Modified Solutions Based On Calcium Sulfate For Architectural Monuments Of Bukhara

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Abstract: In the article, based on the results of the physicochemical analysis of the mortar of the brick masonry of the Ismoil Samaniy and Minaret Kalyan mausoleum, it is shown that these mortars are gypsum-lime mortars with organic and mineral addition. Taking this circumstance into account, as a result of further research, modified solutions were obtained for the restoration of the aforementioned architectural monuments.

Key words:Architectural monument, restoration, brickwork, mortar, gypsum, lime, organic and mineral additives, modified mortar.

1. INTRODUCTION.

Located on the tourist routes of Uzbekistan, repeatable and ancient Bukhara, rich in monuments of monumental architecture, has long and deservedly gained world fame. In this ancient and unique city of Uzbekistan, many outstanding monuments, unique living masterpieces of world architecture, built since the 9th century, are currently preserved, which people living not only in Bukhara, but also in Uzbekistan are proud of. They are known all over the world.

The unique architectural monuments of Bukhara cover a thousand-year interval of the history of Central Asian architecture. These monuments capture building materials and construction techniques that determine the qualities of history architecture. A deep and comprehensive study of the construction business in general and the building materials used in their construction in particular, allows the development of similar modified materials to preserve the value of the restoration of architectural monuments.

Many historical monuments of Bukhara, erected with the use of sulfate binders, despite their long existence, have a good condition under certain conditions of their location, which indicates the use of a modified solution based on calcium sulfate with satisfactory conditions in relation to natural operating conditions.

Therefore, in order to preserve the value of historical monuments during the restoration and restoration of brick architectural buildings and structures, it is advisable to use modified materials, in particular, modified mortars, identical or similar to historical materials.

In order to study the physicochemical compositions and properties of the historical solution and develop the technology of modified building solutions for the architectural monuments of Bukhara, we carried out the corresponding theoretician - experimental studies, the results of which are given in the text of the article.

2. RAW MATERIALS AND RESEARCH METHODOLOGY

To accomplish the set tasks, we studied samples of historical mortars of the Ismail Samaniy mausoleum, the Kalyan minaret and the Abdulazizkhan madrasah, which are unique and original architectural monuments built in the 9th, 12th and 17th centuries, respectively. As we established in the course of experimental research, in the laboratory of the Institute of Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan, together with Professor Z.R. Kadirova, binders based on calcium sulfate were used in the construction of these monuments.

Samples of the Ismoil Samaniy Mausoleum, the Kalyan Minaret and the Abdulazizkhan Madrasah were used in the research in the study of historical masonry mortars. When developing the composition of the modified (identical) mortar, local lime obtained in the shops and combine of the Kagan of the Bukhara region, natural clay (loess-like loam), cementum of local bricks, and vegetable ash of local reeds were used as a mineral additive. Loess loam consists mainly of quartz (SiO_2) and kaolinite $Al_2Si_2O_5(OH)_4$.

The properties of the modified mortars were studied according to the current requirements of the currently valid standards and procedures.

On the basis of the classical technology of building materials, it has been established [1-3] that all the basic physicomechanical and physicochemical properties of building materials, and in particular mortars, masonry cements, fired bricks, are also directly dependent on chemical, mineralogical and fractional compositions the initial components used, the ratio of the main oxides contained in them and the amount of minor oxides, and, consequently, from the chemical compositions of the raw materials from which the final product is obtained. It follows from the foregoing that the operational control of the chemical composition of raw materials is one of the main conditions for obtaining high-quality building material [4-9], in particular, a masonry mortar that meets the specified requirements for physical-mechanical and physical-chemical properties.

In the chemical analysis of various building materials, in particular a solution, as well as hydrated materials, it is important to determine the content of silicon oxides (SiO_2), aluminum (Al_2O_3), iron (FeO + Fe_2O_3), calcium (CaO), magnesium (MgO), sodium (Na_2O) , potassium (K_2O), sulfur (SO_3) and loss on ignition. Much less often it is required to determine the content of other oxides present in small amounts, for example, oxides of titanium (TiO_2), phosphorus (P_2O_5), manganese (MnO_2), chromium (Cr_2O_3), etc. Scheme of carrying out the chemical, i.e. silicate analysis is as follows: after decomposition of the sample, the content of silicic acid was determined by the gravimetric method, with the obligatory subsequent removal of it in the form of silicon tetrafluoride - SiF_4. In the filtrate after separation of silicic acid, oxides of iron, aluminum, calcium, and magnesium were determined complexometrically, and the content of oxides of titanium, phosphorus, manganese, and sometimes chromium was determined photocolorimetrically. The loss on ignition and the content of sodium, potassium and sulfur oxides were determined from individual weighed portions.

It is well known that the majority of chemical and physicochemical processes are accompanied by the release or absorption of heat. The essence of thermal analysis is the study of phase transformations occurring in systems or individual compounds, according to the accompanying thermal effects. For this, the sample under study is gradually heated, continuously recording the temperature according to the readings by automatic recording. The obtained temperature curves make it possible to judge the nature and intensity of thermal effects and the temperatures at which these thermal effects manifest themselves.

The data obtained, in turn, can be used to analyze the mineralogical composition of the material under study and the nature of the phase transformations occurring in it during heating. Differential thermal analysis (DTA) records the changes in the energy of the system during heating. The physical and chemical processes that take place with the absorption or release of heat are expressed on a continuous differential temperature curve by a series of definite endothermic and exothermic effects.

The thermogravimetric method is based on measuring the mass of the test substance during heating, as an indicator of chemical transformations in the test material. This method is an important addition to differential thermal analysis, since the curves of mass change provide additional information and help to more accurately characterize the quantitative side of the ongoing processes.

Phase transformations and regions of stability or changes in solution samples using differential thermal research, i.e. thermographic and thermogravimetric analysis together with Professor Z.R. Kadyrova were carried out on the Hungarian derivatograph of the F. Paulik-I. Paulik-L. Erdey system, which simultaneously recorded the differential curve of thermal analysis with curves of the change in linear dimensions (shrinkage) and weight loss ... Sensitivity of galvanometer, DTA – 1/3, DTG – 1/5, TG - 200, T –900oC, at a heating rate of 10 deg / min in platinum crucibles. The specimen holder is a corundum crucible with a diameter of 10 mm from a standard (Al2O3). Dynamic mode. Differential and temperature recording was performed with a Pt – Pt / Rh thermocouple. The heating curves were recorded at an average weight of 2 g. Simultaneously, on other samples from the test material, changes in linear dimensions were recorded using a torsion balance with a mirror reading.

It is now known that X-ray analysis is a more versatile and currently more perfect method for studying materials than other physicochemical methods. Using it, one can carry out both qualitative and quantitative phase analysis of materials of complex composition, as well as determine the structure of crystal lattices of individual compounds.

Various research methods are used depending on the purpose of the X-ray analysis and the type of object; powder and Debye-Scherer methods for polycrystalline and Laue method for single crystal samples.

Building materials, in particular polycrystalline compounds that bind as bodies, are studied, as a rule, by the powder method and mainly with ionization registration of diffracted X-ray radiation. The great advantage of this method is its high sensitivity in relation to individual minerals and a significant reduction in the analysis time.

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The X-ray diffraction patterns were decoded using a generally known method. When analyzed, the crystals of each individual compound give a specific, inherent only X-ray diffraction pattern with characteristic values of interplanar distances and a certain intensity of the corresponding reflections.

Various researchers have already obtained reliable X-ray diffraction patterns of most of the water crystals and minerals that make up building substances and their hydration products, which are given in various reference books. The most complete list of the radiographic characteristics of various minerals is given in the international card index.

According to the above, the diffraction patterns of the samples of the mortar and clay mortar were obtained by the powder method on an X-ray unit DRON-4.0 MoK□-radiation, Zr-filter. X-ray photographs were taken at a counter disk speed of 2 deg / min. Monocrystalline quartz was used as an internal standard. The wavelength of cobalt radiation is 1.78529 A0, the tube voltage is 25 kV, and the tube filament current is 20 kV.

When identifying the phases, we used tables and reference books compiled by the authors of [10–12], as well as the ASTM card index based on the ASTM X-ray powder diffraction patterns [13].

Thus, the physicochemical analysis of the compositions of the historical materials of the brickwork of architectural monuments and the compositions of modified mortars based on calcium sulfates was studied according to the methods recognized and used at present on operating devices.

3. RESULTS OBTAINED AND THEIR DISCUSSION

The analysis of the world's literary sources showed that in practice, in order to improve the physical and mechanical properties of mortars, during their preparation in ancient times, various organic additives were used [14, 15], in particular sheresh [14-20], camel milk (suzme) [15- 20], wood glue [21], glutinous rice decoction [22,26], egg white [23], dextrin, citric acid, wine [14,24,25], etc. To increase water resistance, ie. reducing the solubility of calcium sulfate in water and creating conditions for the formation of insoluble compounds that protect calcium sulfate dihydrate, in combination with a gypsum binder used mineral fillers - additives with pozzolanic properties [14,15].

The results of our research on the study of the chemical composition of historical building solutions of architectural monuments of Bukhara and modified solutions using the above methods are shown in Table 1 and 2, respectively.

Table №1

The chemical composition of the mortar the mausoleum of Ismail Samaniy and the Kalyan minaret

Name Samples	Content of oxides per air dry matter, wt%									PPP
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	P_2O_5	Cl^-	

1B*)	24,63	4,04	2,40	39,92	3,00	0,68	0,48	0,50	0,01	0,02	23,90
1C**)	21,83	4,09	2,72	38,56	2,00	0,59	0,46	0,56	-	-	24,11
2B***)	15,89	3,22	2,70	40,30	2,50	0,71	0,49	0,61	-	0,02	33,14
3B	55,89	9,78	3,99	10,45	2,70	1,28	1,91	1,89	0,04	0,03	12,37

*)- samples of the upper part of the wall of the Ismail Samoniy mausoleum;

**)- samples of the lower part of the wall of the mausaleum Ismail Samoniy;

***)-samples of the construction of the Kalyan Minaret

-samples of construction Madras Abdulazizkhan

Table №2 Results of chemical analysis of modified solutions

Name Sample	Content of oxides per air dry matter, wt%										PPP
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	P_2O_5	Cl^-	
1M	24,02	4,34	2,70	40,422	3,50	0,60	0,56	0,60	0,02	0,01	23,80
2M	16,05	3,32	2,45	40,22	2,58	0,71	0,5	0,65	-	0,03	33,54
3M	53,79	10,88	4,49	10,95	2,5	1,48	1,51	1,99	0,03	0,04	12,77

Table 1 shows that the chemical composition of the studied samples consists of the following oxides: SiO_2 ,Al_2O_3 , Fe_2O_3 , CaO, MgO, SO_3 ,Na_2O, K_2O. Consequently, the main chemical composition of the samples of solutions from the Ismail Samaniy mausoleum (1B va 1C) consists of calcium oxides of silicon. The main chemical composition of the samples of solutions from the Kalyan minaret (2B) also consists of calcium and silicon oxides. In the studied mortar, the content of PPP was 23.9 and 33.14%, respectively. The obtained composition of the modified solution is similar (table No. 2).

Comparative analysis of the studied compositions of mortars of the mausoleum of Ismoil Samaniy and Minaret Kalyan with data from literary sources showed that if in the masonry of architectural monuments of the 9th - 12th centuries the main content of solutions was calcium oxides of silicon, then the monument of Shokhi-Zinda, built a little later, for example in Samarkand, etc. the composition of the solution consists not only of these oxides, but also of aluminum oxides [14]. Our studies of the mortar of the brickwork of the Abdulazizkhan madrasah (sample no. 3B), built in Bukhara in the middle of the 17th century, the results of which are presented in the same table no. 1 confirmed this opinion.

The composition of the mortar of the brickwork of the Ismail Samaniy Mausoleum and the Kalyan Minaret differs from the architectural monuments of the later period in the lower content of aluminium oxide. On the basis of this position, one can come to a preliminary opinion that clay mixtures were also added to mortars of late times in the seventies.

For a more reliable conclusion on this issue, it was advisable to conduct a DTA analysis. The results of DTA analysis of architectural monuments are presented in Fig. 1-4. It can be seen from the obtained curves that the mineralogical composition of the samples consists of the following thermal effects. At temperatures of 246 and 627 ° C, exothermic effects were observed, and at temperatures of 162, 187, 220, 331, 376, 416, 489, 728 ° C - endothermic effects.

In fig. 1a-4a show the results of X-ray irradiation of samples-samples of the mortar of brickwork of architectural monuments - the Ismail Samaniy mausoleum, the Kalyan Minaret and Madras Abdulazizkhan.

The results of the study of the mortar of the brickwork of these architectural monuments showed that the diffraction maxima appeared at d = 0.756; 0.422; 0.306 and 0.208. These dimensions indicate the presence of gypsum in the solution. In addition, the mixture contains quartz (d = 0.334; 0.245; 0.228 nm), albite (d = 0.310; 0.402 nm) and dolomite (d = 0.290; 0.241; 0.219; 0.202 nm).

In sample samples from the lower part of the Ismail Samaniy mausoleum, the diffraction maxima occurred at d = 0.756; 0.427; 0.306 and 0.208 nm. These dimensions indicate the presence of gypsum in the solution. In addition, the mixture contains quartz (d = 0.334; 0.245; 0.228 nm), basanite (d = 0.606; 0.281 nm), albite (d = 0.310; 0.402 nm), K feldspar (d = 0.324 nm), clinoenetitite (d = 0.893 nm) and calcite (d = 0.187 nm).

The difference in the sizes of the diffusion maxima of the solutions of the upper and lower parts of the brick wall can be explained by the operating environment of the structure. At one time, the lower part of the wall was in a buried state for a long period, as a result of it, aggressive factors of the filled-in soil affected it. As a result, additional K-feldspar minerals, clinoenetitite va calcite, were formed in the composition of the solution in the lower part of the wall.

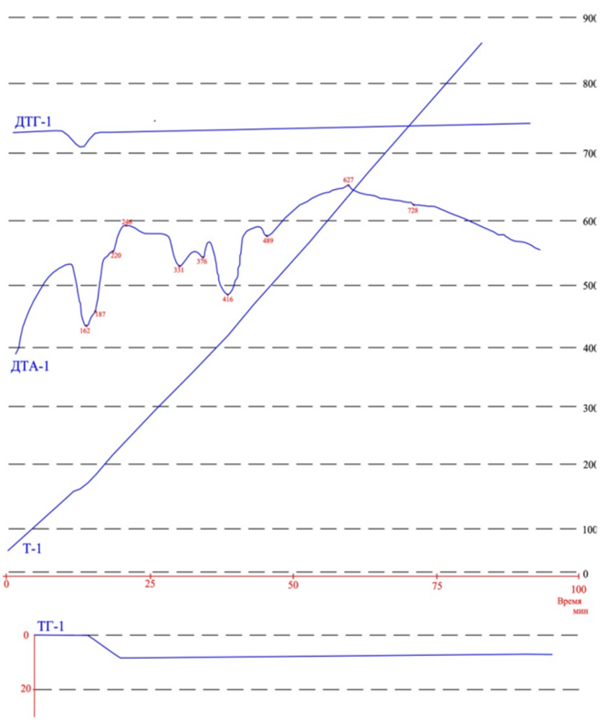

Fig-1. Sample DTA results
mausoleum of Ismail Samaniy №1B
(top of the wall)

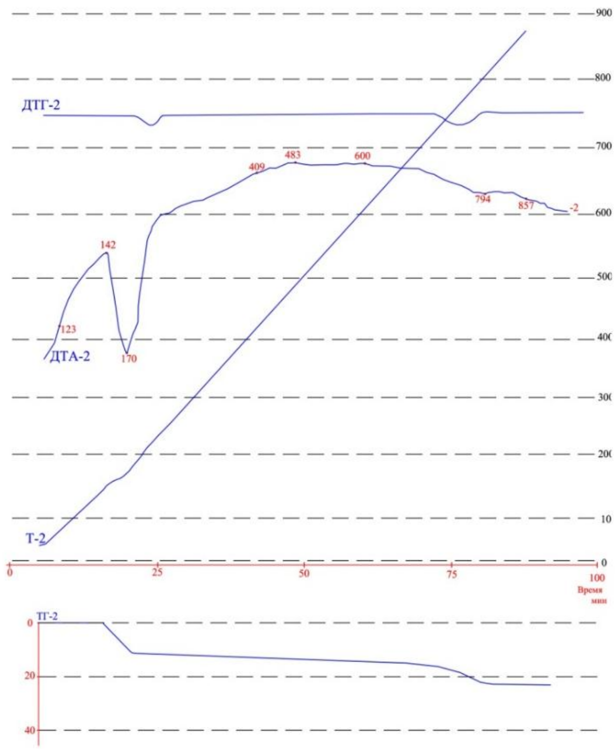

Fig-2. Sample DTA results
mausoleum Ismail Samaniy №1C (lower part of the wall)

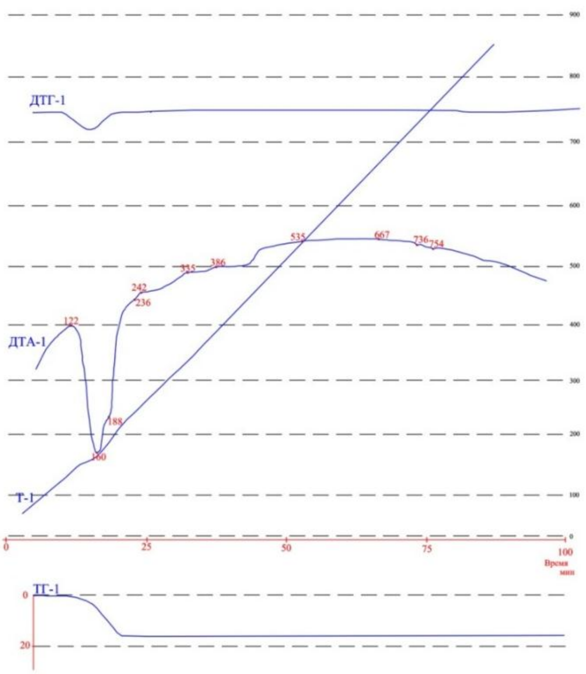

Fig-3. Sample DTA results
Minaret Kalyan №2B

Fig-4. Sample DTA results
Madras Abdulazizkhan # 3B

ISSN 2515-8260 Volume 07, Issue 07, 2020

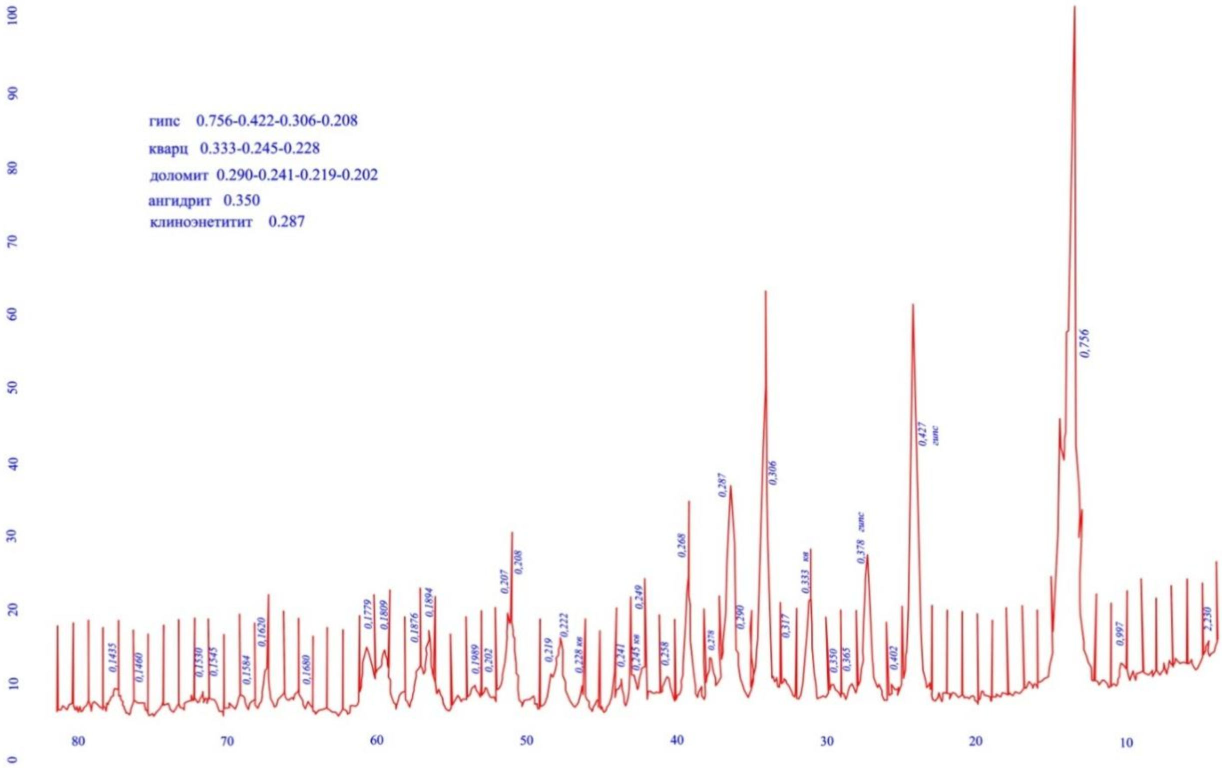

Figure: 1a. X-ray results of sample-sample mausoleum of Ismoil Samoniy №1B

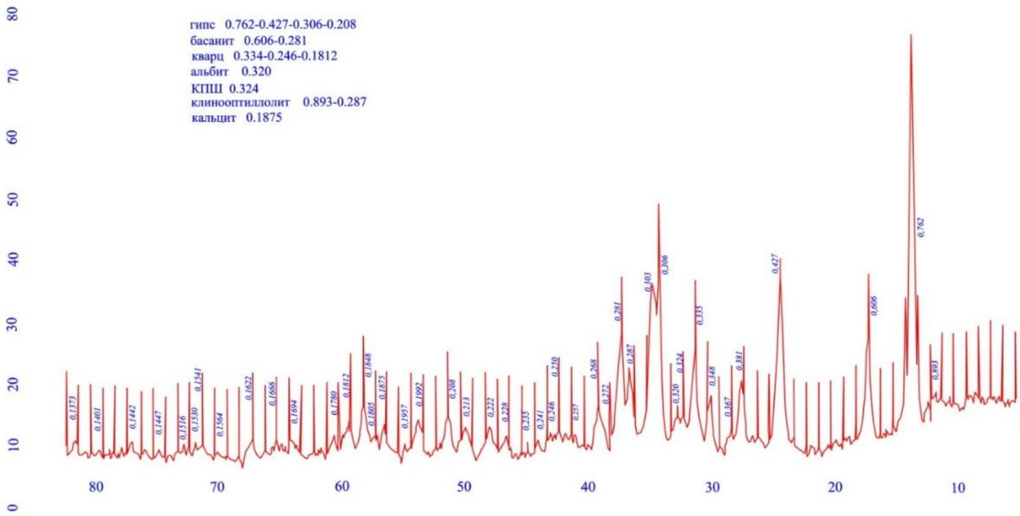

Figure: 2a. X-ray results of sample-sample mausoleum Ismoil Samoniy №1C

ISSN 2515-8260 Volume 07, Issue 07, 2020

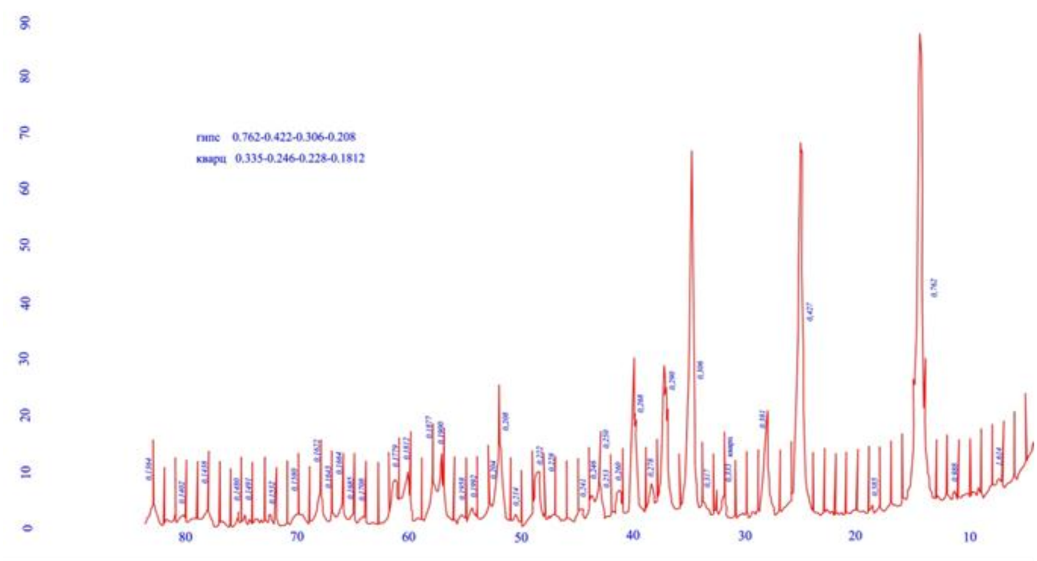

Fig-3a. X-ray results of sample-sample Minaret Kalyan №2B

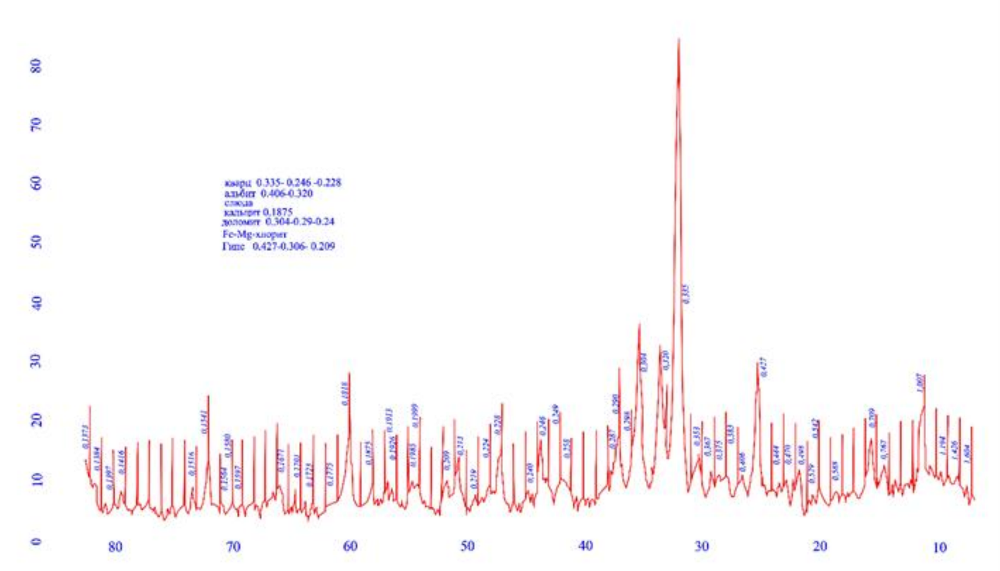

Fig-4a. The results of the roentgenogram of the sample-sample Madras Abdulazizkhan No. 3B

4. CONCLUSION

According to the results of the physicochemical analysis of the mortar of the brick masonry of the Ismoil Samaniy and Minaret Kalyan mausoleum, it can be noted that these solutions are gypsum-lime with organic and mineral addition. Therefore, when developing the technology of a modified solution for the restoration work of architectural monuments of the early period, we took into account these results, which was taken into account in further research. As a result of the research, modified solutions were obtained for the restoration and restoration of architectural monuments of the city of Bukhara's fairy tale.

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