

CONSTITUENT ELEMENTS OF GREEN AND YELLOW GLAZE IN THE POTTERY BRICKS OF PERSEPOLIS

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Abstract. This research paper is devoted to identifying the glazed Achaemenid bricks in Persepolis. So far, some studies have been carried out on the introduction on these bricks, but technical studies have not been conducted. The glazed bricks reviewed in this paper are white, light green, dark green, dark brown, grey and yellow, and each color is surrounded by azure blue lines and separated from each other. Using X.R.D, S.E.M, D.T.A, T.G.A methods and more chemically, the bodies and glazes are identified, the body of this type of bricks is a very porous silica body. The light green, dark green and yellow glazes are made of lead. In the combination of all glazes, there are iron and magnesium, which probably existed in the original composition (base glaze), besides the color effects of impurities. After the extraction of the results of each test separately, the results were compared and the purpose of these tests was to recognize the glazes applied in these pottery bricks and this research is the result of laboratory studies of the authors.

Key word: Persepolis, clay bricks, wet chemistry method, Yellow glaze, Green glaze, Lead glaze.

Introduction

During the Achaemenid period, the decoration of palaces and temples by the paintings on plaster or the colorful tiles was common and numerous examples of these works were achieved in the buildings related to that period. The Image of the eternal soldiers found in the Achaemenid palace in Shush, although it has emerged as a semi-dominant color, but all the features of a wall painting have been used in it.

Shush and Persepolis are among the Achaemenid period buildings that have glazed bricks. Persepolis is undoubtedly one of the most magnificent monuments of the ancient world. Glazed bricks are found in various parts of the building by Schmidt, some of which are located at the Museum of Ancient Iran and some of other museums, including the Persepolis Museum, and those that have been investigated in the eastern wall of the women's palace located at the time of Xerxes, which is used now as the administrative building of Marvdasht cultural heritage.

The discussed examples include Guards (bodyguards), Sphinx Roudro, tiles with lion heads, tiles with, rosette flower with sixteen petals, hands in cloth sleeves, turban series, legs in shoes, etc. The glazes of these bricks are silica as decorated with brown, light and dark green, yellow, white, grey and black. In this study, light and dark green as well as yellow glazes are tested.

Introduction the sample (glazed pottery bricks)

The Achaemenid glazed bricks in Persepolis, located on the eastern wall of the women's palace at the time of the Xerxes (Harem), used as the administrative building of the Marvdasht Heritage. The appearance of the body of this type of bricks is very porous, which looks like a lilac like flint. The glazes on these bricks are painted in white, light green, light green, dark brown, gray and yellow, and these designs are painted by dark blue (blue and azure) lines. The glazes appear to have been constantly degraded over the past years, with physical and chemical changes. As you can see in the images, the surface of the glazes is very rough, rough, and opaque. (Image 1)



Image 1. The surface of glazes is not flat and opaque (Author: 2017)

The quality of these glazes was better during the construction (Akhamanid era). The most of bricks in Persepolis has been exposed to wind, rain and climatic factors in open space, over the time, the glazes have been destroyed. These glaze bricks are mostly big as one side is glazed and it is observed as a colored big design (Image 2).



Image 2. The general design of investigated bricks (Author, 2017)

Usually, one side of the bricks that are not glazed are marked with small colored glazes, these patches and marks can be considered as the signature of the parts maker and can also be indicative of arranging the parts together. Of course, the probability of the first one is greater. (Figures 3 and 4)



Image 3. Colored glaze of marking (Author, 2017)

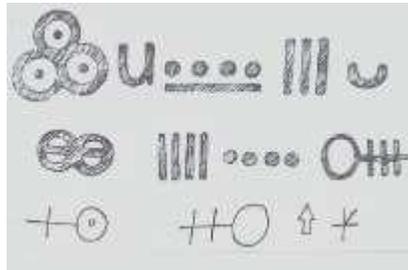


Image 4. An example of marking on bricks (Author, 2017)

Identification methods

There are various methods to identify materials and each method is determined based on the type of material.

Some of these methods include wet chemistry, XRD, XRF, atomic absorption, spectrophotometry, optical microscopy, electron microscopy, XRD, SEM, DTA, TGA, Pixe, and some other methods for analyzing and identifying the composition and some materials to investigate the physical and chemical behavior of materials.

In this study, because of the importance of recognition of colors, we have tried to use more than the methods used to understand and analyze the composition of materials.

Initial tests:

On two small pieces of body samples of sample size, unit weight and volumetric weight were used. These tests were done by immersion method. The calculation results are specified below.

	Sample size	Unit weight	Volumetric weight
Sample A	14.7	1.47	1.34
Sample B	7.90	1.27	1.16

Analysis test of wet chemistry on body (sample 1)

Besides the above tests, chemical analysis by wet method is performed on the studied sample and it was defined that there is about 79% SiO₂ (silica) and 16% Ca₂O₃ (calcium oxide) and analysis of body is as follows.

Oxide %	SiO ₂	R ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	Ca ₂ O ₃	MgO	L.O.I
	79			1.50	16	Little	3

As the appearance of body is similar to the small particles as attached from the pointed angles (e.g. pointed small sand as attached together and there is much empty space) and based on the wet chemistry, we can refer to the followings.

- 1- Small particles of silica as mixed with lime, heated and baked. Lime acts as helping melting and can attach the silica particles.
- 2- It is possible that the composition of body exists as a prepared composition in nature (small sand) as baked without adding other materials.
- 3- It is possible that the body is baked at the temperature in which 16% calcium oxide is not adequate for a composition with high silica percent as the melting aid and high temperature should be prepared¹.

Unless at low temperature, besides calcium oxide, other materials are added as aiding melting and finally during baking, these materials are combined and the phase is changed.

X.R.D , A.S.T D.T.A and T.G.A tests on the body (Sample 1).

On the body sample, besides wet chemistry analysis, X.R.D test and D.T.A tests (thermal analysis) and T.G.A tests (weight change) are performed (Tables 1).

Table 1. The result of X.R.D test of body (author, 2017)

Result	Sample code	Test code
Sio2 ,Quartz, 33-1161, main Phase Cao,28-775, low crystallinty phase	Body	ESHDE-S

Table 2. ASTM ID of Sio2 (Autor, 2017)

The image shows an X-ray diffraction (XRD) pattern for SiO2. The plot displays intensity versus 2-theta angle. Key peaks are labeled with their corresponding d-spacing values (d) and Miller indices (hkl). The most prominent peak is at approximately 23.1 degrees 2-theta, corresponding to a d-spacing of 3.84 Å (110). Other significant peaks are observed at 19.6 degrees (4.60 Å, 200), 16.8 degrees (5.30 Å, 111), and 15.1 degrees (5.90 Å, 040). The pattern is characteristic of amorphous or low-crystallinity silica.

Table 3. ASTM ID of Cao (Author, 2017)

The image shows an X-ray diffraction (XRD) pattern for CaO. The plot displays intensity versus 2-theta angle. Key peaks are labeled with their corresponding d-spacing values (d) and Miller indices (hkl). The most prominent peak is at approximately 28.5 degrees 2-theta, corresponding to a d-spacing of 3.25 Å (100). Other significant peaks are observed at 25.3 degrees (3.53 Å, 110), 20.9 degrees (4.26 Å, 111), and 18.5 degrees (4.81 Å, 200). The pattern is characteristic of calcium oxide.

¹ For pure silica, 1700°C is required to be melted.

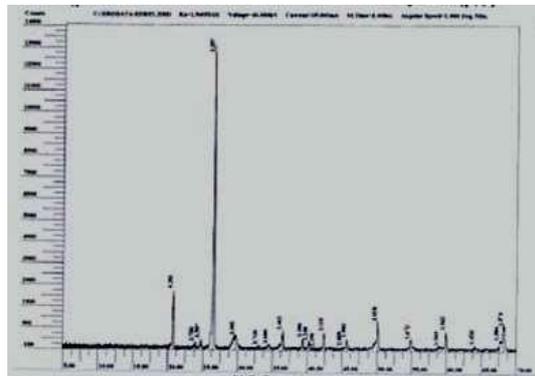


Chart 1. X.R.D test of body (author, 2017)

Table 4. Regarding X.R.D chart of body (author, 2017)

No.	Two Theta	d	I/I0
1	20.73	4.281	19
2	26.53	3.357	100
3	36.43	2.464	10
4	39.38	2.286	8
5	42.38	2.131	6
6	50.88	1.820	15
7	59.93	1.542	9
8	23.88	3.723	2
9	29.35	3.040	4
10	40.22	2.240	3
11	45.73	1.992	4
12	54.83	1.673	4
13	64.02	1.453	2
14	67.70	1.383	6
15	68.23	1.373	7
16	5.83	15.146	1
17	55.33	1.659	1
18	13.32	6.641	0
19	65.77	1.419	1
20	48.57	1.873	0

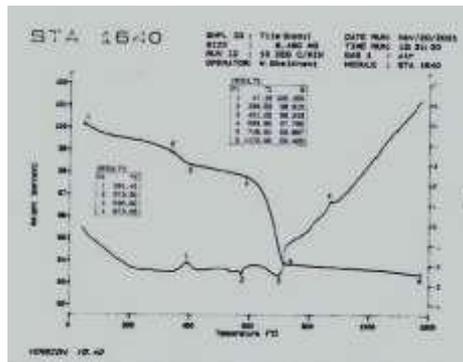


Chart 2. STA chart of body (D.T.A, T.G.A) (author, 2017)

Conclusion of X.R.D, D.T.A and T.G.A tests (sample 1)

By comparing the results of the tests (Table 1 and Figures 1 and 2) with the wet chemistry analysis test, in addition to those discussed in the wet chemistry analysis of the body, the following points are added to the mentioned statements.

- Table 1 and Figure 1 X.R.D confirm the silicon of the above body.

- In the wet chemistry test, the calcium oxide in the composition probably played the role of melting, and according to Chart 2 T.G.A it can be said that calcium carbonate probably was converted into calcium oxide. And weight loss is also the result of this conversion, which is clearly visible in the T.G.A chart at 400 °C.

- Chart. 2 shows that 16% of the calcium oxide existing in the compound was sufficient for the baking operation. As a baking operation at an approximate temperature of less than 800 °C on the body, it causes the body to achieve relative strength, although it is porous, its appearance indicates that the silica particles are totally melting and interconnected in the corners. .

As it was said, the light and dark green and yellow glazes are some of those used in glazed bricks of Persepolis, which we will examine here.

Green Dye Oxides:

"A mixture of copper oxide and lead glaze, proportional to the chemical composition of glaze, can create a variety of green colors [1]. The Iranian blue color can only be made by a mixture of this strong oxide and strong alkali glaze without lead. If we add some boric acid to a green copper glaze, the color of this glaze becomes turquoise and adding 8 to 10% of the tin to the same glaze, the intensity of the turquoise will appear more [2].

"Chromium oxide also turns glazes to green, and even at high temperatures it stays stable. By increasing the amount of zinc oxide in this type of glaze, it removes the dye, and the green color changes to a grayish-greenish and finally brown, so for the production of chromium-colored green, glaze materials should be free of zinc oxide [3].

Green Glaze of Persepolis glaze bricks:

After sampling, this glaze was in the form of flake-shaped layers that was used to prepare the test in powder form (it should be explained that because precise separation of the paint layer from glazed bricks installed in Persepolis was not possible, a percent of the body was colored with glazes, and because of the silica nature of the body, probably a percentage of the silica identified in the glazes was related to the body underneath (Figure 5).



Image 5. Adobe with light and dark green (Author, 2017)

The sample (Sample 2, dark green) was first tested by X.R.D. (Table 5 and chart 3 of X.R.D test). The light green was also tested by X.R.D and S.E.M tests. The results are shown in (Table 6 and Chart. 4 of the X.R.D test and Chart 5 of S.E.M test).

The results of green glaze

Table 5 and Chart XRD No 3 in dark green (sample 2) show the existence of two phases of quartz SiO_2 and " Heden Bergite " $\text{Ca}(\text{Fe}, \text{Mn})\text{Si}_2\text{O}_6$. Table 6 and XRD Graph 4 on light green (specimen 2) identify the same two-phase that is present in the dark green (SiO_2 quartz and Heden Bergite $\text{Ca}(\text{Fe}, \text{Mn})\text{Si}_2\text{O}_6$). In fact, it can be stated that the main phase of the light and dark green is the same and probably the percentage of the dying materials in the composition is different, and maybe in the dark green glaze (sample 2) the dying agent is a percentage higher than the light green of the glaze, or maybe in sample 2 of dark green, in addition to the dying agent of green, the presence or absence of another element can reduce or increase the color of the light and dark green. In addition to comparing the results of the XRD test on light and dark, according to Chart 5, the result of the SEM test is light green; the results show that copper in alkaline glazes produces blue and in the lead glazes, green is created (about below 1% . light green is created , and creates between 2% and 3% dark green).

Table 5. The results of the X.R.D of dark green (Author, 2017)

Result	Sample code	Test code
Quartz, SiO_2 33-1161, main PPhase + $\text{Ca}(\text{Fe}, \text{Mn})\text{Si}_2\text{O}_6$ 41-1372 Hedenbergite	No, 2. Dark green	EDHE1

Table 6. The result of X.R.D test of light green (Author, 2017)

Result	Sample code	Test code
Quartz, SiO_2 33-1161, main PPhase + $\text{Ca}(\text{Fe}, \text{Mn})\text{Si}_2\text{O}_6$ 41-1372 Hedenbergite	No, 2. Light green	EDHE2

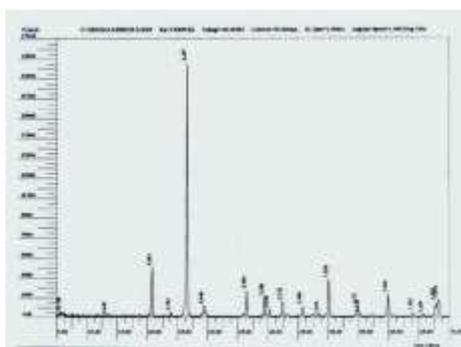


Chart 3. X.R.D test of dark green (Author, 2017)

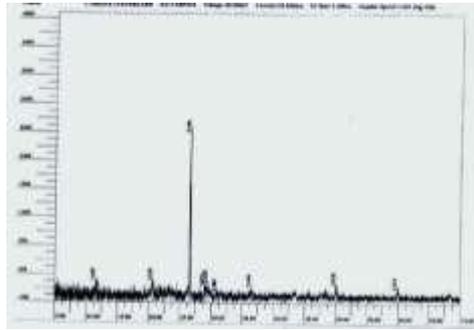


Chart 4. X.R.D test of light green (Author, 2017)

Table 7. X.R.D chart of dark green (author, 2017)

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File Name :C:\XRD\DATA\EDHE1.XRD
Lambda : 1.5405
Peak Lines In Graph Boundaries : 5.00 to 70.00 Degree :
No. Two Theta d I/I0
1 20.73 4.283 100
2 26.53 3.357 100
3 36.47 2.462 4
4 42.38 2.131 5
5 50.12 1.818 9
6 59.92 1.547 6
7 68.19 1.374 8
8 23.95 3.720 2
9 34.73 2.597 1
10 39.73 2.262 4
11 39.38 2.286 3
12 40.22 2.240 2
13 41.18 2.190 0
14 45.72 1.963 3
15 54.85 1.672 3
16 38.98 2.308 1
17 33.03 2.710 1
18 34.47 2.600 1
19 44.02 2.053 1
20 67.63 1.364 2
21 45.08 2.009 1

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Table 8. X.R.D chart of light green (author, 2017)

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File Name :C:\XRD\DATA\EDHE2.XRD
Lambda : 1.5405
Peak Lines In Graph Boundaries : 5.00 to 70.00 Degree :
No. Two Theta d I/I0
1 11.55 7.655 8
2 20.72 4.283 9
3 26.58 3.351 100
4 50.12 1.818 7
5 29.05 3.071 6
6 31.00 2.882 2
7 36.55 2.456 6
8 59.98 1.541 4
9 12.22 7.237 2
10 29.50 3.025 8

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According to the chart 5 of S.E.M test, the presence of pb (lead) in the dark green glaze is considerably noticeable, and it indicates the lead glaze of this sample. In Chart 5, SEM test, there is a major element that can be used as a dying agent in this colored glaze, cu (copper), which is substantially more significant than other elements (other than Si and Ca) . Therefore, due to the lead nature of glaze, the copper in this lead glaze can create green.

The presence of Ca (calcium) in glazes (especially lead glazes) causes the formation of white color (almost causing the enamel to become opaque). It can be said that one of the factors of dark or light color of samples 2 and 3 can be due to the difference of CaO (calcium oxide). It can be said that in light green (sample 2), CaO percentage (calcium oxide) is higher, and it is more likely that the percentage of the main colorant of Cu (copper) in dark green glaze (sample 2) is high.

The presence of gold (Au) in chart 9, SEM test is not due to the presence of gold in the glaze and color combination, but is related to the test system with an electron microscope because under the electron microscope, the electron beam hits the sample. For thermal conductivity, a layer of gold coating, thickness 20nm is drawn on a specimen and the golden peaks in the S.E.M diagram are related to this.

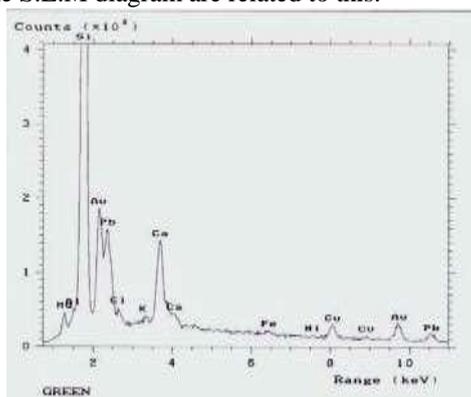


Chart 5. The result of S.E.M test of light green (author, 2017)

Titanium oxide Tio2 makes the lead glazes yellow and whitens the lead-free glazes, but it is yellow again with a small amount of iron oxide in glaze or in Titanium oxide.

The yellow glaze (sample 4) is on some Akhamanid glaze bricks is about pink and brown. (This was evident on sample 4). This glaze looks brighter than gray glaze. There are several reasons for this. One is that yellow glaze is probably lead, but gray glaze is alkaline, or that the physical and chemical deterioration on the surface of the glaze is less than that of the gray glaze, and also in the gray glaze composition, significant amounts of CaO (calcium oxide) and Tio2 (oxide Titan) has caused opaque color.

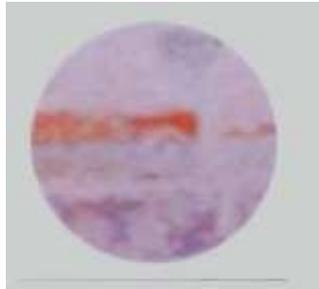


Image 7. Brick with yellow glaze (Author, 2017)

The yellow glaze performed X.R.D test, the results of which are shown in Table 10 and Figure 6 of the X.R.D test, and the S.E.M test was also performed on the above example as shown in Chart 7.

Table 10 shows that the yellow color consists of two phases, one cdPbo3 and one quartz phase with a low crystallization percentage. The peaks in Figure 6 of X.R.D are completely distinct.

Table 10. The result of the X.R.D test of yellow glaze (Author, 2017)

Result	Sample code	Test code
Cd Pbo3, 25-109	NO.5, brown	EDHE4
Quartz,Sio2, 33-1161, low Crystallinity	yellow	

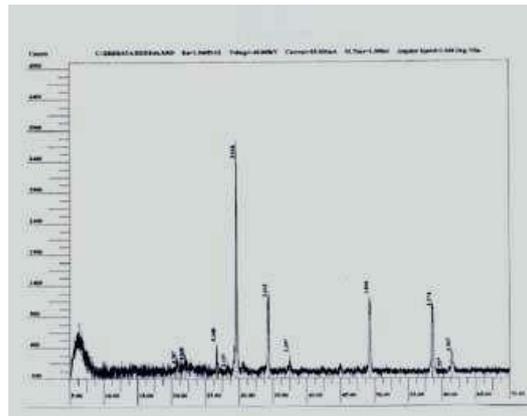


Chart 6. X.R.D test of yellow glaze (Author, 2017)

Table 11. Regarding X.R.D chart of yellow glaze (Author, 2017)

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File Name :C:\XRDDATA\EDHE4A.XRD
Lambda : 1.5405
Peak Lines in Graph Boundaries: 5.00 to 70.00 Degree :
No. Two Theta d I/I0
1 61.48 1.507 9
2 60.15 1.537 -1
3 58.60 1.574 30
4 49.32 1.846 36
5 37.49 2.397 9
6 34.30 2.612 35
7 29.59 3.016 100
8 28.24 3.157 1
9 21.99 4.039 5
10 20.80 4.267 3
11 26.67 3.340 14
    
```

Table 12. ASTM ID card of Cd pho3 (Author, 2017)

Wt %	Vol %	Oxide	Al	SiO ₂	CaO	FeO	Na ₂ O	K ₂ O	PbO	TiO ₂	Cr ₂ O ₃
1.000	10	4.8	1.000	2.1	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.000	10	4.8	1.000	2.1	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.000	10	4.8	1.000	2.1	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.000	10	4.8	1.000	2.1	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.000	10	4.8	1.000	2.1	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.000	10	4.8	1.000	2.1	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.000	10	4.8	1.000	2.1	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.000	10	4.8	1.000	2.1	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.000	10	4.8	1.000	2.1	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.000	10	4.8	1.000	2.1	0.000	0.000	0.000	0.000	0.000	0.000	0.000

In Figure 7 of the S.E.M test, the elements that were significant are as follows: Pb of Pbo (lead oxide), K of Kcl (potassium chloride), Cr of Cr2O3 (chromium oxide), Ca CaO (calcium oxide) Fe of Fe2O3 (iron oxide), Al of Al2O3 (aluminum oxide) and Ti of Tio2 (Titanium Oxide). The presence of Pb (lead) is a clear indication of the presence of yellow glaze, which is one of the main reasons for the high clarity of the yellow glaze, as compared to the gray glaze. As discussed at the beginning of the discussion (yellow glaze), in lead rich acidic glazes, addition of a very small amount of Cr2O3 (Cr2O3) leads to a yellow color at a maximum of one percent at a low temperature.

As the yellow glaze is lead, and as shown in Diagram 7 of S.E.M test, a small amount of chromium oxide is observed, so one of the factors of the yellow glaze is probably the presence of low levels of chromium oxide in the lead glaze.

The presence of Fe of Fe2O3 (iron oxide) can lead to a yellowish color that the glazing environment is a reducing environment, but so far there is no evidence to prove that the baking action is reduced to this Achaemenid glaze bricks (studied color samples). Titanium oxide makes lead glazes yellow, and here we encounter Lead glaze of Titanium oxide. So Titanium Oxide can be mentioned as a potentially probable agent in this glaze.

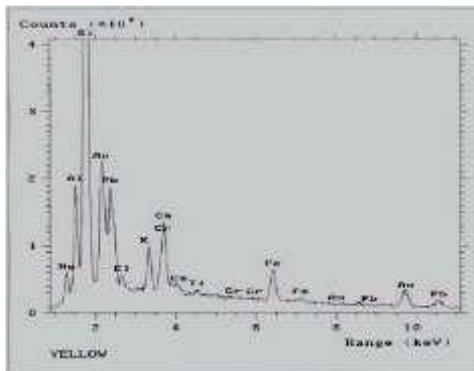


Chart 7. The result of S.E.M test of yellow glaze (Author, 2017)

In general, it seems that two factors of low chromium oxide as little and Titanium oxide are yellow glaze agents. The presence of calcium oxide can be attributed to the tendency of the above-mentioned yellow glaze to be brownish yellow. To make dark yellow glaze with Titanium oxide, you need to add some iron oxides to strengthen yellow, but excess oxide causes a change in color to brown. An increase in the amount of aluminum oxide tends to make the glaze of iron content to the brown (brownish yellow) [1].

With respect to the above mentioned materials and Chart 7 of S.E.M test, in this graph, iron is shown, and also the presence of aluminum oxide in the primary composition of glaze is significantly greater than the S.E.M charts of other colors. So, apart from all other possibilities, a more likely possibility is that the iron oxide is a yellow-colored agent in this glaze and the increase in aluminum oxide has led to a tendency of this color to brownish yellow. According to the analysis, it can be said that to make the yellow glaze (specimen 4), raw materials are used, which contained more iron oxide as impurities and more aluminum oxide in the composition.



Image 8. The microscopic image of yellow glaze (Autor, 2017)

The phases in this sample are with low crystallization percent and phase separation (border of particles) is not definite. To provide yellow similar to sample 4, we can do as follows:

By lead antimonat³, yellow is achieved and it is used to the temperature (1060) SKO2a °C. By changing B2O3 (Brox) (as used as melting aid), alkalines, quartz and iron oxide of this color, other types of yellow can be created (Ibid, 211). Zegger formula for Aventurine glaze⁴ of iron

Sodium oxide Na₂O 0.1 Aluminum oxide Al₂O₃ 0.15 Quartz SiO₂ 0.7
 Brox B₂O₃ 1.25
 Iron oxide Fe₂O₃ 0.75

The materials of above glaze are as:

- 13.5 calcinated brot
- 4.1 percentage of buric acid
- 7.2 percent of calcinated sodium carbonate
- 16% iron oxide
- 5.2% kaolin
- 5.4% quartz

If iron oxide is low, yellow glaze is created.

Conclusion. The appearance of the body of glazed bricks found in Persepolis, which has been investigated in this study, looks very porous and is light yellow such as glossy flint. Sampling of Achaemenid glazed bricks in Persepolis was very small and the experiments on them should be done very carefully. The analysis of the results from the sample which can be summarized as follows: These bricks are a completely silica body with a significant percentage of calcium oxide, which has a temperature of about 800-900 °C for baking temperature. Although this temperature is not enough to bake a completely silica body, this body is not completely dense (silica particles are not completely melted). This temperature has caused the silica particles to stick together in the corner to help for melting.

The simplest possibility is that for each glaze compound, there is only a particular material and without the addition of other materials, the particular glaze of that color is obtained. Probably, there are two basic compounds of lead and alkaline for glazes, or have a base compound (lead or alkaline) that have changed lead or alkaline in some of the materials by adding other ingredients containing coloring agents and they have created glazes with different colors. Green and yellow glazes are lead. The reason of the importance of these glazes than other glazes is their lead as transparency is still clear. In the composition of all glazes, there is iron and magnesium, probably in the main composition of the base glaze, apart from the color effect, it exists as impurities. The main coloring agents in glazes are copper oxide, chromium oxide for green glaze, iron oxide and titanium oxide and low chromium oxide for glaze. The main phase of the green is light green and dark green and as the glaze is made of lead, the presence of copper creates a green color and the change of copper amount can make the green glaze light or dark or can change Ca amount. In a very clear yellow glaze, two titanium dyes and a low amount of chromium have created yellow, and the presence of iron has led to the tendency of this color to brownish-yellow. In the end, we sincerely thank the experts and officials of the laboratory and ceramic research institute of the materials and energy research institute.

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³ Sb₂O₃ white and Sb₂O₅ yellow

⁴ A type of glaze in which there are many small crystals due to sun light as golden particles. The basic glaze is saturated with some oxides as iron, chrome and Titan and the crystals are separated and they form crystals inside the glaze (opposite to the crystal glazes as forming crystals in the surface).