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SYNTHESIS OF MAYOLICA MATERIALS COMPATIBLE WITH HISTORICAL ARCHITECTURAL TILES BASED ON LOCAL MINERAL RESOURCES.

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Abstract: The issue of developing compositions and technological parameters compatible with traditional mayolica materials used in historical monuments, creating ceramic products with high strength and aesthetic characteristics based on local raw materials is considered. A ceramic mass was formed based on Kattabog clay soil, Angren secondary- grey kaolin, aluminosilicate raw materials, and the technological conditions of the firing process were analyzed. The composition of the samples was analyzed using a dispersive X-ray fluorescence spectrometer (XRF), structural bonds and functional groups were characterized using infrared (IR) spectroscopy. Absorption peaks in the range of 909–786 cm^{-1} in the spectrum indicate the presence of tetrahedral coordination [AlO_4] structural units of aluminum. This condition is explained by the restructuring of the aluminosilicate lattice during the firing process, the formation of high-temperature stable phases. The possibility of creating mayolica ceramic materials with physico-mechanical, structural properties compatible with historical architectural tiles based on local raw materials is scientifically substantiated.

Keywords: Mayolica, phase composition, peak, firing range, aluminosilicate lattice, tetrahedral coordination.

Annotatsiya: Tarixiy obidalarda qoʻllanilgan an’anaviy mayolika materiallariga mos tarkib va texnologik parametrlarni ishlab chiqish hamda mahalliy xomashyo asosida yuqori mustahkamlik va estetik xususiyatlarga ega keramika mahsulotlarini yaratish masalasi koʻrib chiqiladi. Kattabogʻ soztuprogʻi, Angren ikkilamchi kulrang kaolini va alumosilikat xomashyolari asosida sopolak massa shakllantirilib, kuydirish jarayonining texnologik sharoitlari tahlil qilindi. Namunalar tarkibi dispersion rentgen-fluoresansiyali spektrometr (XRF) orqali tahlil qilinib, infraqizil (IQ) spektroskopiya yordamida strukturaviy bogʻlanishlar va funksional guruhlar tavsiflanadi. Spektrda 909–786 sm^{-1} oraligʻidagi yutilish choʻqqilari alyuminiyning tetraedrik koordinatsiyadagi [AlO_4] strukturaviy birliklari mavjudligini koʻrsatadi. Mazkur holat pishirish jarayonida alumosilikat panjaraning qayta tuzilishi hamda yuqori haroratda mustahkam fazalar shakllanishi bilan izohlanadi. Mahalliy xomashyolar asosida tarixiy me’moriy koshinlarga mos fizik-mexanik va strukturaviy xususiyatlarga ega mayolika keramika materiallarini yaratish imkoniyati ilmiy jihatdan asoslanadi.

Kalit so’zlar: Mayolika, faza tarkib, pik, pishish orolig’i,alyuminiysilikat panjarasi, tetraedrik koordinatsiya.

Аннотация: В данной работе рассматриваются вопросы разработки оптимальных составов и технологических параметров традиционных майоликовых материалов, сопоставимых с образцами, использованными в исторических памятниках. Целью исследования является создание керамических изделий с высокими прочностными и эстетическими характеристиками на основе местного сырья. На базе суглинка месторождения Каттабог, вторичного серого каолина Ангренского месторождения а также алюмосиликатного сырья. Далее была сформирована керамическая масса и проанализированы технологические условия процесса обжига. Состав образцов был изучен с помощью рентгенофлуоресцентного спектрометра (XRF), а структурные связи и функциональные группы охарактеризованы методом инфракрасной (ИК) спектроскопии. Пики поглощения в диапазоне 909–786 см$^{-1}$

в спектре указывают на наличие структурных единиц алюминия в тетраэдрической координации [AlO_4].

Данное явление объясняется перестройкой алюмосиликатной решетки в процессе обжига и формированием высокопрочных фаз при высоких температурах. Научно обоснована возможность создания майоликовых керамических материалов на основе местного сырья, обладающих физико-механическими и структурными свойствами, идентичными историческим архитектурным изразцам.

Ключевые слова: Майолика, фазовый состав, пик, интервал обжига, алюмосиликатная решётка, тетраэдрическая координация.

Introduction

National architectural heritage is considered one of the vital factors defining the spiritual identity of a nation. In particular, the samples of tiles and majolica used in the decoration of historical monuments are a vivid expression of high artistic, technological potential. Such examples of art are widely manifested in the historical monuments located in our country, specifically in the cities of Bukhara, Samarkand and Khiva.

Presently, preserving and restoring national architectural heritage, as well as its integration into modern construction practices, is considered one of the most pressing tasks. From this perspective, developing a technology for producing mayolica ceramics similar to monumental tiles based on local raw materials holds significant scientific along with practical importance. Utilizing local resources such as Kattabog clay soil and Angren secondary-grey kaolin enables the reduction of product costs, facilitates import substitution, and ensures ecologically sustainable production.

Research Methods and the Received Results

The following analytical methods along with equipment were utilized during the study: elemental analysis via the X-ray spectral method was performed using a SEM EVO MA 10 scanning electron microscope; diffraction analysis was conducted using the powder method on Shimadzu equipment. Infrared spectroscopy (IR spectroscopy), a category of molecular spectroscopy analysis, was employed to investigate the chemical composition as well as, structure of substances by examining the light transmission and reflection spectra of atoms and molecules. In this process, the sample was prepared in the form of a tablet using KBr powder; to obtain high-quality spectra, the particle size of the substance must reach a dispersion level of 2-7 μm.

The kaolin mineral resources in Angren are categorized into two types based on their genetic origin: primary and Angren secondary-grey kaolin [1]. Secondary kaolins are found in grey and reddish varieties. In the process of enriching the AKF-78 grade of kaolin, both grey and reddish varieties of secondary kaolin are utilized.

The physico-mechanical properties of Angren secondary- kaolin are as follows: forming moisture is 21.5%, plasticity relative to Atterberg is 15.58%, drying sensitivity coefficient is 0.68, linear shrinkage coefficient is 6.52%, strength is 2.90 MPa, and bulk density is 1.88 g/cm^3. The plasticity level of Angren secondary kaolin varies within the range of 9 to 15.

Mineralogical compounds of kaolin are mainly divided into two groups. The first group consists of coarse-grained relic minerals. Quartz-potassium feldspar, sericite, garnet, and sillimanite are also added to this. The second group also includes finely dispersed relic minerals of hypergene soils (quartz change, feldspar, fine-grained sericite). Among the soil minerals, kaolin minerals occupy the main place, and the prepared composition, as a result of its heating, produces montromollinite with a mixture layer of hydromica. When obtaining saturated kaolin, minerals in the soil, in which 110% kaolin is absent, naturally influence the technological process. When purifying saturated kaolin, it contains at least 2.0-2.5% mineral impurities. In Europe, saturated kaolin contains 90.4-93.1% kaolinite, 3.2-6.8% muscovite, 1.7-3.3% quartz. The main role in the composition of the mineral kaolin is played by the minerals of the following groups: kaolinite, halloysite, dikkit, and nacrite. All of them structurally represent polymorphic modifications of aluminum silicate: : $Al_2Si_2O_5(OH)_4$, structurally SiO_2 46,54 %; $Al_2O_3$39,5 %; H_2O13,96 % [2-7]. The viscosity of secondary reddish Angren kaolin is characterized by its high sensitivity to iron compounds.. Primary saturated Angren kaolin is characterized by lower viscosity compared to secondary kaolin.

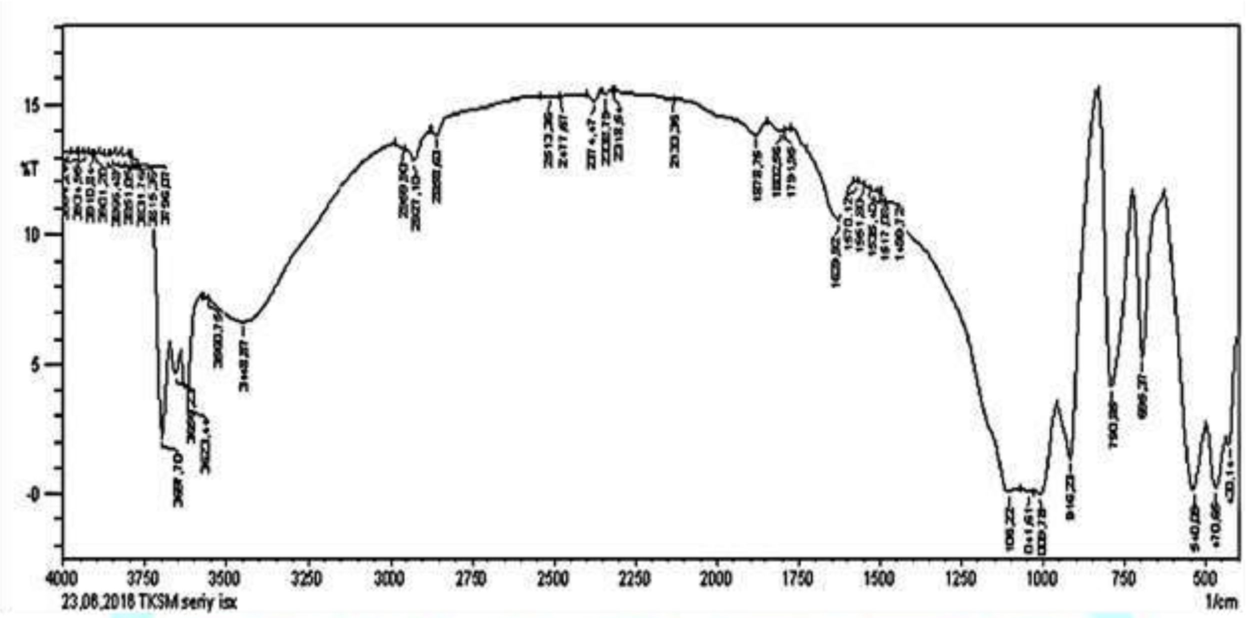

Figure 1. IR spectrum image of Angren secondary grey kaolin.

The α-quartz characteristic of kaolins was identified in the IR spectrum for secondary- kaolin at: 471, 540, 695, 790, 1107 cm^{-1}. The detection of α-quartz peaks in the kaolin sample indicates the presence of free quartz (SiO_2) within the kaolin composition, showing that this quartz is not bound to the kaolinite crystal lattice. The presence of quartz reduces shrinkage during drying, ensures shape stability during firing, and acts as a skeleton (framework). Absorption peaks observed in the 471, 540, 695, 790, 1107 cm^{-1} ranges of the IR spectrum results confirm the presence of the α-quartz phase, the secondary genesis of the studied kaolin sample, as well as, the existence of a free SiO_2 phase within its composition.

To determine the oxide composition of Kattabog clay soil, a high-capacity energy-dispersive X-ray fluorescence spectrometer was utilized. Specifically, the Rigaku NEXCG technology was employed, which features secondary monochromatic excitation and an optical core in a decorative geometry. According to the chemical analysis results, the presence of the following elemental oxides was identified in the soil sample:

Table 1.

Oxide composition of Kattabog clay soil

№	Oxide	Concentration, %
1	Na_2O	2,089
2	MgO	3,054
3	Al_2O_3	13,36
4	SiO_2	58,67
5	SO_3	0,1073
6	K_2O	2,516
7	CaO	10,29
8	Fe_2O_3	5,264
9	CoO	<0,0014
10	Se	0,00008
11	CeO_2	0,0115

Based on the results of the chemical analysis, the presence of 13.36% Al_2O_3 in the soil suggests it belongs to the acidic soil class ; however, the Fe_2O_3 content was found to be 5.264%. Consequently, it is classified as belonging to the medium acidic class.

The plasticity and sand content of the soil sample were investigated under laboratory conditions.

The soil is yellowish in color along with possesses plastic properties; the following results were obtained: the plasticity was determined using the cone apparatus method at 7%, while the sand content was 3.27%. Consequently, this clay soil is considered a plastic raw material and complies with the requirements of UzDSt 2294:2011 [8].

The reserves of local raw material—Kattabog clay soil—were studied for the production of construction industry products, specifically ceramic mayolica, also it was among the first to be applied to the production of mayolica with high physico-chemical properties. The phase composition of Kattabog clay soil was determined using modern physico-chemical analysis methods, including the X-ray spectral method, X-ray fluorescence spectrometer, electron microscopic imaging, and IR spectroscopic analysis; its primary phases consist of kaolinite, quartz, muscovite, orthoclase, and calcite. As a result of investigating the Kattabog soil reserves, it was determined that this soil belongs to the main type of secondary soils—the 'clay' class—and was studied based on physico-chemical analyses [9-10].

The ceramic mass, prepared from local raw materials—Kattabog clay soil, Angren secondary- grey kaolin, and Surxandaryo soil—for mayolica ceramics, was produced under laboratory conditions using the semi-dry pressing method. The required amounts of the mass components were placed in a porcelain mill for grinding, to obtain a slip with 34–35% moisture content. After the mass was dehydrated, a press-powder with a moisture content of 6–7% was formed. The grinding process continued until the residue on a 0063 mesh sieve was no more than 1.5%.

For the conducted research and analysis of the properties, chemical and mineralogical compositions of natural raw materials, a number of raw materials were selected to fulfill the set task. Ceramic mass was prepared under laboratory conditions by the semi-dry pressing method. The required quantities of the batch components were finely ground and introduced into a ball mill to produce a ceramic slip with a moisture content of 34–35%.After dehydration, a press-powder with a moisture content of 6-7% was formed. Grinding continued from a 0.063 sieve to a content of no more than 1.5%. To select the optimal composition of the ceramic mass, the dependence of water absorption, shrinkage, strength, and thermal expansion coefficients on the composition of the experimental samples, fired at a temperature of 1000-1050-1100 ^{0}C, was studied by the Appin method.

The compositions under study were selected based on their physicotechnical properties. OS-5 was chosen as the optimal mass for the majolica pottery. This ceramic was fired at 1100°C and kept in the oven for 1 hour. Expected result achieved:

Figure 2. shows the composition selected as optimal, mass index-OS-4

Infrared spectroscopy (IR spectroscopy), a molecular spectroscopy analysis method, was utilized to study the structure of the ceramic body.

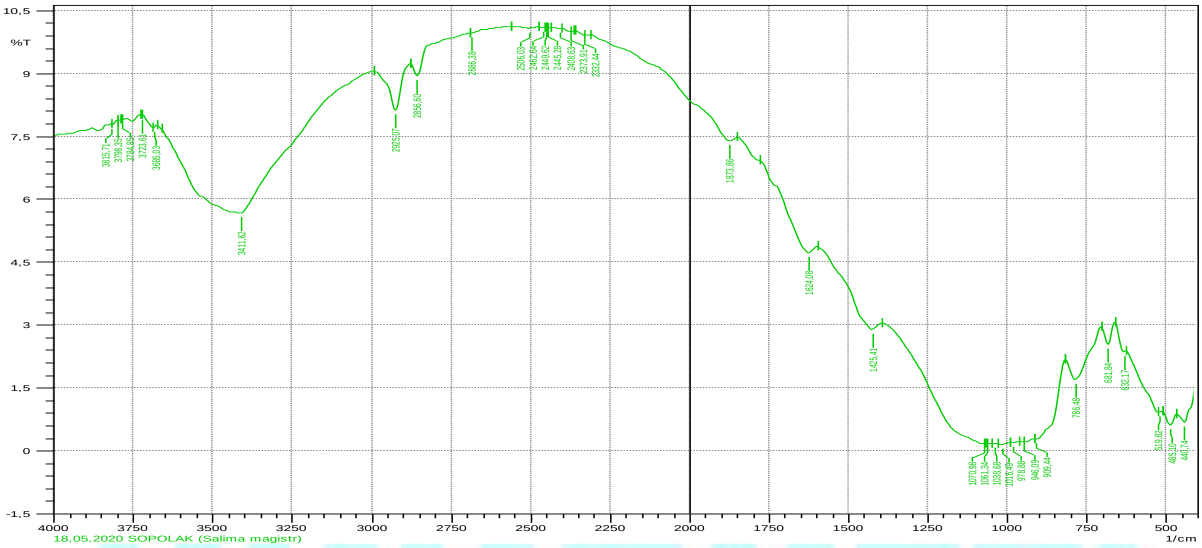

Figure 3. IR spectrum view of OS-4 ceramic body.

The observed wavenumbers in the range of 909.44–786.48 cm^{-1} indicate the presence of the [AlO_4] bond. The 909–786 cm^{-1} range corresponds to the valence vibrations of the Al–O bond and the internal vibrations of the tetrahedral [AlO_4] group. The presence of distinct peaks in this range within the sample demonstrates that aluminum is located in tetrahedral coordination ([AlO_4]) rather than octahedral ([AlO_6]). The presence of [AlO_4] increases structural strength, enhances the chemical stability of the glass phase, and improves mechanical properties. The existence of [AlO_4] in the ceramic mass indicates that aluminum has entered the crystal lattice, aluminosilicate phases (such as mullite or feldspar-based phases) are forming, along with structural restructuring has occurred [11-13]. The absorption maxima in the 909–786 cm^{-1} range confirm the presence of aluminum in tetrahedral coordination ([AlO_4])

within the ceramic mass. Consequently, indicates the formation of aluminosilicate phases at high temperatures and the enhancement of structural stability. [14-15].

Conclusion

It is possible to synthesize mayolica ceramic bodies compatible with historical architectural tiles based on local mineral raw materials. In sintered ceramic materials derived from natural mineral sources, the processes of phase crystallization and microstructural densification determine the mechanical properties of the material [16]. The optimality of the ratio between crystalline and vitreous phases in aluminosilicate systems ensures high strength. The aluminosilicate components within the selected raw materials, such as Kattabog loess soil and Angren secondary grey kaolin, underwent structural restructuring during the firing process, ensuring the formation of stable phases. The absorption maxima observed in the 909–786 cm^{-1} range of the infrared spectroscopy results confirmed the formation of aluminum units in tetrahedral coordination ($[AlO_4]$). This indicates the formation of an aluminosilicate lattice within the mass and the successful progression of thermal restructuring processes.

The structural characteristics of the obtained ceramic samples allow for the achievement of mechanical strength and thermal stability typical of historical tile materials. The identified properties demonstrate that the use of local raw materials can reduce dependence on imported materials, increase economic efficiency, and enable the creation of scientifically grounded materials for the restoration of historical architectural monuments.

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