Improvement of the technology of obtaining mineral binders from loess-like rocks using mechanoactivation

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Abstract. The article presents the results of a comprehensive study of the chemical, mineralogical and granulometric compositions of clay raw materials, as well as thermal properties of loess-like rocks of the Suzanlinskoye deposit using modern methods of physicochemical analysis. A technology for grinding raw materials has been developed, and a proposed process flow chart for obtaining mineral binders from loess-like rocks using mechanical activation has been presented. Using this technology to produce mineral binders ensures higher dispersion and micro-roughness of raw material particles; high concentration of surface and volumetric structural defects, and stabilization of this highly active state before sintering. The research has revealed that 20-minute grinding to 3 μm for mechanical activation of raw materials, the use of man-made waste-defecates as additional raw materials, allows to reduce the temperature to 1200 °C during clinker firing. A new composition of masonry mortars was developed based on mineral binders of grade 200M (H 32.5 class), with a particle size of 3 microns, with the necessary color and chemical and mineralogical indicators for restoration materials of historical heritage.

1 Introduction

Loess-like deposits, traditionally used for the production of building ceramics for centuries, have become widely used as a building material. However, the use of natural clays is complicated by the inconsistency of their properties, which negatively affects the quality of the manufactured products. In the Central Asian republics, including Uzbekistan, the limited reserves of high-quality clay raw materials determine the use of low-plasticity loess-like rocks to produce binders. The resulting products are characterized by reduced strength, insufficient frost resistance, low decorative qualities and a tendency to form efflorescence during operation [1]. Uzbekistan has significant reserves of loess-like rocks and loams, which serve as key raw materials in the production of building ceramics. In the republic, 568 deposits and manifestations of clay rocks have been identified, represented by loess-like loams, clays of various types, argillite clays, kaolins and clay shales. Classification of clay rocks of Uzbekistan by origin includes alluvial, sedimentary (transferred) and

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metamorphosed types. Formation of argillite clay deposits occurred under diagenesis conditions [2].

Production of high-quality binders requires an optimal combination of the raw materials used and the use of modern technological solutions. Regardless of the production method, the key stage in obtaining high-quality binders is the effective preparation of the raw material mass. The main goals of this technological process are the destruction of the natural structure of the clay raw material, its disaggregation and removal of unwanted impurities [3, 4].

Destruction of the natural anisotropic structure of the clay raw material can be achieved in various ways, including by dispersing clay particles or removing water-soluble salts through leaching [5].

Reducing the particle size of the raw components leads to an increase in their contact area, which has a beneficial effect on the sintering process during firing of products. The literature describes studies devoted to the use of mechanochemical activation of raw materials, which, unlike traditional preparation methods, allows changing the physicochemical state of mineral particles at the grinding stage [6].

As part of this work, a study was conducted of the chemical-mineralogical and granulometric compositions, as well as the physicochemical characteristics of loess-like rocks of the Suzanli deposit in order to develop a technology for their processing based on mechanical activation.

To achieve this goal, the following tasks were defined: assessment of the volume of loess-like rocks in Uzbekistan; selection and preparation of samples for the necessary analyses; establishment of the chemical and mineralogical composition, as well as the study of the physicomechanical properties of loess-like rocks of the Suzanli deposit; analysis and interpretation of the results of the experimental studies.

2 Research methods

This study conducted a thorough investigation into the chemical makeup, mineral content, particle size distribution, and heat-related characteristics of clay resources. The research utilized sophisticated physicochemical analytical methods in conjunction with well-established techniques from silicate materials science.

To ascertain the mineral makeup of both initial raw materials and mechanically activated samples, X-ray phase analysis was conducted using a Rigaku Corporation SmartLab3 diffractometer. The technological properties of these materials, encompassing both raw and activated forms, were assessed in accordance with GOST 9169-2021, the prevailing standard within Commonwealth of Independent States (CIS) countries. A comparative analysis of the acquired data was then performed against established findings from relevant scientific literature [7].

The granulometric composition of the initial materials was determined by employing two established techniques: dry sieving and sedimentation analysis, adhering to the guidelines outlined in GOST 21216.2-93 [8].

A sample containing raw materials suspended in water was subjected to gravitational separation. Subsequently, a Shimadzu SALD-7500 laser particle analyzer was used to assess the size distribution of the particulate matter present in the sample.

3 Results of experimental studies

The Suzanli deposit, a loess-like formation, is situated within the Khiva district of Uzbekistan's Khorezm region. A quarry operating at this site is located 4 kilometers southeast of Kasma village and borders the Karakum Desert massif. The quarry spans an area of 28 hectares and exhibits a flat geological topography.

Geologically classified as Upper Quaternary alluvial deposits (Akchadarya complex), Suzanli primarily comprises sands, sandy loams, and loess-like rocks. The productive layer consists of sheet-like loess formations overlying fine-grained quartz-feldspar sands. The upper 0.3 to 0.5 meters contain plant roots and other extraneous materials.

The northern portion of the deposit features finely dispersed aeolian sands, varying in thickness from 0.4 to 2.5 meters. Total estimated reserves amount to 829 thousand cubic meters, with 596 thousand cubic meters registered on the State Committee on Geology's balance sheet and the remaining 233 thousand cubic meters unregistered [9].

The deposit's shape resembles a lens, with a thickness ranging from 3.0 to 4.5 meters, exhibiting localized variations. The dominant color of the loess-like rocks is light brown or gray, and they are composed of minerals arranged in a complex structure [10-12].

Table 1. Results of chemical analysis of loess-like rock samples Suzanli deposit.

Oxide content, wt.%	**№ samples**										Average
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	
SiO_2	52,54	52,55	52,53	52,49	52,56	52,60	52,57	52,51	52,65	52,50	52,55
Al_2O_3	14,72	15,60	15,59	15,27	14,56	15,72	15,39	15,57	15,54	14,51	15,36
CaO	14,04	14,09	14,32	13,31	14,14	14,27	13,48	14,11	13,65	14,55	13,99
MgO	4,70	4,65	4,52	4,62	4,53	4,49	4,48	4,61	4,43	4,42	4,55
Fe_2O_3	7,20	7,44	7,27	7,25	7,44	7,20	7,26	7,23	7,21	7,22	7,28
K_2O	2,76	2,78	2,82	2,75	2,71	2,84	2,72	2,85	2,81	2,74	2,78
Na_2O	2,12	2,08	2,08	2,11	2,02	2,15	2,05	2,14	2,28	2,07	2,11
SO_3	0,18	0,11	0,14	0,14	0,13	0,17	0,12	0,15	0,16	0,12	0,14
TiO_2	0,68	0,66	0,69	0,64	0,65	0,50	0,62	0,63	0,61	0,67	0,64
l.o.p. %	1,06	0,04	0,04	1,42	1,25	0,06	1,31	0,20	0,66	1,20	0,72

Note: Loss on ignition (L.o.p) includes: hygroscopic, constitutional, crystallized water, organic and volatile matter, and carbon(IV) oxide.

This report examines the chemical composition of loess-like rocks from the Suzanli deposit to assess their suitability for ceramic building product manufacturing.

X-ray fluorescence analysis reveals that these rocks are primarily composed of silicon dioxide (SiO_2, 52.55%), classifying them as acidic clay raw material based on aluminum oxide (Al_2O_3) content. The presence of titanium dioxide (TiO2) and iron oxide (Fe_2O_3) suggests potential for use as coloring pigment sources.

However, the relatively low alumina (15.36%) content indicates a limited presence of clay minerals like kaolinite and montmorillonite. Calcium oxide (CaO, 13.99%) and magnesium oxide (MgO, 0.17%), indicative of carbonate inclusions from limestone, could lower the firing temperature of mineral binders.

While the silicon dioxide content meets industry standards for ceramic production, the low aluminum oxide levels hinder the creation of high-quality ceramic bricks. Conversely, the elevated calcium oxide content exceeds acceptable limits, further limiting its applicability in this context.

Preliminary physical observations reveal a light gray coloration and moderate resistance to manual grinding. Foaming upon reaction with hydrochloric acid confirms the presence of carbonate compounds. Granulometric analysis using laser diffraction techniques classifies the rock as coarse clay raw material.

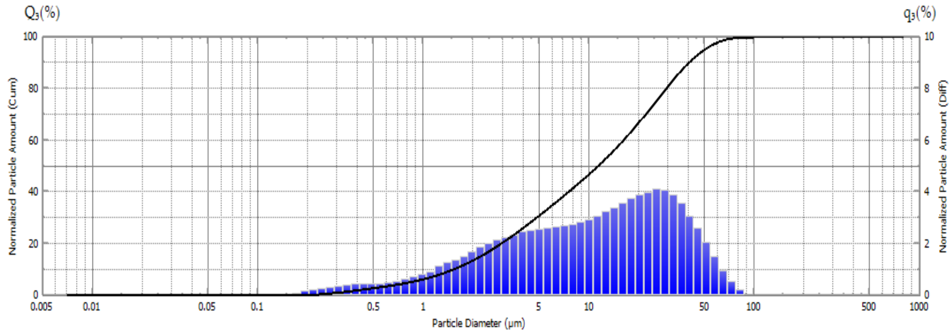
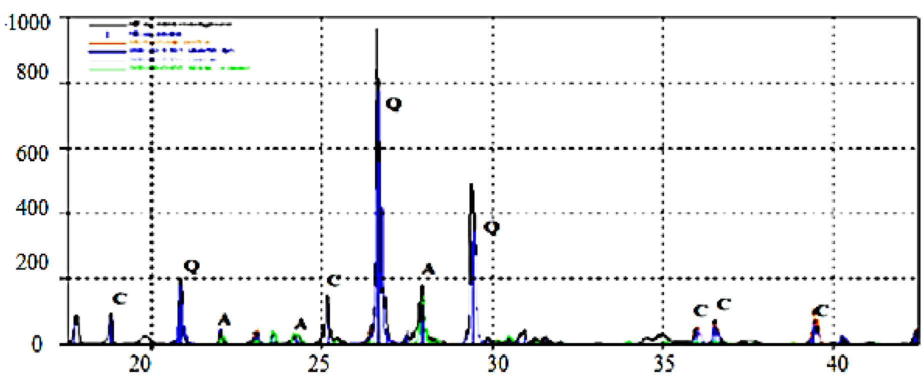


Fig. 1. Granulometric composition of a sample of loess-like rocks from the Suzanli deposit.

The analysis revealed that the raw material exhibits a bimodal particle size distribution, characterized by peaks at approximately 3.5 micrometers and 25 micrometers, resulting in an average particle size of around 9 micrometers.

Examination of X-ray diffraction patterns (Fig. 2) obtained from a sample of loess-like rocks sourced from the Suzanli deposit yielded further insights that there are diffraction maxima of the minerals quartz (SiO_2) (d/n = 0.081; 0.079; 0.102 nm), calcite ($CaCO_3$) (d/n = 0.091; 0.090; 0.102; 0.103 nm), albite (Na (Al Si_3O_8)) (d/n = 0.083; 0.089; 0.091; 0.114; 0.132; 0.079; 0.086; 0.106; 0.108; 0.090 nm).



Q- quartz, A- albite, C-calcite

Fig. 2. X-ray diffraction pattern of a loess-like rock sample from the Suzanli deposit.

To improve the physicochemical characteristics of the raw mix, we used a defecation, a carbonate-containing by-product of sugar production. In the process of purifying the diffusion juice obtained after extracting sugar from beet chips and pre-purifying it by filtration from plant fibers and precipitation of proteins by heating, defecation is used. The waste material produced from sugar refining is characterized by its cream-colored, powdery texture with an oily consistency that readily absorbs moisture and becomes malleable. Analysis of this waste, collected from filters at Khorezm Shakar JSC, reveals a moisture content ranging from 20% to 24%, a density between 2135 and 2380 kg/m³, and a specific volume between 1030 and 1095 kg/m³.

Elemental composition analysis indicates the presence of various components: sugar (1.60-2.10%), pectin substances (1.40-1.65%), calcium carbonate (74.25-80.00%), nitrogen-containing organic substances (5.90-6.01%), nitrogen-free organic substances (8.04-9.50%), lime in the form of various salts (2.80-3.10%), and other mineral substances (2.78-3.91%).

Incorporation of this waste into mineral binders facilitates the formation of alite, belite, and aluminoferrite phases, thereby enhancing their mechanical and chemical properties. Moreover, the organic fraction of the waste creates a reducing environment during firing, enabling the production of clinker that aligns with the color characteristics of traditional masonry mortars.A laboratory ball mill LShM-7500 was used to grind the raw materials. Uralite balls were used as grinding media. The process of grinding the raw mixture was carried out in two stages. Loess rocks were crushed for half the entire grinding time. Then the measured defecate powder was added to the ball mill, and the process of joint grinding continued.

The results of determining the optimal parameters of mechanical activation of loess-like rocks in the presence of defecate are presented in Figure 3.

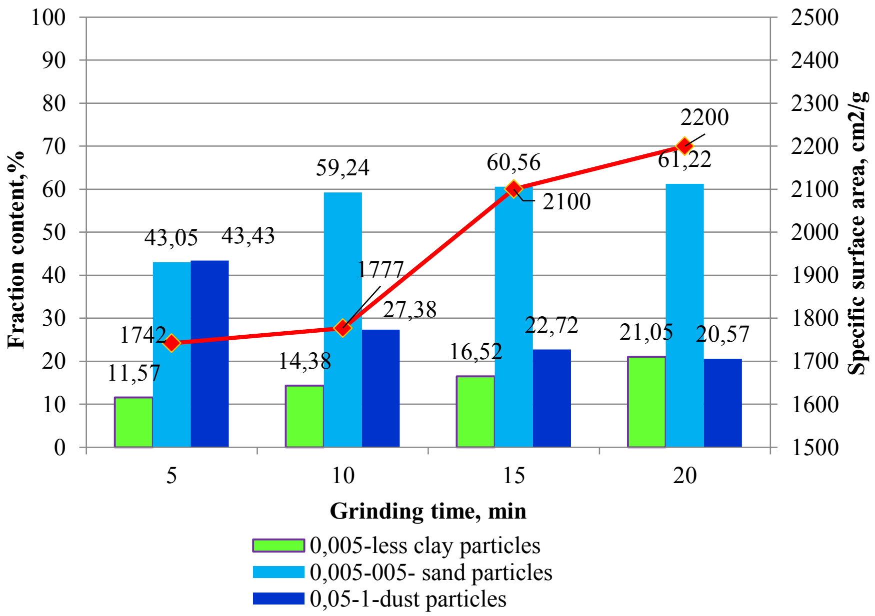
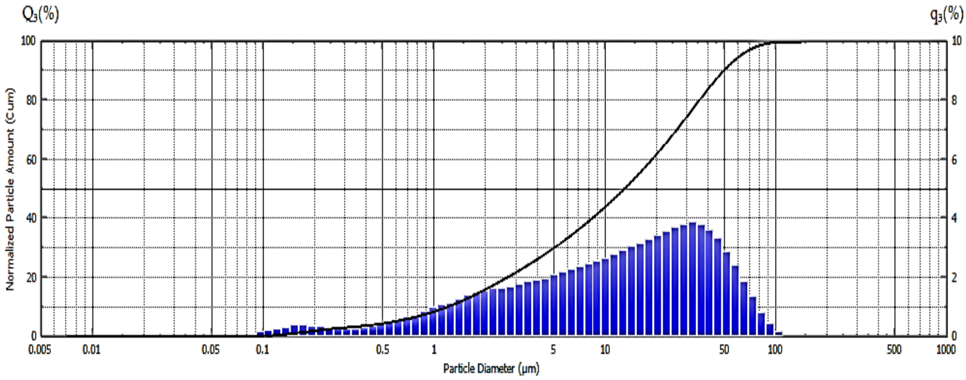
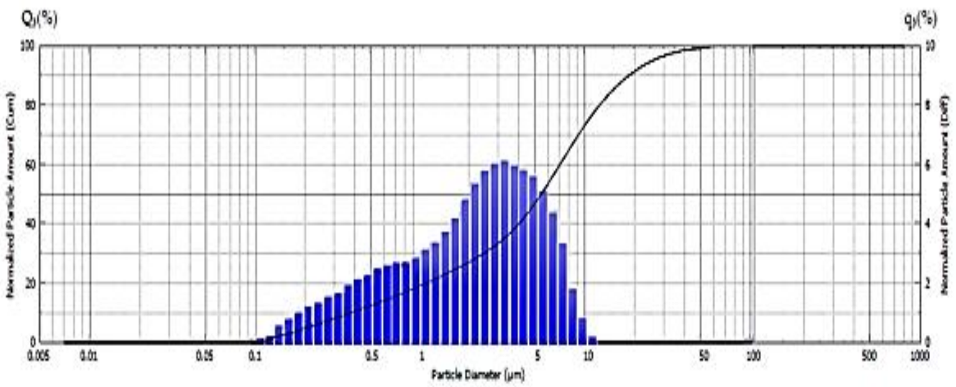


Fig. 3. Change in the granularity of the obtained powder with different grinding durations.

As can be seen from the data presented in Figure 3, grinding the raw material for 20 minutes leads to an increase in the proportion of fine clay and dust particles. To improve the rheological characteristics of the molding mixture, a joint activation of loess-like rock and defecate was carried out. To obtain a composition with binding properties, "loess-defecate" mixtures were used as a base in proportions from 70 to 95%, while the proportion of mechanically activated loess-like rock powder varied from 2 to 27%. Based on the "loess-defecate" mixture, a mass was prepared for the production of a mineral binder. Mechanically activated pressed powder of loess-like rock and defecate was ground to a specific grain surface of 2200 cm2/g, after which the defecate mass was added and dry mixing was carried out. Then the raw mix was moistened to 21.00-22.00% and pelletized to obtain spheres with a diameter of 20.00-23.00 mm. The obtained samples were dried in a laboratory drying oven ШЦ-80-02 ЦП at a temperature of 120 °C until a residual moisture content of 1.0% was achieved and fired in a muffle furnace СНОЛ 120/1200. Heat treatment was carried out at a temperature of 1200 °C with a heating rate of 245 °C/hour and holding at the maximum temperature for 2 hours. The obtained clinker was ground in a ball mill. It was found that mechanical activation of loess-like rocks in a ball mill for 20 minutes leads to an increase in the content of fine clay and dust fractions from 43.05% to 61.22%, while the proportion of coarse sand particles decreases from 11.57% to 21.05%. At the same time, the specific surface area, compared to the initial raw material, increased from 1750 cm2/g to 2200 cm2/g. The study of the dynamics of changes in the initial sample and fractions after grinding for 20 minutes was carried out using a Shimadzu SALD-7500 laser diffraction analyzer. The results of these studies are presented in the form of histograms in Figure 4.



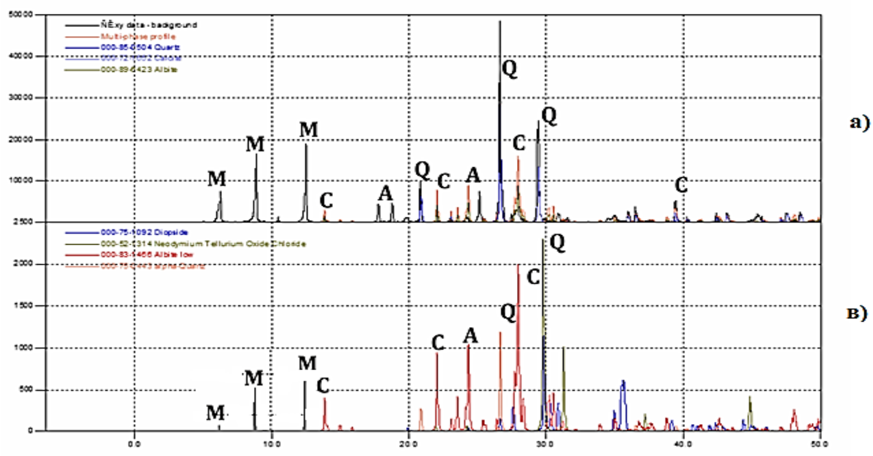
a)



b)

Fig. 4. Histograms illustrating changes in the ceramic mass based on the “loess-defecate” compositions and its particles after mechanical activation: a) original sample; b) sample after mechanical activation for 20 minutes.

It was found that mechanical activation of loess-like rocks in a ball mill for 20 minutes leads to an increase in the content of finely dispersed clay and dust particles from 43.05% to 61.22%, and the amount of coarse sand particles decreases from 11.57% to 21.05%. At the same time, compared to the original raw material, the specific surface area increased from 1750 cm^2/g to 2200 cm^2/g. The dynamics of changes in the initial sample and fractions after grinding for 20 minutes were studied using a Shimadzu SALD-7500 laser diffraction analyzer. The findings are visually represented in the histograms depicted in Figure 4.



Q-quartz, C-calcite, A-albite, M-montmorillonite

Fig. 5. Results of X-ray phase analysis of non-activated (a) and mechanically activated mass (b) for 20 minutes.

Analysis of X-ray patterns of samples subjected to grinding for different periods showed that with increasing grinding duration, characteristic diffraction maxima appear on the diffraction patterns, indicating an increase in the degree of raw material amorphization. Based on this, it can be concluded that the use of this technology in the production of mineral binders provides: increased dispersion and microroughness of raw material particles; high concentration of structural defects both on the surface and in the volume of particles; as well as stabilization of this highly active state before the start of the clinker firing process.

4 Development of a process flow chart

Based on the results of tests carried out in laboratory and semi-industrial conditions, a technological scheme for obtaining a binder was developed, presented in Figure 6.

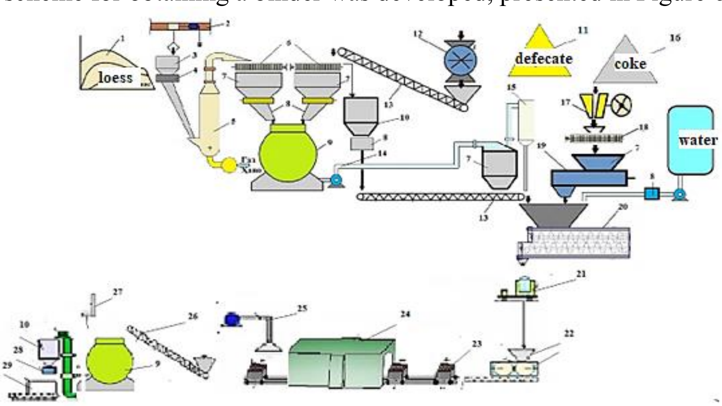


Fig. 6. Flow chart of production of mineral binder composition "loess-defecate": 1- excavation pit; 2-electric hoist-loader; 3-hopper; 4-plate feeder; 5-dryer with aerobic crusher; 6-drum sieve-borer; 7-hoppers; 8-dimensional dispenser; 9-ball mill; 10-coarse fraction hopper; 11-defecate compartment; 12-hammer crusher; 13-conveyors; 14-pneumatic conveyor; 15-cyclone; 16-coke compartment; 17-jaw crusher; 18-sieve; 19-doser hopper; 20-screw mixer; 21- measuring trolley; 22-briquette machine; 23- granule trolley; 24-chamber oven; 25-cooling system; 26-screw conveyor; 27-scales; 28- measuring dispenser; 29-packaging machine.

The conducted studies confirmed the possibility of obtaining a mineral binder using mechanical activation of loess-like rocks of the Suzanli deposit. A new composition of binder solutions with specified color characteristics was developed, taking into account the chemical and mineralogical composition of the original components. To evaluate the binding properties of the developed samples of mineral binder, their physical and mechanical characteristics were determined by the requirements established in GOST 30744-2001. The results of the tests are presented in Table 2. During the studies, it was found that the quality of binders decreases with an increase in the percentage of defecate in the "loess-defecate" mixture. Thus, for mineral binders samples MB-1 and MB-2, the setting time is 45-60 minutes, and complete hardening occurs after 120-150 minutes. While in other compositions, with an increased content of defecate, the initial setting occurs after 80-120 minutes, and complete hardening occurs after 180-210 minutes. The developed material can be used in the restoration and reconstruction of defects in the masonry of walls of historical monuments. In particular, in the presence of deep damage caused by aggressive impacts, when the depth of defects exceeds 3 cm, it is envisaged to remove defective bricks with subsequent replacement with inserts of the required size, fixed with mortar. As a result, a full restoration of defects in the masonry of historical objects is ensured.

Table 2. Physicomechanical properties of mineral binders obtained based on the "loess-defecate" composition.

Samples	Defecate, %	Loess, %	Binder grad GOST 31108 -201 (H 32,5)			km				
								28	14	28
MB-1	70	30	190	60	150	3,0	2,6	5,4	30,3	48,5
MB-2	75	25	200	75	120	3,5	2,8	4,5	34,6	50,4
MB-3	80	20	180	70	160	4,5	2,7	3,7	28,4	45,3
MB-4	85	15	170	80	180	5,0	2,3	3,5	25,5	43,2
MB-5	90	10	160	90	190	5,2	2,2	3,0	20,2	40,4
MB-6	95	5	150	120	210	5,4	2,1	2,5	19,6	38,6

There is a tendency for the grain size of the mineral binder to increase with the content of defecate in its composition. Determination of the bending strength of the developed mineral binders in dynamics showed a decrease in this indicator from 2.8 to 2.1 MPa after 14 days and from 5.4 to 2.5 MPa after 28 days. A similar pattern was observed when determining the compressive strength of mineral binders: the compressive strength decreased from 5.3 to 3.0 MPa after 14 days and from 20.4 to 15.4 MPa after 28 days. As a result, a mineral binder of grade 200 M (strength class H 32.5) with a particle size of 3 μm was obtained. Conclusion.

5 Conclusions

It has been established that during the mechanical activation process, the proportion of fine clay and dust particles increases by 20.01% and 61.12%, while the content of coarse sand particles decreases by 18.87% and the specific surface area increases to 2200 cm2/g, which has a positive effect on the technological properties of loess-like rocks. Changes in the phase composition of "loess-defecate" mixtures during mechanical activation have been revealed.

Based on the conducted research, a process flow chart for the production of a mineral binder based on the "loess-defecate" combination has been proposed, including mechanical activation of raw materials by 20-minute grinding in a F1830×6400 ball mill and the use of defecate (man-made waste) as an additional component, which makes it possible to reduce the clinker firing temperature to 1200 °C. In addition, the developed binder can be used in the creation of building materials intended for the restoration of cultural heritage sites.

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