Identifying the Glaze Structure of Historical Clay Bricks: A Case Study of Persepolis Clay Bricks

Sasan Samanian (samanian_sa@shirazu.ac.ir)
Shiraz University

Sareh Bahmani
Shiraz University

Research Article

Keywords: Persepolis, Glazed Clay Bricks, Gray Glaze, Azure Blue Glaze, X-Ray Diffraction Method, Scanning Electron Microscope Method

Posted Date: June 29th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-3078182/v1

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Abstract

Glazes include a wide range of organic and inorganic compounds. During the Achaemenid period, one of the decoration methods of buildings and palaces was the use of colored glazed clay bricks. This experimental-laboratory research was carried out regarding valid scientific documents.

**Purpose:** to identify the constituent elements of glazes in Achaemenid clay bricks.

**Research Question:** What are the constituent elements and the main coloring factors in gray and azure blue glazes of Achaemenid clay bricks in Persepolis?

This research aims to identify the structure of the glaze of Persepolis clay bricks. Among the different devices that are used to identify minerals, X-Ray Diffraction and Scanning Electron Microscope laboratory methods were used. The XRD device was used to detect the type of material and determine the type of constituent phases and the SEM device was used to determine the amount of constituent elements of the material. The glazes of Persepolis bricks are white, pale green, dark green, dark brown, gray, fawn yellow, and azure blue. In this article, the structure of gray and azure blue glazes was identified and studied. The study samples were physically sampled as a tiny flake-shaped layer of glaze from the building body on the eastern wall of the exclusive women's palace during the time of Xerxes. In total, three samples of gray glaze and three samples of azure blue glaze were selected. According to the results, the existence of silica and porosity of the body and also the existence of iron and magnesium in the composition of the glazes were confirmed, which were probably present in the original composition (base glaze), showing that besides the color effects, they were also present in them as impurities. Based on the structure of gray and azure blue glazes, both glazes are alkaline. The scientific and academic application of this research is for the protection and restoration of brick glazes and also for the use of the Ministry of Cultural Heritage, Handicrafts, and Tourism, as well as students in restoration of cultural and historical artefacts in Art universities.

Introduction

The history of using glazed bricks in the decoration of palaces and temples dates back to the ancient Mesopotamia civilization. Sumerians and Akkadians in 2500 BC established the basis of classical art in the Near East in the ancient period. The Sumerians covered the walls of their buildings with a mixture of unfired clay with black, white, and red colors. The Babylonians decorated the reliefs on the walls of their buildings with glaze. In Babylon, a vast area of multi-colored glazed bricks was obtained, which were assembled to form the main parts of a building (Mortgart, 1969, p. 297) The Elamites used glazed bricks in the decoration of their buildings and palaces in the second millennium BC, and the prominent example of their works is the Choghazanbil ziggurat (Ghirshman, 1992, p. 130).

During the Achaemenid era, the decoration of palaces and temples by painting on plaster coating and using Alvan tiles was extremely popular and many examples of these works were found in the buildings of that period. For example, the image of "Immortal Soldiers" found in the Achaemenid palace in Susa...
and other examples of it, although decorated in colored semi-relief, all the characteristics of a wall painting are used in them; showing the folds of clothes and the decorations of the fabrics are so beautiful and well done that even the type of fabrics can be recognized from these motifs (Tajvidi, 2015, p. 23). Other examples of these decorations have been found in different regions of Iran belonging to the Achaemenid period, including Pasargadae, Persepolis, and some of them have been found in the building known as the treasury in Persepolis. Persepolis is one of the most magnificent and famous buildings of the ancient world, which was built in 518 AD. It was built by the order of Darius I and continued until 330 BC, in which year it was fired by Alexander the Great and the Achaemenid government was extinguished.

This building was excavated by Professor Ernst Hertzfeld and an architect named Professor Crafter between 1310 and 1314 AH. Then in 1314 AH., Eric Schmidt and a group from the University of Oriental Studies in Chicago came to Persepolis to explore and discovered valuable and beautiful works of glazed bricks with plant, geometric, and inscription motifs. The glazed bricks discovered by Eric Schmidt were transferred to various museums, including the Museum of Ancient Iran, for preservation and display, and some of them are kept in the Persepolis Museum, some of them are arranged in the eastern wall of the exclusive women's palace during the time of Xerxes, which was used as a building. The present research is conducted on the samples in the administrative building of Marvdasht cultural heritage. Since these works are exposed to damage caused by erosive environmental and climatic factors, it is very important to identify the constituent elements to protect and preserve them to prevent or reduce further damages. Also, the severe deterioration of the glaze of these bricks, besides making it difficult to study and analyze the technical and aesthetic works of these works, has created certain complications in the way of preserving and displaying them in the historical site. Knowing how to prepare brick bodies and glazing on them, as well as evaluating the optimal conditions to preserve these works, are among the most important goals that demand the necessity of conducting this research.

The studied glazed clay bricks are decorated with a completely siliceous body and with brown, pale green, dark green, fawn yellow, white, gray, and azure glaze. Glazes in Achaemenid glazed bricks in Persepolis are tested and investigated, and the necessity of doing this research is to protect and restore these glazed bricks in Persepolis. This research is question-oriented and has been done in order to answer the following question: What are the constituent elements and the main coloring factors in gray and azure blue glazes of Achaemenid brick in Persepolis?

In the next sections of the article, the background of the research is explored, and then the research method and tests are performed. Also, Achaemenid glazed bricks and especially gray and azure glazes tested in this article are introduced. At the end, the findings are analyzed and the last discussion and conclusions of the analyzes are provided.

**Research Background**

So far, many books, articles, and investigations have been done by various people in connection with the historical site of Persepolis, including Professor Ernst Emile Hertzfeld from 1307 to 1314 AH. He has
published research studies such as the book entitled "Rapport sur l'etat actuel des ruines de Persepolis et propositions pour leur conservation" as well as the book entitled "East Ancient the in Iran" and various other articles, in which the paintings on clay works discovered in this region and also the glazed clay bricks in some parts of Persepolis palaces have been mentioned (Herzfeld, 1307–1314). After that, from 1314 to 1318 AH., Eric Schmidt accepted the responsibility of the exploration in Persepolis and published three volumes of the book entitled "Persepolis" during 1953-1957-1970 in connection with his explorations. This research is based on the findings of the glazed bricks of the same excavations (Schmidt, 1953-1957-1970). Also in 1319 AH., Dr. Isa Behnam has been appointed as the head of Persepolis Scientific Institute and has continued exploring Persepolis. After that, until 1340 AH., Ali Sami has explored in Persepolis and many books and articles have been published by him.

From 1347 to 1352 AH., Akbar Tajvidi has explored Persepolis and published books such as "A look at the art of Iranian painting from the beginning to the 10th century AH.", in which he has explored the decoration of palaces and temples of the Achaemenid period and glazed tiles.

On the other hand, one of the Achaemenid research studies by western scholars is a book called "Achaemenid research" which was translated by Dr. Alirezashapour Shahbazi, in which the views of western scholars regarding the historical site of Persepolis are discussed (Shahbazi, 1975).

Also, Dr. Alirezashapour Shahbazi has published a book entitled "Illustrated description of Persepolis" which introduces the Persepolis building and the measures taken in it, and mentions the bricks of Persepolis and glaze and patterns on them (Shahbazi, 1975).

Michael Raff has published the book entitled "Reliefs and lithographs of Persepolis" which was translated by Hooshang Ghiasinejad (Ghiasinejad, 1994). Hossein Basiri has also published a guidebook for Persepolis, which introduces Persepolis and its conservation and restoration measures (Basiri, 1946).

Khan Yusefnejad has presented an article entitled "Analytical study of Achaemenid glazed bricks of Persepolis by multiple instrumental analysis methods" in the conference "International Symposium on Archaeometry Art: The Getty center and university of California Los Angeles". He studied the Achaemenid glazed bricks of Persepolis using several instrumental chemical analysis methods such as scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), X-ray fluorescence (XRF), and inductively coupled plasma-optical emission spectroscopy (ICP). Then he compared the results with the Susa glaze samples of Apadana Palace and the Elamite glaze samples of Choghazanbil Ziggurat.

In an article entitled "Painted plaster and glazed brick fragments from Achaemenid Pasargadae and Persepolis, Iran" published by Aloiz, Douglas & Nagel in Heritage Science in 2016, in which the plaster-molding and glazed brick in Persepolis and Pasargadae have been investigated. The results show that there are five layers of paint on the Pasargadae plaster, and the floor pieces of Persepolis are completed with lime plaster and two layers of paint, and the brick pieces of Persepolis are made of Silica material and decorated with alkaline glazes. Tilia (1978) in the article entitled "Studies and restorations at Persepolis and other sites in Fars" which he did in the International Association of Mediterranean and
Eastern Studies (Associazione Internazionale di studi sull Mediterraneo e l’Oriente (ISME0)), studied the restorations done in different regions of Fars and also investigated the restorations of Persepolis.


"Color and gilding in Achaemenid architecture and sculpture" is the title of a book by Nagel (2013), in which he investigates the use of color and patterns in the sculptures and reliefs of Achaemenid architecture. Analytical methods used to detect microscopic traces of pigment and analysis of the composition of ancient pigments, the history of color studies in Achaemenid works, show that many cases of preserved pigments have been observed in the past few centuries. In this book, case studies of the color of Darius I façade door are presented.

In a book entitled "Glazed objects and the Elamite glaze industry" written in 1992, Heim examines the glazing industry of Elamite civilization, and in this book, he studies the glazed objects of this civilization.

A Technological Study of the Elamite Polychrome Glazed Bricks at Susa, South-Western Iran" is another article by Holakooei (2013), in which the technological characteristics of the Neo-Elamite glazed bricks discovered in the Acropolis of Susa, South-Western Iran, were analyzed by micro-Raman spectroscopy, differential thermal analysis/thermos-gravimetric analysis (DTA/TG), X-ray diffraction (XRD). The results show that the colored glazes were separated by a Si-rich brown glaze to prevent them from running during foring. Glazed bricks are most likely not fired above 900 degrees Celsius.

Holakooei, Ahmadi, Volpe, & Vaccaro (2016) also in the article entitled "Early Opacifiers in the Glaze Industry of First Millennium BC Persia: Persepolis and Tappe Robat", the matting and coloring agents used in the glazed bricks of Persepolis (middle of the first millennium BC) and the Manni area of Robat Hill (Tappe Robat) in the northwest of Iran (eighth to seventh centuries BC) are investigated. Various analytical investigations show that lead antimonate and brizite (NaSbO3) were used as yellow and white opacifiers in the glazes of Persepolis and Tappe Robat, and also the connection between the Achaemenid glaze industry and the production of Manni glaze in Tappe Robat has been discussed.

Then, since 2001, with the establishment of the Parse-Pasargadae Research Foundation, special attention was paid to the archaeological investigations of Persepolis and the preservation and restoration of the works in it. This foundation formed scientific groups in different and separate branches in Persepolis, in this direction, many archaeological activities have been carried out or are being carried out. Regarding the bricks used in the ancient works of Fars, Seyyed Mohammadamin Emami, et al. (2014) have conducted a research entitled "Archaeometric methods for the structural analysis of the bricks discovered from the brick hill of Persepolis". In this research, the structure of the Tol Ajori of Persepolis
was examined using XRD and XRF analysis, and in the meantime, they also studied the glazes formed during the firing of these bricks.

In an article entitled "Evaluation of the use of X-ray microprobe analysis (XPMA) as a non-destructive method in identifying the chemical composition of historical glazes", Samieh Noghani et al. (2016) investigated the chemical composition of seven-color tile glazes belonging to the Safavid period through elemental, phase, thermal (XRD and XRF), and petrography analyses.

Mir Mohammad Abbasian, has published various books such as "the history of clay and tiles in Iran from the era before ours until now (1991), the glazing industry and its colors (1991), the basics of physical chemistry, non-metallic mineral materials, preparation and production of ceramics, refractory materials, glass, plaster, lime (1991)", in glazing and ceramics, and investigated glazes and their constituent elements.

Bahman Mirhadi (1380) also discussed the method of producing glazes and their constituent elements in the book entitled "Theory and Technology of Ceramic Glazes". There has been no report or research regarding the main coloring agents in the gray and azure blue glazes of the glazed bricks of Persepolis and conducting tests to identify the constituent elements of these glazes (Table 1).
<table>
<thead>
<tr>
<th>No.</th>
<th>Type (article/book)</th>
<th>Author</th>
<th>Title</th>
<th>Date of publication</th>
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<tr>
<td>1</td>
<td>book</td>
<td>Hertzfeld Ernst Emile</td>
<td>&quot;Rapport sur l'état actuel des ruines de Persepolis et propositions pour leur conservation&quot;</td>
<td>1928</td>
<td>Introducing the paintings on clays discovered in this area and glazed clay bricks in some parts of Persepolis palaces.</td>
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<tr>
<td>2</td>
<td>book</td>
<td>Hertzfeld Ernst Emile</td>
<td>Iran in the ancient East</td>
<td>2002</td>
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<td>book</td>
<td>Akbar Tajvidi</td>
<td>A look at Iranian painting art from the beginning to the 10th century AH</td>
<td>1973</td>
<td>Introducing the decoration of palaces and temples of the Achaemenid period and glazed tiles</td>
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<td>4</td>
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<td>Alireza Shapour Shahbazi</td>
<td>Illustrated description of Persepolis</td>
<td>1975</td>
<td>Introducing Persepolis building and its clay bricks, glaze and motifs on them</td>
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<td>Michael Raff</td>
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<td>6</td>
<td>article</td>
<td>Khan Yusef Nejad</td>
<td>Analytical study of Achaemenid glazed bricks of Persepolis by multiple instrumental analysis methods</td>
<td></td>
<td>The Achaemenid glazed bricks of Persepolis have been studied with several instrumental chemical analysis methods and the results have been compared with the Susa glaze samples of the Apadana Palace and the Elamite glaze samples of the Chogha Zanbil ziggurat.</td>
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<td>article</td>
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<td>Painted plaster and glazed brick fragments from Achaemenid Pasargadae and Persepolis, Iran</td>
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<td>The results show that there are five layers of paint on the Pasargadae plaster, and the floor pieces of Persepolis are completed with lime plaster and two layers of paint, and the pieces of Persepolis bricks are made of Silica material and decorated with alkaline glazes.</td>
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<td>9</td>
<td>article</td>
<td>Stodulski, Farrell, &amp; Newman</td>
<td>Identification of ancient Persian pigments from Persepolis and Pasargadae</td>
<td>2013</td>
<td>The ancient Iranian pigments taken from the surface of the limestone reliefs of Persepolis and Pasargadae were studied and identified using a combination of scanning electron and optical microscopes, atomic emission spectroscopy, X-ray diffraction, etc.</td>
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<td>10</td>
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<td>Color and gilding in Achaemenid architecture and sculpture</td>
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<td>book</td>
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</tr>
<tr>
<td>14</td>
<td>article</td>
<td>Seyyed MohammadAmin Emami et al.</td>
<td>Archaeometric methods for the structural analysis of bricks discovered from the Tol Ajori of Persepolis</td>
<td>2014</td>
<td>The structure of the bricks of Tol Ajori area has been investigated using XRD and XRF analysis and the glazes formed during the firing of these bricks have also been investigated.</td>
</tr>
<tr>
<td>15</td>
<td>book</td>
<td>Mir Mohammad Abbasián</td>
<td>The history of pottery and tiles in Iran from before our era until now Glazing industry and its colors Basics of physical chemistry, non-metallic mineral materials...</td>
<td>1991</td>
<td>Examining glazes and their constituent elements</td>
</tr>
<tr>
<td>16</td>
<td>book</td>
<td>Bahman Mirhadi</td>
<td>Theory and technology of making ceramic glazes</td>
<td>2001</td>
<td>Examining the method of glaze production and their constituent elements</td>
</tr>
</tbody>
</table>
Research Method

To identify materials, there are different methods, the application of which is determined according to the type of material. Some of these methods are XRD, XRF, atomic absorption, spectrophotometry, optical microscope, electron microscope, XRD, SEM, DTA, TGA, Pixie method, etc., some of which are used for investigating the behavior and physical and chemical changes of materials.

In this research, since the identification of colors has been intended, it has been tried to use more of the methods that are used to recognize and analyze the composition of materials, because this research was conducted to know the constituent elements of glazes in Achaemenid glazed bricks in Persepolis. This research is experimental-laboratory based on valid scientific documents that have been carried out using the library method and conducting field and laboratory studies. In this regard, by referring to valid scientific documents and conducting library studies and visiting the historical site of Persepolis and taking samples of tiny scaly layers of glaze from the body, physically and carefully separating the color layer from the glazed bricks installed on the eastern wall of the exclusive women's palace during the time of Xerxes and using XRD and SEM laboratory methods, the structure of the researched glazes was identified in 2016 (Table 2). The necessity of doing this research is to protect and restore these glazed bricks in Persepolis.

Table 2

<table>
<thead>
<tr>
<th>No.</th>
<th>Device Name</th>
<th>Model</th>
<th>Manufacturing Country</th>
<th>Test Place</th>
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<tr>
<td>1</td>
<td>(SEM) Scanning Electron Microscope</td>
<td>philips xl30</td>
<td>Netherlands</td>
<td>Central Laboratory of Isfahan University of Technology</td>
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<tr>
<td>2</td>
<td>X-Ray Diffraction (XRD)</td>
<td>panalytical x’pert</td>
<td>Netherlands</td>
<td>Central Laboratory of Isfahan University of Technology</td>
</tr>
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</table>
Introduction of Tests

As stated in the research method, there are various methods for identifying materials. Nowadays, in carrying out research projects, the device methods of identifying items are fast, widely used and original. Among the device methods for mineral identification, XRD, XRF, and SEM devices can be mentioned.

XRD and SEM methods have been used in this research. Diffraction (using X-rays): XRD device, which is mostly used to detect the type of material, determine the type of constituent phases and crystal and structural characteristics such as size, gradation, etc. (Krishner, 1991, p. 1).

Scanning Electron Microscope SEM (Scanning Electron Microscope): The key feature of this device is to identify materials and its extremely high magnification compared to optical microscopes. Besides imaging, new SEM devices can also be used in the analysis to determine the amount of elements that make up materials. In other words, the scanning electron microscope is one of the analytical methods that is used to identify materials and through which chemical analysis, composition, surface characteristics, and microstructure of materials can be examined (Miessler & Tarr, 2011, p. 89).

Achaemenid Glazed Bricks

The Achaemenid cities of Persepolis, Pasargadae and Susa were constructed of stone foundations, embellished by sculpted stone bas-reliefs carved onto interior and exterior walls, door panels, gateways, and stairways. Hundreds were preserved in situ at Persepolis, far less at the other two cities. Their presence (as essences, not decorations) functioned as calm political depictions of historical, religious, political, military, and social realities and protocols, reflecting the king's power and authority. At Persepolis, the first of the three Achaemenid capital cities erected, many hundreds of both glazed and unglazed molded relief bricks have been excavated by French and German excavations respectively (EXCAVATIONS i. In Persia). Also recovered in these cities were a lesser number of glazed, flat, non-relief bricks, depicting the same or similar scenes as those on the relief examples. Both the relief and flat bricks, glazed and unglazed, depicted the same scenes.

Glazed bricks from various palaces in Persepolis were discovered by Eric Schmidt during the exploration and then installed on the eastern wall of the exclusive women's palace during the time of King Xerxes, which is currently used as an administrative building of Marvdasht cultural heritage. It is possible that it was the same during the Achaemenid period (Fig. 1).

The body appearance of this type of brick looks very porous, which is milky and shiny like flint, with white, pale green, dark green, dark brown, fawn yellow, and gray glazes painted and designed. These designs are separated by azure lines.

Considering that the body appearance is like angular grains that are stuck together from sharp corners (like sharp pointed grains of sand that are stuck together and there is a lot of space between them), probably, very fine silica particles were mixed and fired with some lime, which acted as a melting aid and caused the silica particles to stick together. It is also possible that the composition of the body existed as
a ready-made composition in nature and was fired without adding other ingredients. On the other hand, it is possible that the body was fired at a temperature where the amount of 16% calcium oxide was not enough for a composition with a high percentage of silica as a melting aid, so they had to provide a very high temperature[1]. Unless, at a low temperature, besides calcium oxide, other materials have been added as a melting aid, and finally, during firing, these materials have been combined to cause a phase change.

Glazed bricks under research have been exposed to environmental factors (temperature, humidity, light, atmospheric pollutants) for many years, so they have been constantly degrading and undergoing physical and chemical changes. For this reason, it can be seen that the surface of the glazes is very rough, uneven, and opaque.

The studied glazed bricks have relatively similar dimensions and all of them are 9 cm high, 35 cm long, and their width is variable and ranges from 10 to 20 cm. These bricks are almost similar to the Nareh tiles that are used to cover the domes, and the back of the bricks is narrower than the front and is 6 cm. "At the same time, on the side of the bricks that is not glazed, there are small spots of colored glaze marked, which is probably the signature of the maker of the piece." (Hertzfeld, 2002, p. 243) (Fig. 2).

**Introduction of samples for testing**

In order to perform the tests, it was necessary to transfer the samples of studied glazes to the central laboratory of the Isfahan University of Technology. Because the glazed bricks were installed in the eastern wall of the exclusive women's palace during the time of King Xerxes, and it was not possible to transfer them to the laboratory, so sampling was done (Fig. 3).

At the time of sampling, because tiny flaky layers of glaze were physically separated from the body and it was not possible to separate the color layer from the installed glazed bricks accurately, therefore, some of the body was transferred to the laboratory along with the glaze. In addition, at the time of testing to prepare the samples, they were turned into powder. There is a possibility that because of the siliceous nature of the body, a percentage of the silica detected in the glazes was related to the body under the glaze (Table 3).
Gray coloring oxides

"Iron oxide changes the glazes in the oxide firing environment to yellow color, then to red-brown and wine-red, and finally to brown color. The same oxide produces other colors such as bluish gray to dark gray in the reduction firing environment. With the saturation of iron oxide in the glaze, unlike manganese and copper compounds, the metallic state does not appear on its surface, but only the surface of the glaze is opaque" (Abbasian, 1991, p. 115) (Fig. 4).

The examined gray glaze (sample number 1)

Table 4 and XRD Graph 1 and SEM Graph 1 show the test results on gray glaze (Sample 1). Table 4 related to the gray color shows a main amorphous phase and a quartz phase. The appearance of the gray glaze layer is a completely opaque that shows gray with a green undertone.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Sample No.</th>
<th>Result</th>
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<tbody>
<tr>
<td>EDHE3</td>
<td>Gray 1</td>
<td>Amorphous phase (main) + low Content of Quartz. SiO2, 33-1161</td>
</tr>
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</table>

Results-Analysis

According to the results of the XRD test and examination of the SEM Graph 1 and according to the explanations given about the gray coloring oxides, some possibilities for this sample are provided.

In the SEM graph of gray glaze, the presence of aluminum (Al), potassium (K), calcium (Ca), iron (Fe), sodium (Na) elements is significant. These elements are probably from the oxides of aluminum oxide (Al2O3), potassium chloride (KCl), calcium oxide (CaO), iron oxide (Fe2O3), sodium oxide (Na2O). Besides,
the existence of chromium (Cr) and titanium (Ti) which are oxides of Cr2O3 and TiO2, should not be ignored.

The presence of potassium (K), sodium (Na), calcium (Ca), and the absence of lead (Pb) show that the gray glaze is only an alkaline glaze. Copper (Cu), chromium (Cr) and iron (Fe) are the coloring agents, and copper (Cu) and chromium (Cr) in this (alkaline) glaze almost produce a turquoise color. However, Fe (iron) if it is in reduction firing conditions, it causes a gray color, which can be seen in the SEM Graph 2, that iron (Fe) agent is more significant than the two factors of copper (Cu) and chromium (Cr) and it is preferable. Considering the presence of titanium (Ti) agent, although it does not seem very noticeable, this amount can have a significant effect on the opaqueness of the gray color. Of course, probably the presence of titanium oxide (TiO2) was almost unintentionally in the composition of this glaze, although many other oxides may have been unintentionally in the composition of glazes.

"Titanium oxide (TiO2), colors lead glazes in yellow and lead-free glazes in white. However, with the presence of a small amount of iron oxide (Fe2O3) in the glaze or in titanium oxide (TiO2), it turns yellow again. The presence of titanium in large amounts in the glaze makes it opaque" (Abbasian, 1991, p. 116). Finally, due to the alkalinity of this glaze (sample 1) and most likely the main cause of the gray color in the presence of iron (Fe), calcium (Ca), and titanium (Ti) (of Fe2O3, CaO, TiO2 oxides), the alkalinity of this glaze is less transparent than other glazes. The presence of gold (Au) in Graph 2 of the SEM test is not the reason for gold in the combination of glaze and color, but it is related to the testing system with the electron microscope device. Because under the electron microscope, the electron beam hits the sample and for electrical, thermal conductivity, a 20 nm thick layer of gold coating is drawn on the sample, and the gold peaks in the SEM Graph are related to this issue.

Figure 5 shows a microscopic photo of the surface of the gray glaze, which is magnified 2700 times. In the microscopic image prepared from the surface of the glaze, the gray color can be seen. The phases in the color are not well separated from each other, and the boundary between the crystal grains is not completely clear, and they are shown almost as a single phase. Therefore, this image shows the surface of the sample and does not show the shape of phases and crystal particles.

**Blue azure oxides**

"With the gradual increase in the amount of cobalt compounds (CoO) in the glaze, pale blue to dark blue colors are created, and usually different blue colors are from the mixture of cobalt compounds (CoO) with aluminum oxide (Al2O3) and it even has some zinc oxide (ZnO).

Cobalt (CoO) compounds with phosphate and arsenate give a violet-blue to dark purple color, which becomes more intense by adding some magnesium oxide (MgO)" (Sabia, 1999, p. 123).

"By substituting alkaline materials instead of lead oxide (PbO) in the glaze, the color of the glaze tends to blue-green, and when the level of complete alkalinity is reached, its color becomes completely blue"
Blue azure glaze examined sample 2

After sampling, this glaze was as flake-shaped layers. It is necessary to mention that it was not possible to separate the color layer from the glazed bricks installed in Persepolis, a percentage of the body under the color was taken with the glaze, and due to the siliceous nature of the body, probably a percentage of the silica was detected in the glaze, related to the body under the color. The azure blue glaze is designed on the glazed bricks as lines around the patterns, and the rest of the colors on the bricks are separated from each other by these lines (Fig. 6).

Azure blue can only be produced by a mixture of this oxide and a strong lead-free alkaline glaze. If some boric acid is added to a green glaze, the color of this glaze becomes turquoise, and by adding 8 to 10% of tin to the same glaze, the intensity of the turquoise color appears more (Pampuch, 1976, p. 78).

The examined sample (blue azure sample 2) was first subjected to XRD test (Table 5 and Graph 3 of XRD test). Also, azure blue glaze was subjected to SEM test and the results are shown in Graph 4.

Examining the results of azure blue glaze

Table 5 and XRD Graph 3 in azure blue color (sample 2) show two phases of quartz Sio2 and "Heden Bergite" Ca (Fe, Mn) Si2o6. Besides the results of the XRD test on the azure blue color and according to Graph 4, which results from the SEM test on this color, investigations show that copper causes blue color in alkaline glazes and green color in lead glazes.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Sample No.</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDHE1</td>
<td>2</td>
<td>Quartz, Sio2 33-1161, main PPhase + Ca(Fe,Mn)Si2o6 41-1372 Hedenbergite</td>
</tr>
</tbody>
</table>

Sample 2 (azure blue) was subjected to SEM test, the result of which can be seen in SEM Graph 4. In this Graph, apart from silica, which is the main glaze material, Fe from iron oxide (Fe2o3), Ca from calcium oxide (CaO), K from potassium chloride (Kcl), and Cu from copper oxide (Cuo) are seen.

At first, the use of cobalt oxide (CoO) in the composition of the glaze is estimated by observing the azure blue glaze. However, the examination of the result of the SEM test, which is presented in the Graph 4, shows that there is no cobalt (CoO) in the azure blue glaze. Because this glaze (Sample 2) was placed on a piece of glazed brick that was located directly under the SEM device, the probability of error in the test sampling is very low. Besides, Graph 4 shows the absence of lead (Pb), therefore, the above glaze is
alkaline. As it was previously mentioned, in lead glazes, by substituting an alkaline agent instead of lead oxide (PbO) until the alkalinity is complete, first the green color turns green to blue-green and then completely blue.

Here, the possibility is that by replacing the alkaline agent instead of the lead agent (in lead glazes), they got azure blue glaze. Basically, at that time, by adding a raw material containing alkaline substances instead of a raw material containing lead (such as a syringe, etc.), they did a color conversion (green to blue).

The presence of iron (Fe) in SEM Graph 4 cannot show the blue color factor in the above glaze compositions. However, if cobalt oxide (CoO) was proved in the above sample (azure blue colored glaze), surely the azure blue color of this glaze was influenced by cobalt, although copper (Cu) is also present in the composition. Figure 7 shows the SEM microscopic image of azure blue glaze.

Considering the alkalinity of glaze sample 2 and copper oxide (CuO) as a coloring agent, it is possible to get an azure blue glaze almost similar to the examined glaze (Sample 2) by the formula presented in Table 6.

**Table 6. The formula of an azure blue glaze**

<table>
<thead>
<tr>
<th>Silica SiO2</th>
<th>1.7</th>
<th>Aluminum oxide Al2O3</th>
<th>0.05</th>
<th>Sodium oxide Na2O</th>
<th>0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Potassium oxide K2O</td>
<td>0.7</td>
</tr>
</tbody>
</table>

In addition, 3% of copper oxide (CuO) should be added to the above composition.

This glaze for SK03a[2] is 1040°C. If we want to assume a lead glaze and consider cobalt as the coloring agent, the formula presented in Table 7 can be used.

**Table 7. Lead glaze formula with cobalt coloring agent**

<table>
<thead>
<tr>
<th>Quartz SiO2</th>
<th>1.7</th>
<th>Aluminum oxide Al2O3</th>
<th>0.17</th>
<th>Lead oxide PbO</th>
<th>0.55</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boric acid B2O3</td>
<td>0.1</td>
<td>Zinc oxide ZnO</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium oxide CaO</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barium oxide BaO</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithium oxide Li2O</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Discussion**
According to the analysis of the results of the experiments, quartz was identified as the main constituent phase of the bricks, which are dispersed in fine-grained and uniform brick texture, and the glaze used on the bricks is based on alkaline compounds. Also, because of the severe erosion of glazes, which now shows itself with pale color and the creation of many holes on the surface of the glaze, it is very difficult and important to recognize the historical structure of the glaze. According to the laboratory and structural studies of Achaemenid glazed bricks in Persepolis, and although the soil of Marvdasht has a high percentage of impurities such as iron oxide and calcium oxide, it can be classified as relatively high-quality bricks. The preparation process of all the samples has been the same, both in terms of processing and preparation of raw materials and to fire techniques, and this can show the attention in the selection of raw materials and predetermined steps for firing bricks. With glazes, tests have been carried out with the focus of identifying the constituent elements of the glaze and checking the condition of the surface in terms of the amount of wear and erosion process. For this purpose, SEM and XRD methods provided the desired information about glazes in a complementary manner. At the same time, they confirmed the previous studies in this field and identified the elements that make up the glazes, which had not been done before.

**Conclusion**

According to the studies, the appearance of the glazed bricks found in Persepolis looks very porous and is milky and shiny like flint, and the siliceous nature of the bricks is confirmed. The quartz phase has been identified as the crucial phase of the brick, and the observation of quartz grains with angular corners is a proof that these materials have been eroded from the parent stones to be used as fillers. The quartz grains are distributed in almost the same sizes in the texture of the brick, which shows that these fillers are well kneaded.

The gray and azure glazes used in glazed bricks are alkaline, and the reason for the opaqueness of these glazes, besides passaging time and the effects of environmental factors, can also be their alkalinity. There are iron and magnesium in the composition of all glazes, which, apart from the color effects in the main composition of the base glaze, also have an effect as impurities. The XRD test on the gray glaze shows a main amorphous phase and a quartz phase, and the appearance of the gray glaze layer is a completely opaque color, which shows the gray color with a green undertone.

The SEM test on the gray glaze shows the presence of aluminum (Al), potassium (K), calcium (Ca), iron (Fe), sodium (Na) elements, which are probably from aluminum oxide (Al2o3), potassium chloride (Kcl), calcium oxide (Cao), iron oxide (Fe2O3), and sodium oxide (Na2O). In addition, chromium (Cr) and titanium (Ti), which are oxides of Cr2O3 and TiO2, should not be ignored. The presence of potassium (K), sodium (Na), calcium (Ca) and the absence of lead (Pb) also shows that gray glaze is just an alkaline glaze.

The XRD test on the azure glaze shows two phases: quartz SiO2 and “Heden Bergite” Ca (Fe, Mn) Si2O6. SEM test on azure glaze other than silica, which is the main glaze material, Fe from iron oxide (Fe2O3), Ca
from calcium oxide (CaO), K from potassium chloride (KCl), and Cu from copper oxide (CuO) are observed. The results are used in the conservation and restoration of Achaemenid glazed bricks in Persepolis and also in the instructing students in restoration of cultural and historical objects in different stages. In addition, it will be very effective in the protection and restoration policies of Persepolis.

In this regard, future research can include issues such as the identification of the elements that make up the glazes of other Achaemenid clay bricks in Persepolis, as well as the identification of the elements that make up the glazes of Achaemenid clay bricks in other buildings of this period, or simulating the glazes in the Achaemenid glazed bricks in Persepolis or other buildings of this period, and finally, that the restoration of the Achaemenid glazed bricks in Persepolis and other buildings of this period should be explored.

Declarations

Funding declaration

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

Data availability statement

All data generated or analyzed during this study are included in this published article (and its supplementary information files).

Competing interests

The authors declare no competing interests.

Authors' contributions

S.Samanian conceived and designed the analysis, S.Samanian & S. Bahmani collected the data, both authors contributed data or analysis tools, both authors performed the analysis and wrote the article and reviewed the article.

References


**Footnotes**

1. About 1700 degrees Celsius is required for pure silica to melt.
2. The number of the Seger cone indicates the approximate firing temperature of the glazes, and the number a03 indicates the firing temperature of 1040 degrees Celsius.

**Graphs**

Graphs 1 to 3 are available in the Supplementary Files section

**Figures**

![Figure 1](image-url)
Layout of the investigated bricks (author, 2016)

Figure 2

Colored marking glaze (author, 2016)
Figure 3

Selected samples (author, 2016)
Figure 4

Examined brick with gray glaze (author, 2016)
Figure 5

Microscopic image of gray glaze (author, 2016)
Figure 6

Examined brick with azure glaze (author, 2016)
Figure 7

Microscopic image of azure blue glaze (author, 2016)

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- G1.png
- G2.png
- G3.png
- G4.png