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RELATIONSHIP OF PROPERTIES, PHASE COMPOSITION, AND MICROSTRUCTURE OF CLINKER BRICK

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Clinker brick was obtained on the basis of polymineral raw materials, including low-melting and refractory clays, loams, and granitoid screenings in the plastic method of manufacturing. The interrelation of the physical and chemical properties of products was determined as a function of the mass content of the components and the oxide composition of the charge, and the optimal temperature/time regimes of firing were determined — 1150 ± 5°C with exposure of 4 h at an optimal temperature. The data obtained on the oxide and mineral composition make it possible to predict the composition of the charge for producing clinker brick, the heat-treatment regimes, and the properties of the products.

Key words: clinker bricks, frost resistance, sintering, glass phase, mechanical strength, water absorption, oxide composition.

The demand for clinker bricks in Belarus has increased more than three-fold In the last few years. This type of product is not produced at home-grown enterprises.

The objective of this research is to synthesize the compositions of ceramic bodies and determine the process parameters for the production of clinker bricks based on regionally available polymineral raw materials.

The choice of the sources of raw materials and the selection of the charge composition of clay bodies for the production of clinker bricks is a rather complex material science task, and it is based on the study of the chemical and mineralogical composition and sieve tests and sedimentation analysis of the components of the raw mixture [1 – 4]. Such studies are used not only to select the composition of the charge, but also to obtain information on drying and firing regimes that secure required product quality. This task is especially real for Belarus, which does not have high-quality clay raw materials — refractory and high-melting clays.

In this connection we took into account the information accumulated from other researchers on the body compositions required for producing clinker ceramic based on the characteristics of the initial raw materials [4 – 6].

In the normative/technical documentation of Belarus (STB 1787–2007), clinker bricks are divided into two classes — A and B.

Class-A solid clinker bricks are used for masonry and wall cladding in hydraulic structures as well as for the construction of sidewalks and perimeter walks.

Class-B clinker brick can be solid or hollow, and it is used for masonry and wall cladding of buildings and structures.

To develop the compositions for the bodies of clinker bricks we used a multicomponent system of raw materials, including several clay materials of various mineral and granulometric composition [7]. Granitoid screenings of fraction < 1 mm, formed at the RUPP Granit (Belarus) as the waste from stone-crushing of granites, were the fluxing component, acting as a leaner at the first stages of firing.

The high-melting clay from the Gorodnoe deposit in the Brest region, loam from the Fanipol' deposit in the Minsk region of Belarus, as well as added clay imported from Russia (Bolshaya Karpovka deposit in the Kursk region) were used as clay raw materials for the fabrication of clinker products.

The chemical composition of the starting components used for research is given in Table 1.

The compositions of the experimental bodies for obtaining clinker ceramics included (%[3]): clay from the Gorodnoe deposit — 5 – 15; loam from the Fanipol' deposit — 35 – 55; granitoid screenings of the fraction indicated above — 20 – 40. BK-0-make clay was introduced in the constant

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[3] Hereinafter in the text, unless otherwise stated, the weight content, %, is indicated.

TABLE 1. Chemical Composition of the Initial Raw Materials Used for the Production of Clinker Bricks

Raw materials	Weight content of oxides, %								LOI
	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	MgO	CaO	TiO_2	
Gorodnoe clay	62.12 – 68.23	15.56 – 18.31	4.76 – 6.23	0.10 – 0.23	1.00 – 1.15	0.74 – 0.98	0.50 – 1.44	0.72 – 1.18	7.03 – 9.72
Bol'shaya Karpovka BK-0 clay deposit	65.50 – 71.45	16.04 – 19.61	3.20 – 5.02	0.04 – 0.15	0.27 – 0.51	0.06 – 0.11	0.12 – 0.16	1.43 – 1.86	6.27 – 8.20
Fanipol' loam	75.94 – 81.42	8.94 – 10.25	2.01 – 2.85	0.66 – 0.82	1.41 – 1.64	1.20 – 1.47	1.28 – 1.58	0.50 – 0.71	2.95 – 4.37
Granitoid screenings	57.20 – 65.13	11.75 – 17.31	7.16 – 9.48	3.28 – 5.16	2.10 – 3.18	3.10 – 3.73	3.98 – 5.12	0.60 – 1.32	0.10 – 0.30

amounts of 10 – 20%. The components were varied in steps of 5%.

All of the raw materials used in this work were pre-dried to moisture content ≤ 1% and then ground to passage through a No. 1 sieve (51 holes/cm^2). The resulting mixture was mixed, moistened to 17 – 19%, and left to stand for at least 7 days; then, after thorough kneading, the samples were molded for the investigations. They were dried at temperature 105 – 110°C for 6 h. Firing of the samples was performed in the temperature range (1050 – 1150) ± 5°C with steps of 25°C and 4 soaking at the maximum firing temperatures. The total firing duration was 36 h.

The fired samples had a uniform color ranging from brownish-orange to chocolate-brown. There were no defects in the form of deformations, notches, or delaminations, including lime inclusions.

The physicochemical properties of the samples were assessed using standard methods of ceramic production. Appearance indicators and the presence of lime inclusions were investigated according to STB 1160–99 and water absorption, density, and frost resistance by the volumetric method of freezing samples — according to GOST 7025–91, the ultimate strength in compression and bending — according to GOST 8462–85, and, abrasion — on an LKI-2 setup, according to GOST 13087–81. The specific effective activity of native radionuclides was determined in accordance with GOST 30108–94 using an RUG-92-2 radiometer.

Thermal analysis of the materials and raw mixtures was performed to within ± 0.1°C, using a DSC 404 F3 Pegasus calorimeter from Netzsch (Germany), in the temperature range 25 – 1200°C and a neutral environment.

The phase composition of the samples was studied using a D8 Advance x-ray unit (Brucker, Germany); radiation — CuK_α; detector — scintillation counter. The Joint Committee on Powder Diffraction Standards international card index and the Diffract Plus software (Bruker) were used to identify the crystalline phases.

The cleavage microstructure of the ceramic samples was investigated using scanning the microscopes TESCAN MIRA 3 (Japan) and JSM-5610 LV with an EDX JED-2201 JEOL chemical analysis system (Japan).

The results of the determination of the physicochemical properties of fired samples of clinker ceramics are presented in Table 2.

As follows from Table 2 the physicochemical properties of the samples fired at 1050 ± 5°C do not meet the specifications for clinker bricks. The values of the water absorption of samples fired at 1100 ± 5 and 1150 ± 5°C are equal to 3.5 – 8.2 and 3.2 – 4.7%, respectively; this indicator naturally decreases with increasing heat-treatment temperature.

The mechanical strength of the samples at these firing temperatures meets the requirements of the standard, and its values are 74 – 81 and 78 – 96 MPa in compression and 10 – 16 and 11 – 18 MPa in bending.

TABLE 2. Physicochemical Properties of Fired Specimens of Clinker Ceramics

Indicator	Values of the physicochemical properties of specimens fired at temperature, °C		
	1050 ± 5	1100 ± 5	1150 ± 5
Total shrinkage, %	3.6 – 4.5	4.9 – 6.1	6.4 – 7.7
Water absorption, %	6.4 – 10.7	3.5 – 8.2	3.2 – 4.7
Mechanical strength, MPa:			
in compression	40 – 48	74 – 81	78 – 96
in bending	5 – 6	10 – 16	11 – 18
Frost resistance, cycles	75 – 100	150 – 180	150 – 180
Apparent density, kg/m^3	$(2.06 – 2.11) \times 10^3$	$(2.17 – 2.50) \times 10^3$	$(2.19 – 2.54) \times 10^3$
Wearability, g/cm^2	1.0 – 1.2	0.3 – 0.7	0.2 – 0.4
Specific efficiency of natural radionuclides, Bq/kg	170 – 175	170 – 185	170 – 185

TABLE 3. Optimal Body Compositions for Producing Clinker Bricks

Components of raw mixture	Weight content of components, %, compositions with index			
	15–1	17–2	9–3	20–3
Gorodnoe clay	20	30	20	20
Fanipol' loam	40	30	35	30
Granitoid screenings	30	25	30	30
Bolshaya Karpovka clay	10	15	15	20

The frost resistance on bulk freezing of samples lies in the range of 150 – 180 cycles. The apparent density is equal to $(2.17 – 2.54) \times 10^{-3}$ kg/m^3 and wearability — 0.2 – 0.7 g/cm^2.

The total shrinkage indicators also depend on the firing temperature and are equal to 4.9 – 6.1% for specimens fired at 1100°C and 6.4 – 7.7% at 1150°C.

The specific effective activity of native radionuclides lies in the range 170 – 185 Bq/kg with standardized value 370 Bq/kg.

Analysis of the physicochemical properties of products in terms of the chemical composition of the investigated bodies showed that the optimal compositions correspond to the following limit of the oxide content, %: SiO_2 — 63.1 – 67.8; Al_2O_3 — 15.2 – 17.8; the sum of alkaline oxides ($Na_2O + K_2O$) and alkaline earth metals ($CaO + MgO$) — 5.5 – 6.5; the sum of $Fe_2O_3 + TiO_2$ — 5.2 – 7.1. These intervals of the oxide content are close to the values obtained by other researchers [2].

The mineral composition of the optimum range of ceramic bodies for producing clinker ceramics made it possible to establish the following content of minerals (%): 7 – 10 kaolinite; 14 – 18 montmorillonite; 6 – 8 illite; 7 – 9 feldspars; 35 – 39 quartz; 2 – 3 muscovite and biotite; 7 – 10 glauconite; 4 – 6 chlorite; 1 – 3 calcite; 2 – 4 ferruginous minerals; and, 2 – 3 other minerals. The obtained results are in agreement with the data of [5, 6].

We found that for the optimal composition range the oxide ratio $(SiO_2 + Al_2O_3)/(Na_2O + K_2O + CaO + MgO + TiO_2 + Fe_2O_3)$ should be 6.0 – 6.4.

Raising the content of the sum of Al_2O_3 and SiO_2 above the specified amount does not afford the required values of the physicochemical properties of the samples, which may be the reason for the polymorphism of free quartz present in the raw material composition.

The performed research made it possible to determine the optimal compositions of raw mixtures, including (%): high-melting clay from the Gorodnoe deposit — 20 – 30; loam from the Fanipol' deposit — 30 – 40; granitoid screenings of fraction < 1 mm — 25 – 30; Bolshaya Karpovka BK-0 clay deposit — 10 – 20.

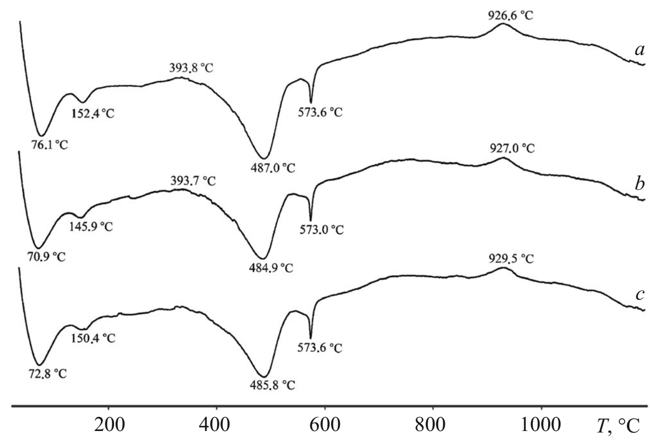

Fig. 1. DSC curves of the experimental compositions: *a*) 15–1; *b*) 17–2; *c*) 9–3.

Some clinker brick body compositions, which are optimal in terms of physicochemical properties, are shown in Table 3.

The thermal analysis of the raw mixtures of the experimental ceramic bodies established that on heating the processes occurring in them are identical. This is illustrated in Fig. 1.

The endothermic effects observed at temperature peaks 70.6 – 78.1°C are due to the removal of the molding and the hygroscopic moisture from the samples. On raising the temperature, adsorption-bound and interlayer molecular moisture is removed from hydromica, montmorillonite, and glauconite, which is due to a shallow endothermic effect at temperature 143.7 – 153.2°C.

The exothermic effects with maxima in the temperature range 346.8 – 362.3°C are due to the structural rearrangement of Fe^{2+} into Fe^{3+} in the iron-containing components of the raw material (muscovite, biotite, glauconite, and so on). Endothermic effects with a maximum at temperatures of 482.7 – 493.6°C are associated with the removal of hydroxyl moisture from montmorillonite, chlorite and hydromica, which are constituents of the ceramic body, as well as with partial amorphization of the matter.

Weak endothermic effects with maxima at 573.0 – 575.0°C are explained by the removal of the remaining constitutional moisture and destruction of the structure of montmorillonite, chlorite, kaolinite, and glauconite.

The formation of low-temperature anorthite is due to exothermic effects at the maximum 927.0 – 933.2°C.

X-ray phase analysis of samples fired at 1150°C showed the presence of crystalline phases of α-quartz, anorthite, mullite and hematite (Fig. 2).

The presence of a developed halo in the x-ray diffraction patterns indicates the formation of a significant amount of the vitreous phase. On raising the firing temperature the diffraction maximum of mullite becomes more intense, and

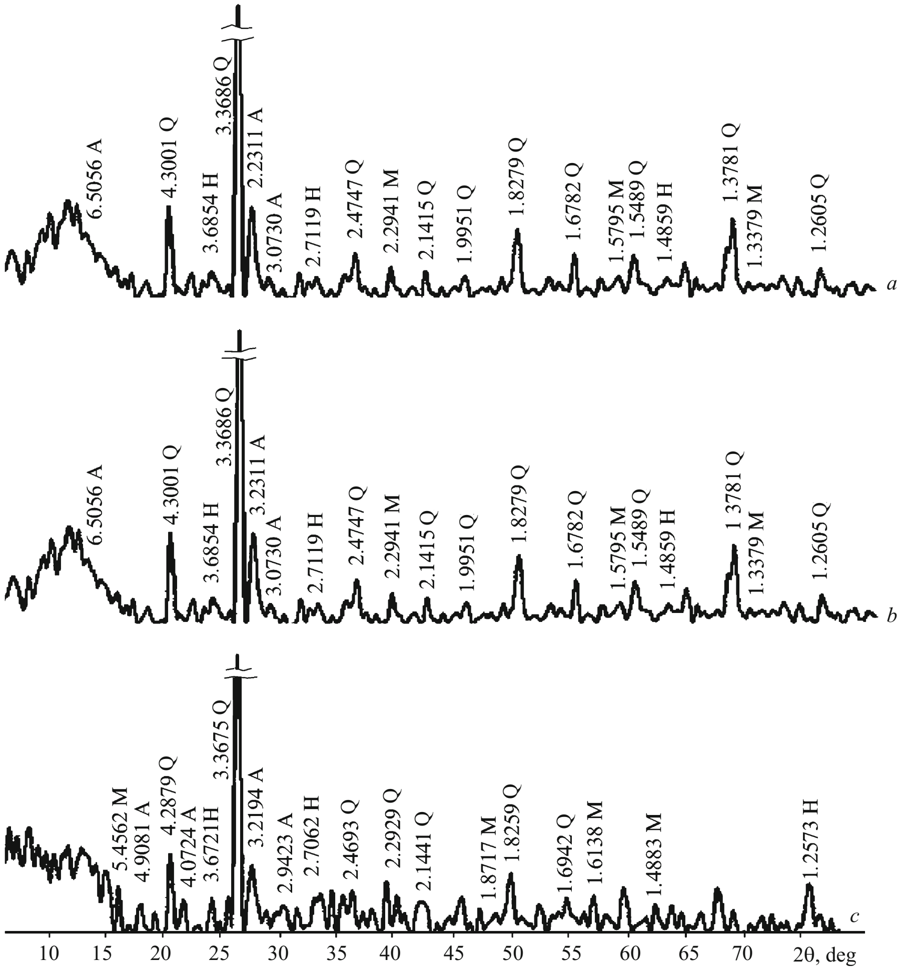

Fig. 2. X-ray phase analysis of samples of clinker bricks with compositions (interplanar distances are given in angstroms): *a*) composition 15–1; *b*) composition 17–2; *c*) composition 9–3; Q) quartz; M) mullite; A) anorthite; H) hematite.

α-quartz and hematite less intense, which may indicate the dissolution of these phases in the melt.

The performed studies made it possible to establish that the sintering of ceramic bodies is achieved due to the formation of a well-developed crystal structure cemented by a glassy phase. The high degree of compaction of the ceramic body of the products due to plastic formation also plays a positive role.

Of the clay minerals present in the experimental raw materials the montmorillonite component is characterized by the highest content of fluids and low dispersion (less than 5 μm), which, along with fine impurities — free iron hydroxide and micaceous minerals, leads to the active formation of the melt. Clay particles larger than 5 μm in size, represented by sandy and dusty fractions, as our studies have shown, remain inert for a long time and interact little with the melt.

Among all the products of thermal transformations the most significant role belongs to the amorphized aluminosilicate component, which is formed from clay minerals as a result of their amorphization and destruction of the crystal lattice. The main part of the clay substance during heat treatment after amorphization passes into the melt. Low-melting BK-0 clay and loams melt especially easily. Subsequent reactions take place with the participation of the melt, which makes it possible for various minerals to form crystals relatively quickly.

Crystallization products from the melt are formed mainly at the annealing temperature 1150°C. They predominate, though the products of solid-phase reactions also play an important role.

As melts cool, a glassy phase is formed; Na_2O and K_2O play the most significant role in crystallization — increasing it.

The color of the products depends on the amount of iron-containing impurities.

The most significant impression about the features of the formation of the densely sintered structure of the experimental samples of clinker bricks is due to the electron-microscopic study of their structure with an analysis of the chemical composition at their local points, which is illustrated in Fig. 3.

Mullite plays a significant role in the formation of physical and chemical properties of clinker brick samples. The growth of mullite crystals is observed with an increase in the firing temperature from 1100 to 1150°C, which contributes to the transformation of isometric nuclei, which apparently

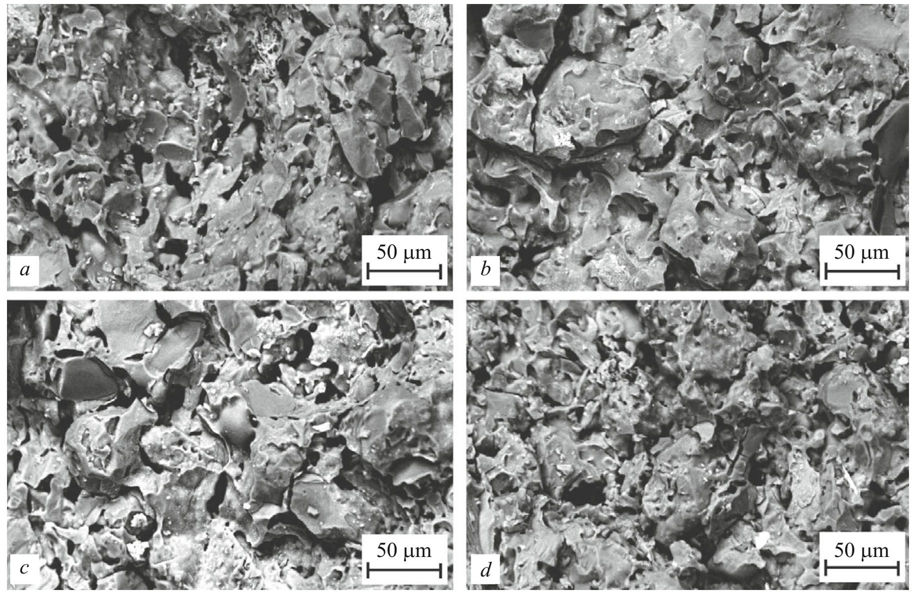

Fig. 3. Microstructure of samples of clinker ceramics with the compositions: *a*) 7–1; *b*) 15–2; *c*) 9–1; *d*) 20–1.

appear due to solid-phase interaction, into longer and thinner needles, which are rarely scattered in the structure of the sample.

Of note is that at firing temperature 1050°C no mullite was found in the samples. At higher firing temperature 1100°C the mullite phase is recorded in the form of 0.03 – 0.08 μm long needle-like formations both in x-ray diffraction patterns and in electron microscopic images. The crystal habit changes as the temperature is raised (see Fig. 3). There are both needle crystals and short-columnar crystals close to prismatic in shape. Their crystallization is observed mainly at the interfaces between the amorphous clay substance and the glass phase. This may indicate the crystallization of mullite with the fluids present in the ceramic bodies (oxides of iron and alkali metals) having a direct effect on this process. The size of these formations increases to 0.5 – 2.0 μm. The clearest habit of crystals is observed at firing temperature of 1150°C, which makes it possible to judge the formation of secondary mullite. Its maximum amount is typical for samples containing 35 – 40% granitoid screenings, which may indicate the formation of mullite from feldspar minerals that are part of the granitoids, which form a melt on firing.

Analysis of the microstructure of clinker bricks fired at the optimum temperature (1150 ± 5°C) in the optimal composition zone shows that the samples are characterized by a high degree of sintering and the minimum number of open and closed pores. Open pores are predominantly oriented (slit-like), sometimes with enlargements and constrictions; their size is 10 – 110 μm. Closed pores and capillaries are also predominantly slit-like, often sinuous and oriented in the direction of crystalline formations. They reach 5 – 130 μm in size.

Local chemical analysis revealed the presence of a significant amount of micro-heterogeneities of relic origin in the structure of all experimental samples, which did not pass into the melt during the formation of the structure of the samples, as well as a number of crystalline new formations.

Almost always present are quartz grains ranging in size from 30 to 460 μm, in habit close to non-isometric shape, relatively smooth (Fig. 4*a*), with surface chipping (Fig. 4*b*), and sometimes with a fractured structure (Fig. 4*c*). The boundaries of relict grains are slightly melted, surrounded by a glassy phase.

Feldspar grains close in chemical composition to anorthite $Ca[Al_2Si_2O_8]$ are usually parent in the structure (Fig. 4*d*). The habit of the crystals is close to prismatic with well-discernible face irregularities and the presence of cleavage cracks. The crystals reach 140 – 510 μm in length and 100 – 300 μm in width. The presence of grains similar in chemical composition to albite Na $[AlSi_3O_8]$ (Fig. 4*e*), whose crystals have a prismatic shape, is also noted. It is obvious that feldspar minerals are formed from a melt enriched in CaO and Na_2O.

The investigations have confirmed the conclusion of [8] that the presence of feldspar grains less than 0.5 mm in size in clinker brick is preferable: they afford the formation of a glass phase with a thermally altered clay substance. The presence of ferrous minerals in the charge also facilitated this process.

In connection with the use of raw materials containing a significant amount of CaO, its combination with ferrous impurities, which are mineralizers, form other crystalline neoplasms on sintering. Among them, first of all, are the frequently encountered pyroxenes. They have the form of elongated prismatic crystals with dimensions 10 × 100 μm or large formations with dimensions 75 × 150 μm, and in isolated cases — 150 × 250 μm. Studies of the chemical composition of these new formations allow us to classify them

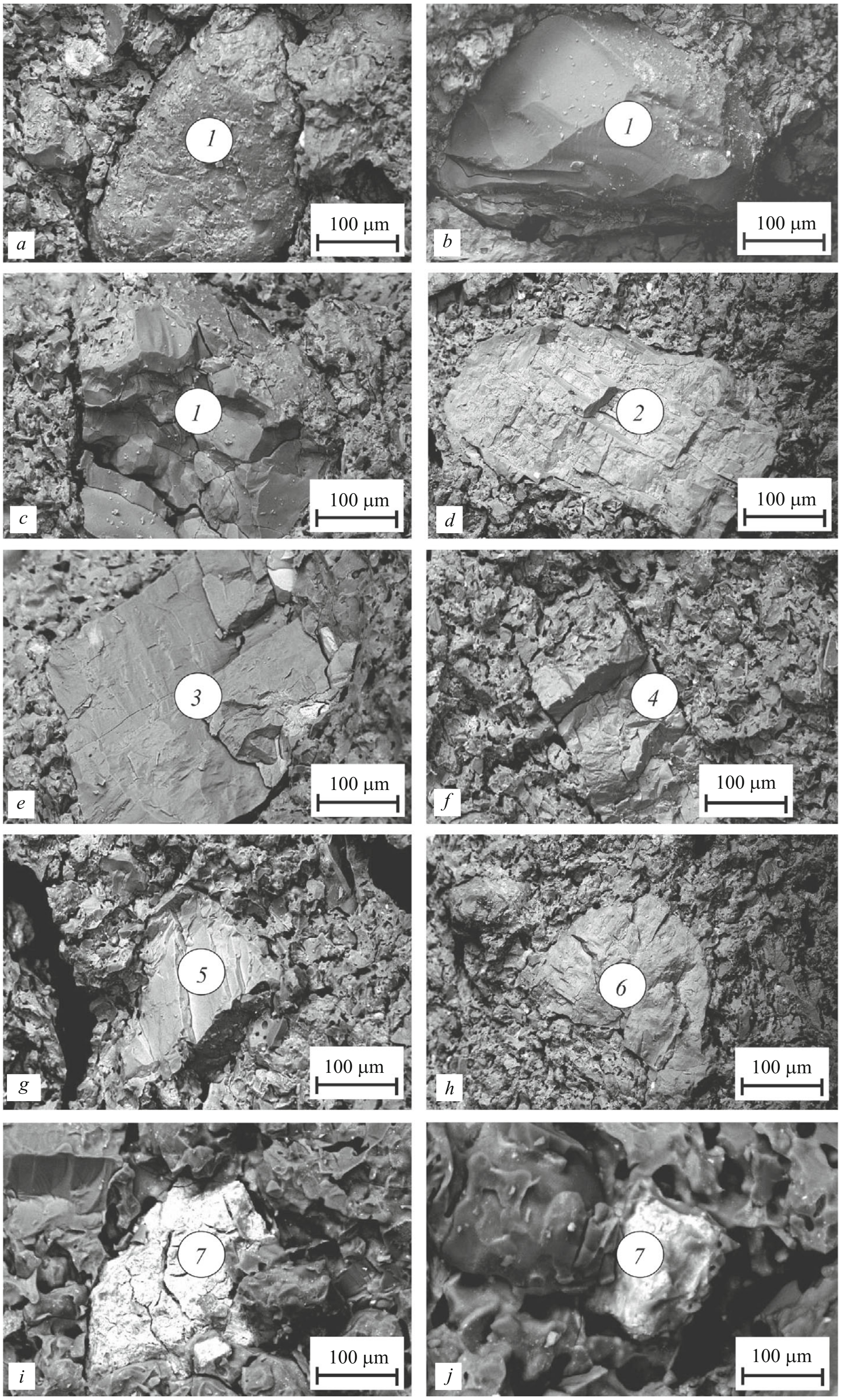

Fig. 4. Crystalline inclusions in the microstructure of clinker bricks of optimal compositions 17–2: *1*) quartz; *2*) anorthite; *3*) albite; *4*) augite; *5*) aegirine; *6*) hedenbergite; *7*) hematite.

as augite $Ca_4(Mg, Fe)_3Al[(Si, Al)_2O_6]$ (Fig. 4*f*), aegirine $NaFe(Si_2O_6)$ (Fig. 4*g*), hedenbergite $CaFe(Si_2O_6)$ (Fig. 4*h*), or a transitional phase — aegirine-augite, aegirine-hedenbergite.

When free oxygen acts on a silicate melt containing Fe^{2+} ions oxidation of the latter with crystallization of hematite is observed. It is formed in the form of randomly arranged lamellar formations of various sizes, length 15 – 270 μm and width 30 – 150 μm (Fig. 4*i* and *j*). The boundaries of the crystals are corroded.

As the firing temperature of the samples increases from 1050 to 1150°C, partial dissolution of hematite in the melt is noted, providing the color of the formed glassy phase. However, even at high firing temperatures hematite is present in the structure of the material.

The presence of iron-containing components gives the material a rich, uniform color. The performed studies allow us to conclude that the liquid phase formed on firing, which has a significant viscosity, increasing with increasing temperature, acts as follows. From the physical standpoint, due to surface tension it contributes to the convergence of the solid particles of a body. Moreover, chemical interaction is also present due to the dissolution of minerals, followed by the precipitation of thermodynamically stable crystals from the melt. A significant amount of the melt also leads to the interaction of the products of thermal decomposition of loams, clays, and other constituent components of the raw mixture.

At the same time crystals of predominantly prismatic or acicular, and less often lamellar, habit are formed, and on subsequent cooling are cemented by the glass phase and perform a reinforcing role that increases the mechanical strength of the material structure.

It was also established that the dehydration reactions of the minerals of clays, micas, hydromicas, and carbonate components of ceramic bodies, and the oxidation of the present organic inclusions must be completed before the liquid phase forms in significant amounts. This is necessary so that burnout of organic components of the bodies, reduction of iron ions Fe^{3+} to Fe^{2+}, and removal of hydration moisture and decomposition products of carbonates occured before a liquid phase forms and prevented fusion of the forming pores. Total completion of gassing processes before the formation of the melt also avoids the formation of a black core in the products.

In the course of the present investigations the compositions of polymineral clay bodies, the temperature/time regimes of firing of clinker ceramics, and the interrelation of the physicochemical properties of product samples with their structure and phase composition were established. It is shown that clinker ceramics can be obtained on the basis of raw materials available in Belarus, which factory tests conducted at Keramin OJSC (Minsk) have confirmed.

The products manufactured in the factory by plastic molding were fired in an industrial gas-flame furnace at temperature 1120°C. The firing duration was equal to 20 h, and the soaking time at the maximum temperature was equal to 2.5 h. A clinker brick was characterized by water absorption 4.5%, density 2190 kg/m^3, mechanical strength grade 400, frost resistance grade 100, and radiation quality 1st-class. A clinker brick corresponds to class B according to STB 1787–2007 ‘Ceramic clinker bricks. Technical conditions.’

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