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The Role of Metal Oxides in Manufacturing the Glaze

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Abstract: Tile making, one of the Mineral Chemistry Industries, is known as an ancient practise used for the decorating of historical buildings. There have been many modifications in the chemical and mineral structures of tiles during different eras-however, these changes were mostly developed in mineral oxides. The reason for using a few special elements in making tiles and comparing the used elements in one era to elements used in another era, is shown in six samples from 150 year old glazes to determine these changes: yellow, black, turquoise, blue, dark turquoise and brown. These samples were all analyzed by the PIXE method and the results have shown some differences in compounds. These varieties are mostly because of Nickel and Zirconium usage in their combinations which were used to matte yellow colors in famous Qajar tiles.

Key words: Tiles · Nickel · Zirconium · Element analysis · Mineral oxides

INTRODUCTION

Glaze is highly regarded as one of the important cultural manifestations of Iran used in Iran's historical tiled buildings. Glaze is extracted from minerals found in nature and its application began in the 4th century BC in Iran. In the beginning, the glaze was applied first on pottery and then on bricks. [1] Tiles have two sections: [1]

- The first part is ceramic, which derives from clay and is made by variable degrees of purity. Clay usually has 20 to 25% silica. Major types for tiles are from different kinds of ceramics [2].
- The second part of a tile is glaze; a glass material with different chemical combinations and is used for three reasons [3]:

For Beauty

- For creating a stable phase for bricks used in decorating parts.
- For creating a protective layer for precious buildings against chemical damages and environmental changes such as humidity and Ultraviolet (UV) lights [4].

The raw materials of glaze are as follows [5]:

Sio2 Silica: Is used to make glaze like glass

Kaolin: Will keep the enamel particles suspension

Feldspar: Provides the enamel's saturation

Flux: Brings down the glaze melting point

Metal Oxides: Tile colors depend on the used metal oxides. These oxides show different historical times. For instance, the dominant colors in the Achaemenian era were green; the Safavid era colors were blue and the colors of the Qajar era were yellow. Some of these metal oxides are copper oxide, cobalt oxide, manganese oxide, Ferro oxide, Lead oxide, Tin oxide and etc [6]. The same historical methods are used for making today's tiles; however, there are some considerable improvements in manufacturing technologies. For example, for improving the tile quality and creating different colors in glaze, the mixture and combination of a few different oxides are used [6]. In this article, the principles of tile manufacturing based on elemental analysis have been studied. For this reason, tile samples from Qajar and Safavid for elemental analysis have been chosen. The comparison of results has shown some differences and some similarities between Qajar, Safavid and today's tile manufacturing. Their metal oxides were discovered as different [6, 7].

Experimental: Qajar and Safavid glaze analysis and today's glaze examinations have been done by machines and studied as follows:

- Blue glaze analysis as old as 326 years (Safavid) by SEM EDX methods.

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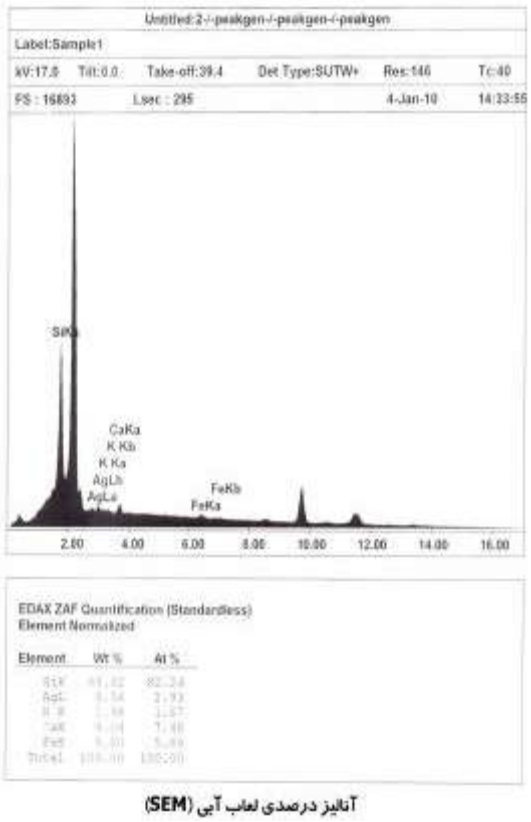
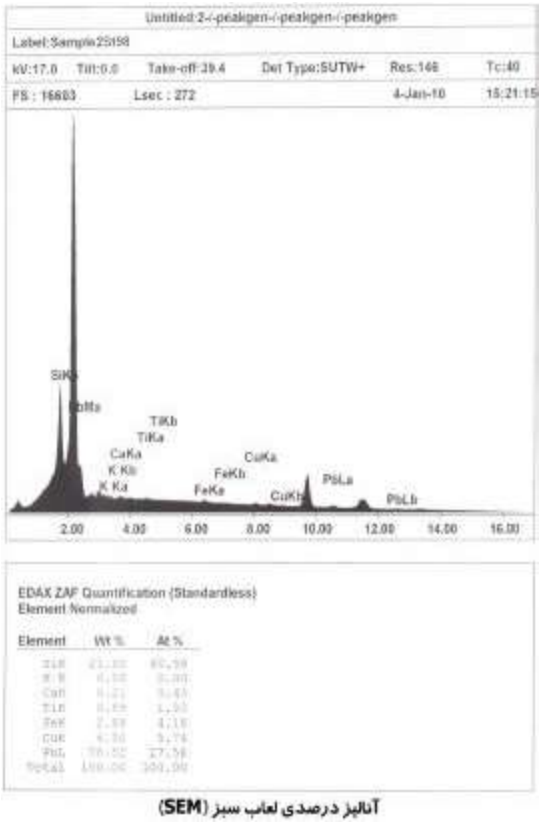


آنالیز درصدی لعاب آبی (SEM)

Blue glaze percentage analysis (SEM)
(Table and Graph 1)



آنالیز درصدی لعاب سبز (SEM)

Green glaze percentage analysis
(Table and graph 2)

The glaze sample for this experiment has been gathered from buildings residue from Safavid in Ardebil located in West-North of Iran. The analysis depth of this method is high and microscopic pictures can be prepared from the glaze, which are the reasons behind choosing this method. (Table and Graph 1) The results of analyses in percentage are as follows: Silica 69.89, Potassium 1.98, Calcium 9.04, Ferro 9.60 and Silver 9.56 Between 33 elements used for coloring the glaze traditionally in Iran, there is no name of silver. Among these 33 Oxides, 16 are the most important compounds of glaze (Pbo Oxide, Sodium and Potassium, Lithium, Calcium, Strontium, Barium, Aluminum, Titan, Zirconium, Zinc, Manganese, Silicon, Boron, Phosphor and Fluorine) [6]. The four analyzed Oxides are among these Oxides listed. It is possible that silver is used as a coating in lab methods.

Green glaze analysis as old as 326 years (Safavid) by SEMEDAX methods (Table and Graph 2).

Silicon Oxide 25.00, Calcium Oxide 0.21, Titanium Oxide 0.88, Ferro Oxide 2.88, Copper Oxide 40.50 and Pbo Oxide 70.52 were among 16 main ingredients of glaze; however, Ferro and Copper Oxides were popular for their colors.

Glaze Analysis as Old as 150 Years (Qajar) by PIXE Methods: The glaze samples were gathered from Zanjan Province in North-West of Iran and the results of the analyses are shown in Table 3. These analyses have been done by PIXE methods. The advantages of these methods are [8-10]: In comparison with XRF methods, its sensitiveness is 10 times more.The analysis depth is not high so it is a non-destructive method for samples – which is why the XRF and XRD methods have not been chosen [11-13]. As it is shown in the following table, the characteristics of Qajar tiles are distinguished by their differences from Safavid Tiles. The differences are mainly seen in Zirconium Oxides and Nickel Oxides used in yellow glaze.

A- A sample of yellow glaze from Dokhan Inn
B- A sample of yellow glaze from Dokhan Inn
C- A sample of yellow glaze from Dokhan Inn
D- A sample of yellow glaze from BiBi Khanom Mosque

E1- A sample of blue glaze from Jaame mosque in Zanjan
E2- A sample of brown glaze from Jaame mosque in Zanjan.

Table 3: The percentage of elements' consistency in Zanjan glaze samples

Sample	MgO	Al_2O_2	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	Ti_2O_3	MinO	Fe_2O_3	Cu_2O	ZnO	SnO_2	PbO	Others
A(Yellow)	-	1.79	20.82	-	-	3.91	-	1.48	0.12	-	0.48	0.06	-	4	62.27	ZrO_2: 503, NiO: 0.04
B(Yellow)	1.56	4.12	17.68	-	12.73	2.31	0.61	5.85	0.05	-	0.6	0.02	0.02	2.69	44.42	ZrO_2: 7.34
C(Yellow)	6.36	8.06	25.06	5.14	-	1.56	-	1.22	0.11	-	0.4	0.08	0.06	2.48	49.42	NiO: 0.05
D(Yellow)	-	4.48	30.66	3.15	-	2.68	-	1.17	0.11	-	0.24	0.05	-	-	53.18	ZrO_2: 4.28
E1(Blue)	-	4.45	54.9	12.43	3.55	0.78	4.32	2.83	0.13	0.04	0.95	3.79	-	-	11.83	-
E2(Brown)	-	2.81	45.41	-	6.52	0.91	5.76	6.13	-	0.1	0.29	0.08	0.08	-	19.86	ZrO_1: 12.05
E3(Yellow)	-	3.42	24.52	6.86	9.55	1.58	0.89	3.65	0.07	-	0.32	0.08	-	2.71	46.35	-
E3(Black)	-	7.34	40.33	4.36	18.76	0.56	2.24	12.3	0.33	6.98	2.04	0.15	-	-	4.61	-
F(Turquoise)	3.94	6.1	48.58	7.96	1.45	-	1.51	2.6	0.06	0.05	0.2	1.29	-	2.16	24.1	-
F(Dark Tur.)	4.45	6.33	42.61	6.7	1.27	-	1.93	1.89	-	0.05	0.24	2.33	-	2.43	29.77	-

Table 4: The percentage of elements' consistency in modern glaze samples

SAMPLE	AL_2O_3	SiO_2	Cl	K_2O	CaO	Ti_2O_3	MnO	Cr_2O_3	Fe_2O_3	MgO	CuO	PbO
A YELLOW	1.6	44.75	3.18	0.87	1.32	0.11	-	-	0.48	-	-	50.2
A1 YELLOw	5.12	63.9	2.6	033	2.46	0.08	-	-	0.15	1.5	0.02	32.4
B BLUE	3.46	77.6	1.2	2.9	1.44	0.03	-	-	0.9	-	2.56	17.8
C BLACK	6.54	34.50	0.8	1.30	4.0	-	3.78	-	1.80	-	-	47.4
C1 Black	2.30	39.30	3.92	0.16	2.51	-	3.34	0.01	0.8	-	0.1	55.1
D BROWN	1.82	38.80	5.80	0.66	5.3	-	0.08	-	0.32	-	0.4	54.32
D1 BROwn	1.67	41.40	1.10	4.9	0.20	0.03	7.4	1.8	0.1	-	0.23	36.7
E TURQUOISE	4.3	67.4	-	1.3	2.98	0.09	-	-	0.82	0.23	2.76	20.32
E1 TURQUOISE	4.6	56.83	1.53	0.68	2.19	0.06	-	-	0.6	0.1	1.18	26.92
F GREEN	5.18	82.8	2.7	2.16	5.5	-	-	-	1.3	-	0.33	-
F1 GREEN	4.56	70.53	0.9	3.12	2.5	0.4	0.04	-	1.68	-	0.76	-

E3- A sample of yellow glaze from Jaame mosque in Zanjan.
E3- A sample of black glaze from Jaame mosque in Zanjan.
F-A sample of turquoise glaze from khanom mosque in Zanjan.
F-A sample of dark turquoise glaze from khanom mosque in Zanjan.
4- Analysis of today's glaze by PIXE methods (Table 4)

RESULTS AND DISCUSSION

According to these tables (1,2,3,4) resulted from three kinds of glaze analyses, we are shown that in glaze structures, Sio2 Silica or Flint was the most important of acid oxides network forming. In addition, it was also the base for glaze composition. Lead Oxide or Pbo is from alkaline oxides used in glaze manufacturing and has Flux roles; most often, a high percentage of that is used in making glaze. Sodium and Potassium oxides sometimes replace Pbo and role as a Flux. However, Sodium oxide is used less and Potassium oxide is used as Feldspar because these two oxides reduce the Viscosity more than enough. As a result of this, there would be very fine cracks. Calcium oxide (CaO) is added as Calcium carbonate ($CaCO_3$) to the glaze and has Flux effects on it. This oxide prevents forming fine cracks on the glaze and increases the glaze stabilities. Alumina Oxide (Al_2O_3) in two different states, alkaline oxide and acid oxide, are used as a Flux in the glaze. This oxide increases the glaze suspension states in water and its chemical durability. The other oxides such as Copper oxide, Ferro oxide, Manganese oxide, Nickel oxide, Titanium oxide, Zinc oxide and Chromium oxide are used for coloring the glaze. The amount of their usage depends on the desired color needed for the glaze. The important point of these results was that the Zirconium oxide was only used in yellow and brown glazes belonging to 150 years ago (the Qajar era). This oxide, which was in the group of main acids, was used to matte the glaze. Zirconium oxide not only increases the glaze resistance against acids, intensifies the color stability, controls glaze texture unity and prevents forming fine cracks, but also reacts with Scillies, which is the main element of glaze. As a result, this combination produces Zirconium Silicate. Then, ZrSio4

reduces Silica in the glaze. As Table 4 shows, in the glazes with Zirconium, as the amount of Zirconium increases the amount of silica reduces and consequently the glaze will be matted. The reason for making matte glaze is that usually the glazes are transparent and reflect the bright light, whereas in matte glaze, the rays are not reflected harmonically and the light is decomposed which is visually very important.

CONCLUSION

There are differences and similarities found in the studies of Safavid tiles, Qajar tiles and today's tiles. The differences are from various metal oxides (main elements of glaze) and coloring oxides. In general, the usage of main oxides from 326 years ago until present has been considered as a main skill; meanwhile, that each era had been harmonized with former in glaze kinds and usage or decoration styles. Metal oxides as main or coloring compounds of glaze were commonly utilized and yet are produced as before. However, the existence of Zirconium oxide caused particular differences between today's glaze and 150 year old glaze. Usage of too much yellow in this era confirms the existence of this component because as it matted the glaze, it also decomposed the light and caused uniformity in the glaze material – thus, increasing the chemical stability of the glaze. Finally, this article has discussed the methods and basics of making glaze from 326 years ago until now. Moreover, the Zirconium oxide and Nickel oxide roles as distinguished aspects of making glazes in one era were considered the dominant color of this era.

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