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THE INFLUENCE OF SALT DEPOSITS ON THE PRESERVATION OF THE HISTORICAL AND ARCHITECTURAL MONUMENT OF THE MAUSOLEUM OF KHOJA AHMED YASAWI

Abstract. *The article presents the results of environmental monitoring of the state of the mausoleum of Khoja Ahmed Yasavi, which is a monument of architecture and history. Mechanisms of processes of formation and development of salt deposits on its building structures are considered. The prospective application of the sorption method for the elimination and inhibition of corrosive salt destruction processes of monuments is shown based on the superimposition of compressing with the complexing agent Trilon B (disodium salt of ethylenediaminetetraacetic acid).*
Keywords: *Khoja Ahmed Yasawi mausoleum, environmental monitoring, salt efflorscence, destruction of construction materials, compressor cleaning method, Trilon B.*

Introduction

The mausoleum of Khoja Ahmed Yasawi, located in the southeastern part of Turkistan, is an outstanding monument of medieval architecture, a masterpiece of architecture. This priceless historical and architectural monument has been on the World Heritage List of UNESCO from 2003 under No. 1103. This monumental complex has about 34 rooms, different in size and functional purpose. The large entrance portal and the main halls - Kazandyk and Gurkhana are located on the longitudinal axis and are the main construction elements. There are Askhana, Kitaphana, Mosque on the western side, Kudukkhana, Small Aksaray, Big Aksaray on the eastern side [1].

The construction material of the monument is burnt square bricks varying in size from 25-27 cm, 4,5-5 cm thick. The main walls are assembled of clay mortar arches and the domes are of ganch (a type of ancient gypsum). Three facades and two large domes are covered with glazed tiles. The architectural-artistic state of the monument is in difficult natural and climatic conditions, characterized by hot climate and significant temperature drops of outside air, as well as under the constant aggressive influence of abiotic and biotic factors.

From year to year, there is a threat for the destruction of this monument of history and culture increase due to the influence of negative environmental factors. These factors include excessive pollution of the atmospheric air (acid and salt precipitation), soils, groundwater salinization, heavy traffic (exhaust gases, vibration, etc.), and expansion of the construction of residential and industrial complexes [2-4].

In-depth knowledge about the environment status of monuments, about construction materials, and about the impact of environmental factors on them will make it possible to objectively assess the existing problems and find ways to solve them.

Development of new and improvement of existing methods, methods for extending the viability of the historical and cultural monument are becoming more relevant in the context of the dynamic development of tourism in the region. Five clusters have been identified geographically in the framework of implementation of the "Concept for development of the tourism industry until 2020 in Kazakhstan" [5]. The South Kazakhstan cluster will be positioned as a "Heart of the Great Silk Road." The main tourist products that will be developed in this cluster include cultural tourism, wherein the town of Turkestan with the mausoleum of Khoja Ahmet Yasawi, are presented as key places of tourist interest, in addition, theses objects are included in the UNESCO's International Serial Cross-border Nomination "The Great Silk Road" [6]. So the preservation of cultural heritage moved beyond national interests and became worldwide.

At present, one of the reasons for the decrease in service life of building structures of historical architectural monuments is the corrosion processes in them due to the formation of salts or the so-called "salt efflorescence" in the technical literature. Formed salt deposits, apart from the destruction and decrease of operational indicators, lead to the deterioration of architectural expressiveness of monuments [7-8].

The technology of monuments' surface cleaning has many features and is of scientific and practical interest. One of the problems faced by restorers is the conduction of monuments' cleaning from historical contamination. Usually, the exposure time of these contaminants is several centuries, they have a fairly complex composition and are firmly fixed on the surface, since they were repeatedly exposed to solar radiation, wind pressure, and anthropogenic factors, including acid and salt rain during this period.

The aim of this work is to assess the current state of the monument, to consider the problems of destruction of the mausoleum as a consequence of environmental factors, and to find ways to preserve the structure.

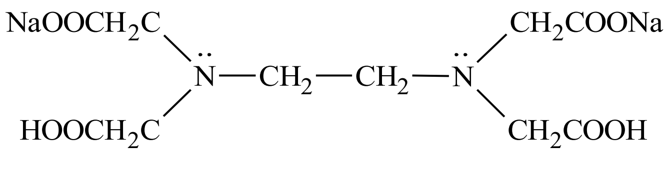
Materials and methods

The following indicators are considered as priority parameters for environmental monitoring of the monument: temperature, humidity and atmospheric composition, quality, and quantity of salt sediments on construction structures. The following methods were used to assess the condition of the mausoleum: field survey, including photographic evidence; visual expert assessment and laboratory studies.

The scalpel was used to analyze the qualitative composition of salt efflorescence from the accumulated areas. After weighing and taking the sample in a quantity of 100-200mg, the sample was dissolved in distilled water of 5-10 ml volume. The non-dissolved part was then separated and the quality analysis of sediment and filter was carried out.

An analysis of atmospheric air samples was carried out containing dust, methane, hydrogen sulphide, sulfur gas, ammonia, carbon dioxide, carbon monoxide, oxides of nitrogen, hydrocarbons, dioxins and mercaptans with the help of gas analyzer GANK-4. Other instruments, complying with modern requirements, have been used for experimental studies, namely: Fluorate-02-2M, pH-meter, KFK-3-01-30MZ, atomic absorption spectrophotometer, Testo-443 instrument, and certified methods. Experimental data on the monitoring of ambient air and groundwater inside the mausoleum and in the environment, necessary for considering the formation of salt efflorescences, were reviewed in the papers [9-11].

Experimental studies have been carried out to reduce the generation of salt deposits and to stop the destruction of construction structures. So-called compressive method, widely known in many countries of the world, has been used to remove salt deposits and inhibit the salinity accumulation process for preventing and preservation the stability of historical monuments. A sorption exchange process is used to abolish the salt layers formed on the surface of the walls and foundations. An ordinary ash-free filter papers impregnated with distilled water or water solutions of the complexing agent were used as a sorption material. While conducting the purifying process of construction structures from salt deposits having the property to generate a strong soluble complex with alkali earth and other metals, the 0,05 N solution (dissolving 9,3 g in 1 L of water) of dinatrium salt of ethylenediaminetetraacetic acid (trilon B) was used as complexing agent [12]. Trilon B has the following chemical formula:



Trilon B forms a complex compound with the majority of metal cations in the proportion 1:1:

$$Me^{2+} + [H_2T]^{2-} \leftrightarrow [MeT]^{2-} + 2H^{+}$$

$$Me^{3+} + [H_2T]^{2-} \leftrightarrow [MeT]^{-} + 2H^{+}$$

$$Me^{4+} + [H_2T]^{2-} \leftrightarrow [MeT]^{0} + 2H^{+}$$

The compressor method uses a multilayer filter paper impregnated with a 0,1% trilon B solution and is put on salt efflorescences. A compressor cover shall be kept on the surface until completely dry. The soluble salts, which are located both on the surface of construction materials and accumulated in the internal volume, go over into a layer of paper in this method.

Results and discussion

As we have previously established, the destruction of the mausoleum is due to the rising of saline groundwater, polluted precipitation, abrupt climate change, poor quality of renovation works, non-conformance of used materials in the composition of historical samples in the restoration, as well as by various anthropogenic factors with the participation of people [13-15].

A visual inspection of the indoor and outdoor areas was initially carried out to identify the causes of salt formation. This made it possible to detect the presence of spallings, the superimposition of salts, and the occurrence of joints (cracks) in different parts of the mausoleum. Cracks usually create favourable conditions for the development of moulds, fungi, algae, etc. Furthermore, these biological organisms will participate to some extent in destructive processes.

Presence of cracks was detected by visual inspection in the bearing of north-west pylon in Mosque, Kazantdyk. Saline surfaces have been found in many carved curb stones, as well as glazed destruction on the colonnettes. Kazandyk and Gurhana paneling are in satisfactory condition. There are salt efflorescences and slight biodamages in the premises of Mosque, Big and Small Aksaray, Kudukhana. The largest damage of the mausoleum structure to salt efflorescences, except for the front wall from the south-west, is found in all three exterior walls.

The mausoleum is not heated, therefore there are often problems related to temperature and humidity inside the building and the accumulation of carbon dioxide and other gases in the air. These problems often occur when there is a crowd of visitors in autumn-winter and early spring. In this connection, particular attention should be paid to ventilation, avoiding the formation of condensate, which has a destructive effect on unique paintings.

The condensate is formed when the wet air touches the cooler walls inside the premise. In addition, water vapours in the air are transformed into tiny droplets and are deposited on the internal surfaces of walls, pylons, and floors. This results in moisture saturation of the mausoleum's bearing elements. When the water is saturated, the heat conductivity of the walls is increased, the salts dissolve and crystallize. It is known that the water increases by 9% during freezing and the porous stone of any strength can break when the water is fully saturated. Transfer of water from one aggregative state to another causes swelling, loosening, detachment from the plaster lining, and scaling.

The temperature and humidity conditions in all mausoleum premises were monitored daily at different seasons of the year to avoid undesirable processes leading to corrosive events and to create favourable conditions for preservation of the monument (table 1).

Table 1 – Temperature and humidity inside and outside of the mausoleum of Kh.A.Yasawi

Spring, 03.03.21.	Meteorological data inside/outside of the mausoleum		Difference		Summer, 01.08.21.	Meteorological data inside/outside of the mausoleum		Difference	
	f%	°C	*f*%	°C		*f*%	°C	*f*%	°C
	Kazandyk					Mosque			
00.00	27,1/23,5	28,8/29,8	3.6	1,0	00.00	23,0/19,3	31,7/34,9	3.7	3,7
09.00	38,0/21,7	28,1/30,1	6.3	2,0	09.00	30/24,8	30,3/36,0	5.2	3,3
12.00	69,0/61,7	26,7/23,3	7.3	3,4	12.00	20/14	33,1/35,7	6.0	4,6
15.00	81,2/74,8	24,1/20,1	6.4	4,0	15.00	15/8	34,0/40,8	7.0	6,8
18.00	63,5/56,4	23,7/21,9	7,1	1,8	18.00	16/10,2	33,6/39,9	5.8	5,3
21.00	59,0/54,2	23,9/24,1	4.8	0,2	21.00	19/14,7	33,2/36,6	4.3	3,4
Autumn, 04.11.20	Kudykkhana				Winter, 15.01.20	Kitchen			
00.00	60,2/55,1	5,9/10,9	5,1	5,0	01.00	75,0/84,0	-0,9/-4,5	9,0	-3,6
09.00	69,0/55,9	6,4/13,5	13,1	7,1	06.00	75,0/84,1	-1,2/-4,1	9,1	-2,9
12.00	69,4/81,6	7,8/14,2	-12,2	6,4	10.00	76,0/81,0	-1,5/-4,2	5,0	-2,7
15.00	75,0/93,0	9,9/9,9	-18,0	0	16.00	77,2/73,2	-0,6/-1,8	4,0	-1,2
18.00	78,0/93,1	9,8/5,5	-15,1	-4,3	20.00	70,0/76,5	0,8/0,6	6,5	0,2
21.00	78,2/91,0	9,0/3,9	-12,8	-5,1	23.00	72,3/82,2	0,6/0,4	9,9	0,2

The condensate formation does not occur if the difference between the external and internal temperature is more than 3^0C and the relative humidity is more than 70%. We have reached this conclusion on the basis of experimental results. A very simple experiment with empty glass bottles was conducted to determine the need for additional ventilation. The bottles, which were inside, were taken outside, if they were covered with condensate, there was no need for ventilation.

Maintaining the normal temperature and humidity inside the building of the mausoleum complex is an opportunity to eliminate the condensation process and thus to reduce its contribution to corrosion processes.

It is known from the literature, the origin of all physical and chemical, chemical, and biological processes is water. The main evil causing the salt formation on the surface of construction structures is capillary water rising from the base up the walls [16-17]. Changes in humidity and temperature on different surfaces of the items cause osmotic pressure, as a result of which diffusion of soluble salts to the external surface happens on the capillary porous structure of the material, which results in the formation of salt efflorescences.

Compared to condensation water, the groundwater, as it rises from the capillaries of the brickwork, causes significant damage. The groundwater, unlike condensation moisture, contains inorganic and organic salts, including salts of humus acid. The water of this composition contributes to the development of moulds, algae, mosses, and other types of vegetation and microorganisms.

Figure 1 presents the results of photographic evidence of some places in the mausoleum, which have been destructed by salt efflorescences and mosses (Fig. 1).

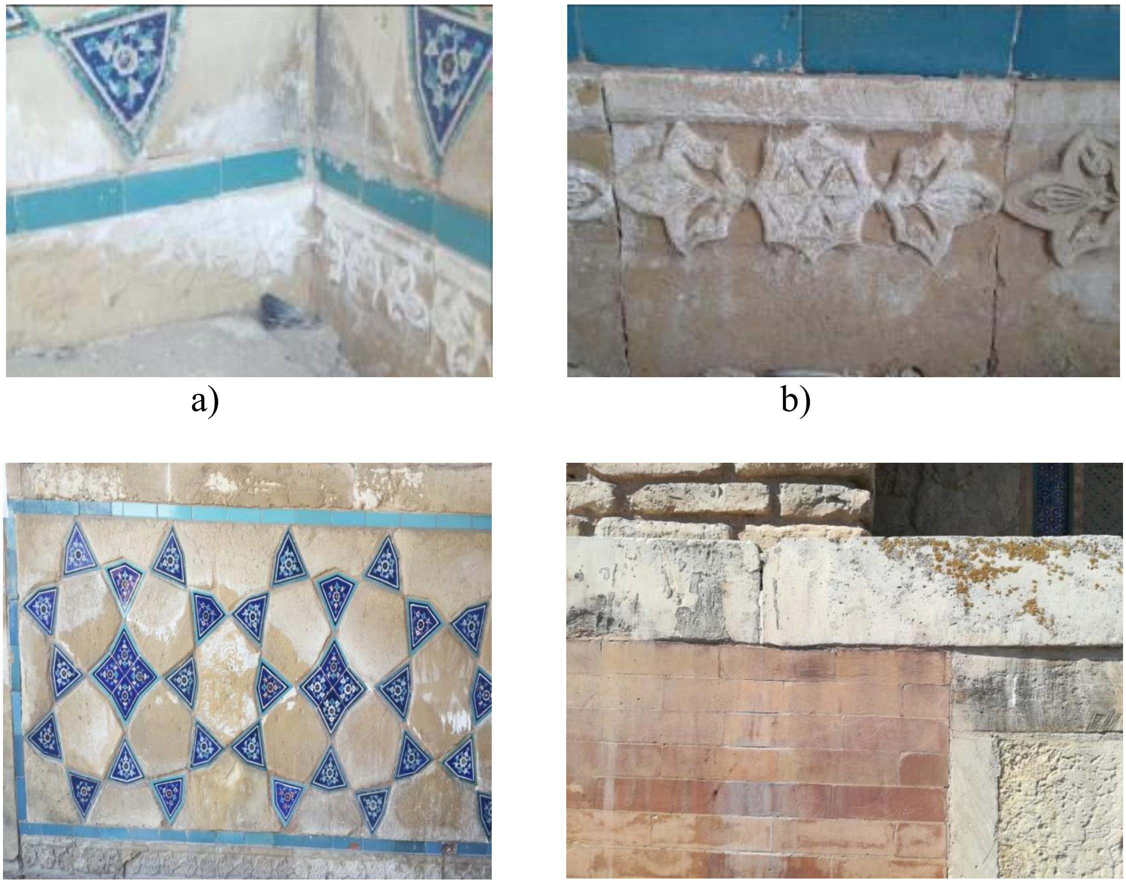


Figure 1 – Salt deposits on different areas of the foundation and walls (a, b, c) and moss on the brick surface (d) [author's material].

Decomposition of carbonates and qualitative determination of carbon dioxide is based on the following reactions:

We collected stone salt powder saturated with salt and research was conducted. The presence of nitrates, chloride, sulphate, carbonate, phosphates, silicate, humates, calcium, magnesium, sodium, etc., was determined based on the results of salt efflorescences analysis. Many of these salts are soluble, insoluble calcium carbonate dominates in the composition of salt efflorescences. The presence of this salt was determined by processing the salt efflorescences with a solution of hydrochloric acid (1), in which the gas is released and the nature of which is determined by passing through a solution of calcium hydroxide (2). Carbonate decomposition and carbon dioxide quality determination are based on the following reactions:

$$CaCO_3 + HCI \rightarrow CaCI_2 + H_2O + CO_2 \text{ (decomposition)} \quad (1)$$

$$CO_2 + Ca(OH)_2 \rightarrow H_2O + CaCO_3\downarrow \text{ (white mud)} \quad (2)$$

Salt efflorescences contain salts able to form crystalline hydrate with varying amounts of water ($Na_2SO_4 \cdot 10H_2O$, $CaSO_4 \cdot 2H_2O$, $MgSO_4 \cdot 7H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, etc.). When the salts change from one modification to another, there is a change in the total salt volume. The transition of salts to crystalline hydrates or, conversely, to an anhydrous state depends on the atmospheric air temperature and humidity. Construction products are under a lot of strain from these salt changes, which leads to destruction.

If groundwater, temperature, and humidity parameters of the environment participate in the deposition of salts on the building structures inside the premises, then salinity, dust, and gas contamination of atmospheric air, bird manure on the floors, domes, roofs of buildings, natural climatic (temperature, humidity, wind) and other environmental factors have a significant impact on the external part of the structure and salt formation process and on composition of salts.

A very large gathering of birds are observed in the mausoleum complex, which causes a great problem as the products of their life activities have a destructive effect on the architecture. Tons of manure with the highest concentration of nitrogen and phosphorus corrode the monument. Weekly cleaning of manure does not solve the problem. The number of birds, especially pigeons, is constantly increasing due to the persistence and fertility of wild (synanthropic) birds. It is inhumane to kill birds, and effective scaring methods are not invented. To find a solution to this problem is a crucial task.

It is known from the literature data, the nitrogen in poultry manure is mainly represented as uric acid [18]. $C_5H_4N_4O_3$ uric acid is first converted to ureal $CO(NH_2)_2$ and then to ammonium carbonate $(NH_4)_2CO_3$which is further decayed to ammonia, carbon dioxide and water:

$$C_5H_4N_4O_3 + O + H_2O = C_4H_6N_4O_3 \text{ (allantoin or glyoxylic diureide)} + CO_2 \quad (3)$$

$$C_5H_4N_4O_3 + H_2O = 2CO(NH_2)_2 + HCOCOOH \text{ (glyoxalic acid)} \quad (4)$$

$$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3 \quad (5)$$

$$(NH_4)_2CO_3 = 2NH_3 + CO_2 + H_2O \quad (6)$$

Ammonia is then converted to nitric oxide and nitric acid (7-8) by interacting with air oxygen, which contribute to the intensive corrosive and other destructive processes on the mausoleum’s building materials:

$$4NH_3 + 7O_2 = 6\, H_2O + 4NO_2 \quad (7)$$

$$4NO_2 + 2H_2O + O_2 = 4HNO_3 \quad (8)$$

The abundance of sulphates, nitrates, carbonates, hydrocarbons, and other salts in salt efflorescence can be explained by the occurrence of physical and chemical, chemical, and biochemical transformations involving contaminants of the external environment in the monument’s materials.

Analyzing the literary data and the results obtained in the study of salt composition, in order to inhibit the destruction processes of the building materials and to create conditions for the elimination of salt deposits on their surfaces, we concluded that the use of the sorption method would be a good perspective. Additionally, apart from salt efflorescence, purification conditions are created by transitioning salts inside the building material into a tightly bonded state, which minimizes the transition ьб===бpossib8ility of salts to crystalline hydrates. Trilon B, selected as a complexing agent, enters an exchange reaction with the formation of stable complex compounds.

Figure 2 shows the implementation of the compressor method and the area of salt efflorescence cleared with a single overlap (Fig. 2).

a) b)

Figure 2 – Example of overlaying the compress (a) and the area of salt cleared with a compressor method using the solution of Trilon B (b) [author's material].

Conclusions

It has been established that the formed salt efflorescence on the surface of the mausoleum foundation, walls, and facades according to the composition is multicomponent. The predominant components are the salts of sodium, calcium, and potassium, mainly in the form of sulphate, chloride, nitrates, carbonates. The bulk of salt efflorescence consists of calcium carbonate, which is insoluble in water or in precipitation.

It is noted that the main factors contributing to the monument corrosion are the following: a) transition of salts to crystalline hydrates and back into a waterless state, depending on climatic conditions; b) changes in the solubility of calcium carbonate from microclimate conditions inside the premises, namely, when carbon dioxide accumulates, the transition to soluble bicarbonate state; c) accumulation of poultry manures, which are sources of construction aggressive uric and nitric acids and humic acids, which are fertilisers for evolution of mosses and other vegetation; d) capillary rise of groundwater salts; e) air pollution by release of various anthropogenic sources.

The prospective application of the sorption method for the elimination and inhibition of corrosive salt destruction processes of monuments is shown based on the superimposition of compressing with the complexing agent Trilon B.

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ВЛИЯНИЕ СОЛЕВЫХ ОТЛОЖЕНИЙ НА СОХРАННОСТЬ ИСТОРИКО-АРХИТЕКТУРНОГО ПАМЯТНИКА МАВЗОЛЕЯ ХОДЖИ АХМЕДА ЯСАВИ

Аннотация. *В статье приведены результаты экологического мониторинга состояния мавзолея Ходжи Ахмеда Ясави, являющегося памятником архитектуры и истории. Рассмотрены механизмы процессов образования и развития солевых отложений на его строительных конструкциях. Показана перспективность применения сорбционного метода для ликвидации и ингибирования процессов коррозионного солевого разрушения памятника* *на основе наложения компресса с комплексообразователем Трилон Б (динатриевая соль этилендиаминтетрауксусной кислоты).*

Ключевые слова: *Мавзолей Ходжи Ахмеда Ясави, экологический мониторинг, высолы, разрушение строительных материалов, компрессный метод очистки, Трилон Б.*

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ҚОЖА АХМЕТ ЯСАУИ ТАРИХИ-СӘУЛЕТ ЕСКЕРТКІШТЕР КЕШЕНІНІҢ САҚТАЛУЫНА ТҰЗДЫ ШӨГІНДІЛЕРДІҢ ӘСЕРІ

Аңдатпа. *Мақалада сәулет және тарих ескерткіші болып табылатын Қожа Ахмет Ясауи кесенесінің жағдайына экологиялық мониторинг нәтижелері келтірілген. Кешенді қосылыс түзуші Трилон Б-ны (этилендиаминтетрасірке қышқылының динатрий тұзы) жабыстыру компресін жасау негізінде ескерткіштің тұзбен бұзылуын жоюға немесе тежеуге пайдалану болашағы бар сорбциялық әдіс екені көрсетілді.*

Түйін сөздер: *Қожа Ахмет Ясауи кесенесі, экологиялық мониторинг, тұз шөгіндісі, құрылыс материалдарының бұзылуы, компресс тазару әдісі, Трилон Б.*