The Use of Anhydrite (CaO.SO3) for the opacification of low-temperature ceramic Glaze

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ABSTRACT

This study attempts to search the effect of anhydrite (CaO.SO3) in the opacification of low temperature glaze as an alternative to the commonly used opacifiers. The hemihydrate gypsum (Plaster of Paris) (CaO.SO3.0.5H2O) was used as a source of anhydrite. Gypsum was added in multiple proportions to two types of alkaline glaze (NaK) and lead (Pb), which were applied to a whiteware body, the samples were burned at two temperatures (900°C and 1050 °C), and two opaque samples were selected for each type of glazes. Several analyses, examinations and calculations were done for analyzing and discussing the results, and it appeared that the cause of the opacity was the optical disturbances resulting from solid particles and gas bubbles suspended in the glazes.

Keywords: Opacity in Glaze, Suspension Particles, Gypsum-Anhydrite.

Introduction

The structural properties of ceramic materials and the knowledge of their chemical behavior allowed researchers and ceramists to invest in the preparation of various glazes, including white or colored (opaque) glaze, which is widely used in ceramic products as it covers the pottery body with a glaze layer that can be used as a base for decoration. There are several methods of opacifying glaze, the most important and best of which is the use of opacity agents (ZrO_2, SnO_2 and TiO_2), but they are expensive, so many attempts and experiments have been made to find better and cheaper means and alternatives.

In this research, we will try to use a natural material that is available and cheap, which is calcium sulfate hemihydrate ($CaSO_4.0.5H_2O$) (Plaster of Parise) as a source of Anhydrite and anhydrous calcium sulfate (Ca.SO4) as an alternative. Anhydrite is used because it is white in color and is resistant to thermal decomposition to about (1250 C°), so its presence in low-temperature glaze (800-1100°C) means that part of it remains unmolten (solid phase), while the decomposed part produces large amounts of gas (SO_3) as well as (Cao), the presence of these phases leads to a disturbance of the light and this results in a white opacity.

There were no studies or research available on this subject, except for (Chinese) laboratory experiments published in the year (2016) in which anhydrite and other materials were used to opacify ceramic glaze that matures at high temperatures (1210-1230 C°). (1)

1. Theoretical aspect.

1.1 Opacity in Glaze:

Optically, the glaze is classified into two types: The first is transparent, which has one refractive index, being homogeneous in composition, that is, when light falls on the air-glass interface, it passes through the glass before it is reflected, scattered, or absorbed because it does not contain suspended particles or phases other than the glass phase.

As for the opaque, it obstructs the passage of light. The opacity occurs due to the particles suspended in the vitreous liquid (Suspension Particles), solid, liquid, or gaseous, which cause diffusion, reflection, and refraction of the incident light because of the formation of a heterogeneous substance.

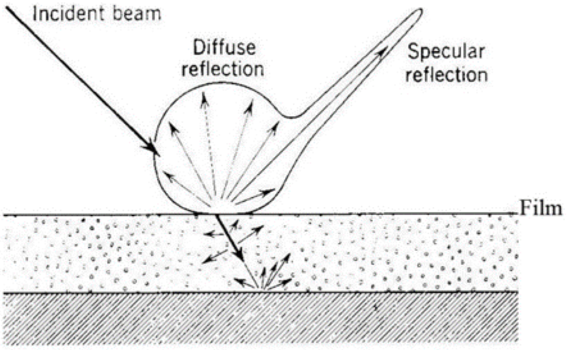

Figure (1.1) Reflection and scattering of light in glaze containing suspended particles.

The factors affecting the formation of opacity are:

1- The difference in the refractive index between glaze - continuous phase and suspended particles - discontinuous phase causes scattering of the transmitted light, noting that the refractive index of alkaline glaze is (1.5-1.6) as for lead glaze, it is (1.6-1.8) (Hamer, 1975, p.70), (Taylor &Bull, 1986, p.112).

2- The size gradient of the particles is an important factor in the spread of light in all directions due to the scattering of light as a result of refraction and reflection. When the size of the particle is less than (0.4μm) or close to the wave length, the particles are unable to repel light rays, thus decreasing the value of opacity (Singer & Sonja, 1963, p.585).

3- The shape of the crystal: if it is flat, it is more capable of the event of opacity than round crystals when the rest of the factors are equal (Allam, 1964, p.p. 162-163) (Mayanard, 1980, p.p.40-41).

4- The concentration of suspended particles in the glaze leads to an increase in the scattering of light and an increase in the opacity value.

5- The color of the opaque material, as it has a direct effect on absorbing some wavelengths of the incident light on the surface of the glaze, so the white particles reflect most of the incident rays, while the color material increases the absorption and leads to an increase in the effect of the opacity (Allam,1964, p.162).

There are several phases that cause opacity in glaze, they are:

1- Crystals that are insoluble or do not dissolve easily in the glass molten (Rhodes, 1973, p.201).

2- Recrystallization after regulating burning and controlling temperature and cooling (Taylor & Bull, 1986, p. 112).

3- The presence of two immiscible vitreous liquids (liquid/liquid) phase (Taylor &Bull, 1986, p.112).

4- Gases are formed inside the glaze layer as a result of the interaction of some compounds and the liberation of their gases (Hamer, 1975, p.p.206-207).

1.2 Bubbles in Glaze:

Glaze contains large quantities of gases, part of which remain within the composition of the liquid, and some are released in the form of bubbles of different sizes, which may be few and small, or in large numbers, and with large sizes that may be greater than the average thickness of the glaze (Taylor & Bull, 1986, p.217)

Type	Size (µm)
Blister	400-800
Orange peal	200-400
Eggshell	100-200
Bubble	80-100
Visible with hand lens	60-80
Barely visible with hand lens	40-60

Table (1.1) size and type of bubbles.

The source of the gases that form the bubbles are:

1- Chemical water (water of crystallization) in the form of hydroxyl groups bonded with the constituent elements of glass and clay compounds.

2- Air bubbles trapped in the slip glaze, as they rise either from excessive addition of the wetting agent or through the glazing process of (porous) pottery pieces where the bubbles are confined between the layers of the glaze (Kingery, 1967, p.528).

3- Through the decomposition process of some compounds, some gases are released, such as CO_2, F, Cl, SO_3 and others (Hamer, 1975, p.27).

4- From the process of disintegration of the crystal structure upon heating or when changing the valency.

As for the causes of bubbles growing and confining inside the glaze:

1- Thickness (molten) of the glaze: a great thickness leads to a longer time for the bubble to rise to the surface, and consequently, its diameter increases.

2- Surface tension: The low surface tension helps in the penetration of bubbles, while the high tension works to trap bubbles within this layer, which leads to their gathering and growth (Singer & Sonja, 1963, p. 86), (Xiong, 2004, p. 16).

3- Viscosity: Viscosity makes it difficult for bubbles to merge and grow, and by reducing the elastic limit (the Yield point) it facilitates the process of bubble growth, as bubbles are present in large numbers and small sizes in high viscosity glaze, but in low viscosity the bubbles are few and large (Taylor & Bull, 1986, p.219) (Xiong, 2004, p. 28).

1.3. Gypsum-Anhydrite:

Gypsum is hydrated calcium sulfate ($CaSO_4.2H_2O$). It is one of the common minerals in sedimentary rocks. It is found in the form of thick layers intertwined with layers of limestone and shale and is often found within the rock salt layers. Sulfur salts with low solubility are deposited during the process of evaporation of salt water and the body is formed as a result of hydration of the mineral anhydrite ($CaSO_4$). With this process, an increase in size occurs and the mineral is also found in volcanic areas as a result of the interaction of sulfur fumes with limestone rocks (Al-Busaili, 1980, pp. 168-169) (Jamil, 1980, pp. 46-47).

1- Natural features:

Colorless, white, gray, yellow, red, and brown due to the presence of some impurities, hardness (2), density (2.32), refractive index (1.519- 1.529).

2- Chemical properties:

Hydrocalcium sulfate consists of CaO 32.6%, SO_3 46.5% and H_2O 20.9%. When the mineral is heated to a temperature of (100-175 or 200 C°), it loses 1.5 parts of its water of crystallization to turn into a semi-aqueous (Hemihydrite) or what is known as (Plaster of Paris) (Norton, 1974, p. 275) which consists of $CaSO_4$ 8.93% and H_2O 6.2% (Singer & Sonja, 1963, p. 158), and by continuous heating to about 500 C°, it turns into anhydrite, which contains CaSO4 100%. This process is known Calcination, and then at a temperature of (1100-1000C°), anhydrite decomposes to CaO 41% and SO_3 59% (gas), which continues to be liberated to about 1250 C°.

$$2(CaSO_4.2H_2O) \xrightarrow{120-200C^{\circ}} 2CaSO_4.H_2O + 3H_2O \uparrow$$

$$2CaSO_4.H_2O \xrightarrow{500C^{\circ}} 2CaSO_4 + H_2O \uparrow$$

$$2CaSO_4 \xrightarrow{1000-1100C^{\circ}} 2CaO + 2SO_3 \uparrow$$

The presence of (SO_3) gas in the glaze leads to the formation of bubbles (Hamer,1975, p.151) in different numbers with it being related to the type of glazes, noting that (SO_3) gas has a density of 2.76 g/cm^3 (in relation to the density of air) (2) and a refractive index of 1.409 In 20 Cº (3).

2. Laboratory Procedures:

2.1 Chemical analysis:

The chemical analysis of the materials that make up the pottery and the glass was carried out.

oxide% Chemical) compound (4)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO3	H_2O	Total
Plaster of Paris	0.69	trace	trace	38.0	0.09	1.0	-	54.0	6.2	99.88
Silica Sand	98.08	0.33	0.06	0.09	0.03	0.03	0.02	0.07	0.22	98.93
Kaolin	47.62	35.86	0.97	0.17	0.33	0.25	0.4	0.07	12.88	98.55

Table (2.1) Chemical analysis

2.2. The ceramic body:

The ceramic body has been prepared from:
Kaolin: 80% + ground silica sand: 20%.
Glazes are not affected by color therefore; this mixture was used because it is white. The specimens were formed in the form of tiles, measuring (4 x 8 cm) with a thickness of (2 cm) and fired at (1000 C°).

2.3 Grain size of the opaque material:

The volumetric gradient is an important factor in determining the value of refraction, scattering, and light reflection. After the grinding process (2 hours / liter), a sifting was carried out, where a measurement of (200 mesh) (B.S.410) was adopted. Then the granular measurement of the opaque substance (Gypsum of Paris) was carried out using a microscope, as about 35-40 grains were measured, then the smallest and largest measurements were fixed, as well as the average, which is the sum of all the results, and divide them by the number of readings. Here it should be noted that the longest axis of the molecule is adopted (5).

Opacifying material	Smallest size	Biggest size	Average
Plaster of Paris	32.5	71.3	56.7

Table (2.2) shows the smallest and largest size and average particle size (µm)

2.4 Composition of glaze:

Experiments were conducted for mixtures of glaze that are created at low temperatures (Earthenware) (1050 and 900 C°) and two types of transparent glaze were chosen: alkaline and lead, as shown in the two tables.

Glaze	Components	900 C°	1050 C°
alkaline (NaK)	Soft alkaline (6)	60%	50%
	Kaolin	10%	15%
	Silica sand	30%	35%

Lead (Pb)	Lead monosilicate Kaolin Silica sand	70% 10% 20%	60% 15% 25%

Table (2.3) percentages of lead and alkaline glazes components according to temperature.

Grs.	Ox.	Alkaline Glaze (KNaO)				Lead Glaze (PbO)			
		900 C°		1050 C°		900 C°		1050 C°	
		%	F.U.	%	F.U.	%	F.U.	%	F.U.
RO R2O	Na_2O	10.8	0.8	9.0	0.8	-	-	-	-
	K_2O	4.1	0.2	3.5	0.2	-	-	-	-
	PbO	-	-	-	-	55.3	1.0	47.4	1.0
R_2O_3	Al_2O_3	12.2	0.6	13.4	o.7	4.6	0.2	7.0	0.35
RO_2	SiO_2	63.1	5.0	66.0	5.8	40.1	2.7	45.0	3.75
	B_2O_3	9.7	0.7	8.0	o.6	-	-	-	-

Table (2.4) Percentages and Formula Units of glazes.

2.5 Addition of opacifying material:

Plaster of Paris (the source of the opacifying substance) was added in ascending proportions in the two types of glazes to obtain the best opacity values.

Temperature	Alkaline Glaze%	Lead Glaze%
900 C°	2 ،4 ,6 ، 8 ،…………،22	1 ،2 ، 4 ، 6 ، 8 ,……،20
1050 C°	2 ، 4 ، 6 ، 8 ،…………،22	2 ، 4 ، 6 ، 8،…………،20

Table (2.5) Percentages of adding opacifying material

2.6 Firing and cooling of glaze:

1- Firing process:

After placing the specimens in the klin, and for making sure that there is no moisture that might cause a defect in the glaze layer, the specimens were heated to 110 C° for two hours at a rate of (50 C°/h) and then the method of fast firing was adopted (Taylor &Bull, 1980, p.104). In comparison with conventional firing, which depends on raising the temperature according to specific times and according to the type of glaze, this firing raises the temperature to the maximum power of the klin.

Thus, the average of firing can be obtained from the following relationship: (Abu Safiya, 1982, p. 42)

$$\text{Heating average} = \frac{\text{Temperature rise}}{\text{Firing Time}}$$
$$= \frac{T1 - T2}{t}$$

Since:

T1 = the temperature at which the rapid burning began (100°C).

T2 = Maturing temperature.

t = number of g hours to maturing temperature.

For example:

$$\text{Heating average at 900 C°} = \frac{100-900}{5} = 160\ \text{C°/h}$$

Temperature	Firing hours	Average of the increase in temperature
900 C°	5	160 C°/h
1050 C°	7	130 C°/h

Table (2.6) Number of glaze firing hours and the rate of increase in temperature.

The reason for choosing (fast firing) is to reduce time because the length of the period leads to an increase in the reaction rate of the components, and thus, the glaze loses the cause of opacity, which are the suspended particles, as (programmed) firing gives a greater chance for these particles to disappear (Taylor & Bull, 1986, p.105).

2- Cooling program:

After reaching the maturing temperature, we leave the kiln to cool down while keeping the observation hole and the ventilation hole closed to prevent rapid cooling that leads to stresses that may cause problems in the glaze layer, such as an increase in the rate of crystallization (if there is a possibility of its occurrence) or the breaking of the glaze layer.

As for calculating the rate of the decrease in temperature, it was according to the following relationship:

$$\text{Cooling Average} = \frac{\text{The decrease of temperature}}{\text{cooling time}} = \frac{T1 - T2}{t}$$

Since:
T1 = the lowest temperature at which the kiln is opened (100°C).
T2 =maturing temperature.
t = number of cooling hours to (100 C°).

$$\text{Cooling average at 900 C°} = \frac{100 - 900}{12} = 67\ \text{C°/h}$$

Temperature	Cooling hours	Average in the decrease in temperature
900 C°	12	67 C°/h
1050 C°	15	63 C°/h

Table (2.7) Number of cooling hours and the rate of decrease in temperature

2.7 Determining the specimens:

Two specimens were selected for each type of glazes based on the highest percentage of opacifiers addition that gave the highest value of opacity before the surface of the glaze became (matt). The type of opacity and color were determined, according to the type of glaze, temperature, and percentages of addition (gypsum) (Hemihydrite), the source of (Anhydrite). paragraph (1.3).

Glaze	Temp C°	(7) Plaster of Paris% (G)(8)	Anhydrite %	CaO%	SO_3%	Opacity and glossy	Color (9)
NaK	900 1050	14 16	13 15	5.3 6.2	7.6 8.8	3-O 4-O	gray white pale white
Pb	900 1050	10 14	9.4 13	3.9 5.3	5.5 7.6	2-O 3-O	whiteish yellow yellowish white

Table (2.8) Specifications of specimens
O = Opaque (opaque), 2- 4 = (Gloss gradient)

2.8 Glaze Experiments:

A slip glaze was applied by spraying glaze mixtures with a thickness of about (1 mm) on ceramic tiles with dimensions of (4cm x 3cm), and after firing, the thickness of the glaze became about (0.48-0.53 mm), and the measurement was taken through the cross sections.

3. Examinations and Results:

A number of tests were conducted on the glazes to determine the causes of opacity as follows:

3.1 Microscopic examination:

The specimens were examined to identify the content of the glaze layer.

Glaze	Bubbles (μm)	Suspension Particles (μm)
NaK900G14	High percentage، small :10-20 Medium: 20-40 Large: 50-40	1- White, leftover material 2- Yellow, few but large sizes measuring about 50 3- Red, very few and measures 50-20
NaK1050G16	Difficulty distinguishing because of the degree of whiteness	Difficulty distinguishing details due to high opacity.
Pb900G10	Difficult to distinguish, the sizes are between 10-30 and there are white colloidal lumps.	1- white, high residue, size 10-30 2- red, very few and in size 20-40
Pb1050G14	Difficulty distinguishing because of the degree of whiteness	1- white leftover material 30-10 2- brown and red, small 30-10

Table (3.1) results of microscopic examination.

3.2 Mineral analysis (X.R.D.):

The examination revealed the crystallized or insoluble minerals in the glazes therefore; the chemical composition, color, density, refractive index, and construction systems were identified. The examination was done to the specimens that were fired at (1050 C°), while the specimens that were fired at (900 C°), the percentage of insoluble materials is expected, and mostly have a known composition. This was concluded from the microscopic examination.

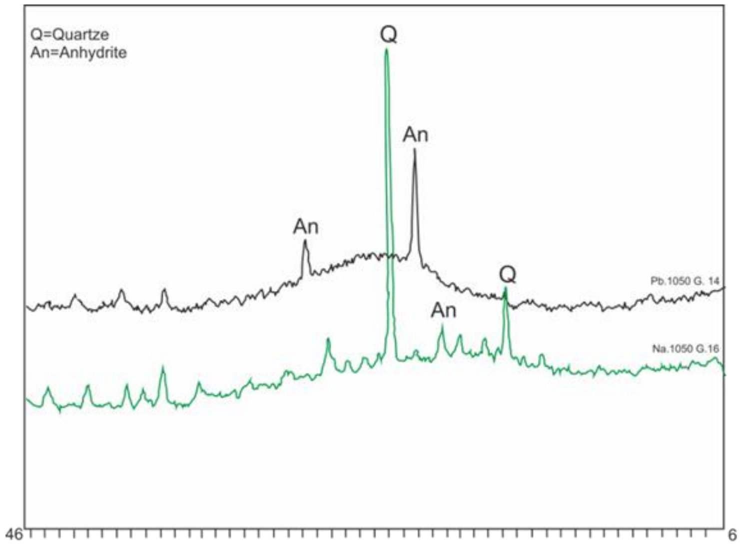

Figure (3.1) The minerals of glazes at (1050°C) using (XRD).

Mineral	Chemical formula	Specific gravity	refractive index	crystal system	color
Anhydrite	$CaSO_4$	2.97	1.567	Orthorhombic	white
Quartz	SiO_2	2.65	1.553	trigonal	colorless

Table (3.2) Properties of minerals of glazes at (1050°C) (10).

3.3 Calculating the density of transparent glaze:

Density is important in determining the reflectance ratio and the value of the optical refractive index. The densities of glazes range between (2.125-8. 120 g/cm^3), as the lowest density glazes are borosilicate then alkali, and the highest density glaze is lead glaze (Allam, 1964, p. 133).

Density was measured using powders of glazes through the use of pycnometer (50 ml), and the following relationship was applied: (Akroyd, 1969, pp49-50): (Zamzami, 1996, p. 82).

$$Density = \frac{Wd - Wc}{(Wx - Wc) - (Ww - Wd)}$$

Since:
Wc = Weight of empty beaker.
Wd = Weight of beaker + powder.
Ww = Weight of beaker + water + powder.
Wx = Weight of the beaker + water only.

Glaze	Density g/cm^3
NaK900G14	2.45
NaK1050G16	2.49
Pb900G10	7.15
Pb1050G14	6.47

Table (3.3) Density of glazes

3.4 Refractive Index Measurement:

The refractive coefficients of glazes were measured by the Immersion Method and using the Becke line by a polarized light microscope, whereby a quantity of glaze powder is immersed in an oily liquid with a known refractive index and the Becke line (which is a luminous line surrounding the grain) is observed, where it moves according to the refractive index of the immersed material and the oily liquid. The liquid is changed until it is difficult to distinguish this line which means that the refractive index of the granule is the refractive index of the liquid. (Al-Jubouri, 1989, p. 110-115), (Bloss, 1961, p.52).

Glaze	Refractive index
NaK900G14	1.670
NaK1050G16	1.678
Pb900G10	1.800
Pb1050G14	1.790

Table (3.4) Refractive index of glazes

3.5 Optical Reflection and spectral analysis:

a- The percentage of light reflection was measured according to the type of glazes, the maturing temperature, and the degree of opacity, by which this percentage increases.

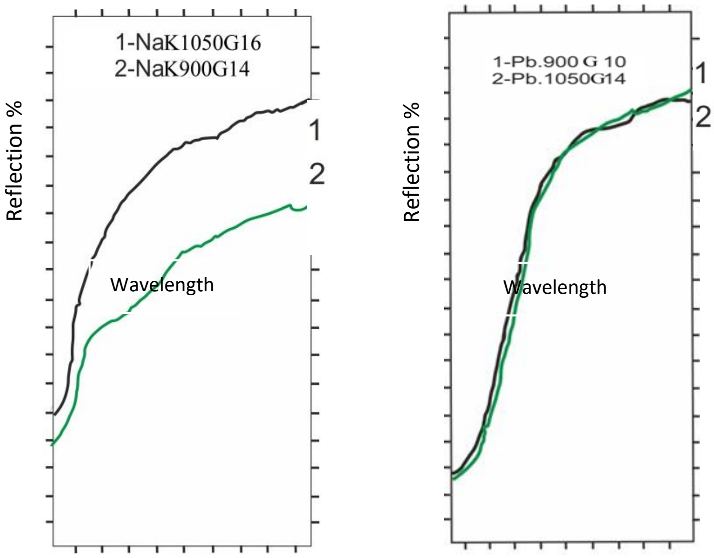

Figure (3.2) Reflectivity of glaze specimens.

b- To know the values of the main color spectral (B.G.R.), the glazes were analyzed using Photoshop.

Glaze	R	G	B
NaK900G14	250	220	182
NaK1050G16	253	228	210
Pb900G10	255	235	192
Pb1050G14	255	232	198

Table (3.5) Optical spectral ratios (B.R.G.) for glazes.

4.Discussing the results:

4.1 Microscopic examination results:

a- Bubbles:

Controlling the formation of bubbles and determining their proportion, type, and size in the glazes are not possible because they are affected by several factors and cannot be subjected to a rule (Telller, 1979, p. 31).

- The most important factors affecting the presence of bubbles:

Viscosity and surface tension, with their increase, the gases remain confined to the glazes layer, and when they decrease, their percentage decreases (as the rise in viscosity corresponds to the rise in surface tension) (Hamer, 1975, p.287). Table (4.1).

Glaze	Surface tension dyn / cm
Nak900G14	22.5
NaK1050G16	19.74
Pb900G10	11.64
Pb1050G14	10.12

Table (4.1) Surface tension values for glazes (11)

The fast-firing method works to confirm the opacity, as it does not give enough time for the components of the glaze to form a liquid with a high fluidity, which results in a glaze liquid with sufficient viscosity and surface tension to hinder the merging and liberation of gas bubbles. In addition to that, the liberation of gases does not occur at a specific temperature, rather, it is within a thermal range, and for this reason, this type of firing does not allow materials that contain gases in their composition to decompose easily, and this leads to the continuation of the release of gases until the end of the firing range.

Another factor that contributes to the trapping of bubbles is the critical melting point (Eutectic point) (Hamer, 1975, p.114), at which, vitrification occurs for the surface of the glaze layer (Britt, 2004, p.46), as a viscous liquid is formed that prevents the gases from penetration after being separated from their compounds. This occurs at the beginning of the firing range due to the sudden high temperature of fast firing.

In addition, the thickness of the glaze layer has an effect on the liberation of bubbles. An increase in the thickness, causes an increase in the distance that the bubble travels to rise to the surface (as the strength of the fluid resistance is directly proportional to the degree of viscosity, the diameter of the bubble, and its velocity) according to Stokes' law (Pearson, 1982, p. 48).

From the foregoing, and through the microscopic examination of Table (3.1), we note that at a temperature of (900 C°), the alkaline glaze, which has a eutectic temperature of about (825 C°), contained bubbles of relatively large sizes because the phase of (vitrification) and then (melting) occurred late which means that the reactions occur near the end of the thermal range (Table 2.6), which, in turn, led to the formation of a glassy liquid with high viscosity and surface tension, so it formed pressure inside the glaze and its surface that allowed the merging of gas bubbles.

While in lead glaze which has a eutectic temperature of about (600 °C) (Alhindawi, 1997, p.201), the bubbles are difficult to distinguish due to their fineness which is a result from their inability to merge because of the low viscosity and surface tension.

The opaque substance ($CaO.SO_3$) is resistant to heat and decomposition, especially at low temperatures, so the high percentage of gases (bubbles) in alkaline glaze is caused by it being more effective for interaction with these substances (Table 2.8) compared to lead glaze, which is characterized by weak interaction and inability of peptization of high proportions of these substances (Alhindawi, 1997, p.204), and therefore the percentage of liberated gases is low. As for the glazes of (1050 C°), the examination showed difficulty in distinguishing its content due to (white opacity) which is due to the high concentration of fine bubbles of (SO_3) gas, which is liberated at this high temperature at a high rate, and at this temperature, there is a decrease in viscosity and surface tension which disallows the merging of micro bubbles.

In general, the viscosity of lead glazes is much lower than that of non-leaded glazes at the same temperature (Singer & Sonja, 1963, p.538).

The opacity occurs as a result of bubbles visible through magnification of the glass, but there may be very fine bubbles (ultrafine) that cannot be distinguished by magnification of the glass and are not distinguished by the ordinary microscope, and this may be a colloidal liquid. Whatever the size of the bubbles, they lead to the scattering of light and the formation of opacity (Hamer, 1975, p. 70, 206)).

b- Solid particles suspended in glaze:

From Figure (3.1) and Table (3.2) it is noted in all specimens that the solid particles are non-molten materials, and were not formed as a result of the recrystallization process due to the fast firing mechanism that leads to incomplete decomposition of the opacifiers, especially as it is heat-resistant, as well as the cooling mechanism that lowers the viscosity rapidly which hinders the movement of ions to form a crystalline structure (Hamer, 1975, p.92) (Taylor & Bull,1986, p.p.118-119). As the eutectic solution melts into the glaze (a eutectic mixture) first, then the excess of the formation melts by a continuous rise in temperature, and this excess may not get enough time to reach complete fusion (Allam, 1964, p. 54) (This means that part of the material remains not fusible).

Lead glaze, in addition to being poorly reactive with earth materials, is one of the materials that resist crystallization (Al-Badri, 2003, p.89), this mean that (unmolten) suspended particles are high in (anhydrite and quartz) compared to the alkaline glaze, in which the melting is relatively high, indicating that the structure of glaze is the result of the reaction of oxides, so the components either decompose and enter the reaction, or their molecules remain suspended in the liquid and separated from it.

At a temperature higher than (1000 C°), the percentage of calcium oxide (CaO) resulting from the decomposition of anhydrite ($CaO.SO_3$), which interacts with the components of glaze and melts at the melting temperature of the mixture to act as a fusion aid (Allam, 1964, p. 14), thus, calcium oxide, at a temperature less than (1100 C°), is ineffective, as it is an (anti-flux).

10% or more of (CaO) can be absorbed by low-temperature glaze, so its presence in these ratios (Table 2.8) is ineffective and may cause a slight loss in the gloss of glaze (Hamer, 1975, p.p.42,287), so it is noted that the opacity of the glaze at (1050 C°) is higher than at (900 C°), and alkali glaze is relatively higher than lead glaze, where the temperature and the type of glaze are influential in decomposing ($CaO.SO_3$) and liberating its content.

- From Table (3.3), lead glazes have a higher density compared to alkaline glazes, and this is caused by the specific densities of flux oxides: (Na_2O - 2.3 g/cm^3), (K_2O - 2.32 g/cm^3), and (PbO - 9.33 g/cm^3) (Hamer, 1975p.343), and the densities of suspended substances in the glaze liquid (Quartz and Anhydrite) (Table 3.2), as well as gases, which are mostly (SO_3), as the difference between the densities of the opacity phases (gases and solid) and the density of the alkaline glassy phase is relatively low compared to the lead glassy phase where the difference is large. This causes optical disturbances, leading to the formation of opacity.
- The refraction coefficients of the phases constituting the glaze and their different values are determined by the density values, according to which, the refractive coefficients change (Tables 3.4 and 3.2) (Ali, 1973, p. 220), as the increase in the percentage of differences increases The intensity of the light scattering through the glaze which leads to a high opacity value, and as mentioned above, the differences between the phases (gaseous and solid) and alkali glaze are low compared to lead glaze due to the high refractive index of (PbO) which is (2.61).
- Increasing the concentration of the opaque substance increases the percentage of the spread of its phases in the glaze, which leads to higher values of refraction coefficients and light reflections and thus, an increase in opacity. The concentration does not only mean the percentage of the added opacifier, but rather the percentage of materials produced after interaction with transparent glaze, that are insoluble substances, and the materials resulting from the decomposition of the dissolved part that are gases and others. Tables (3.2 and 3.1).
- The sizes and shapes of the opaque phases are, in general, relatively large (Table 2.2). As for their irregular shapes, the solid ones are insoluble materials due to grinding and corrosion during firing and interaction, so they disperse light from multiple points and in different directions. As for the bubbles, they are regular in shape which leads to the light

suffering from uniform scattering. (Kingery, 1967, p.p.527,531) (Al-Sharbati, 1982, p. 213) Figure (1.4)

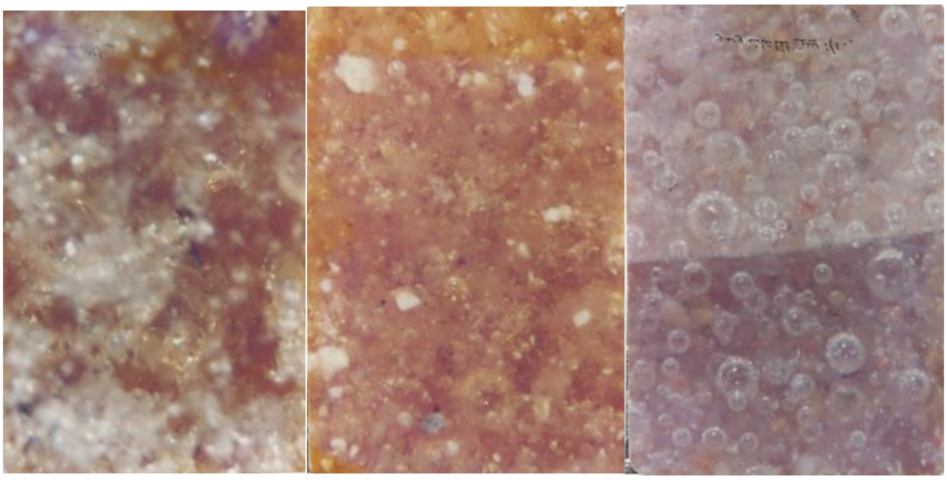

Figure (4.1): Solid particles and bubbles suspended in the glazes.

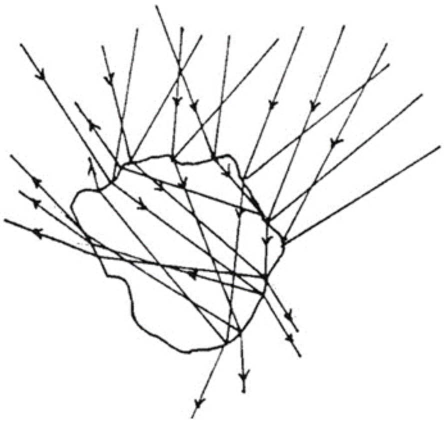

Figure (4.2): Scattering of light from an irregular particle.

- The optical properties of the phases that form the glazes (liquid, solid and gas) in terms of color, transparency, and opacity.

Phases	Material	Color	transparency and opacity
Liquid	Alkaline glaze Lead glaze	colorless yellowish	transparent transparent
Solid	Anhydrite ($CaO.SO_3$) Quartz (SiO_2)	white colorless	opaque transparent
Gas	sulfur trioxide (SO_3)	Colorless (12)	transparent

Table (4.2) The phases that formation the glazes and their optical properties.

Table (4.2) shows that the yellowish (lead glaze) is more absorbent of light, and this raises the value of the refractive index compared to the colorless (alkaline glaze), while (anhydrite) is a strong reflector of light because of its whiteness, and (SiO_2 and SO_3) are colorless. In general, the light suffers from scattering during its penetration through all transparent or opaque components.

- It appears in Figure (3.2) that the percentage of light reflection in the alkaline glazes (1) (NaK900G14) is less than the (2) (NaK1050G16) due to the high percentage of the opaque substance, the high temperature, and the release of a large percentage of (SO_3)

and (CaO), which caused the formation of a white colloidal cloud, but in lead glazes, the reflectivity is equal in the (1) (Pb900G10) and (2) (Pb1050G14) as a result of the equal value of opacity and color at a high rate despite the difference in the percentage of opaque substance and the firing temperature, and it is thought that the glaze that has a melting base (PbO), and because of its low interaction with earthen materials, as mentioned above, it is less absorbent of high percentages of these materials which means that the glaze liquid is saturated with an excess of the reaction, so the increase in the percentage of the opaque substance does not affect the opacity value even if the temperature increased.

Since the research specimens have a glossy surface, it should be noted that the film layer (13) affects the reflection and penetrating ratios of light. Figure (1.1).

From Table (3.5), it is noted that the digital values of the color spectra have determined the degree of white and colored opacity, where the alkaline glaze showed a higher degree of whiteness than in lead glaze in which the whiteness leans to a yellowish white, as the highest value (255) for each of (B.G.R.) means the glazes are whiter (Al-Bahnassi et al., 2011, p. 32).

Conclusions:

1- The opacity produced by anhydrite ($CaO.SO_3$) in low-temperature glazes is the result of incomplete decomposition and gas bubbles that result from decomposition.

2- The main reasons for the opacity of lead glaze are the lack of complete fusion of the opaque substance, while the opacity of the alkaline glaze is caused by the liberated gases.

3- The degree of opacity of alkaline glaze is whiter than lead glaze because (PbO) has a yellowish color.

4- Other materials can be used to achieve the opacity of one of the three phases after identifying their properties.

Endnotes

(1) patents.google.com/patent/CN104529543B/en

(2) https://pubchem.ncbi.nlm.nih.gov/compound/sulfur-trioxide

(3) www.vaxasoftware.com/doc_eduen/fis/inrefraction.pdf

(4) Kaolin, Silica Sand, Gypsum-Plaster of Paris (Slot).

(5) The lens used has a magnification of 500, so the results are multiplied by x 0.002 or 500/1 to convert to (mm)

(6) Wenger Ltd., p.p.4-5

(7) Plaster of Paris - CaO.SO4.1/2H2O

(8) G: dark material symbol

(9) Korneup, 1981.

(10) (Mason & Berry, 1968, p.p. 363-364,410-412)

(11) http://webmineral.com/data/Anhydrite.shtml#.YSu2HLDXLIU)

(12) The surface tension was calculated using the surface tension coefficients of the glaze-composition oxides (Singer, 1963, p.539).

(13) echa.europa.eu/registration-dossier/-/registered-dossier/15436/4/2.

(14) The film: a very thin slice, which is the surface part of the glaze layer, and is often transparent and pure due to its direct exposure to heat which leads to complete melting and low viscosity, which produces a layer free of suspended solids and gas bubbles (Hamer & Hammer, 2004, p.186) (Alhindawi, 1997, p.21).

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