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ANALYSIS OF CLAY TYPES AND THEIR BINARY SYSTEMS

The objects of study were the Mali Budyshcha and Opishnia clays of two deposits in the Poltava region (Ukraine), binary systems of these clays, and ceramics based on them. It is noted that the efficiency of the practical use of these clays can be increased taking into account the peculiarities of their mineralogical composition. The features of the qualitative mineralogical composition of clays were studied by the methods of chemical, X-ray phase and thermal analysis. The amount of rock-forming minerals was determined using the new computer program «Mineral». It has been established that with an increased content of quartz in both samples, the Mali Budyshcha clay is characterized by a combination of clayey rock-forming minerals – 18.8 % montmorillonite, 12.1 % kaolinite, 17.9 % feldspar and 7 % calcite. According to the intensity of characteristic diffraction peaks and the plane of the endothermic effect with a maximum at 550–575 °C, Opishnia clay is marked by a significantly higher content of kaolinite – 48.1 %. Large values of the quantitative ratio of oxides SiO_2:Al_2O_3 and the content of alkaline earth and alkaline oxides of the RO+R_2O type determine the ratio of Mali Budyshcha clay to the group of low-melting clays with a fire resistance of 1230 °C, in contrast to refractory clay (1620 °C). It has been established that in the range of maximum firing temperatures of 950–1100 °C, samples of Mali Budyshcha clay differ from Opishnia clay in changes in average density from 1.90 to 2.28 g/cm^3 versus 2.00–2.09 g/cm^3, a decrease in water absorption from 15.3 to 5.0 wt % versus 12.0–9.1 wt %. It is shown that the use of binary systems of the studied clays has a significant effect on the chemical and mineralogical composition, the degree of sintering, and the physical and mechanical properties of ceramics. When varying the quantitative ratio of clays from 4:1 to 1:1, the content of kaolinite changes the most – from 19.3 to 30.1 %. An increase in the content of kaolinite in binary systems leads to a gradual expansion of the possible temperature range of firing. At the same time, in comparison with Mali Budyshcha clay, Opishnia clay achieves a decrease in water absorption, an increase in density and strength.

Keywords: *chemical-mineralogical composition of clays, ceramic-technological properties, strength of ceramics, binary clay systems.*

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1. Introduction

The supply of raw materials, which in composition and properties corresponds to the chemical technology for the manufacture of ceramic materials of a certain purpose and assortment, is the basic part of modernization projects for existing and new enterprises [1, 2]. It is clear that the efficiency of such projects increases with approaching the base of raw materials [3–5]. The criteria for determining this base take into account the features of the chemical and mineralogical composition, the processes of structure formation and technology [6]. To a large extent, this concerns the production of ceramic bricks [7, 8].

The technology for manufacturing ceramic bricks has gone through a centuries-old path from the empirical choice of clay raw materials, manual molding, natural drying and low-productive firing to scientifically based industrial production [9, 10]. At the same time, at the first stage, when choosing raw materials, priority was given to its molding properties in terms of plasticity and color after firing. Now more attention is paid to industrial reserves, chemical and mineralogical composition as factors of indicators of technological properties of masses for plastic formation [11, 12] and physical and mechanical properties of brick after drying and firing.

The importance of a comprehensive analysis of the chemical and mineralogical composition of clay raw materials in the development of ceramic masses and optimization of technological parameters was determined by the works [13–15]. Research and development in this direction have been developed [16–18] and have become relevant in the technology of ceramic bricks due to the growing use of polycomponent masses in its production. In this regard, this work has been done.

The objects of research are the Mali Budyshcha and Opishnia clays of two deposits in the Poltava region (Ukraine), binary systems of these clays, and ceramics based on them.

The aim of research is an in-depth analysis of clays and an assessment of the effectiveness of their complex application in ceramics technology.

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2. Research methodology

In this work, modern physicochemical research methods were used [19–21]. Testing of technological and physical-mechanical properties of raw materials and ceramic materials was carried out in accordance with current standards [22, 23].

X-ray phase analysis (powder preparation) was performed using a DRON-2 diffractometer (Russia) (Cu Kα 1–2 radiation, voltage 40 kV, current 20 mA, speed 2 deg/min). Thermal analysis was carried out using a Paulik-Paulik-Erdei (OD-1000) derivatograph (Hungary).

Calculations of the quantitative mineralogical composition of clay were carried out on the basis of data from chemical, X-ray phase and thermal analyzes using the Mineral computer program [24].

In accordance with modern ceramic technology, masses of a certain composition were prepared by dosing components by mass, mixing and homogenization, plastic molding, drying and firing.

All samples of the experimental masses, the performance of which was compared, were dried and burned out together to exclude the possibility of a difference in the degree of heat treatment.

3. Research results and discussion

The investigated raw materials differ significantly in chemical and mineralogical composition and physicochemical properties. According to the qualification of DSTU B V.2.7-60-97 in terms of Al_2O_3 content (Table 1), a sample of Mali Budyshcha clay belongs to the group of acid (14 %), a sample of Opishnia – to semi-acid (14–28 %). At the same time, the sample of Mali Budyshcha clay differs from the pishnia clay by almost twice as much quantitative ratio of oxides SiO_2:Al_2O_3 (6.1 vs. 3.2). And also 3.5 times higher content of alkaline earth CaO+MgO and alkaline Na_2O+K_2O oxides, three times more iron oxides, which generally leads to increased fusibility.

The results of X-ray phase and thermal analyzes indicate significant differences in the studied raw materials in terms of their qualitative mineralogical composition (Fig. 1–4). Obviously, with an increased content of quartz in both samples, the Mali Budyshcha clay is characterized by a combination of clayey rock-forming minerals – montmorillonite, hydromica, kaolinite, feldspar, and calcite. According to the intensity of characteristic peaks (7.14 and 3.57 Å) and the plane of the endothermic effect with a maximum at 550–575 °C, Opishnia clay is distinguished by a significantly higher content of kaolinite.

Table 1

The chemical composition of clay

Sample name	The content of oxides, wt %									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	Na_2O	K_2O	l. o. i
Mali Budyshcha	68.54	11.25	4.43	0.70	4.40	1.22	0.27	0.74	1.96	6.58
Opishnia	65.22	20.38	1.52	1.77	1.10	0.52	0.34	0.22	0.55	8.69

Note: l. o. i. – loss on ignition

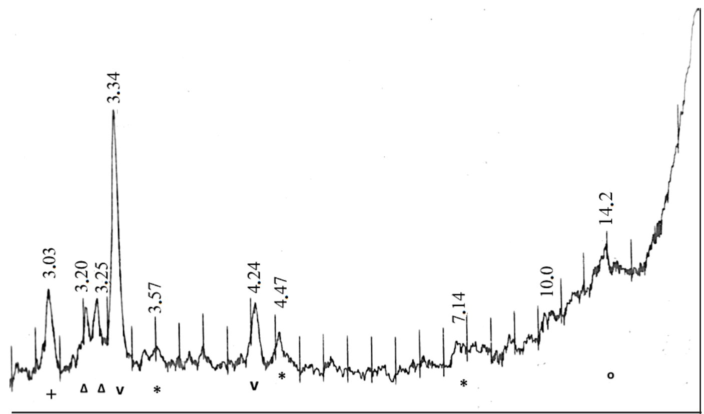


Fig. 1. X-ray diffraction pattern of Mali Budyshcha clay: v – quartz; ✳ – kaolinite; o – montmorillonite; Δ – feldspar

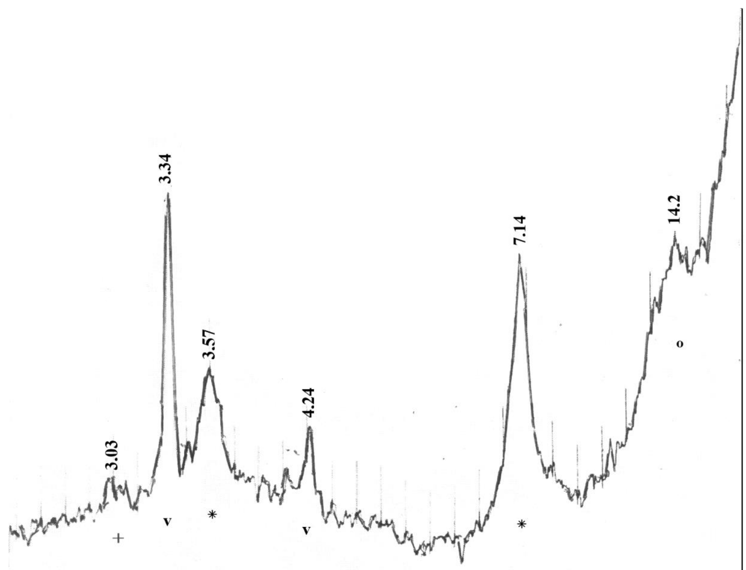


Fig. 2. X-ray diffraction pattern of Opishnia clay: v – quartz; ✳ – kaolinite; + – calcite; o – montmorillonite

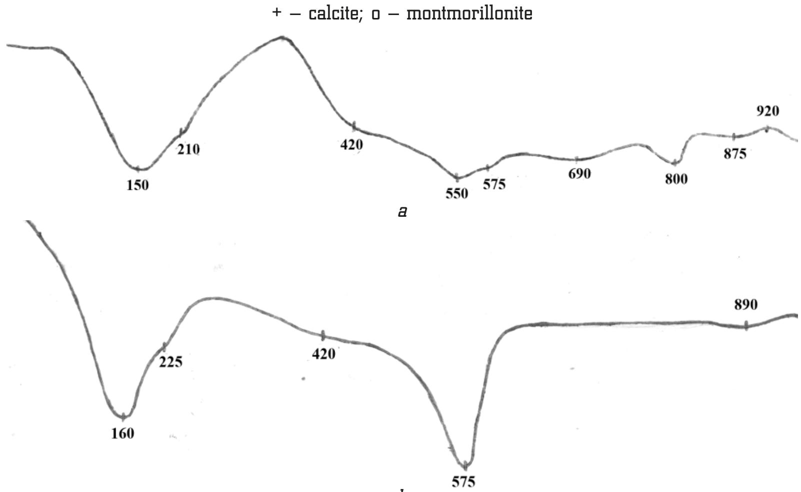


Fig. 3. X-ray diffraction pattern of clay samples: *a* – Mali Budyshcha; *b* – Opishnia

According to the results of computer calculations of the quantitative mineralogical composition according to the qualification of DSTU B V.2.7-60-97, a sample of Mali Budyshcha clay belongs to the group of polymineral clays, and a sample of Opishnia clay belongs to montmorillonite-kaolinite (Table 2).

In terms of fineness (Table 3), a sample of Mali Budyshcha clay, according to the content of 8.6 wt % of particles of fractions <0.001 mm, belongs to coarsely dispersed ones, according to the content of 46.8 wt % of particles of fractions <0.01 mm – to low-dispersed ones. 19.25 wt % of particles of fractions <0.001 mm refers to low-dispersion, according to the content of 65.05 wt % of particles of fractions <0.01 mm – to medium-dispersed.

These characteristics of the chemical-mineralogical composition and dispersion of the studied clays determine the indicators of their ceramic-technological properties.

Thus, the low-dispersion, low-dispersion Mali Budyshcha clay differs from the highly plastic Opishnia clay by more than 3.5 times less plasticity number and belongs to the group of moderately plastic ones (Table 4).

Table 2

Mineralogical composition of clay

Clay	The content of rock-forming minerals, wt %							
	kaolinite	montmo-rillonit	quartz	microcline	albite	calcite	iron hy-droxides	rutile
Mali Budyshcha	12.1	18.8	41.3	11.6	6.3	7.0	4.0	0.7
Opishnia	48.1	8.0	38.5	–	–	1.6	1.3	1.8

Table 3

Clay dispersion

Sample	Content (%) of particle fractions (mm), %					
	>0.25	0.25–0.05	0.05–0.01	0.01–0.005	0.005–0.001	<0.001
Mali Budyshcha	0.13	0.62	52.45	18.25	20.00	8.55
Opishnia	3.04	4.31	25.60	20.30	25.50	19.25

Table 4

Ceramic-technological properties of clay

Sample	Properties indicators	
	plasticity number	fire resistance, °C
Mali Budyshcha	7.9	1230
Opishnia	28.6	1620

Large values of the quantitative ratio of oxides $SiO_2:Al_2O_3$ та and the content of alkaline earth and alkaline oxides of the $RO+R_2O$ type determine the degree of refractoriness of Mali Budyshcha clay, which, according to DSTU B V.2.7-60-97, belongs to the group of fusible, in contrast to refractories.

The tests carried out made it possible to assess the degree of sintering of the studied clays during firing. It has been established (Fig. 4) that in the range of maximum firing temperatures of 950–1050 °C, both samples are characterized by the same intensity of changes in water absorption and average density. However, the levels of these indicators differ.

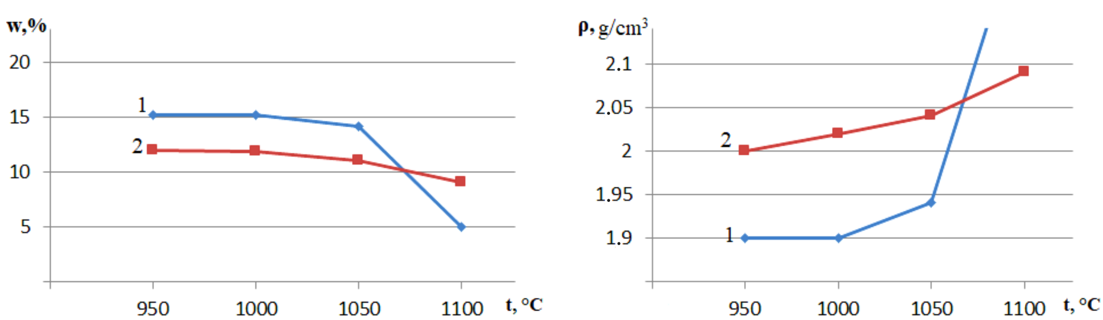
Significant differences in sintering appear with an increase in the maximum firing temperature. In the range of 1050–1100 °C, samples of Mali Budyshcha clay are characterized by an increase in shrinkage from 1.0 to 5.4 %, an average density from 1.94 to 2.28 g/cm^3, and a decrease in water absorption from 14.2 to 5.0 wt %.

The use of binary systems of the investigated raw materials with varying the quantitative ratio of Mali Budyshcha and Opishnia clays from 4:1 to 1:1, which made it possible to evaluate the effect of changes in the chemical and mineralogical composition on the degree of sintering and physical and mechanical properties of ceramics.

The analysis performed shows (Table 5) that with the indicated variation in the quantitative ratio of the studied clays, the content of kaolinite changes the most – from 19.3 to 30.1 % or by 10.8 %.

The content of other rock-forming minerals varies much less: montmorillonite and microcline by 3.2–3.5 %, calcite and albite by 1.6–1.8 %, quartz and iron hydroxides by 0.8–0.9 %, rutile by 0.3 %.

As the test results show (Table 6), an increase in the content of kaolinite in binary systems leads to a gradual expansion of the possible temperature range of firing, while, compared with Mali Budyshcha clay, a decrease in water absorption, an increase in density and strength is achieved.



a *b*

Fig. 4. Dependence of water absorption and density of ceramics from Mali Budyshcha and Opishnia clay on firing temperature: *a* – water absorption *w*; *b* – density ρ; 1 – Mali Budyshcha clay; 2 – Opishnia clay

Table 5

Mineralogical composition of clay

Sample code	Quantitative ratio of clays	The content of rock-forming minerals, wt. %							
		kaolinite	montmorillonit	quartz	microcline	albite	calcite	iron hydroxides	rutile
M53	4:1	19.3	16.6	40.7	9.3	5.0	5.9	3.5	0.9
M54	7:3	22.9	15.6	40.5	8.1	4.4	5.4	3.2	1.0
M55	3:2	26.5	14.5	40.2	7.0	3.8	4.8	2.9	1.1
M56	1:1	30.1	13.4	39.9	5.8	3.2	4.3	2.6	1.2

Table 6

Physical and mechanical properties of ceramics

Sample code	Temperature range of firing, °C	Water absorption, wt. %	Average density, g/cm^3	Bending strength, MPa
M53	950–1100	14.2–10.1	1.94–2.07	15–25
M54	950–1150	13.7–1.9	1.96–2.37	16–41
M55	950–1200	12.4–1.6	1.99–2.26	18–29
M56	950–1200	13.2–3.7	1.96–2.22	14.5–30

The direction of the effective use of the data of the above analysis can be the production of ceramic bricks with an increase in the strength of products (Fig. 5).

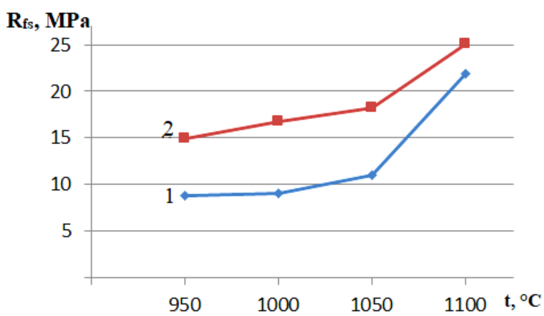


Fig. 5. Strength of ceramics made of: 1 – Mali Budyshcha clay; 2 – binary mass

This study is limited to the clay varieties of the two deposits. However, the possibility of controlling the composition and properties of ceramics when using binary systems of clays of different mineralogical types can be implemented in other similar developments.

Promising directions for the further development of this research are the development of technological parameters for the production of ceramic bricks and consumer goods with the integrated use of polymineral Mali Budyshcha and montmorilonite-kaolinite Opishnia clays.

4. Conclusions

According to the instrumental methods of analysis, the features of the qualitative mineralogical composition of the Mali Budyshcha and Opishnia clays of the Poltava region deposits were determined and computer calculations of the mineral content were carried out. It has been established that with an increased content of quartz in both samples, the Mali Budyshcha clay belongs to polymineral clay, and the Opishnia clay belongs to motmorilonite-kaolinite clay.

Large values of the quantitative ratio of oxides SiO_2:Al_2O_3 and the content of alkaline earth and alkaline oxides of the RO+R_2O type determine the ratio of Mali Budyshcha clay to the group of low-melting clays with a fire resistance of 1230 °C, in contrast to refractory clay (1620 °C).

It has been established that in the range of maximum firing temperatures of 950–1100 °C, samples of Mali Budyshcha clay differ from Opishnia clay in changes in average density from 1.90 to 2.28 g/cm^3 versus 2.00–2.09 g/cm^3, a decrease in water absorption from 15.3 to 5.0 wt. % versus 12.0–9.1 wt. %.

It is shown that the use of binary systems of the studied clays made it possible to significantly influence the chemical and mineralogical composition, the degree of sintering, and the physical and mechanical properties of ceramics. When varying the quantitative ratio of clays from 4:1 to 1:1, the content of kaolinite changes the most – from 19.3 to 30.1 %. An increase in the content of kaolinite in binary systems leads to a gradual expansion of the possible temperature range of firing. At the same time, in comparison with Mali Budyshcha clay, Opishnia clay achieves a decrease in water absorption, an increase in the density and strength of ceramics.

Conflict of interests

The authors declare that there is no conflict of interest regarding this study, including financial, personal nature, authorship or other nature that could affect the research and its results presented in this article.

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Data availability

Data will be provided upon reasonable request.

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