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The Influence Of Ceramic Masses Obtained By Sintering On Wall Ceramics

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Abstract. The production of wall ceramics, despite the improvement of technology, still remains quite energy-intensive.

Production in Ukraine is mainly carried out from loamy raw materials and requires high firing temperatures of 1000–1050 ^{0}C, and, accordingly, high costs of fuel and energy resources, the cost of which is constantly growing.

The existing main directions for reducing the firing temperature of wall ceramics (dispersion of raw materials, introduction of fuel-containing and other additives), when using low-quality loams, do not give the expected effect, and the firing temperature remains within the range of 950–970 ^{0}C, and their use in combination is often constrained by the lack of a general theoretical basis for the processes of formation of the structure and physical and mechanical properties of ceramic material.

Thus, reducing the firing temperature in the production of wall ceramics is an urgent problem, which may be be solved by controlling the formation of the structure and properties of ceramics obtained from activated aluminosilicate raw materials modified with Na - Fe -containing compounds.

Key words: wall, ceramics, firing, nanomaterials, waste, construction, microdistricts

Aim research is to create physicochemical principles for the production of wall ceramics at low firing temperatures by modifying activated aluminosilicate raw materials with Na-Fe-containing compounds.

Research methods. Theoretical studies were conducted based on the analysis and systematization of scientific ideas about the mechanisms of physical and chemical aspects of the formation of the structure of wall ceramics. Experimental studies were carried out using mathematical methods of experimental planning.

The phase composition and microstructure of the materials were studied using a set of instrumental methods of physical and chemical analysis: X-ray phase analysis (Dron-4 diffractometer, Philips PW1820 X-ray diffractometer), dilatometric analysis (DKV-4 A dilatometer), and electron microscopic analysis (Selmi REM-106I scanning electron microscope). The physical and mechanical properties of the obtained materials were studied using standard methods in accordance with current regulatory documents.

Results of the study. Coal enrichment waste contains an insufficient amount of clay particles. Therefore, in our studies, coal enrichment waste was mixed with mechanically activated loam. Samples were formed from the resulting raw mix with a moisture content of 16.7%, which were fired at 800 and 870 ^{0}C, and then the strength was determined [2]. The conducted studies revealed that with an increase in the loam content from 10 to 30%, the strength and average density of the samples increases, and with a higher content, it decreases (Fig. 1). Thus, the optimal loam content in the raw mix of coal enrichment waste and loam is 30% [2].

According to the working hypothesis, part of the loam during its mechanical activation by grinding was replaced by red mud containing iron and sodium cations. The presence of water-soluble sodium salts during the grinding process created an alkaline environment, which intensified the dispersion and grinding of a larger number of colloidal particles. Grinding was

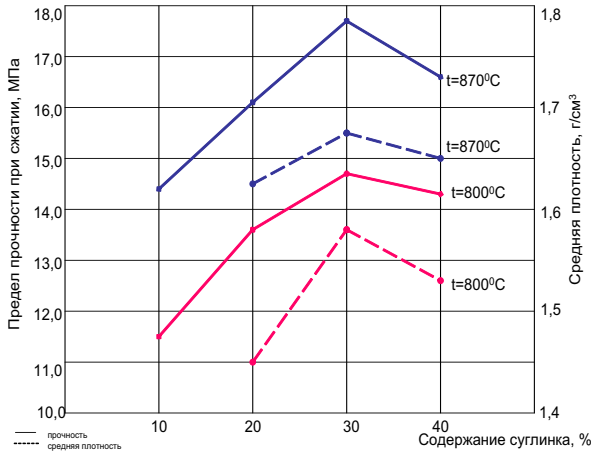


Fig. 1. Strength and average density of brick depending on the content of mechanically activated loam

carried out for 2 hours at a suspension humidity of 40%. The resulting suspension was mixed with dried and partially mechanically activated coal enrichment waste in runners. The samples were fired at a temperature of 870 ^{0}C and then tested for strength [2].

Loam and red mud in the raw mix of coal beneficiation waste on the strength and average density, simplex lattice mathematical planning of the experiment was used. The initial parameters were the content of the components: X_1 – content of coal beneficiation waste from the central processing plant, X_2 – loam, X_3 – red mud. The content of coal beneficiation waste varied from 70 to 90%, loam 10–30%, red mud 0–20% [2]. The matrix of the experiment planning and the output parameters of the samples are given in Table 1.

Table 1 Planning matrix and output parameters of the material

Content of components in coded scale			Natural content of components, % by weight			Compressive strength of the material, MPa, after firing at temperature 870 ^{0}C
1	0	0	90	10	0	14,4
0	1	0	70	30	0	17,8
0	0	1	70	10	20	20,2
0.5	0.5	0	80	20	0	16,1
0.5	0	0.5	80	10	10	19,6
0	0.5	0.5	70	20	10	24,7
0,333	0,333	0,333	71,7	21,7	6,66	20,8

According to the data in table 6, the influence coefficients for the studied raw material compositions were calculated using standard formulas. Based on the results of planning and conducting the experiment, a mathematical model was obtained that adequately describes the dependence of the compressive strength of wall ceramics when its composition changes:

$$R_{\text{compress}} = 14{,}4X_1 + 178X_2 + 20{,}2X_3 + 9{,}2X_1X_3 + 22{,}8X_2X_3 - 6X_1X_2X_3.$$

Based on the obtained model, a diagram of "composition - compressive strength" of samples of ceramic material obtained after firing at 870 ^{0}C was constructed (Fig. 2). The diagram shows that the highest strength for three-component ceramic masses is achieved with the following content of components, wt. %: coal enrichment waste - 70; loam - 20; red mud - 10, and for two-component ceramic masses with the content of components, wt. %: coal enrichment waste - 80; loam - 20. Patents for utility models were obtained for the developed compositions [3, 4].

Let us consider the section of the diagram "composition - strength" (Fig. 2) with a constant content of coal enrichment waste - 70%, passing through the composition with maximum strength (Fig. 2). The diagram shows that with an increase in the content of red mud from 0 to 10%, the strength of the fired sample increases. This is due to an increase in the content of colloidal particles in the raw mix, obtained both by activation and by increasing the content of iron cations in it, binding particles of silica, alumina and aluminosilicates.

The decrease in the strength of the sample after firing with an increase in the content of red mud is associated both with an increase in the thickness of the layer of iron-containing compounds and a weakening of the interaction in the contact zones, and due to greater shrinkage during the firing process, leading to the appearance of a greater number of defects in the contact zones.

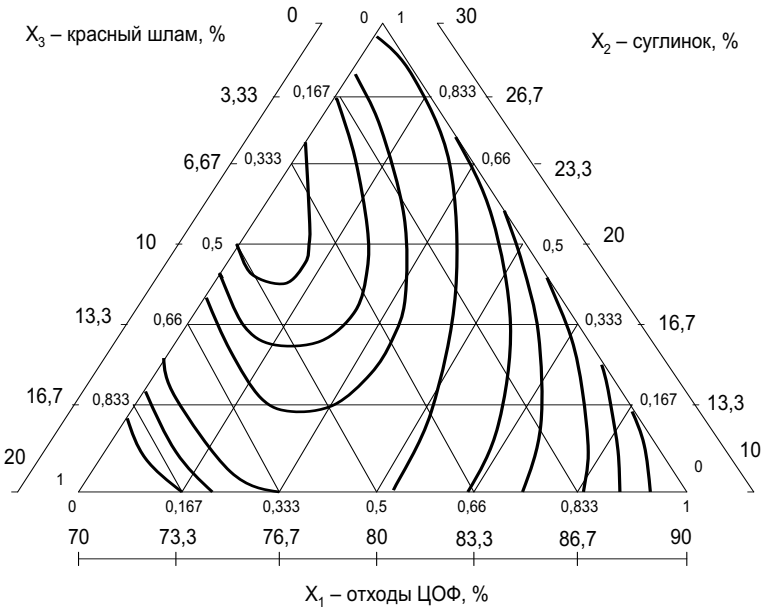


Fig. 2. The diagram of the state “composition – compressive strength” of wall ceramic samples of the studied system

Based on dilatometric studies of raw material with the following composition, wt. %: waste coal from the central coal preparation plant - 70; loam - 20; red mud - 10, studies were conducted to determine the duration of isothermal holding at a firing temperature of 870 ^{0}C, heating to 220 ^{0}C with a holding time of 1 hour to remove all types of water to adsorption, raising to 600 ^{0}C with a holding time of 1 hour to burn out hydrocarbon compounds.

Raising the temperature to 870 ^{0}C with isothermal holding for 0,5; 1; 1,5 hours. The results of the studies (Table 1) indicate that isothermal holding for 1 hour is optimal.

The optimal duration of isothermal holding for samples from complex activated raw materials is holding for 1 hour, which is adopted when firing the samples. In this case, there are no traces of underburning or overburning in the samples.

The study of the structure of ceramic material from a complex activated raw material mixture revealed the features of the formation of a structure that differs in mineral composition and the size of dispersed particles and their location.

In the initial period of sintering, during the combustion of carbon and low oxygen pressure, a reducing environment is created in the material, facilitating the transition of iron oxides to the ferrous form and a decrease in the melting temperature of the melt in the contact zones due to the

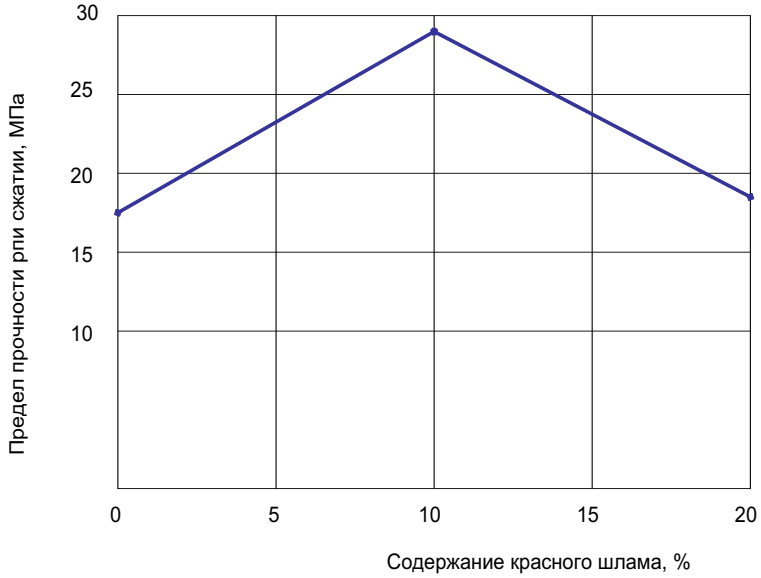


Fig. 3. Dependence of the compressive strength of the material on the content of red mud

Table 1 Research results

Duration of isothermal holding, h	Compressive strength, MPa	Average density, kg/ m^3
0,5	28,4	1500
1,0	31,6	1450
1,5	27,8	1420

formation of low-temperature eutectics in the system $Na_2O - SiO_2 - Al_2O_3$, $FeO - SiO_2$, $FeO - Al_2O_3 - SiO_2$. The appearance of the melt during interaction with silica particles of various levels, as well as dehydrated and delaminate clay particles with reactive compounds of sodium and iron, ensures the intensification of sintering processes.

X-ray phase analysis studies were carried out using a standard technique on a DRON-4 diffractometer with Bragg-Brentano focusing; decoding was performed using reference literature. The results are shown in Figure 5 [2]. X-ray phase analysis data show that the samples of mechanically activated ceramic mass (coal enrichment waste – 80%, loam – 20%), fired at 870 ^{0}C, contain more silica than the samples of complex-activated ceramic mass (coal enrichment waste 70%, loam – 20%, red mud – 10%), which is determined by comparing the intensities of diffraction maxima with d = 0,333–0,337 (Fig. 4) [4,5].

In samples from the mechanically activated mixture (Fig. 10), feldspars are present in significantly smaller quantities, identified by interplanar distances d = 0,641; 0,405; 0,381; 0,322; 0,288; 0,175; 0,144; 0,142 nm. In addition to the minerals listed, these samples contain dehydrated chlorite leaflets (d = 0,769; 0,352; 0,288; 0,205; 0,141; 0,2129 nm) of the introduced coal enrichment waste, as well as dehydrated hydromica leaflets (glauconite) (d = 0,457; 0,369; 0,258; 0,175; 0,163; 0,151 nm) and a small amount of dehydrated montmorillonite leaflets (d = 0,457; 0,262; 0,258; 0,151; 0,148; 0,131; 0,129 nm) [2]. Enrichment waste – 70; loam – 20; red mud – 10 quartz , the samples from the complex-activated raw material mixture (Fig. 3) also contain large amounts of: feldspars (d = 0,665; 0,376; 0,323; 0,2988; 0,286; 0,177; 0,149 nm), dehydrated chlorite

leaflets (d = 0,725; 0,492; 0,35; 0,286; 0,14; 0,1308 nm) and dehydrated hydromica (glauconite) leaflets (d = 0,35; 0,258; 0,151; 0,1289 nm) (Fig. 3) [2]. Additionally, in comparison with the samples from the mechanically activated raw material mixture (Fig. 10), the samples from the complex-activated mixture contain compounds containing sodium, iron, quartz and alumina in the form of ferrosilite (d = 0.323; 0.298; 0.258; 0.252; 0.229; 0.213; 0.182; 0.169; 0.159; 0.154; 0.14; 0.137; 0.1288 nm), almandine $Fe_3Al_2Si_3O_{12}$ (d = 0.187; 0.1406; 0.120 nm), aegirine (d = 0.198; 0.182; 0.167; 0.154; 0.137; 0.134; 0.128 nm) (Fig. 4). This indicates that a greater amount

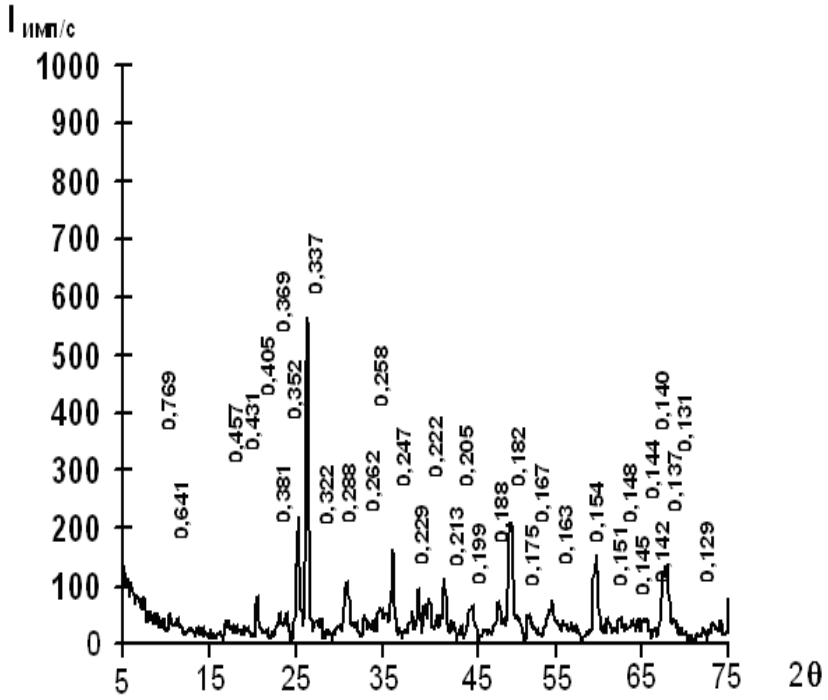


Fig. 4. Diffraction pattern of a sample fired at 870 ^{0}C, with the following composition, wt. %: coal enrichment waste – 80; loam – 20

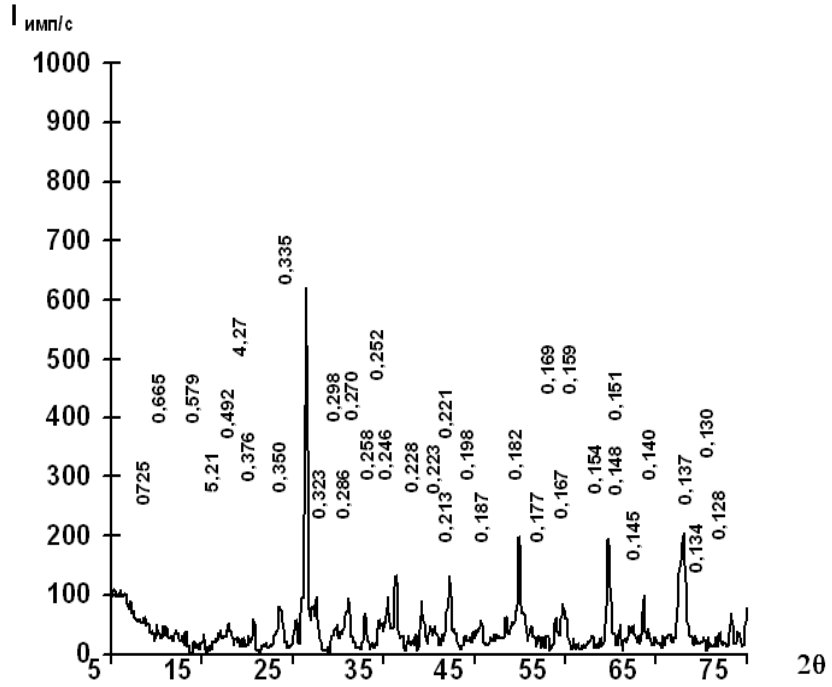


Fig. 5. Diffraction pattern of a sample fired at 870 0C, with the following composition, wt. %: coal

of silica reacted and formed a greater number of compounds in the contact zones, which united quartz grains, feldspars, and dehydrated clay particles into a monolith. These compounds are represented by ferrosilite, almandine, and aegirine [2].

Structural analysis was carried out using a Selmi REM-106I scanning electron microscope; the results are shown in Figures 5–6 [2].

The material based on a mechanically activated two-component ceramic mass consisting of wt.%: coal enrichment waste – 80; loam – 20, has a virtually uniform structure, the microstructure of the material is represented mainly by particles 5–20 μm in size, between which smaller particles – 0.5–2 μm – are located (Fig. 12). In addition, larger particles are present in significant quantities. The material is also permeated with pores of various configurations 0.2–10 μm in size, formed as a result of the burnout of organic compounds contained in coal enrichment waste. Particles 10–20 μm in size mainly have a lamellar configuration. Particles of 0.5–2 μm in size are connected to each other, as well as to particles of larger sizes (10–20 μm), by discrete contacts that unite all the particles into a monolith (Fig. 5, 6); these contacts are glassy and crystallized compounds of low-melting eutectics, and also probably iron cations [3].

Colloidal spherulites may be hematite or amorphous silica of the opal type. Plates and leaflets in microaggregates are connected to each other by the cleavage- cleavage, base-cleavage and base-base types (Fig. 8). In granular, plate-like and leaf-shaped microaggregates, particles and microaggregates are connected to each other by bridges of compounds formed (crystallized) from eutectic melts. In colloidal microaggregates, particles and microaggregates are probably connected to each other by Fe^{3+} cations [2].

The material from the complex activated raw mix, including 70% of coal washing waste, 20% of loam, 10% of red mud, as well as the material from the mechanically activated raw mix, including 80% of coal washing waste and 20% of loam, are characterized by a virtually homogeneous structure (Fig. 7). The microstructure of the material is represented by: plates 1,5–5 μm in size; leaflets 4–5 μm in size; granular microaggregates of particles 0,4–1 μm in size; microaggregates of colloidal particles 0,15–0,2 μm in size. Lamellar and leaf-shaped

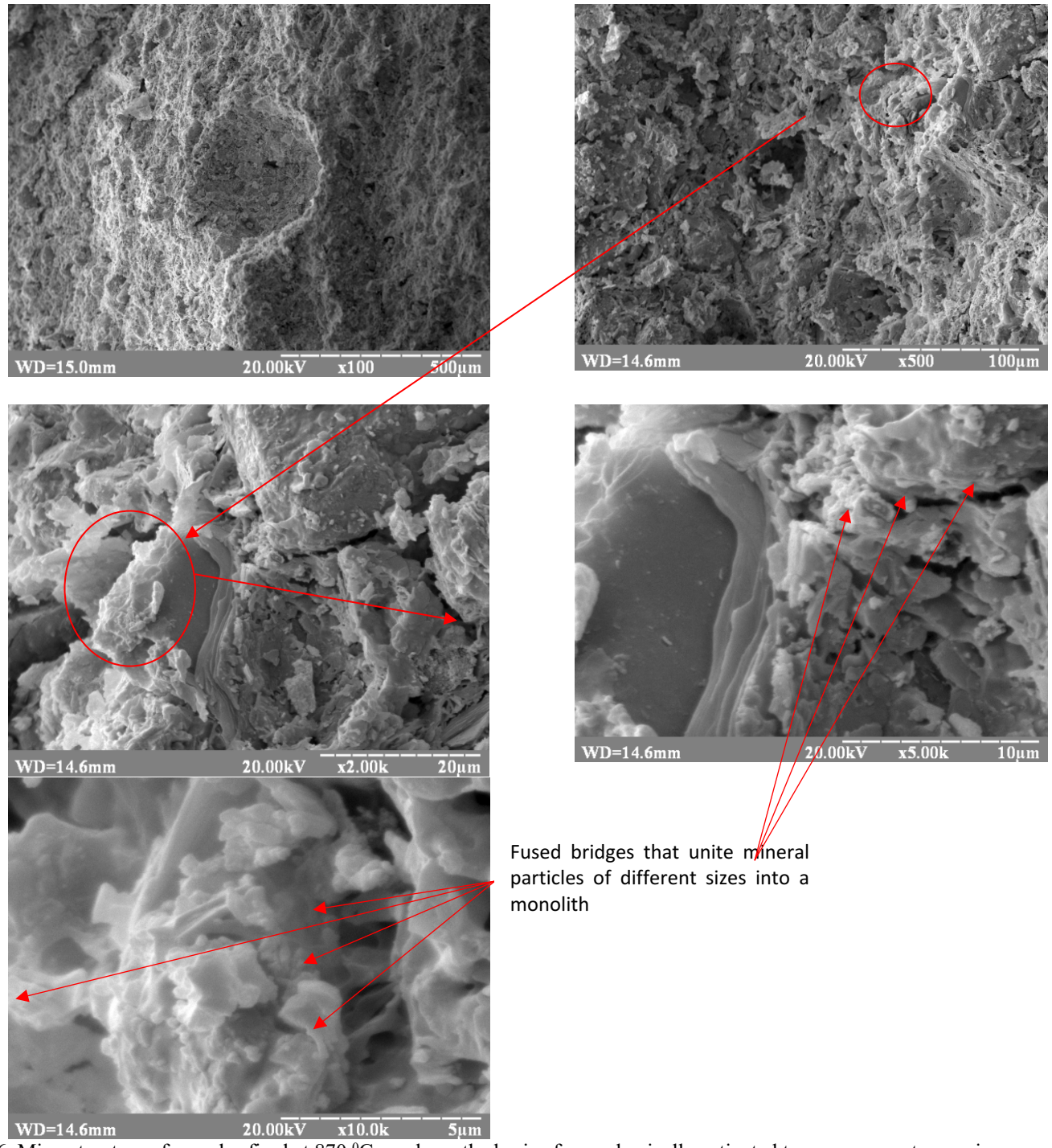


Fig. 6. Microstructure of samples fired at 870 ^{0}C, made on the basis of a mechanically activated two-component ceramic mass consisting of 80% coal enrichment waste and 20% loam

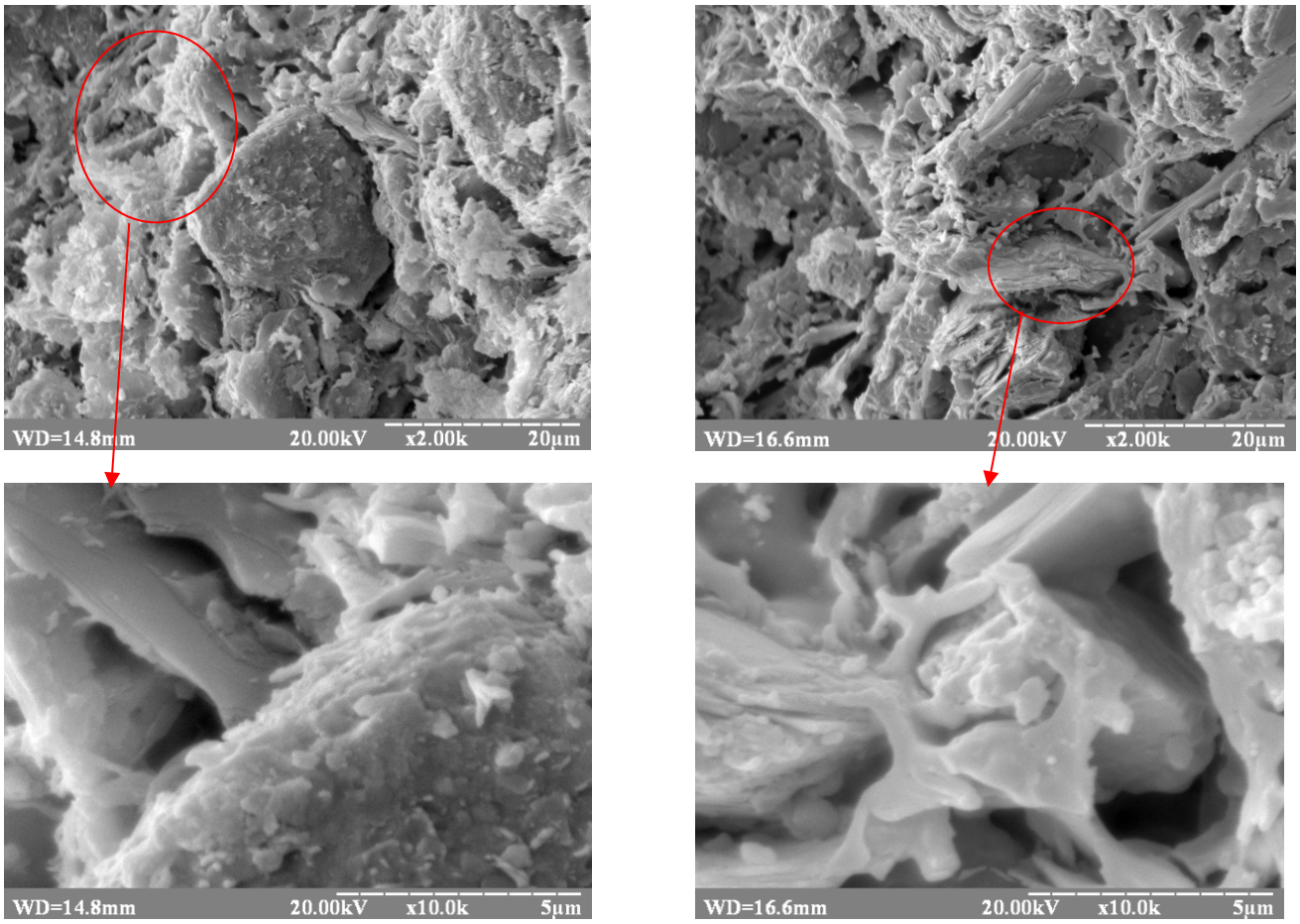
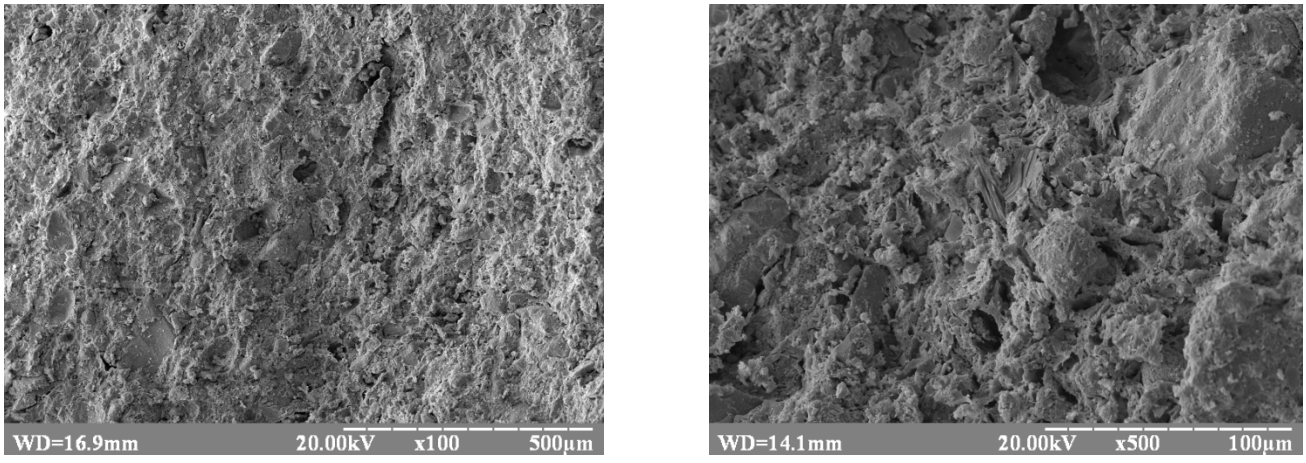


Fig. 7. Microstructure of samples fired at 870 ^{0}C made on the basis of a mechanically activated two-component ceramic mass consisting of 80% coal enrichment waste and 20% loam



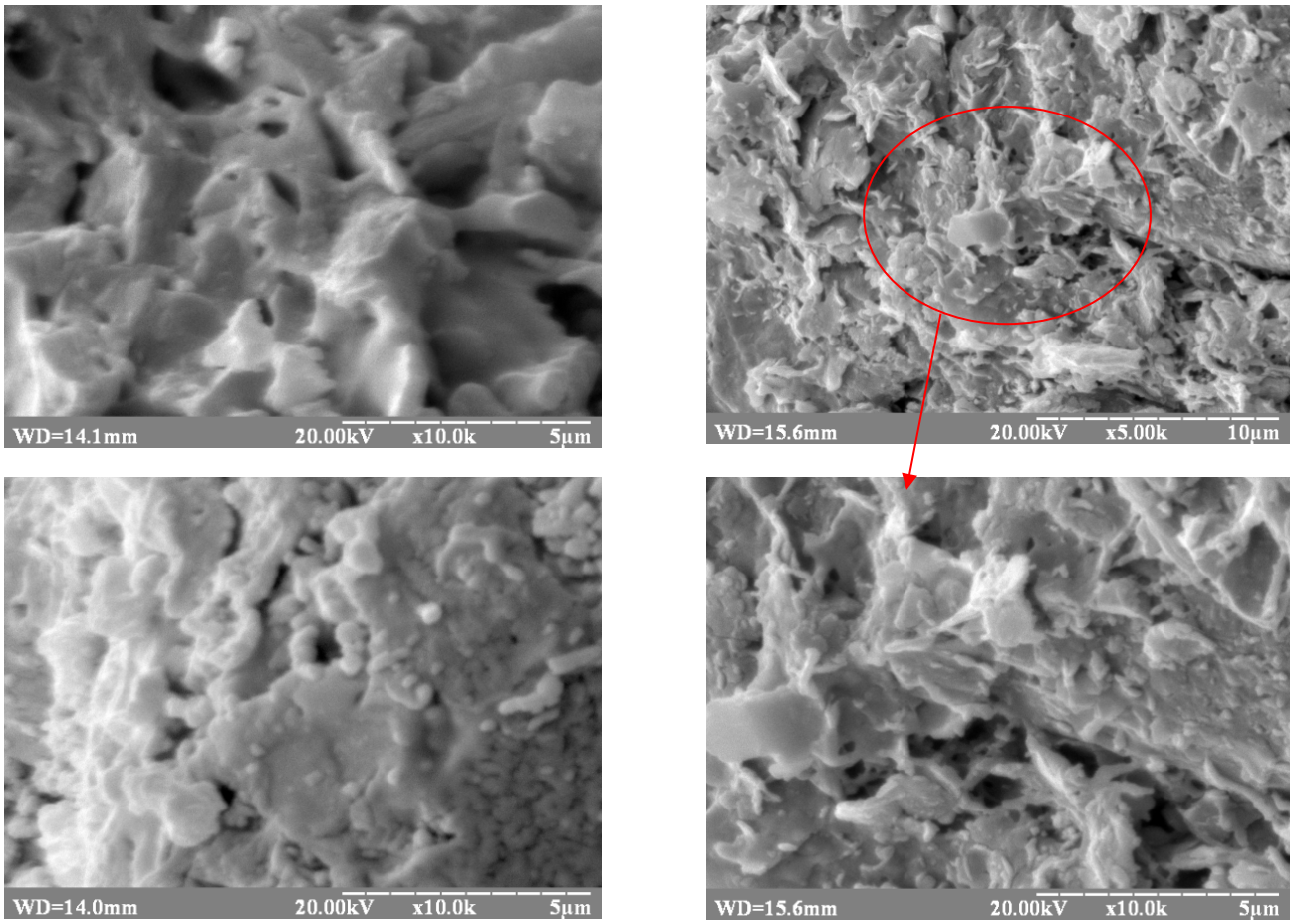


Fig. 8. Microstructure of samples fired at 870 ^{0}C, made from complex-activated raw materials of the following composition, wt. %: coal enrichment waste – 70; loam – 20; red mud – 10

microaggregates indicate the presence of dehydrated chlorite and montmorillonite particles in the structure of the material, and granular microaggregates indicate the presence of dehydrated mica.

A comparison of the SEM images of the structure of materials (samples) fired at 870 ^{0}C in Figures 7, 8 and 14 shows that the samples from complex-activated raw materials contain a larger amount of granular particles measuring 0.4–1 μm, microaggregates of colloidal particles appeared, and also more compounds formed from low-melting eutectics [2].

The greater amount of colloidal silica particles in samples made from complex activated raw materials, determined by X-ray phase analysis, as well as particles of 0,4–1 μm in size and colloidal hematite particles, determined by electron microscopic analysis, leads to a greater number and contact area of particles per unit volume of the sample, and, consequently, higher strength [3, 4].

Conclusions

1. When studying loess-like loams of the Sursko-Pokrovskoe deposit, it was found that they are characterized by a low content of aluminum oxide – 7,01-8,61%, iron oxide – 2,15-3,3%, the content of SiO_2 is 63,4-70,2%. Therefore, to improve their properties, it is advisable to carry out mechanical dispersion of raw materials, and when introducing a Na - Fe - containing component, chemical activation will also take place, i.e. a complex activated system: "loam - coal enrichment waste - Na - Fe -containing component red mud".

2. Using the simplex-lattice method of experimental planning, mathematical dependencies were obtained for the strength and density of wall ceramic bricks obtained at low firing temperatures on the ratio of raw components, which made it possible to determine rational compositions of raw mixtures;

3. Physicochemical methods of analysis (XRD, SEM) have determined that during the formation of the ceramic shard structure, the fluxing effect in the contact zones is exerted by compounds containing sodium and iron cations, causing intensive formation of melts in them with subsequent crystallization at lower temperatures in the form of ferrosilite, aegirine, and almandine. The microstructure of the obtained materials is represented mainly by particles 5–20 μm in size, between which there are smaller particles 0.4–2 μm in size, contacting through bridges.

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