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Study of Ceramic Masses Obtained Using Raw Materials of Technogenic Origin

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Absract

Waste from industrial coal preparation contains an insufficient amount of clay particles. In studies, coal preparation waste was mixed with mechanically activated loam. From the resulting raw material mixture with a moisture content of 16.7%, samples were molded, fired at 800 and 870 ^{0}C, and then the strength was determined. The conducted research revealed that with an increase in the loam content from 10…30%, the strength and average density of the samples increases, and with a higher content it decreases.

Studies of the phase composition and microstructure of materials were carried out using a complex of instrumental methods of physicochemical analysis. The physical and mechanical properties of the resulting materials were studied using standard methods in accordance with current regulatory documents. Studies of the system "loam – coal preparation waste – Na-Fe-containing red mud" were carried out using: red mud from enterprises was used as a clay component of loess-like loam, coal preparation waste from a central processing plant and as a Na-Fe-containing component.

Material from a complex activated raw material mixture, including 70% coal processing waste, 20% loam, 10% red mud, as well as material from a mechanically activated raw material mixture, including 80% coal processing waste and 20% loam, is characterized by an almost uniform structure. Lamellar and leaf-shaped microaggregates indicate the presence of dehydrated particles of chlorite and montmorillonite in the structure of the material, and granular microaggregates indicate the presence of dehydrated mica.

A comparison of SEM images of the structure of materials (samples) fired at 870 ^{0}C indicates that in samples from complexly activated raw materials there are more granular particles 0.4–1 μm in size, microaggregates of colloidal particles have appeared, as well as more compounds formed from low-melting eutectics.

Keywords: mixed, raw material, red mud, structure, granular, compounds

Introduction. 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.

The existing main directions of reducing the firing temperature of wall ceramics (dispersion of raw materials, introduction of fuel-containing and other additives), when using low-grade loams, do not give the expected effect, and the firing temperature remains in the range of 950–970^{0}C.

Thus, reducing the firing temperature when producing wall ceramics is an urgent problem that can 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.

The purpose of the study is to create the physicochemical basis for the production of wall ceramics at low firing temperatures by modifying activated aluminosilicate raw materials with Na-Fe-containing waste compounds.

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

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

Raw materials. Studies of the system «loam – coal preparation waste – Na-Fe-containing red mud» were carried out using: loess-like loam as a clay component (Tables 1, 2, 3, Fig. 1, 2), coal preparation waste from the Central Concentrating Plant in Pavlograd (Table 1, 4, Fig. 3, 4) and red mud from the Zaporizhzhye aluminum smelter was used as a Na-Fe-containing component (Table 1, 5, Fig. 5, 6) [1].

Table 1: Characteristics of raw materials

Name of raw materials	Chemical composition, mass. %	Mineralogical and granulometric composition
Loess-like loam	SiO_2 – 70,2; Al_2O_3 – 7,01; Fe_2O_3 – 2,15; CaO – 5,07; TiO_2 – 0,58; MgO – 1,55; Na_2O – 0,71; K_2O – 1,85; SO_3 – 0,08; CO_2 – 4,9; ппп – 8,7	Quartz, kaolinite, muscovite, microcline, clinochlore, albite, calcite, rutile. Granulometric composition: 1250 microns – 27.32%; 630 μm – 23.07%; 315 μm – 19.51%; 140 μm – 14.63%; 80 microns – 4.88%; < 20–10.59%. Drying sensitivity coefficient – 0.81. The plasticity number of loam is 8.76 (moderately plastic). Air shrinkage – 7.4%. Fire shrinkage – 0.70% and total – 8.1%
Coal processing waste	SiO_2 – 59,0; Al_2O_3 – 17,9; Fe_2O_3 – 4,4; CaO – 0,55; MgO – 1,65; MnO – 0,025; P_2O_5 – 0,120; K_2O – 2,8; Na_2O – 0,65; TiO_2 – 1,0; п.п.п. – 11,2	Quartz, calcite, nacrite, clinochlore, muscovite, kaolinite, illite, pyrite. Granulometric composition: 40.86 microns – 25%; 16.36 μm – 25%; 8.407 μm – 25%; 3.211 μm – 15%; 1.296 μm – 10%
Red mud	Al_2O_3 – 16,6; SiO_2 – 10,5; Fe_2O_3 – 40,7; CaO – 12,1; TiO_2 – 4,2; Na_2O – 6,3 ; ппп – 9,4	Hematite, boehmite, quartz, magnetite, diaspore, calcite, sodium aluminosilicates. Granulometric composition, wt. %: 1... 0.05 mm – 32%; 0.05…0.005 mm – 62%; 0.005…0.002 mm – 4%; 0.002 mm – 2%. Granulometric composition: 167.5 microns – 25%; 123.9 μm – 25%; 86.08 μm – 25%; 48.14 μm – 15%; 1.619 microns – 10%. The average value is 88.05 microns, the maximum is 105.9 microns.

Research results. Coal preparation waste contains an insufficient amount of clay particles. Therefore, in our studies, coal preparation waste was mixed with mechanically activated loam. From the resulting raw material mixture with a moisture content of 16.7%, samples were molded, 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…30%, the strength and average density of the samples increases, and with a higher content it decreases (fig. 6). Thus, the optimal content of loam in the raw mixture of coal processing waste and loam is 30% [2].

In accordance with the working hypothesis, part of the loam, when mechanically activated by grinding, was replaced with 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 carried out for 2 hours at a suspension humidity of 40%. The resulting

Table 2: Values of the granulometric composition of undispersed loess-like loam

Grain content, mass. % <	27,32	23,07	19,51	14,63	4,88	10,59
Grain size, microns	1250	630	315	140	80	<20

Table 3: Values of particle size distribution of dispersed loess-like loam

Grain content, mass. % <	10	15	25	25	25
Grain size, microns	1,205	2,977	9,172	20,99	43,55

The average grain size of dispersed loess-like loam is 15.58 μm, the maximum is 41.68 μm.

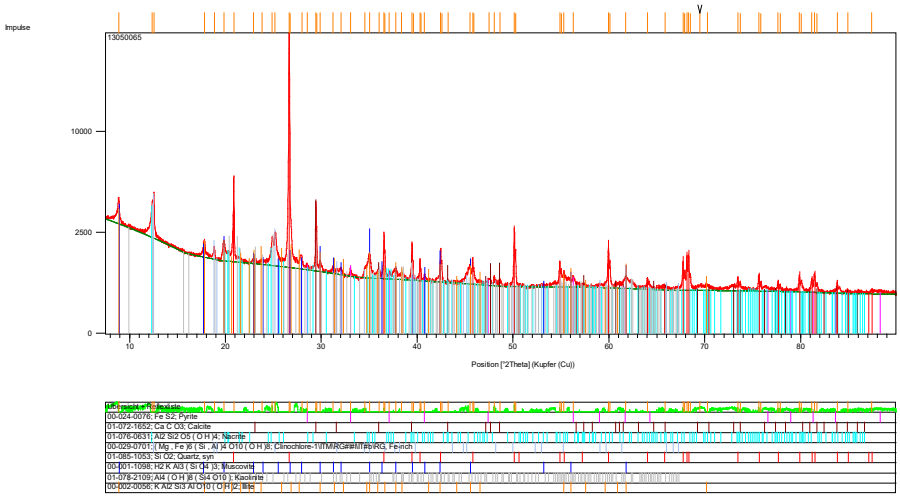

Fig. 1: X-ray diffraction pattern of coal preparation waste from the Pavlograd central processing plant

Table 3: Values of the granulometric composition of coal preparation waste from the Pavlograd CPP

Grain content, mass. %<	10	15	25	25	25
Grain size, microns	1,296	3,211	8,407	16,36	40,86

The maximum particle size is 16.40 μm, the average value is 14.17 μm.

suspension was mixed with coal preparation waste that was dried and partially mechanically activated in the runners. The samples were fired at a temperature of 870 0C and then tested for strength [2].

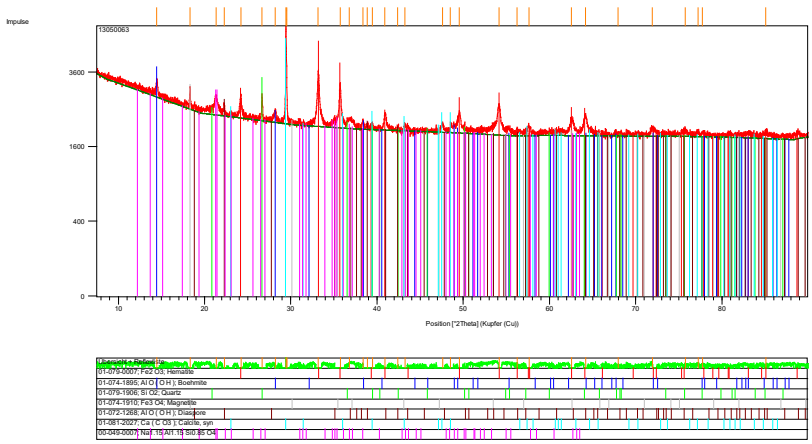

Fig. 2: X-ray diffraction pattern of red mud

Table 4: Values of granulometric composition of red mud ZALK

Grain content, mass. % <	1	15	25	25	25
Grain size, microns	1,619	48,14	86,08	123,9	167,5

The average value is 88.05 microns, the maximum is 105.9 microns.

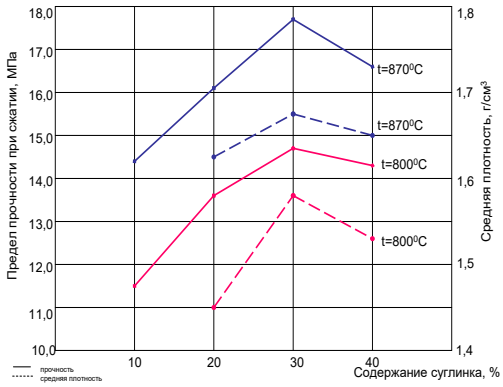

Fig. 3: Strength and average density of brick depending on the content of mechanically activated loam

To determine the effect of the content of loam and red mud in the raw mixture of coal enrichment waste on strength and average density, simplex lattice mathematical planning of the experiment was used. The content of components was taken as the initial parameters: X1 – content of coal preparation waste from the central coal processing plant, X2 – loam, X3 – red mud. The content of coal preparation waste varied from 70…90%, loam 10…30%, red mud 0…20% [2]. The experiment planning matrix and sample output parameters are given in table 6.

Table 5: Planning matrix and material output parameters

Contents of components in coded scale			Natural content of components, % by weight			Ultimate 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 table 5, 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:

Rсж = 14,4 X1 + 17,8 X2 + 20,2 X3 + 9,2 X1X3 + 22,8 X2X3 – 6X1X2X3 .

Based on the obtained model, a “composition – compressive strength” diagram was constructed for samples of ceramic material obtained after firing at 870 0C (fig. 3). The diagram shows that the greatest strength for three-component ceramic masses is achieved with the following component content, wt. %: coal preparation waste – 70; loam – 20; red mud – 10, and

for two-component ceramic masses with component content, wt. %: coal preparation waste – 80; loam – 20. Patents for utility models were obtained for the developed compositions [3].

Let us consider the cross-section of the "composition – strength" diagram (fig. 3) at a constant content of coal preparation waste – 70%, passing through the composition with maximum strength (fig. 4). The diagram shows that as the red mud content increases from 0…10%, the strength of the fired sample increases. This is due to an increase in the content of colloidal particles in the raw mixture, obtained both due to activation and due to an increase in the content of iron cations in it, which bind particles of silica, alumina and aluminosilicates.

The decrease in the strength of the sample after firing with an increase in the red mud content is associated both with an increase in the thickness of the layer of iron-containing compounds and 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.

Based on dilatometric studies of raw materials with the following raw material composition, wt. %: coal preparation waste from the Central Concentrator Plant – 70; loam – 20; red mud - 10, research was carried out to determine the duration of isothermal exposure at a firing temperature of 870 0C, heating to 220 0C with a hold time of 1 hour to remove all types of water to adsorption, raising to 600 0C with a hold time of 1 hour to burn out hydrocarbon compounds. Raising the temperature to 870 0C with an isothermal hold of 0.5; 1; 1,5 hour. The results of the studies (table 6) indicate that isothermal exposure for 1 hour is optimal.

Table 6: Research results

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

The optimal duration of isothermal exposure for samples made from complexly activated raw materials is an exposure of 1 hour, which is adopted when firing samples. At the same time, 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.

During the initial period of sintering, during the combustion of carbon and low oxygen pressure, a reducing environment is created in the material, which promotes the transition of iron oxides into the ferrous form and a decrease in the melting temperature of the melt in the contact zones due to the appearance of low-temperature eutectics in the system Na2O–SiO2–Al2O3, FeO–SiO2, FeO –Al2O3–SiO2. The appearance of a melt upon interaction with silica particles of various levels, as well as dehydrated and delaminated clay particles with reactive compounds of sodium and iron, ensures the intensification of sintering processes.

X-ray phase analysis studies were carried out according to standard methods on a DRON-4 diffractometer with Bragg–Brentanno focusing; interpretation was carried out according to reference literature. The results are shown in figures 1, 2 [2]. X-ray phase analysis data show that in samples from mechanically activated ceramic mass (coal preparation waste - 80%, loam - 20%), fired at 870 0C, there is more silica than in samples from complex activated ceramic mass (coal preparation waste 70%, loam – 20%, red mud – 10%), which is determined by comparing the intensities of diffraction maxima with d = 0.333…0.337 (fig. 1, 2) [2].

The samples from the mechanically activated mixture (fig. 1) contain significantly less feldspars, 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 above minerals, these samples contain dehydrated leaves of chlorite (d = 0.769; 0.352; 0.288; 0.205; 0.141; 0.2129 nm) of the introduced coal preparation waste, as well as dehydrated leaves of hydromica (glauconite) (d = 0.457; 0.369; 0.258; 0. 175 ; 0.163; 0.151 nm) and in small quantities dehydrated montmorillonite leaves (d = 0.457; 0.262; 0.258; 0.151; 0.148; 0.131; 0.129 nm) [2].

In addition to quartz, samples from the complexly activated raw material mixture (fig. 1) also contain large quantities of: feldspars (d = 0.665; 0.376; 0.323; 0.2988; 0.286; 0.177; 0.149 nm), dehydrated chlorite leaves (d = 0.725 ; 0.492; 0.35; 0.286; 0.14; 0.1308 nm) and dehydrated leaves of hydromica (glauconite) (d = 0.35; 0.258; 0.151; 0.1289 nm) (fig. 1) [2]. Additionally, in comparison with samples from a mechanically activated raw material mixture (fig. 1), samples from a 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 Fe3Al2Si3O12 (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. 1). This indicates that more silica reacted and formed a larger number of compounds in the contact zones, uniting 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 2–4 [2].

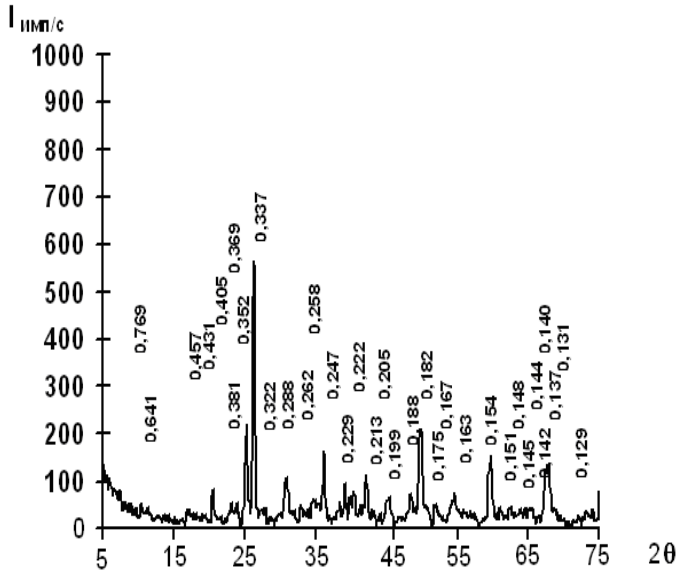

Fig. 4: X-ray diffraction pattern of a sample fired at 870 0C, the following composition, wt. %: coal preparation waste – 80; loam – 20

Material based on mechanically activated two-component ceramic mass, consisting of wt.%: coal preparation waste – 80; loam – 20, has an almost uniform structure, the microstructure of the material is represented mainly by particles 5–20 μm in size, between which there are smaller particles – 0.5–2 μm (fig. 2). 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 combustion of organic compounds contained in coal preparation waste. Particles measuring 10–20 μm generally have a plate-like configuration. Particles 0.5–2 μm in size are connected with each other, as well as with larger particles (10–20 μm) by discrete contacts that unite all particles into a monolith (fig. 2, 3); these contacts are glassy and crystallized compounds of low-melting eutectics , and also probably iron cations [2].

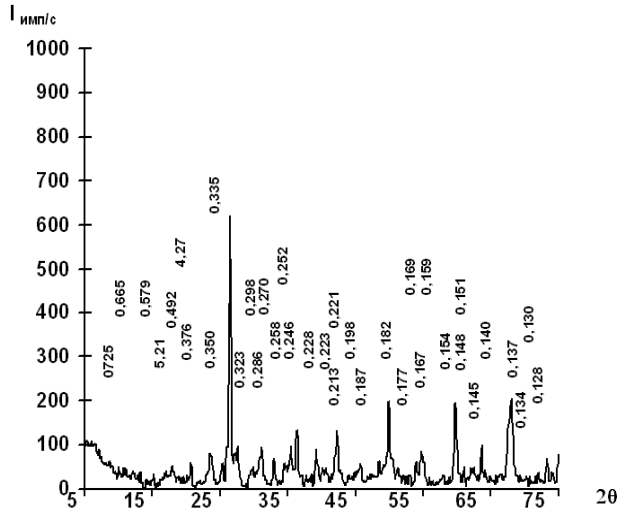

Fig. 5: X-ray diffraction pattern of a sample fired at 870 0C, the following composition, wt. %: coal preparation waste – 70; loam – 20; red mud – 10

Material from a complex activated raw material mixture, including 70% coal preparation waste, 20% loam, 10% red mud, as well as material from a mechanically activated raw material mixture, including 80% coal preparation waste and 20% loam, is characterized by an almost uniform structure (Fig. 14). The microstructure of the material is represented by: plates measuring 1.5–5 microns; 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 microaggregates indicate the presence of dehydrated particles of chlorite and montmorillonite in the structure of the material, and granular microaggregates indicate the presence of dehydrated mica.

Colloidal spherulites may be hematite or opal-type amorphous silica. The plates and leaflets in microaggregates are interconnected according to the types cleavage - cleavage, basis - cleavage and basis - basis (Fig. 4). In granular, lamellar and sheet-like microaggregates, particles, as well as microaggregates, are interconnected by bridges of compounds formed (crystallized) from eutectic melts. In colloidal microaggregates, particles, as well as microaggregates, are probably connected to each other by Fe^{3+} cations [2].

A comparison of SEM images of the structure of materials (samples) fired at 870 ^{0}C in figures 3, 4 and 5 indicates that in samples from complexly activated raw materials there are more granular particles 0.4–1 μm in size, microaggregates of colloidal particles have appeared, and there are also more compounds formed from low-melting eutectics [2].

A larger number of colloidal silica particles in samples made from complex activated raw materials, determined by X-ray phase analysis, as well as particles 0.4–1 μm in size and colloidal hematite particles, determined by electron microscopic analysis, leads to a larger number and area of particle contacts in per unit volume of the sample, and therefore higher strength [3].

Conclusions

1. Studying the loess-like loams of the Sursko-Pokrovsky 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%, SiO_2 content is 63.4…70, 2%. To improve their properties, it is advisable to perform mechanical dispersion of raw materials.

2. Using the simplex-lattice method of experiment planning, mathematical dependences of the strength and density of ceramic wall bricks obtained at low firing temperatures on the factors of the proportions of raw materials components were obtained;

3. Physicochemical methods of analysis (XRF, SEM) have determined that during the formation of the structure of a ceramic shard, compounds containing sodium and iron cations have a fluxing effect in the contact zones, causing the intensive formation of melts in them with subsequent crystallization in the form of ferrosilite, aegirine, almandine, which speeds up the technological operation and increases the efficiency of the technological process by 32%.

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