Представлені результати комплексних досліджень, спрямованих на розробку рецептурно-технологічних параметрів отримання об'ємно забарвлених клінкерних керамічних матеріалів широкої кольорової гами. Доведена можливість отримання керамічного клінкеру при використанні полімінеральної глинистої сировини за температури 1,000 °C. Показана доцільність заміни у складі мас високовартісних керамічних пігментів техногенними матеріалами, що містять оксиди металів змінної валентності: відходами видобування лужно-земельних сієнітів, збагачення пегматитів та виробництва феротитанових сплавів. Це відкриває перспективи для зниження собівартості виробництва клінкерних керамічних виробів. Досліджено вплив складу сировинних композицій на процеси кольоро- та фазоутворення керамічного клінкеру залежно від характеру пічної атмосфери. Встановлено, що забарвлення клінкерної кераміки в коричневий колір в умовах окислювального випалу обумовлено наявністю фаз гематиту α-Fe_2O_3 та Mn_2O_3. При випалі у відновлювальному середовищі вироби набувають кольору від темно-коричневого до чорного за рахунок утворення магнетиту Fe_3O_4 та гаусманіту Mn_3O_4. Теракотовий колір виробів обумовлений наявністю фаз гематиту та геденбергіту $CaFeSi_2O_6$. Умовою отримання клінкерної кераміки жовтого кольору є обмеження у складі вмісту Fe_2O_3 до 3 мас. % та наявність рутилової фази TiO_2. Проілюстровано вплив на характеристики колірності клінкерної кераміки сумарного вмісту оксидів металів змінної валентності Σ(Fe_2O_3+FeO+MnO+Mn_3O_4). Визначено співвідношення фазоутворюючих оксидів (Fe_2O_3+Mn_2O_3)/(FeO+Mn_3O_4), Fe_2O_3/(Al_2O_3+CaO) і TiO_2/(Al_2O_3+CaO) та встановлені межі їх варіювання, що забезпечують формування кольоротвірних фаз, відповідальних за отримання виробів бажаного кольору в умовах окислювального і відновлювального випалу

Ключові слова: клінкерні керамічні матеріали, полімінеральні глини, техногенні матеріали, інтенсифікатори спікання, кольоротвірні фази

UDC 666.741.1(047); 666.3/7
DOI: 10.15587/1729-4061.2018.150659

STUDYING THE PHYSICOCHEMICAL REGULARITIES IN THE COLOR- AND PHASE FORMATION PROCESSES OF CLINKER CERAMIC MATERIALS

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1. Introduction

There has been an active development of construction industry lately; industrial production of ceramic building materials demonstrates a stable growth. At the same time, there is an annual increase in the segment of clinker ceramic products, which indicates their advantages such as durability, environmental safety, as well as bioresistance, which prevents contamination of structures by fungi, mosses, and algae. In the construction industry, clinker ceramics are used for internal and external decoration of buildings, paving squares and roads, arrangement of waterproofing facilities, pools, collectors, etc. [1, 2]. Large range of sizes, shapes and textures of the clinker brick make it possible to implement any architectural solutions; however, modern designs require expanded range of colors for products [3]. This task can be resolved through the surface or volumetric coloration of clinker ceramics [4]. Comparison of the effectiveness of these methods testifies to unambiguous advantages of volumetric coloration of products under condition of using affordable high-temperature dyes, specifically anthropogenic materials, which containing oxides of variable valence [5, 6]. Determining the ways for targeted color-formation in order to obtain the volumetrically colored ceramic clinker of desired colors and shades is an important scientific and practical task. In this regard, it appears relevant to study patterns in the processes that form color-creating phases during manufacture of clinker ceramics under conditions of oxidative and reductive annealing.

2. Literature review and problem statement

Technological principles for the volumetric coloration of clinker ceramics of brown color are outlined in paper [7]; the results indicate the effectiveness of utilization of granite and basalt rocks screenings as a fluxing and coloring component of masses. However, data on the phase composition of materials are not associated with the process of color-formation in products. The work by authors of [8] addresses the peculiarities of forming a microstructure in the volumetrically colored clinker brick; however, no patterns in the formation of color-creating phases were considered. Studies aimed at understanding the processes and patterns in the phase-formation and coloration of ceramics mostly focus on majolica and pottery products, as well as construction ceramics, whose annealing temperature does not exceed 1,050 °C. Thus, paper [9] reports results of research into phase composition of the light-colored facing brick, whose color-formation processes are defined by the formation of phases with high values for coefficient of reflection: wollastonite, anorthite and pyroxene.

The dependence of color on phase composition of pottery ceramics, annealed in a neutral environment, was established by authors of work [10]. A study into characteristics of coloration in products from the annealing of mixtures of fusible clays and glauconite rocks made it possible to determine that an increase in temperature to 1,000 °C and in the duration of annealing to 4 hours leads to the increased amount of Fe^{3+} ions that are included in the hematite composition. As a result, the products of annealing acquire a red-brown coloration. It is shown that the enhancement of this color can be achieved by introducing finely dispersed glauconite to the mass. Paper [11] also noted the existence of a close connection between the emergence of high-temperature crystalline phases and the color of ceramic bricks, obtained under conditions of oxidative annealing at a temperature of 1,000 °C. It is shown that the high content of iron oxide (5–7 % by weight) provides for a red-brown coloration of products only under condition for the formation of the hematite phase. For the case when iron ions are included in the composition of other phases (mullite, meta kaolinite, facite pyroxene), products acquire yellow, beige, and light-brown colors. These data indicate the possibility for a controlled phase-formation to ensure the required color for ceramic products; however, the data derived do not take into consideration the influence of a furnace atmosphere, while the established patterns in color- and phase-formation relate to the ceramic materials, whose annealing temperature does not exceed 1,000 °C. At the same time, the authors of [12] emphasized that an increase in the annealing temperature of ceramics, obtained based on iron-containing clays leads a substantial change in the shades of red color, which is predetermined by the presence of hematite. It is shown that products that were exposed to oxidative annealing at a temperature of 1,000 °C acquire darker shades, which is associated with an increase in the size of iron oxide particles. However, the impact of the annealing atmosphere on the processes of color- and phase-formation of materials was not addressed. It should be noted that modern furnace units make it possible to purposefully change the atmosphere of annealing, which greatly expands the possibility to control coloration of products. As noted in papers [13, 14], obtaining ceramics of dark colors is possible through the application of reductive annealing when using iron-containing clays. This technology opens up additional avenues to control the process of color-formation via targeted formation of phases that contain metals of variable valence. Thus, paper [15] emphasizes the dependence of color on the content of pyrometamorphic phases (anorthite, galenite, facet pyroxene, hedenbergitis) in the composition of ceramics, annealed in the temperature range of 850–1,050 °C. Authors of the work also examined the features of phase composition of oxidative and reductive annealing. It is known that the formation of ceramic clinker occurs at higher temperatures (1,000–1,200 °C), which significantly changes the mechanisms of phase-formation and makes it impossible to apply the patterns, established by the authors, in the color- and phase-formation of ancient ceramics.

Thus, there is no doubt that there is a close relationship between color and phase composition of ceramic products, which to a large extent depends on the duration and temperature of annealing, as well as the composition of a furnace atmosphere). Despite the practical relevance of results, reported in most studies, related to obtaining volumetrically dyed clinker ceramic products, the physical-chemical regularities of the color-formation process have not been addressed in detail. The lack of certainty concerning the interrelation between the formulation of raw material compositions, the chemical and phase composition of clinker ceramics, and the coloration of products, necessitates the present research.

3. The aim and objectives of the study

The aim of this research is to define the influence of composition of the ceramic clinker on the characteristics of coloration, and to develop masses in order to obtain clinker products in a wide range of colors based on the polymineral clay raw material.

To accomplish the aim, the following tasks have been set:

– to develop the masses that would ensure obtaining ceramic products with a high degree of sintering and in a wide color range;

– to define the characteristics of coloration for the obtained samples and to establish dependences based on the composition of clinker ceramics and the annealing conditions;

– to explore the phase composition of clinker ceramics, annealed under conditions of oxidative and reductive annealing;

– to identify the regularities in the formation of color-creating phases that ensure the obtaining of clinker products of different colors.

4. Materials for the development of ceramic masses and methods to study phase composition and properties of clinker products

The basic raw materials used in the study included the polymineral not-sintered clay from the Luzhkivske deposit and the kaolinite-hydromica clay from the Artemivsk deposit.

The additives applied for the intensification of sintering and phase-formation included the waste from pegmatite enrichment (TOV "Georesurs", Ukraine), the waste from ferrotitanium production (NVP TOV "Mateko") and the screenings formed during extraction of alkaline earth syenites from Kalchik field (Donetsk oblast). The coloring component used to obtain clinker products of brown color was the manganese ore from PAT "Ordzhonikidze GZK". The composition of raw materials based on the results of the performed chemical analysis is given in Table 1.

Samples were prepared by plastic moulding from masses with a moisture of 20 %. After drying to a residual moisture content of 2 %, the annealing was performed at a temperature of 1,000 °C under conditions of oxidative (CO/CO_2~2) and reductive (CO/CO_2~15) environment with an-hour-long aging at maximal temperature. The total duration of annealing was 10 hours.

Phase composition of the samples was determined at the diffractometer DRON-3M. Properties of clinker ceramics were determined according to standard procedures in accordance with DSTU B V.2.7-245:2010. Color characteristics were determined using the device *Chroma meter* CR-410 in line with the system $L^*a^*b^*$. Random measurement errors do not exceed 5 %.

5. Research results

5. 1. Development of raw material compositions

When developing clinker masses, we applied the simplex plan of the experiment according to a special cubic model. Factors X_i (i=1...3) were based on content of raw materials that are included in the masses' composition: clay Artemivsk (CA) – 50÷65 %, ferrotitanium production waste (FTW) from NPV TOV "Mateko" – 10÷25 % and pegmatite enrichment waste from (PEW) from TOV "Georesurs" – 25÷40 %. In this case, the content of not-sintered polymineral clay from Luzhkivske deposit was 40 % by weight (with a ratio of green to brown clays as 1:2).

An analysis of sample sintering characteristics at a temperature of 1,000 °C revealed that the use of raw material compositions within the examined factor space ensures the obtaining of light-colored ceramic brick with water absorption W= =2.8–4.8 % and strength to compression σ_{compr}= 50–70 MPa.

Color characteristics of ceramic samples are given in Table 2.

Table 1

Chemical composition of raw materials based on the results of chemical analysis

Raw materials	Content of oxides based on chemical analysis, % by weight									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	MnO_2	Na_2O	K_2O	I.L.
Clay, Luzhkivska	62.52	13.41	6.16	0.88	1.32	0.69	–	0.81	1.49	6.10
Clay, Artemivska	72.70	19.30	1.12	1.28	0.6	–	–	0.82	1.95	5.00
Ferrotitanium production waste	–	78.70	1.30	20.0	–	–	–	–	–	–
Pegmatite enrichment waste	74.55	14.29	0.74	0.08	0.45	0.25	–	4.48	4.41	0.75
Screenings of syenites	68.80	15.10	3.00	–	2.33	1.77	–	4.40	3.76	0.72
Manganese ore	23.16	2.00	–	–	–	–	74.84	–	–	–

Table 2

Color characteristics of the clinker brick samples

Color characteristics	Sample designation according to the simplex-plan						
	1	2	3	12	13	23	123
Oxidative annealing							
Color							
L, %	78.05	75.34	77.67	75.44	77.83	73.01	84.02
*a**	16.74	21.36	18.81	20.30	19.68	27.11	17.76
*b**	45.71	32.05	43.12	30.08	40.30	44.03	35.07
Reductive annealing							
Color							
L, %	74.90	73.05	70.65	72.11	77.11	70.95	80.02
*a**	7.30	7.72	6.81	5.30	7.05	5.33	4.24
*b**	43.22	40.12	45.03	55.26	50.32	62.15	48.56

5. 2. Determining and analysis of color characteristics of samples

Study into the color characteristics of clinker bricks, annealed in the oxidative environment has shown that they have quite high indicators of lightness (L=73–84 %), which decrease to the level of 70–80 % under conditions of reductive annealing. High positive values of coordinate b^* (compared to coordinate a^*) indicate the dominance of the yellow component of color. For the samples obtained at reductive annealing, the value of coordinate b^* increase that affects the enhancement of the yellow component and the color saturation of samples in general. An analysis of the influence of formulation of raw material compositions on the color characteristics of samples $L^*a^*b^*$ has made it possible to determine the compositions of masses, which ensure obtaining clinker bricks of various shades of peach and yellow colors (Table 2, Fig. 1). Our study had shown a possibility to obtain a light-colored ceramic clinker of different colors within the range of peach-pink and beige-mustard colors under conditions of oxidative and reductive annealing, respectively.

In order to obtain ceramic clinker of brown color, the composition of masses based on the polymineral Luzhkivske clay was supplemented with manganese ore in the amount of 3–5 % by weight (exceeding 100 %). The base raw material mixture used contained green and gray-brown Luzhkivske clay (in the ratio 2:1) and the waste from alkaline earth syenites from Kalchik deposit, which act as the sintering intensifiers. Upon annealing at a temperature of 1,000 °C, we obtained ceramic materials in different shades of brown color, which, based on the sintering level, meet requirements for the clinker brick (W=4.5–5.5 %; σ_{compr}=40–43 MPa). A visual comparison of the samples showed that under conditions of reductive environment the products acquire dark brown and black colors.

Based on a comprehensive analysis of operational properties and color characteristics of the obtained samples, we recommend the following formulations of raw material compositions (Table 3) for the production of clinker ceramic products of the most sought-after colors [3].

5. 3. Determining the phase composition of clinker ceramics

We defined the qualitative phase composition in the products of annealing (Fig. 2) for the obtained samples of ceramics, annealed at a temperature of 1,000 °C under conditions of weakly-oxidative and reductive furnace atmosphere using the method of X-ray phase analysis (XPA). The following color-creating phases were identified in the phase composition of sample of the brown clinker, annealed in an oxidative environment: hematite α-Fe_2O_3 (d=0.269; 0.251; 0.243; 0.220; 0.169; 0.148 nm) and Mn_2O_3 (d=0.272; 0.166; 0.1846; 0.384 nm). The presence of these phases predetermines the rich red-brown coloration of products. The annealing of samples in the reductive environment is accompanied by the emergence of gaussmanite Mn_3O_4 (d=0.492; 0.309; 0.277; 0.249; 0.162; 0.154 nm), which, together with Mn_2O_3, gives products cold shades of dark brown color.

We identified the phases of hematite α-Fe_2O_3 (d=0.269; 0.251; 0.243; 0.220; 0.169; 0.148 nm) and hedenbergitis $CaFeSi_2O_6$ (d=0.294; 0.298; 0.323 nm), which belongs to the group of pyroxenes, in the samples of terracotta clinker, annealed in the oxidative environment. Formation of the latter becomes possible owing to the presence of alkaline earth syenites in the composition of the ceramic mass. But in the composition of samples, annealed in oxidative environments, due to the incomplete reduction of Fe_2O_3 to FeO, there appears magnetite Fe_3O_4 (d=1.48; 2.52; 2.95 nm). The presence of these phases in the disperse state gives the products a darker color that is visually perceived as light brown. In the absence of magnetite, products acquire the classic terracotta color with a red tint.

The phase composition of yellow clinker is represented mainly by mullite $Al_6Si_2O_{13}$ (d=0.54; 0.3437; 0.2699; 0.2554; 0.243; 0.2296; 0.220 nm), quartz SiO_2 (d=0.426; 0.3347; 0.2458; 0.2282; 0.2238; 0.2128; 0.198 nm) and rutile TiO_2 (d=0.3239; 0.2458; 0.2282 nm). In this case, the color-creating phase is precisely rutile. But the composition of the cream-colored clinker has no compounds of metals with variable valence that give ceramics their saturated colors. This fact indicates that a small amount of Fe_2O_3, which arrives along with the raw material (Artemivsk clay and the waste of pegmatite enrichment) is in the melt, whose presence is indicated by the large-size halo at the samples' radiographs.

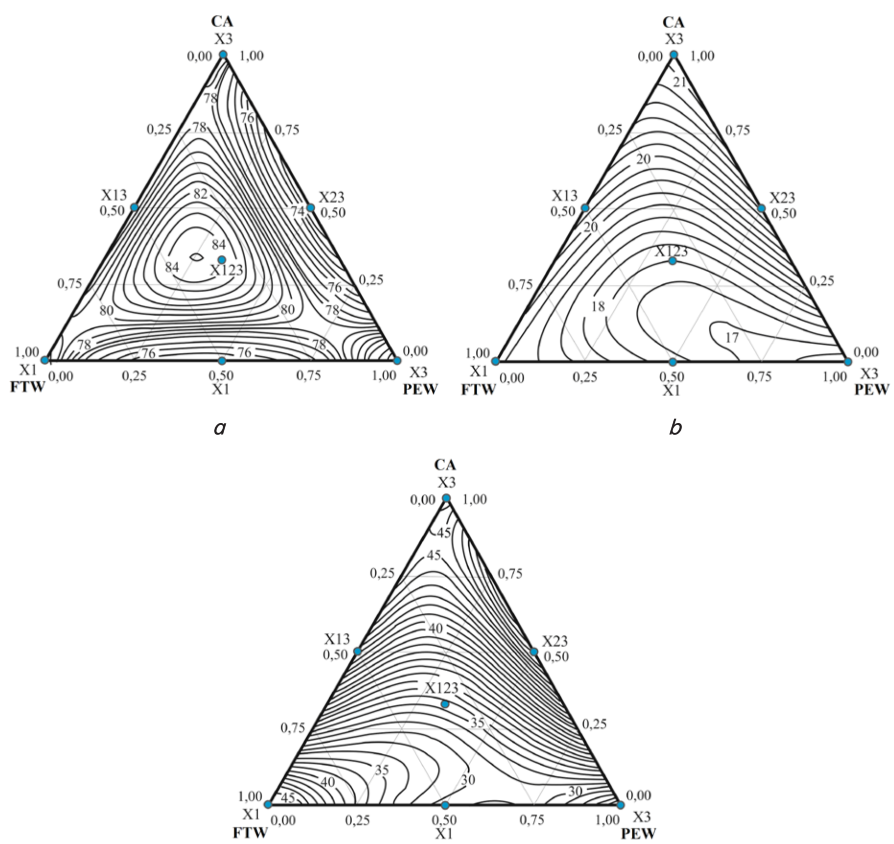

Fig. 1. Dependences of color characteristics of the clinker ceramic materials, obtained under conditions of oxidative annealing, on the composition of masses: *a* — lightness L^*; *b* — coordinate a^*; *c* — coordinate b^*

Table 3

Composition of mixtures for obtaining colored clinker products

Raw materials	Content of components for obtaining products of the predefined color, % by weight			
	creamy	yellow	terracotta	brown
Clay, Luzhkivske, green	–	13.4	55.0	55.0
Clay, Luzhkivske, gray-brown	–	26.6	27.5	27.5
Clay, Artemivsk	85.0	38.0	–	–
Waste of Lozuvate pegmatite enrichment from TOV «Georesurs»	15.0	15.0	–	–
Waste of ferrotitanium production from NPV TOV «Mateko»	–	6.0	–	–
Screenings from Kalchik granosyenites from PrAT «Kalchiksky karyer»	–	–	17.5	14.5
Manganese ore from Ordzhonikidze GZK	–	–	–	3.0

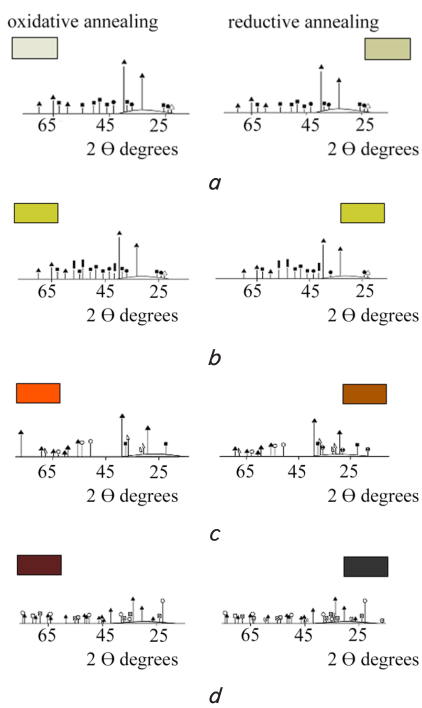

Fig. 2. Bar radiographs of ceramic clinker samples of different color, annealed in the oxidative and reductive environment: *a* – creamy; *b* – yellow; *c* – red; *d* – brown. ▲ – quartz; ● – albite; Δ – microcline; ⊾ – hedenbergite; ■ – mullite; ▌ – rutile; ○ – hematite; ❸ – magnetite; ⊡ – gaussmanite; ⊠– Mn_2O_3

It should be noted that the compositions of the lightly-colored samples of clinker (creamy and yellow) contain residues of feldspars: albite $NaAlSi_2O_6$ (d=0.403; 0.378; 0.368; 0.319 nm) and microcline $KAlSi_2O_6$ (d=0.422; 0.380; 0.329; 0.216; 0.180 nm), which did not dissolve in the melt during annealing.

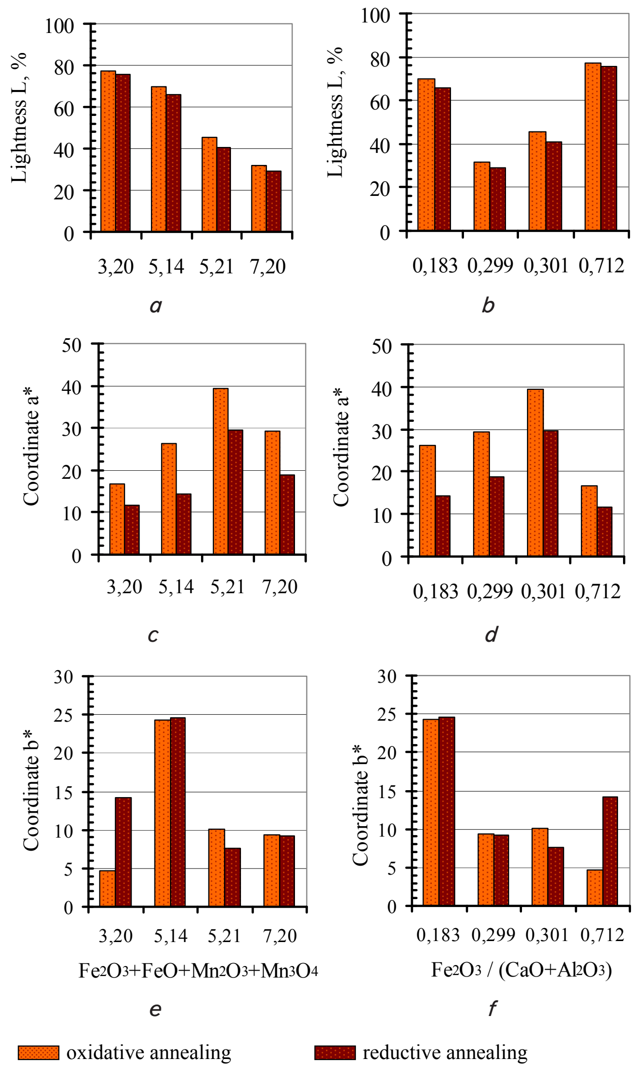

Fig. 3. Dependence of color characteristics of ceramic clinker, annealed at a temperature of 1,000 °C on the content of $\Sigma(Fe_2O_3+FeO+Mn_2O_3+Mn_3O_4)$ and the ratio of $Fe_2O_3/(Al_2O_3+CaO)$: *a* – lightness *L*, *b* – coordinate *a**, *c* – coordinate *b**

5. 4. Determining patterns in color-formation in correlation with the chemical and phase composition of clinker ceramics

The next phase of our study implies defining patterns in the color-formation by clinker ceramics by determining the effect of the chemical and phase composition on colorimetric characteristics of materials according to the model $L^*a^*b^*$, which is one of the most informative ones at present [16]. The study has shown that for the case of clinker ceramic products, the most sensitive parameter to the atmosphere of annealing is the coordinate a^*, which characterizes the red component of ceramics color. And lightness L^* almost do not depend on the composition of a furnace atmosphere. As regards the coordinates b^*, the impact of the atmosphere of annealing is notable only for the case of lightly-colored products.

Obviously, lightness L^* is a function of the total content of coloring oxides $\Sigma(Fe_2O_3+FeO+MnO+Mn_3O_4)$: an increase in their amount in ceramic clinker leads to a decrease in the value for lightness indicator L^* (Fig. 3).

In order to study the dependence "composition–color" of clinker products taking into consideration the chemical composition of raw materials and the content in technological mixtures (Tables 1, 3), we calculated chemical composition of the annealing products of ceramic masses. We also determined the total content of oxides of metals with a variable valence $\Sigma(Fe_2O_3+FeO+MnO+Mn_3O_4)$ and the ratio of phase-forming oxides, which reflect the peculiarities of color-formation in a ceramic clinker, in particular: $(Fe_2O_3+Mn_2O_3)/(FeO+Mn_3O_4)$, which takes into consideration the oxidation degree of these oxides, and $TiO_2/(Al_2O_3+CaO)$ and $Fe_2O_3/(Al_2O_3+CaO)$, which reflect the content of oxides, in the composition of color-creating and uncolored phases. The specified ratios were applied to evaluate the dependence of color characteristics of clinker ceramics on the composition of an annealing atmosphere. It was established that the color-formation of the dark-colored ceramic clinker reflects more accurately the ratio $(Fe_2O_3+Mn_2O_3)/(FeO+Mn_3O_4)$. In this case, in order to analyze the color-formation of lightly-colored clinker products, depending on the available coloring oxide, it is appropriate to employ correlations $Fe_2O_3/(Al_2O_3+CaO)$ or $TiO_2/(Al_2O_3+CaO)$.

As the above data show, the value for lightness L^* of products from oxidative and reductive annealing differs insignificantly (Fig. 3, *a*). With an increase in $\Sigma(Fe_2O_3+FeO+Mn_2O_3+Mn_3O_4)$ there is the strengthening of the red component in the color of products from oxidative annealing (Fig. 3, *b*), which is explained by the dependence of a given indicator on the content of oxides of metals with variable valence. In this case, for products exposed to regenerative annealing such a tendency is not observed due to incompleteness of the processes to reduce iron oxides $Fe_2O_3 \rightarrow FeO$ and manganese $Mn_2O_3 \rightarrow Mn_3O_4$. Coordinate b^* (Fig. 3, *b*) has the positive values that indicates the presence of the yellow component in the products' color. The influence of reductive atmosphere is more notable for lightly-colored products, for which the sum of coloring oxides is 3.20 % by weight.

An analysis of dependences of color characteristics of the lightly-colored samples (Fig. 4) revealed that with an increase in ratio $Fe_2O_3/(Al_2O_3+CaO)$ there is an increase in the values for coordinate a^*, an increase in the share of the red component of products' color, to a larger extent for products exposed to oxidative annealing (Fig. 3, *b*).

The maximum values for coordinate b^* are observed at a ratio of $Fe_2O_3/(Al_2O_3+CaO)=0.183$, regardless of the conditions for annealing. This indicates that the condition for obtaining the yellow clinker products is not only limiting $Fe_2O_3 \leq 3$ % by weight, but maintaining the ratio of phase-forming oxides $Fe_2O_3/(Al_2O_3+CaO)$ at the level ~0.18. A decrease in the value for this ratio will ensure obtaining products of light shades (straw, vanilla, etc.). With an increase in the value for this ratio to 0.712 the enhancement of the yellow component of color is observed only under conditions of reductive annealing. Thus, obtaining the desired shades for lightly-colored clinker products is possible by changing the ratio of $Fe_2O_3/(Al_2O_3+CaO)$ within 0.1–0.2 and adjusting the atmosphere of annealing, which affects the red component of color.

It is known that the rutile modification of titanium dioxide that exists at temperatures above 1,000 °C colors ceramic products in yellow color. TiO_2 is conventionally used for obtaining the yellow clinker products. As evidenced by results reported in papers [5, 11], the presence of the elevated content of CaO and Al_2O_3 oxides leads to the formation of phases, which lighten the color of ceramics. Thus, to obtain clinker ceramics with a desired shade of yellow color, one should take into consideration the ratio of oxides $TiO_2/(Al_2O_3+CaO)$. It was established that an increase in this ratio to ~0.11 leads to substantial growth in the values for coordinate b^*. Satisfying a given condition would make it possible to obtain the ceramic clinker of saturated yellow color regardless of the composition of the furnace atmosphere.

6. Discussion of results of studying patterns in the processes of color- and phase-formation of clinker ceramics

An analysis and generalization of research results allowed us to establish a reasonable connection between the color characteristics of clinker products, their phase and chemical composition. The merit of this research is in obtaining data about the transformation of the phase composition of ceramic clinker depending on annealing conditions, in particular the character of the furnace atmosphere. A change in the color of ceramics based on the iron-containing raw materials is predetermined by the oxidation-reducing processes associated with a change in the degree of iron oxidation as a transient metal with the unfilled *3d*-layer of electrons. The paper shows the way in which a change in the color characteristics of the ceramic clinker occurs, depending on the direction of processes that transfer oxygen, which define the transformation of oxide forms of iron. The most significant degrees of oxidation for the processes of color-formation in clinker ceramics are 0, +2, +3, which are characteristic of the existence of iron in the form of hematite, wustite, or magnetite, and give products the red, brown, and black coloring, respectively. It is shown that the presence of one or another oxide form of iron is predetermined not only by excess or lack of oxygen in the furnace environment, but also by the content of various oxide forms of iron, as well as their ratios to other phase-forming oxides, including the oxides of transient elements that define the conditions for forming more complex iron-containing compounds, specifically hedenbergitis. The regularities established could open new opportunities for the controlled formation of color-creating phases when annealing the clinker ceramics.

Based on the results of this research, we recommended the compositions for raw material mixtures (Table 3), which ensure the desired shades of four basic colors for clinker products (creamy, yellow, terracotta, and brown). The recommendations provided would be useful for modern production of clinker ceramic materials, including those that operate on low-grade polymineral clays. Application of large-tonnage industrial waste in the composition of masses could significantly reduce the cost of ceramic clinker production. Specifically, an economic effect when using the screenings of granosyenites amounts to 0.22 UAH/standard unit, while the replacement of titanium dioxin with the waste from ferrotitanium production will make it possible to reduce the cost of the conditional unit of products by 2.2 times. The present work does not take into consideration a possibility to use other oxides of metals with variable valence (Cr, Co, Cu) as colorants. Therefore, in the future, it might be appropriate to study regularities in the color- and phase-formation of the ceramic clinker, colored by the compounds of these metals, as well as to search for affordable raw materials to implement our developments under industrial conditions.

7. Conclusions

1. By applying polymineral not-sintered clays and the anthropogenic raw materials, we have developed formulations for raw material compositions, which ensure the obtaining of clinker ceramic products at a temperature of 1,000 °C, and are characterized by a wide color range, as well as a set of high operational properties (water absorption W=4.5–5.5 % compressive strength σ_{compr}=40–43 MPa). Replacement of costly pigments with the anthropogenic materials will make it possible to reduce the cost of the volumetrically colored clinker ceramics by 2.2 times.

2. The phase composition of clinker ceramics, obtained under conditions of oxidative and reductive annealing, has been investigated. It was established that the main color-creating phases of brown ceramic clinker is hematite α-Fe_2O_3 and Mn_2O_3. A shade of color depends on the atmosphere of annealing, which is predetermined by the progress of processes that reduce oxides of iron and manganese and the formation of magnetite Fe_3O_4 and gaussmanite Mn_3O_4. A terracotta color of products is due to the presence of highly-disperse hematite α-Fe_2O_3 and hedenbergite $CaFeSi_2O_6$. The main color-creating phase of yellow clinker products is rutile. The phase composition of the lightly-colored clinker is represented by mullite, quartz, and the residues of feldspar minerals that do not produce any coloring action.

3. In order to study the physical-chemical patterns in the color- and phase-formation of clinker ceramics, we identified the color characteristics of samples. That has made it possible to define the dependences of color components that determine certain shades on composition of the ceramic clinker and the atmosphere of annealing. The reduction annealing changes the shade of products' color to a colder one, which is predetermined by the reduction of oxides of iron $Fe_2O_3 \rightarrow FeO$ and manganese $Mn_2O_3 \rightarrow Mn_3O_4$. A shade of yellow color significantly depends on the presence in a material of oxides with variable valence and the degree of their reduction at product annealing. An increase in the ratio $TiO_2/(Al_2O_3+CaO)$ to ~0.11 enables obtaining the ceramic clinker of saturated yellow mustard color. Obtaining the desired shades of lightly-colored clinker products is possible by changing the ratio $Fe_2O_3/(Al_2O_3+CaO)$ within 0.1–0.2 and by adjusting a composition of the annealing atmosphere.

4. Formation of the hematite phase depends on the content of iron oxide: provided the content is up to 3 % by weight, Fe_2O_3 is in the melt; when increasing the content of iron oxide, hematite is crystallized in the ceramic clinker. In this case, in the presence of a reductive atmosphere at annealing, there occurs the transformation α-$Fe_2O_3 \rightarrow Fe_3O_4$. The reduction of manganese oxide Mn_2O_3 to gaussmanite Mn_3O_4. proceeds in the similar manner. The formation of complex iron compounds, specifically hedenbergite ($CaFeSi_2O_6$), which change the coloring of ceramic clinker, is possible in the presence of a significant amount of oxide CaO. Hedenbergitis forms at annealing the ceramic masses based on polymineral clays with an elevated content of iron oxides under condition of using the calcium-containing raw materials. In order to obtain the lightly-colored ceramic clinker, the amount of coloring oxides in the composition of masses must be as low as possible (not exceeding 3 % by weight), which would prevent the formation of color-creating compounds. An essential condition for obtaining products of yellow color is the introduction of titanium-containing materials in order to form rutile.

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