Studying The Composition And Properties Of Binary Clay Systems

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Abstract

The article presents results of study of the composition and properties of clays taken from two deposits in the Kyiv region. The features of the mineralogical composition of clays were determined by the methods of instrumental analysis and computer calculations. The possibility of regulating the mineralogical composition of ceramic masses based on binary systems of clays was noted. The effect of improvement of physical and mechanical parameters of ceramics from the raw materials studied is shown.

Keywords: *clay, composition, properties, firing, phase formation, ceramics.*

Introduction

Formulation of the problem. Providing raw materials, which in terms of composition and properties correspond to the technological possibilities of manufacturing ceramic materials of a certain purpose and assortment, is a problematic component of the work of existing and projects for the creation of new enterprises [1-3].

Relevance of research. The solution to this problem is connected with the constant involvement in the technological processes of ceramic production of new types of raw materials of different genesis, which increases the relevance of a comprehensive analysis of the composition and properties of the raw materials.

The purpose and objectives of the article. The aim of this work was a comprehensive analysis of the features of the composition and technological properties of clays from two deposits of the Kyiv region, as a raw material base for the restoration and development of the regional production of building ceramics.

Analysis of research and publications. The technology of ceramics manufacturing has passed a centuries-old path from the empirical selection of clay raw materials, manual shaping, natural drying and low-productive firing to scientifically based industrial production [4]. At the same time, at the first stage, when choosing raw materials, primary importance was attached to its formative properties in terms of plasticity and color after firing, and in modern times - industrial stocks, chemical and mineralogical composition as factors of indicators of technological properties of masses and physical and mechanical characteristics of products after drying and firing [5 - 7].

The criteria for the selection of ceramic raw materials take into account the peculiarities of the chemical and mineralogical composition, structure formation processes and technology [7].

The importance of a complex analysis of the chemical and mineralogical composition of clay raw materials for the development of ceramic masses and optimization of technological parameters is substantiated by well-known works [8-10]. Research and development in this direction have been developed [11-14] and have become relevant due to the constant expansion of the raw material base for the production of ceramics.

At the same time, is clear that the efficiency of enterprises increases with the approach to a raw material base [15-17], in the direction of which the presented work was performed.

Experimental part

This work used a combination of modern physical-chemical research methods with standardized testing of technological and operational properties of raw materials and ceramic materials [18-21].

X-ray phase analysis (powder preparation) was performed using a DRON-2 diffractometer (Cu Kα 1-2 radiation, voltage 40 kV, current 20 mA, speed 2 degrees/min), thermal analysis - using a derivatograph of the Paulik-Paulik-Erdei system (OD-1000).

Calculations of the quantitative mineralogical composition of the clay were carried out on the basis of data obtained from chemical, X-ray phase and thermal analyzes using the computer program "Mineral" [22].

According to the modern technology of ceramics, the mass of the specified composition was prepared by dosing the components by mass, mixing and homogenization, plastic forming, drying and firing.

All samples of experimental masses, the indicators of which were compared, were dried and fired together in order to exclude the possibility of a difference in the degree of heat treatment.

The objects of the study were Shakhrovska and Muzychanska clay deposits of the Kyiv region, the binary systems of these clays and ceramics based on them.

The studied raw materials differ significantly in terms of their chemical and mineralogical composition and physical and chemical properties.

According to the qualifications of DSTU B V.2.7-60-97, according to the content of Al_2O_3 (Table 1), the sample of Shakhrovska clay belongs to the semi-acidic group (14-28 %), the Muzychanska clay sample belongs to the acidic group (< 14 %). At the same time, the sample of Muzychanska clay differs from that of Shakhrovska by a higher quantitative ratio of SiO_2: Al_2O_3 oxides (5.4 vs. 3.9), a larger amount of alkaline oxides Na_2O+K_2O (1.9 vs. 0.1%) and iron oxides, which generally cause increased melting point

Table 1. **Chemical composition of clay raw materials**

Sample	*Content of oxides, %*									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	Na_2O	K_2O	в.п.п
Shakhrovska	68.25	17.40	3.83	0.98	0.94	0.50	0.03	-	0.06	8.20
Muzychanska	71.51	13.13	5.10	0.87	1.34	1.01	0.27	0.20	1.17	5.44

The results of X-ray phase and thermal analyzes show that the samples of the studied raw materials are characterized by approximately the same qualitative mineralogical composition (Figs. 1-3). At the same time, a comparison of the intensity of characteristic shown by X-ray peaks and planes of endothermic effects indicates a relatively higher content of kaolinite in the sample of Shakhrovska clay, and montmorillonite in the sample of Musychan clay.

According to the quantitative mineralogical composition (Table 2), both samples are close to the group of montmorillonite-kaolinite clay raw materials, but differ significantly in the content of the main rock-forming minerals. The quantitative ratio of minerals – kaolinite : montmorillonite : quartz is 5.3:1:5.9 for the Shakhrovska clay and 1.5:1:3.1 for the Muzychanska clay. At the same time, Muzychanska is also distinguished by the presence of a significant amount of feldspars.

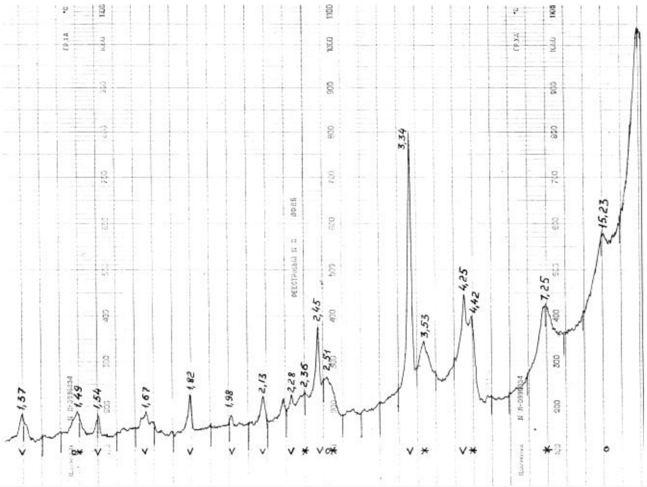

Figure 1. X-ray diffraction of Shakhroivske deposit sample: v quartz, * kaolinite, o montmorillonite

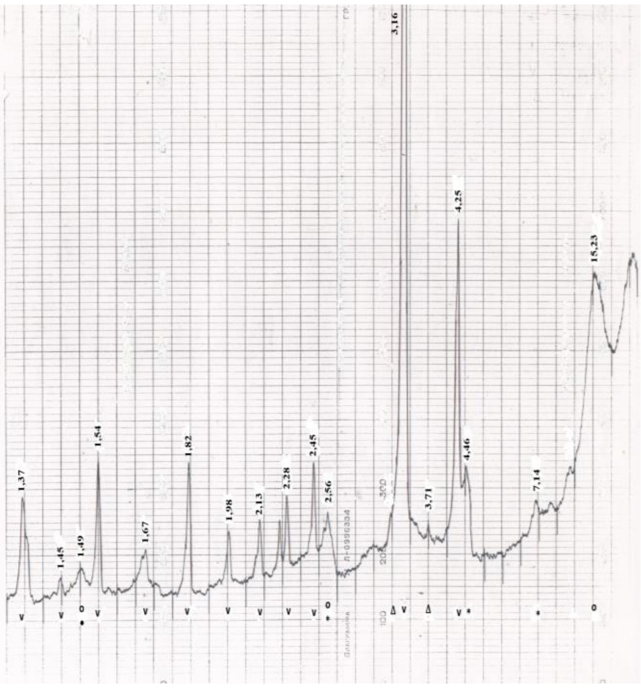

Figure 2. X-ray diffraction of Muzechanske deposit sample: v quartz, * kaolinite, o montmorillonite, ∆ feldspar

Table 2. **Mineralogical composition of clay raw materials**

Sample	*Mineral content,%*				
	kaolinite	montmorillonite	quartz	iron hydroxides	feldspar
Shakhrovska	40.8	7.7	45.3	3.8	-
Muzychanska	23.5	15.5	48.0	4.9	6.9

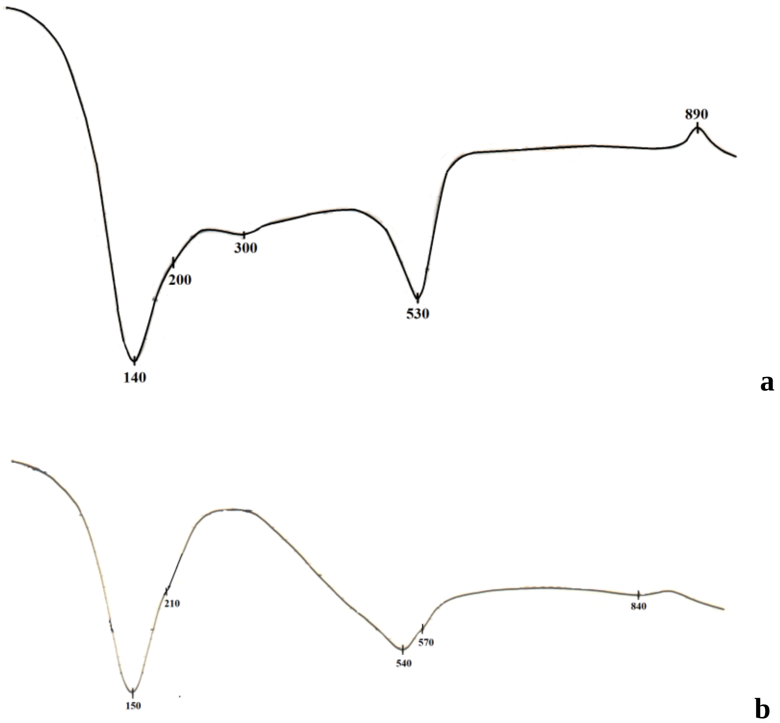

Figure 3. DTA samples of Shakhrovska (a) and Muzychanska (b) clay

According to dispersion (Table 3), the sample of Shakhrovska clay with a content of 119.5 wt.% of particles of fractions < 0.001 mm belongs to low dispersion, and with a content of 70.5 wt.% of particles of fractions < 0.01 mm - to medium dispersion. The sample of Muzichanska clay with a content of 22.85 wt.% of particles of fractions < 0.001 mm and 52.55 wt.% of particles of fractions < 0.01 mm belongs to low dispersion.

Table 3. **Dispersion of clay raw materials**

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
Shakhrovska	4,71	8,14	16,65	18,65	32,35	19,50
Muzychanska	0,67	1,18	45,60	17,35	12,35	22,85

The specified characteristics of the chemical and mineralogical composition and dispersity of the studied clays determine the indicators of their ceramic and technological properties.

The analysis of ceramic-technological properties showed (Table 4) that according to the plasticity of the test clay samples according to DSTU B V.2.7-60-97 they belong to 2 groups: Shakhrovska - highly plastic (number >25), Muzychanska - moderately plastic (number 7-15).

Shahrovska clay belongs to the refractory groups (>1580 °C). Muzychanska - to the low-melting group (< 1350 °C).

Table 4. **Plasticity and fire resistance of clay raw materials**

Sample	*Property indicators*	
	plasticity numbe	fire resistance,**^{0}C**
Shakhrovska	25.8	1610
Muzychanska	13.4	1150

The conducted tests revealed significant differences in the degree of sintering of the studied clays during firing (Fig. 4). Clay samples of Muzychanska clay in the range of maximum firing temperatures of 950-1150 °C differ from those of Shakhrovska clay by lower water absorption (12.0-5.7 vs. 15.0-10.5 wt.%) and higher average density (2.00-2. 26 against 1.90 - 2.11 g/cm^3). However, in the range of maximum firing temperatures of 950-1050 °C, samples from Musychanska clay are inferior to samples from Shakhrovska clay in terms of flexural strength, which is 6.0-10.6 against 10.2-14.2 MPa.

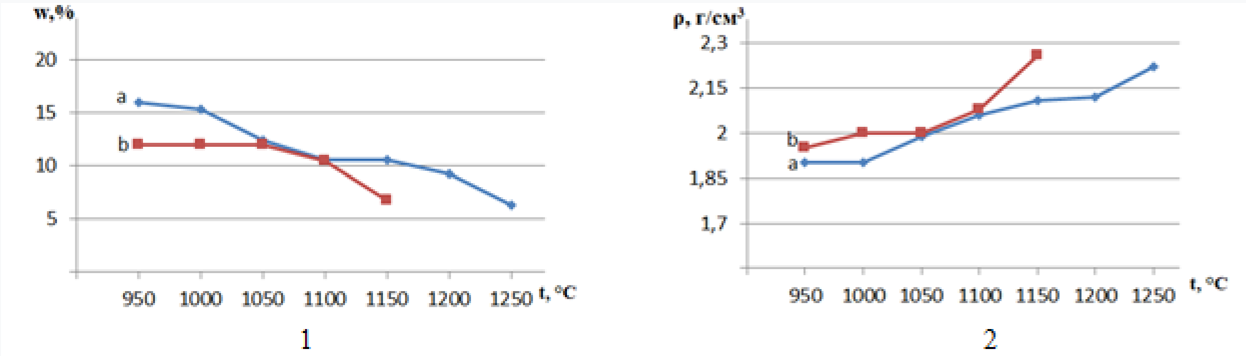

Figure 4. Dependence of water absorption w (1) and density ρ (2) of Shakhrovska (a) and Muzychanska (b) clay ceramics on the firing temperature

The use of binary systems of the raw materials studied made it possible to evaluate the influence of changes in the chemical and mineralogical composition on the degree of sintering and physical and mechanical indicators of ceramics.

It is obvious (Table 5) that with the variation of the quantitative ratio of Shakhrovska and Muzychanska clays from 4:1 to 1:4 in relation to the chemical composition, there is a change in the quantitative ratio of SiO_2: Al_2O_3 oxides from 4.2 to 5.1, the amount of alkaline oxides Na_2O+ K_2O from 0.3 to 1.1% and iron oxides from 4.1 to 4.9%.

Table 5.**Chemical composition of binary masses**

Mass code	*Content of components,%*		*Chemical composition, %*				
	Shakhrovska clay	Muzychanska clay	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O
K24	80	20	68.90	16.55	4.08	0.04	0.28
K23	60	40	69.55	15.69	4.34	0.08	0.50
K22	50	50	69.88	15.26	4.46	0.10	0.62
K21	40	60	70.21	14.84	4.59	0.12	0.73
K20	20	80	70.86	13.98	4.85	0.16	0.95

As for the mineralogical composition (Table 6), with the indicated variation of the ratio of components in binary systems, the quantitative ratio of the main rock-forming minerals changes – kaolinite: montmorillonite: quartz from 1.9:1:3.4 (K20) to 4:1: 4.9 (K24).

Table 6. **Mineralogical composition of binary masses**

Mass code	Quantitative ratio of clays	*Mineral content, %*				
		kaolinite	montmorillonite	quartz	iron hydroxides	feldspar
K24	4:1	37.3	9.3	45.8	4.0	1.4
K23	3:2	33.9	10.8	46.4	4.2	2.8
K22	1:1	32.2	11.6	46.6	4.4	3.4
K21	2:3	30.4	12.4	46.9	4.4	4.1
K20	1:4	27.0	13.9	47.5	4.5	5.5

As the results of testing (Table 7) show, changes in the mineralogical composition of binary systems significantly affect the properties of ceramics. Thus, in the interval of maximum firing temperatures of 950-1100 0C, ceramic samples from mass K22 differ from samples from Musychanska (m1) and Shakhrovska (sh1) clays by lower water absorption, greater density and strength.

Table 7. **Physical and mechanical properties of ceramics**

Sample code	Temperature firing interval,^{0}C	*Property indicators*		
		water absorption,%	density, g/sм^3	bending strength, MPa
m1	950-1100	12.7-10.4	1.95-2.08	6.0-12.9
sh1	950-1100	16.0-10.6	1.90-2.06	10.2-14.2
K22	950-1100	10.2-6.3	2.08-2.24	14.8-19.6

This effect is also manifested when using high-speed firing modes. So, when fired in a roller furnace at a maximum temperature of 1020 °C for 42 minutes. ceramic samples from the K22 mass are characterized by a bending strength of 21.2 MPa against 7.8 MPa for samples of Muzychanska clay and 13.2 MPa for samples of Shakhrovska clay.

A number of specified features of physical and mechanical indications have been established with the special features of the structural characteristics of ceramics prepared from the additional binary masses.

So, according to the data of X-ray phase analysis (Fig. 5), the samples from the K22 mass after firing at a maximum temperature of 950 ° C are characterized by the rumination of the ridges of the main rock-forming minerals - kaolinite and montmorillonite, the presence of a system of crystalline phases of quartz-hematite with a small amount of glass phase (over the area of diffuse halo).

At the maximum temperature of firing1050 °C, there is an increase in the number of glass phase and hematite and an ear of modifying transformation of β-quartz into α-cristobalite. With a further increase in the maximum temperature, the processes intensify. with the development of a system of crystalline phases mullite-cristobalite-quartz-hematite.

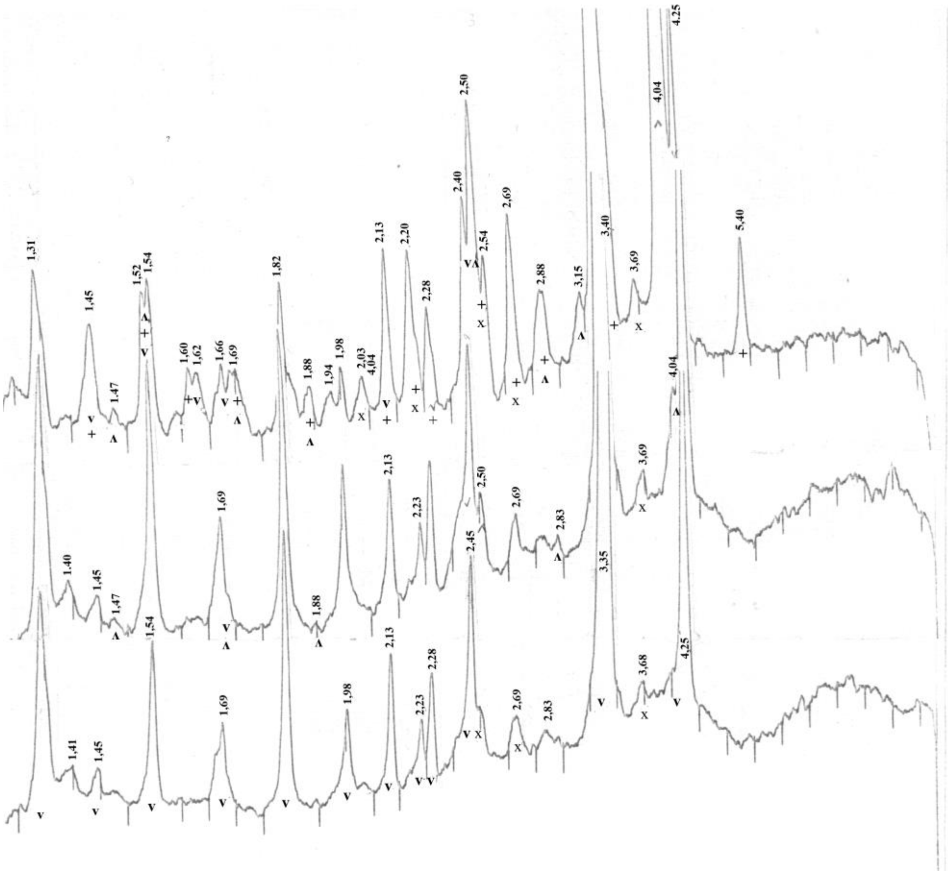

Figure 5. X-ray diffraction of samples K22 after firing on 950 (a), 1050 (b), 1250 °C (c):

v quartz, ^ cristobalite, + mullite, x hematite

The results of porosity determination are correlated with the above data on the degree of sintering and the development of the glass phase (Table 8).

Table 8. **Dependence of porosity of K22 ceramics on iring temperature**

Types of porosity	Maximum firing temperature,°C		
	950	1050	1250
general	21.3	16.1	15.1
open	21.2	15.7	12.2
closed	0.1	0.4	2.9

Conclusions

Employment of compositions of clay raw materials of different chemical and mineralogical composition is one of the effective means of influencing the technological parameters and properties of ceramics.

Usage of binary systems of clays studied allows to adjust the quantitative ratio of rock-forming minerals, the degree of dispersion and plasticity, to influence the formation of phase composition and porosity during firing with an improvement of the physical and mechanical characteristics of ceramics.

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