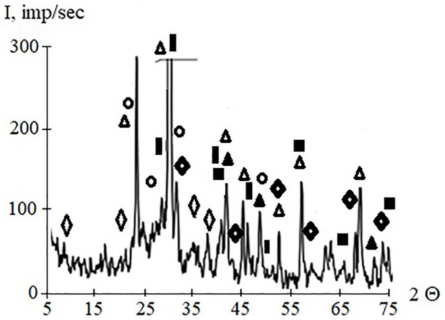

Fig. 4 X-ray diffraction of black clinker brick; Δ–β- quartz; o – microcline; ▌– mullite; ◊ – biotite; ■ – hematite, ♦ – hausmannite, ▲ – cuprite

Table 4 The reference data for decoding X-ray phase analysis

Phase name	The most important diffraction maxima of the phases by which they are identified are d, Å	JCPDS or ICCD files and numbers to the results of XRD
β-quartz	4.25; 3.35; 2.45; 2.29; 1.82; 1.54; 1.37	46-1045
Microcline	4.22; 3.83; 3.70; 3.49; 3.37; 3.26	02-0613
Mullite	3.42; 3.39; 2.69; 2.54; 2.20; 2.12	88-2409
Biotite	9.92; 4.97; 4.47; 3.48; 3.32; 2.99; 2.86; 2.57	025-1388
Hematite	2.69; 2.51; 1.84; 1.69; 1.49	33-0664
Hausmannite	3.09; 2.76; 2.49; 2.04; 1.79; 1.58; 1.54	080-0382
Cuprite	2.46; 2.13; 1.51; 1.29	05-667

Table 5 Main performance indicators of ceramic products

Ceramic charge	Water absorption, %	Compres-sive strength, MPa	Frost resistance, cycles	Color products
Light	5.0	36	155	Grey Hex: #8B847A Grey 50% HSV: (35°, 12%, 55%)
Red	4.8	35	165	Brown: Red Hex: #B06362 Coral Tree HSV: (1°, 44%, 69%)
Black	4.5	48	178	Black Hex: 010409 Black HSV: (218°, 89%, 4%)

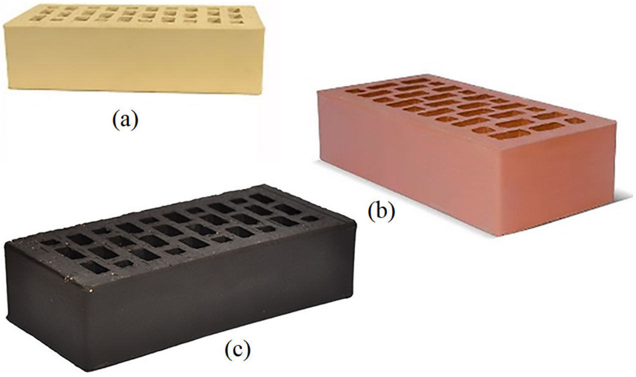

Fig. 5 Ceramic clinker brick "Kerameya"; (a) Pearl; (b) Ruby; (c) Basalt

Red clay is low-melting substance, that melts at the temperature of 1050–1070 °C. Adding of coloring oxides of Fe and Mn (Table 2) to the charge based on low-melting red clay allows reducing the sintering temperature to 1030–1040 °C. Then, as a result of sintering process, the rich brown products color can be obtained, but it is impossible to produce black bricks this way.

For this purpose, we decided to compose the base charges of two clays: fire resistant light clay and low-melting red clay. Adding of the first clay to the mass composition increases the product sintering interval and prevent the deformation, while low-melting red clay ensures sintering of the ceramic material.

Received base charges with a firing temperature of 1100 °C had the predominance of light or red clay; then coloring components were applied to their composition (Table 2). Black samples were obtained on the basis of ceramic charge 4. These samples had all necessary principal properties of clinker ceramics.

The phase composition of black ceramic bricks after sintering (Fig. 4) is represented mainly by quartz SiO_2, microcline $KAlSi_3O_8$, mullite $Al_6Si_2O_{13}$, residues of biotite $K(Mg, Fe)_3[Si_3AlO_{10}][OH, F]_2$, as well as hematite α-Fe_2O_3 and hausmannite Mn_3O_4, which is consistent with the studies' results [13]. Unlike low-temperature porcelain [14], clinker ceramics contains only small amounts of mullite, but its presence indicates the completeness of the sintering process. Cuprite Cu_2O is weakly identified on the X-ray image since its content is at the limit of the device resolution.

The reducing environment formed by the presence of 6.2 wt.% of carbon in charge and its burning during the sintering process contributes to the formation of entire black ceramic bricks.

The Mn: Fe: Ti: Cu ratio is equal to 4.2: 7.7: 0.5: 1.1, and the total content of metallic elements in black charge is 13.5 wt%. The content ratio of elements per 100% of the pure pigment should be as shown in Fig. 6.

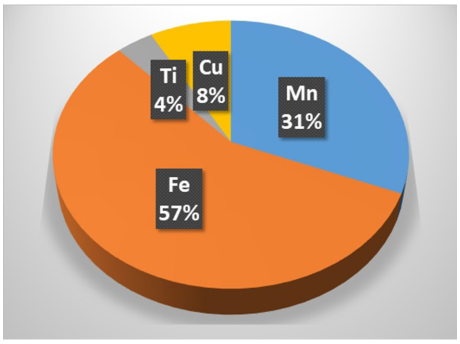

Fig. 6 Ratio of metallic elements in black ceramic pigment

If raw charge contains metal oxides with variable valence, then, in order to obtain the black clinker, it is necessary to recalculate the content of coloring oxides, which should be artificially added, so that the specified ratio is maintained.

Regarding the effect of coloring oxides on the main properties of ceramic bricks, Table 5 demonstrates the increase in the density of the sintered material, which in its turn provides its higher mechanical strength and frost resistance compared to the basic compositions samples.

The obtained results are consistent with the data of following researchers [15], who also showed the positive effect of the ferromanganese component.

5 Conclusions

Volume-colored black ceramic construction materials have been obtained, and the correlation between the elemental composition of the ceramic charge, main operational properties of products and phase composition of sintered material has been established.

Samples of black-brown construction ceramics have been obtained by adding metal oxides of variable valence to the base charge with the predominance of light clay. It was established that the addition of Fe_2O_3 in the amount of 3.33 wt% and Mn_3O_4 in the amount of 6.67 wt% to the charge is effective for the formation of black clinker.

The phase composition of ceramic bricks after sintering is represented mainly by quartz, microcline, mullite, residues of biotite, as well as hematite and hausmannite.

It was established that in order to form the black color of ceramic shards, it is sufficient to take 13.5 wt% of metals with variable valence at the ratio of Mn: Fe: Ti: Cu equal to 4.2: 7.7: 0.5: 1.1.

This ceramic mass is used for the production of ceramic bricks at "Kerameya" enterprise (Sumy, Ukraine). The results of this work are of practical and scientific interest as they substantiate the formation of black clinker ceramics phase composition.

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