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تهیه آزمایشگاهی لعابهای رنگی سرامیکی بدون سرب با استفاده از لعاب‌سازی سنتی ایرانی

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چکیده: در این کار پژوهشی، یکی از فناوریهای سنتی ایران در زمینهٔ ساخت سرامیک که پیش از این چگونگی آن انتشار یافته بود مورد استفاده قرار گرفته است. رنگ لعابهایی که در آن زمانها استفاده می‌شد معمولاً آبی بودند که برای ظروف و بسترهای سرامیکی بسیار مناسب بوده‌اند. لعابهائی با رنگهای دیگر یا ساخته نمی‌شدند و یا اگر ساخته می‌شدند گزارشی از آنها در دست نیست. هدف اصلی این کار پژوهشی، بررسی سازوکار تهیهٔ لعابهای رنگین بدون سرب و تعیین فاکتورهای اصلی آنها به روش آزمایشگاهی به صورت فرایندهای ترکیبی بر پایهٔ روش سنتی یاد شده است.

واژه‌های کلیدی: *فن‌آوری لعاب‌های سنتی ایرانی، لعابهای رنگی سرامیکی.*

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A Special Laboratory Method to Prepare Colored Ceramic Glazes Without Lead, Using a traditional Glazing Technique

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Abstract: In this research, an ancient Iranian ceramic technology, which was published previously for the first time, has been used to produce various colored ceramic glazes. The color of such ancient glazes was always blue and the suitable body for that is unique due to high quartz content. There is no report of other color productions in productive workshop and scientific publications. The basic purpose of this research was to study the laboratory preparation of colored glazes without lead using the "sedimentations process". As a result of a series of experiments, we prepared colored ceramic glazes to determine the main factors in this process based on the unique oriental technique.

Keywords: *Traditional glazing Technique, colored ceramic glazes*.

1. Introduction

1.1 The system produce

An ancient Iranian glazing technology was published in 1968 by Wulff and Koch [1]. They group found a lot of information about the production of this ancient ceramic coating technology during their trip to Iran and through visiting a production workshop in the city of Ghom. They discovered that the preparation of this ancient glazing technology has survived and is used in work instruction of Egyptian glazier makers, "Egyptian faience". Today the main parameters of making this kind of glaze are still unclear. A lot of ceramic glazed objects from ancient times contain copper based salts as a coloring pigment, which is responsible for the blue color [3, 4]. But, there are no cracks on the glaze surface as observed macroscopically by Berger and Brand [2]. The glazes and the bodies contain high silica and such glazing technology is based on the reaction between the component of a mixed powder called;"coating powder" or "developing powder" and the body during the firing process. Such process can be refered to the cementation process [1, 2]. Glaze formation on the body depends on several parameters namely: the temperature, the heating time, amount of the coating powder and inorganic pigments [5, 6].

1.2 Ceramic glazes

Glazed ceramic tiles are the most common building material, usually glazed tiles are produced from frits (glasses quenched in water) which are mixed with water and additive to yield glazes slips, this slips are applied on the surface of body tiles. Ceramics and glasses have been utilized since antiquity and their development is currently area of rapid scientific and technological progress. Glazes are amorphous ceramic with a so high viscosity that can be considered rigid. Ordinary glass which is a mixture of sodium carbonate or sodium sulfate lime- stone and sand. Microstructure of glass consists of the silicate – tetrahedron framework, [SiO_4], in the three- dimensional network within which sodium and calcium ions are embedded [7, 8].

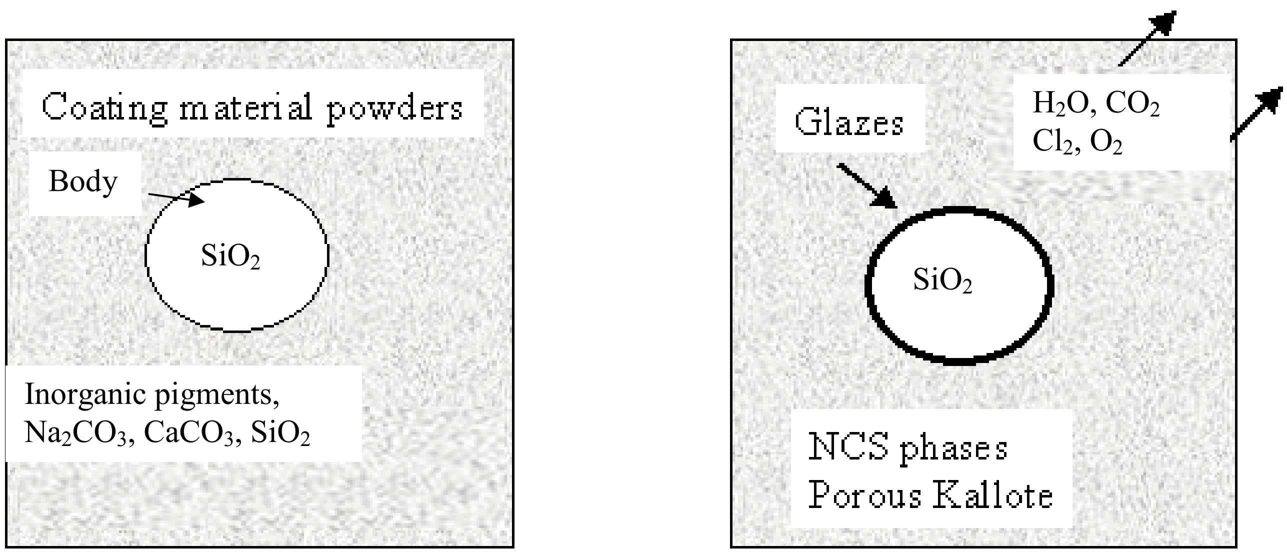
In this paper, we investigate the basic factors about preparation of glazed ceramic objects using the ancient ceramic coating technique. This kind of glazing was applied and experimental analysis method such as X–Ray diffraction analysis (XRD), Scanning Electron Microscopy (SEM) and (XRF) were also used.

2 Experimental

The starting powders for glazing of the ceramic body were based on quartz-sand and water. Due to their hardness and good glass formation with the coating powder, it is a promising candidate for this kind of traditional glazing technology.

The basic inorganic materials for the preparation of the coating powders consist of sodium carbonat, calcium carbonat and quartz. The thermodynamic calculations of the equilibria in the Na_2O – CaO – SiO_2, (NCS) oxide system have been well performed [5]. An inorganic pigment is mixed together with the coating powder. In some samples NaCl and Al_2O_3 were mixed with the coatings powders to increase the limpidity of the glazes.

In a typical synthetic procedure for preparation of NCS glazes the quartz sand as the support body was mixed with a few drops of water and subsequent in to specific forms, i.e., ball–shaped or cone-shaped. Then placed in a ceramic dish which contains the coating-powder. The coating powder was prepared by weighing and blending the selected materials and then covering the support (body) with the coating powder (Fig. 1). We select the synthesis conditions by using the phase diagram shown in Figure 2. The Body (support) covered with the coating powder was fired in an electric furnace. To remove generated gases formed during calcination, the temperature was kept at 350-400C for one hour during the heating process. The furnace was then heated with 10^0C/ min. up to 1000 ^{o}C for three hours. All samples were cooled down to room temperature. After the heating process, a porous part with special color was seen around the glazing body. This porous material is called “Kallote”. Kallote was easily separated from the glaze-surface. Then the clear glaze appeared. The best temperature and heating time was obtained during a series of experiments.



(a) **(b)**

Fig. 1. Schematic procedures of the experimental setup of the cementation and calcination processes for the preparation of traditional ceramic glazes; (a) Before sintering, the system consist of ceramic support of quartz and coating powders of NCS and inorganic pigments; (b) After calcinations and sintering formation of glazes and the porous solid solution of amorphous NCS and Kallote.

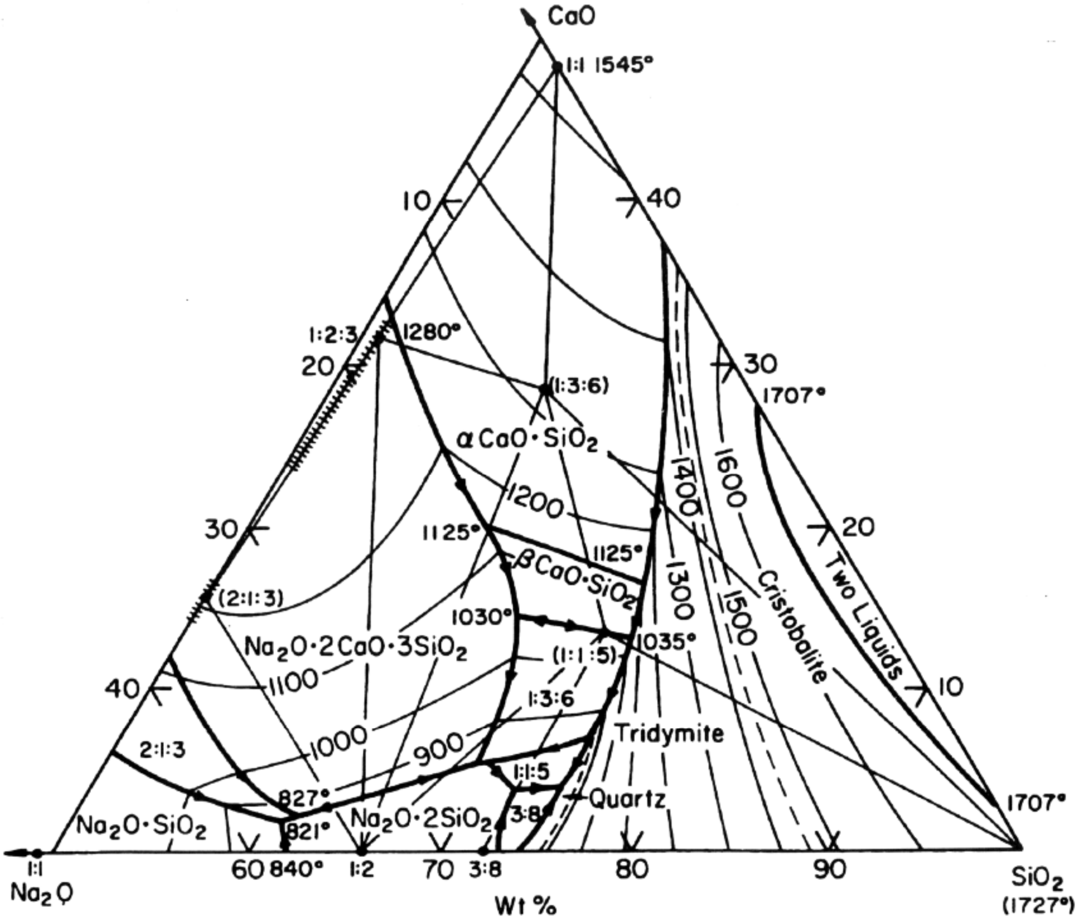


Fig. 2. The ternary diagram of; Na_2O-CaO-SiO_2 (NCS). The appropriates-district of glazes $N_1C_{2.2}S_3$ phases in the system is remarkable.

With increasing temperature and gaseous bubbles from coatings powder, the solid-solutions of NCS (Na_2O – CaO- SiO_2) and inorganic pigments formed, then the glazes and the Kallote have the same chemical composition but differ in Si amount and different physical state (e.g. glazes and porous Kallote).
The processes, which supposed to be happened, during the preparation of traditional ceramic glazes are show in Figuer 1.

Table 1 showed characteristics and color spectrum of glazes by using different inorganic pigment material; also the color of its Kallote is mentioned in this table. After cooling to room temperature glazes showed homogeneous surfaces but kallote tiles showed inhomogeneous porous and defects as bubbles in their microstructure.

Structure and the phases of the Kallote thus of the glazes and raw materials was determined by X-Ray Diffraction, using a Bruker D8 Advance from 20-60 ^{o} in 2θ with a step size of 0.01^o and step time of 1 second with a Cu-Kα radiation source fixed of 45 kV and 40 mA. The diffraction patterns were compared with JCPDS-sheets.

A scanning electron microscope (SEM) was used to study the microstructure and the morphology of the starting NCS materials, glazes and porous NCS Kallote.

The question which at once can be occur with some knowledge of ceramic technology is that; in what way during firing all place on the surfaces of silicon body will be glazed (glazing formation). This can be explained by the study of phase equilibria $N_xC_yS_z$ in the formation of the ternary system of Figure 2.

3. Results and Discussion:

In this study the preparation and sintering of the coating powders were investigated. Quartz sand, SiO_2, is used as ceramic Body and Na_2CO_3, $CaCO_3$, SiO_2 and inorganic pigments as coating materials.

Table1. The result of sintered ceramic body, using "sedimentation methods", coating powder material of NCS, and inorganic pigments, melting of coatings powder and body occurs at 1000 C and heating time is 3hrs. The colors of inorganic pigments of kallote and glaze are compared in this table.

Chemical formal of the Pigments	The color of the Pigments	Color of the Kallote	The color of the glazes
$\alpha - Fe_2O_3$	Brown-reddish	Brown-red*	White
$CoCO_3,H_2O$	Dark blue	Blue-black*	Dark blue
Al_2O_3	White	White	White
$CuCl_2$	Blue	Blue-dark brown*	Blue
MnO_2	Brown-green	Green-light brown	Light violet*
TiO_2	White	White	White
Y_2O_3	White	White	White
$BaCl_2$	White-blue	Blue-whitish	Light blue
$NiCl_2$	Green-gray	Light brown-gray*	Brown-gray*
AgCl	White	Light brown*	Light brown*
CdO	White	White	White
$Cr(NO_3).H_2O$	Green-yellowish	Green-yellow*	Green
$Ce\ (NO_3)_3.6H_2O$	White	White	White
Nd_2O_3	Light violet	Light violet	Light red – light green*
$BiCl_3$	White	White	White
β - Ce_2O_3	White-blue	Light blue – white *	White-light blue*
Zr.2.4 penl.Cl	White	White	White

*Heterogenous

3.1 Phase formation

The composition of coatings powder studied from the ternary system, phase formation of Na_2O-CaO–SiO_2. Figure 2 shows the system of NCS solid solutions. In this figure the region of obtained phases is remarkable. The system contains sodium meta-silicate, calcium meta-silicate. Glazes were easily formed by solid state–reaction between mixture of coating powder and its ceramics body, it was found that the best amount of the basic materials using for coating powder was: Na_2CO_3 (4.1 gr.), $CaCO_3$ (10.1 gr.) and $Si0_2$ (3.2 gr.).

XRF analysis of the elements in glazes shows a ratio corresponding to; sodium oxide, calcium oxide and silicon dioxide as; $N_1C_{2.2}S_3$ and for the kallote a ratio of; $N_1C_2S_{1.3}$. That is, noteworthy that the Si number of the glazes is more than the kallote. This result yielded enlightening due to replacement of Si from body across the coating powder during firing -process and to culminate in the glazes formation Therefore, this topochemical-reaction occur due to transport of siliceous from the body to the coating powder. This phenomena can be explain for the mechanism of this kind of glazing- formations.

The formation of NCS phases was initiated at the calcination temperature of 400^{o}C with dwelling time of one hour and the NCS phase formation in the sintered ceramics in sintering temperatures ranging from 1000 to 1050^{o}C with dwelling time of three hours, the basic mixed material as composition of coating powder, NSC glaze phases and the Kallote are determined by XRD and EDX.

3.2 Characterization

Figure 3a shows XRD diffragtogram of mixed coating powders Na_2CO_3, $CaCO_3$ and $Si0_2$. Figure 3b shows XRD pattern of coating powder of the blue glaze. The Kallotte was found to contain a very low amount of Cobalt oxide, which was used as the blue pigment mixed together with the Kallote that contains a Sodium oxide, Calcium oxide and Silicon oxide with (1:2:1.3) ratio respectively.

The glaze contains Sodium-Calcium–Silicate phases ($N_1C_{2.2}S_3$), the intensity of the diffraction peaks of glazes is higher than the Kallote ($N_1C_2S_{1.3}$), this indicates that the glaze is more crystalline than the Kallote. Due to very low amount of Cobali oxide pigment usually XRD diffraction lines are very weak, further more the glazes contain less cobalt oxide than the kalotte.

The microstructure, SEM, fracture morphology images of the glazes and Kallotte are demonstrated in Figure 4, it is clear that the Kallote due to calcinations during heat treatment has a porous texture. Such phenomenon is not remarkable in the case of usual glazing technology, on the other hand the glazes surfaces has glassy structure the microstructure of glazes is fine and homogeneous. As seen from the figure 4b the some $N_1C_{2.2}S_3$ crystals are formed on the surface of glazes.

Table 1 shows the result of preparation of different colored glazes. This table shows also the colors of inorganic pigments that were added to the coating powder, and also illustrates the colors of high porous part around glazes (Kallote) as well as the colors of glazes. Based on our experiments and according to the recent reports (1-3), we found the best condition for heating temperature as 1000^{o}C, and heating time for 3 hours.

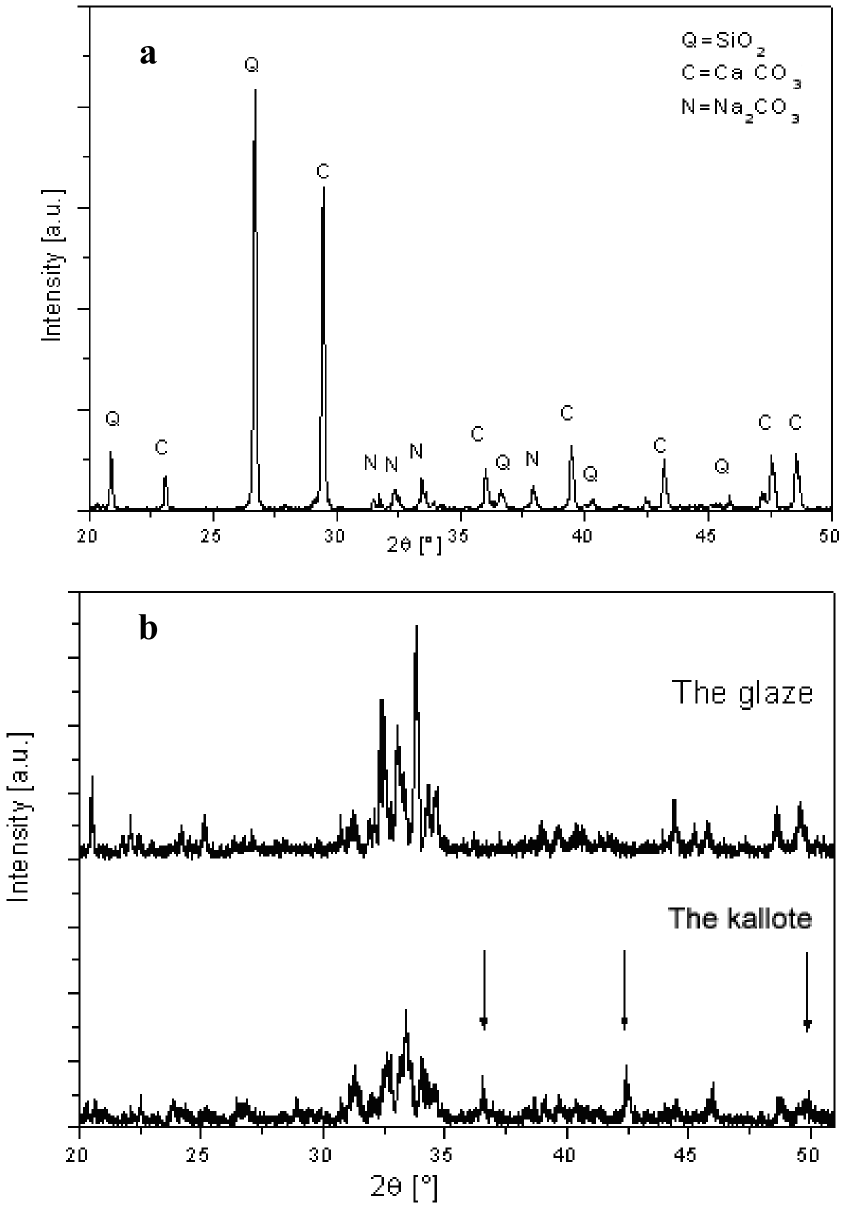
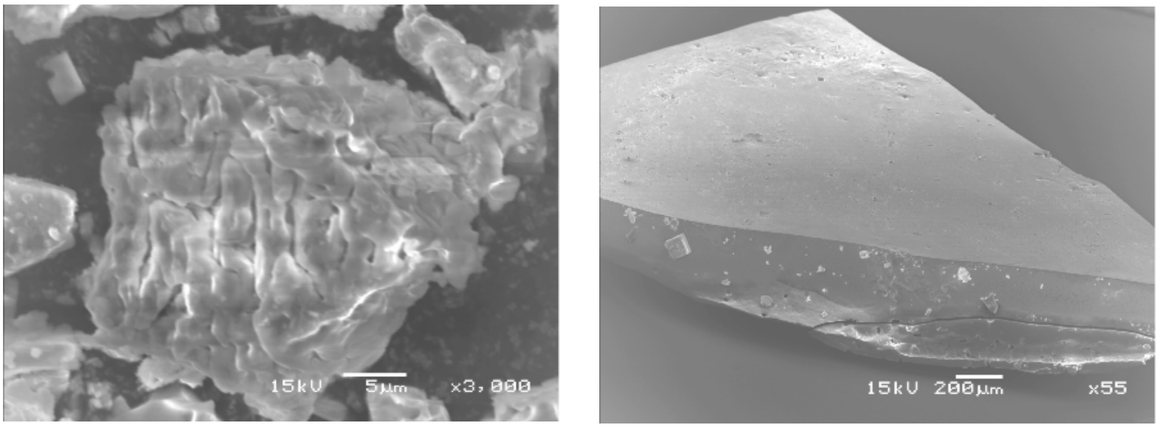


Fig. 3. **A**) X-Ray diffraction pattern of the raw materials for the coatings powders. Q=Quartz (SiO_2), C=Calcite ($CaCO_3$), N=Sodium Carbonate (Na_2CO_3). **B)** X-ray diffraction pattern of the porous part around the glazes (Kallote) and of the surfaces of glazes. The arrows indicate the presence of the CoO-pigment.



(a) (b)

Fig. 4. SEM image showing the microstructure and morphology of: (a) porous Kallote and (b) The glazed side.

There are many factors affecting the microstructures of the reaction-synthesized glazes such as particle size of row material and there purety, heating and load programs, reaction mechanism including formation of phases, reaction-kinetics, diffusion coefficients of the component (atoms or ions), phase composition, heating atmosphere, the type of inorganic colorants. The same reactions–mechanisms don't result different microstructure of the glasses, however the color of the glazes due to use different inorganic pigment will be changed.

The porous kallote considered as the lightweight ceramic material, with a number of applications. Fabrication of porous ceramic can be done by calcinations of mixture of materials after sintering (10, 11).

Due to different diffusion coefficient of transition elements as inorganic pigments during glazing the formation of color different agglomerates and states of solid solution modifications, structure and chemical bonding can reach spectrum. We could not find available data for diffusion mechanism of the Fe, Co, Al, Cu, Mn, Ti, Y, B, Ni, Ag, Cd, Cr and Ce in this work therefore it should be studied separately.

We found that the glaze – color intensity is not only dependent on the amount of inorganic pigments, but also depends on the amount of raw materials of glazes. Therefore, glaze formation is not only dependent on the amount of a certain compound but also dependent on a suitable quantity range for each raw material of coating powder. This range of materials can be determined by phase diagram.

Brown pigment of Fe_2O_3 shows a special characteristic in comparison to the other pigments, so that usingFe_2O_3 as pigment has no effect on glazes colors. Surprisingly by using this pigment, glazes colors will always be white.

It is mention that the blue color intensity on the surface of glazes was stronger than inside the object, this is due to the fact that the concentration of pigment is located at the outside of the surface and decreases towards the body center.

By using the new characterization techniques, it is possible to study comprehensively this kind of ancient glazing technology.

In order to obtain suitable materials (high–tech) for this kind of traditional ceramic, basic investigation of technical properties on microstructure of all glaze surfaces, related to its color intensity and spectrum of the glazes surfaces, and effective parameters on the processing has been achieved.

It should be mentioned that determination of the following subjects must be reviewed separately.

1) Thermodynamic study of the glaze formation according to the amounts of different pigments, and basic materials of coatings powder using thermal process.

2) Theoretical and experimental works to find physical-chemistry phenomena which depends on the mechanism of glazing formation, and further relationship between surface phenomena and solid-state reactions.

3) Diffusion mechanism which are acting on glaze produced and quartz body.

4) presence of different atoms in the raw material in relation to the color of glazes, changing the coatings powder colors after heating, and the difference between color of Kalotte and color of glaze.

4. Conclusion

There are various results and questions that are followed by this research. They are important in scientific, historical, and archaeological points. The results presented and discussed along the present work show that; for the first time a special traditional colored ceramic without lead has been fabricated, all colored glaze samples showed good behavior in color and hardness. The processing cost is not high.

The investigated kallote composition obtained by XRD showed low crystallization, the three dimensional porous kallote that evolves gases during calcinations may be an alternative to fabricate porous ceramic materials; porous silica ceramic material have a number of application. This kind of pore structures after sintering can be categorized to the lightweight structure materials.

One of the observed subjects is the effect of brown-reddish pigment of $\alpha - Fe_2O_3$ that shows an anomalous aspect. This pigment usually is used as brown-red color, but it is also used as brown-reddish pigment in ceramic factories. We have found that in the "sedimentation methods" Fe_2O_3 has no effect on glaze color. By using this pigment, the color of glazes is always white but the color of its kalotte would be brown-reddish. This anomalous phenomenon could be studied by using instrumental methods of analysis, crystal-structure and phase –diagram investigation.

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