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ARAŞTIRMA MAKALESİ / **RESEARCH ARTICLE**

THE USE OF ALTERNATIVE RAW MATERIAL IN STONEWARE GLAZES

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ABSTRACT

In this study, Kütahya region's perlite with high alkali oxide content, at the present time not being assessed in the ceramic industry, was used in stoneware glazes replacing albite, orthoclase and ulexite in the starting batches. New glaze recipes were composed by adding perlite to the standard glaze composition consisting of quartz, kaolin, ulexite, albite and orthoclase. The effects of such a compositional modification on the optical parameters and melting properties of the relevant glazes fired at 1160 °C were investigated. The chemical (XRF) and mineralogical analysis (XRD) of fluxes were also determined.

Keywords: Flux, Stoneware glaze, Glaze properties.

STONEWARE SIRLARINDA ALTERNATİF HAMMADDE KULLANIMI

ÖZ

Bu çalışmada stoneware sır bileşiminde yer alan albit, ortoklas ve üleksitin yerine Kütahya'dan temin edilen alkali oranı yüksek, seramik endüstrisinde bugüne kadar değerlendirilmemiş perlit hammaddesi kullanılmıştır. Perlitin, kuvars, kaolen, üleksit, albit ve ortoklas içeren standart sır reçetesine ilave edilmesiyle yeni reçeteler oluşturulmuştur. 1160 ^{o}C'de renksiz ve renklendirici oksit ilavesi ile pişirilen sırların optik parametreleri ve ergime özellikleri üzerinde bu bileşimsel uyarlamaların etkileri saptanmıştır. Aynı zamanda ergiticilerin kimyasal analizleri (XRF) ve minerolojik bileşimleri (XRD) belirlenmiştir.

Anahtar Kelimeler: Ergitici, Stoneware sırları, Sır özellikleri.

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1. INTRODUCTION

The most challenging materials to adapt for glaze-use are hard igneous rocks, such as granites, granodiorites and basalts. Once prepared, they may make wonderful glazes with virtually no additions. Having at one stage been entirely molten (hence their igneous description) they can be melted again in the kiln to give thin impermeable glassy coatings to clays (Sutherland, 2005). Perlite is an acidic volcanic glass. This name comes from its pearl-like small spheres lusters obtained when some types of perlite to get broken, meanwhile the name is derived from the word "perle" which means pearl. Perlite is a kind of expandable rock with heat treatment, becoming very light and porous structure after expansion process ended. The word "perlite" is used for both raw perlite as well as for the product obtained from expansion of perlite. Perlite rocks may differ from each other in terms of color and structure. The color of crude perlite may change from transparent light gray to bright black. When perlite is expanded its color turns to white completely. The most important feature in perlite is 2.5 % bonded water being in the hydrated vitreous silica structure and, of which provides the stability of perlite. When perlite is suddenly heated to 750-1200 °C, due to the removal of bonded water in the body, an expansion results in foam aggregate consisting of glassy grains. It is expandable up to 20 times by volume comparing to its original volume. This product is called as expanded perlite (The Working Group's Report of the Mining Special Expertise Commission, 2001).

Stoneware glazes become a part of body after firing and enhance mechanical strength of the final products. Their surfaces vary from shiny to textured structure. Gasses in furnace atmosphere play an important role on the development of glaze characters and lead to lower melting points of some glaze and body constituents. This type of glaze usually contains feldspar up to 50 % and fine silica as 20 %. Moreover, there is also a balance between earth alkali. Stoneware glazes are highly resistant to scratching and acid attacks. Depending on the customer's demand, they can be transparent, colored, crystalline or matte. In stoneware production feldspar and sometimes lead-based glazes are chosen. Stoneware thought to be used as kitchen and tableware have to be covered by special glazes that are resistant to chemical corrosion, may be rock-like in color and texture, may reflect and reveal the earthy origins of pottery. The character of these glazes is very difficult to simulate at lower temperatures (Behrens 1971, Karasu 2003, Rhodes 1973).

In this study, Kütahya region's perlite raw material with high alkali levels, which are at the present time not being assessed in ceramic sector, was used instead of albite, orthoclase and ulexite in stoneware glaze and colour and melting properties of glazes were investigated.

2. EXPERIMENTAL STUDIES

The Seger formula of standart transparent stoneware glaze (S1) including sodium feldspar, potassium feldspar, ulexite, kaolin and quartz is given Table 1.

Table 1. Seger formula of the standart transparent stoneware glaze.

Glaze No	Seger Formula		
S1	0.402 Na_2O 0.186 K_2O 0.412 CaO	0.500 Al_2O_3	4.396 SiO_2 1.031 B_2O_3

The chemical analysis (XRF) and mineralogical analysis (XRD) of the starting raw materials were determined. By adding perlite taking from Kütahya to the standard glaze composition consisting of quarts, kaolin, ulexide, albite and orthoclase, new glaze recipes were composed. After weighing the glaze compositions the batches were, first of all, milled for 30 min. The resultant slurries were sieved through 60 μm and their liter weight (1400 gr) and viscosity values were controlled. Then, they were applied onto stoneware bodies. Optical parameters of the coloured glazed samples, which were fired at 1160 °C directly, were investigated by Minolta 3600-d spectrophotometer.

Throughout the whole study a total number of 6 different stoneware recipes were tried, in which the perlite concentration was raised up to 70 %. Of these recipes the standard body (S1) and those with the perlite addition as 20 % (S2), 20 % (S3), 40 % (S4), 30 % (S5) and 70 % (S6) replacing Na-feldspar, K-feldspar, ulexite, kaolin and quartz in the starting recipe were reported hereby (Table 2).

Table 2. Recipes of the standard (S1) and perlite added glazes

Raw Materials	S1	S2	S3	S4	S5	S6
Sodium Feldspar	20	20	-	-	20	-
Potassium Feldspar	20	-	20	-	20	-
Ulexite (U)	30	30	30	30	-	-
Quartz (Q)	20	20	20	20	20	20
Kaolin (K)	10	10	10	10	10	10
Perlite (P)	-	20	20	40	30	70

Since the study was mainly concentrated on the art objects, firing strength values have not been, in the first place, measured. Besides the measurements of optical parameters, characterization studies with XRD and hot stage microscope were also conducted.

3. RESULTS

In XRD analyses of perlite the glassy behavior was observed (Figure 1). Chemical analysis of the raw materials used in the study is presented in Table 3.

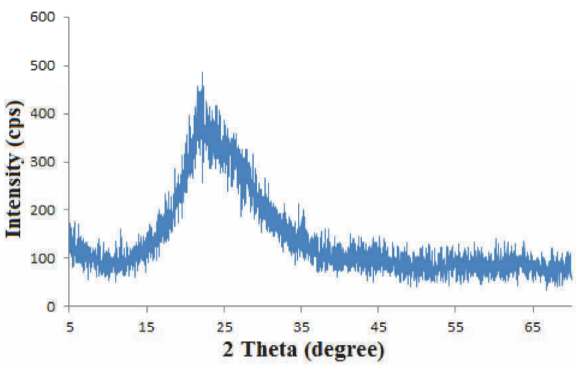


Figure 1. The XRD pattern of perlite raw material.

Table 3. Chemical analysis of the starting raw materials used in the study (wt. %)

Oxides	Na-F	K-F	U	K	Q	P
SiO_2	68.87	67.06	2.87	69.12	99.50	71.74
Al_2O_3	17.46	17.15	-	18.98	-	12.87
Fe_2O_3	0.06	0.16	0.20	0.80	-	0.94
CaO	0.58	0.14	15.45	1.30	-	0.95
MgO	0.03	-	1.54	1.51	-	0.21
Na_2O	12.08	2.64	6.48	0.25	-	3.65
K_2O	0.25	12.65	0.18	2.93	-	5.16
TiO_2	0.27	-	0.04	0.80	0.07	0.26
B_2O_3	-	-	38.67	-	-	-
*L.I.O	0.40	0.20	34.57	4.31	0.43	4.22

*L.I.O: Losses on ignition.

From XRF analysis, the materials having 0.94 % Fe_2O_3 by weight of perlite results in effective impact on the color of fired glaze, depending upon the firing temperature. Ferric compounds intrinsically present in varying concentrations in traditional ceramic raw materials being used for glaze and body. These compounds act as a colorant in different ways, and the coloring effect varies according to the composition of glaze, weight percentage in the material and kiln firing atmosphere. Fe_2O_3, TiO_2, and other impurities lead to the discoloration of raw materials (pink,red,brown) afterfiring (Rhodes1973).

The particle size distribution curve for used perlite is given in Figure 2. According to the results the average particle size of perlite is 16.149 µm, d (0.1) value is 5.206 and d (0.9) value 39.005 µm.

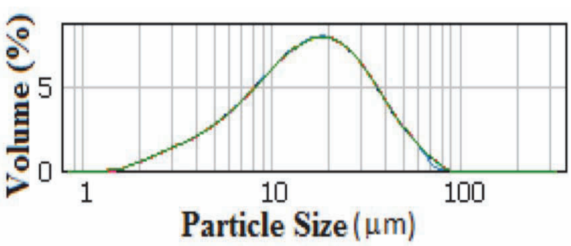


Figure 2. The grain size distribution curve for perlite.

From Figure 3 the hot stage microscope analysis of perlite indicates the sintering and softening temperatures of perlite being 1066 ºC and 1262 ºC respectively.

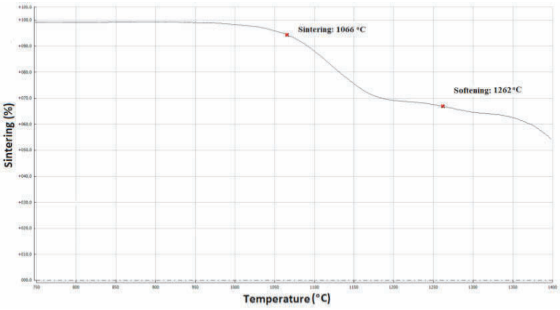


Figure 3. The sintering curve of perlite.

According to the dilatometer analyses, the thermal expansion value (α) of perlite at 400 ºC is 54.3 ($x10^{-7}$ 1/ºC). In Figure 4, the natural and firing (at 1160 ^{o}C) appearance of perlite are presented. As seen, the natural color is gray and firing one is light buff.

Natural Appearance 1160 ^{o}C

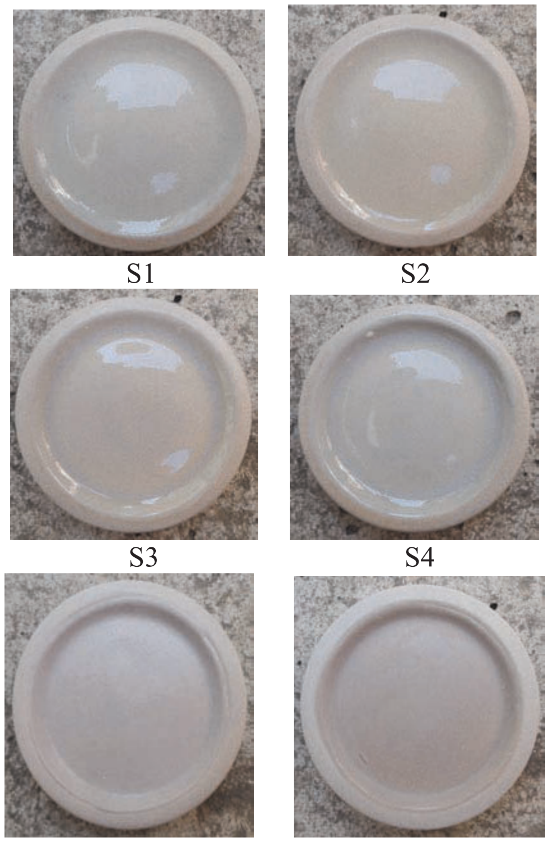
Figure 4. The raw and firing (at 1160 ^{o}C) colors of perlite.

After milling of perlite it was applied onto stoneware body as thin and thick layer then, fired at 1160 ^{o}C (Figure 5).

A thick glaze application A thin glaze application

Figure 5. The raw and firing (at 1160 ^{o}C) colors of perlite.

The glazes prepared by replacing perlite with other constituent in the composition were applied onto bodies and fired. There is no significant change in the color (Figure 6). Only a very slight darkening was observed. In glazes S5 and S6, light and dark buff colors are seen.



S1 S2
S3 S4
S5 S6

Figure 6. The color effects of perlite in alkaline and boron glazes.

Table 4 illustrates the optical parameters of S1-S6 glazes. It is clearly noticed that whiteness (L*) decreased and redness (a*) raised with the increase of perlite put into the standard glaze.

Table 4. The optical parameters of standard (S1) and perlite added glazes

Recipe No	L*	a*	b*
S1	70.81	0.88	8.95
S2	64.07	0.64	7.19
S3	69.77	1.11	10.27
S4	67.37	1.30	7.81
S5	68.44	2.49	7.81
S6	59.55	3.58	9.81

The effect of 3 % CoO and CuO incorporations into the standard and perlite added glazes on the color and texture can be seen from Figures 7 and 8. By classic cobalt blue and cupper green included the different color and texture effects were obtained depending on the glaze composition and the amount of perlite used. In the glaze contained copper oxide (S2), in which perlite was added as 20 % instead of potassium feldspar, a similar color (green copper) and surface characteristics were experienced, comparing to the standard glaze (S1). When it is added as 20 % instead of sodium feldspar (S3), the resultant color turns from green to turquoise and the textured surface forms; when it is used rather than the total amount of feldspar (40 %) (S4), the turquoise color appears. If it is used instead of ulexite (S5) at the same rate, the color is light olive green. In the boron-free glaze (S6) the use of perlite results in major dark olive-green color.

In case of cobalt oxide addition to perlite consisting glaze, S2 and S3 glazes result in a cobalt blue color relatively close to the standard one (S1). In case of using perlite instead of total amount of feldspar (40 %) dark blue color has become blue (S4). In the 30 % perlite added glaze (S5), the color is nearly black, matte dark blue. A silk matte texture in black color is observed on the surface of plate, when perlite is increased to 70 %. It is assumed that this color appears for glazes having low amount of Fe_2O_3, while ferric oxide in perlite is to be effective in the color change of glazes with copper and cobalt oxides. Tables 5 and 6 illustrate the optical parameters of S1-S6 glazes with 3 % CuO and CoO additions.

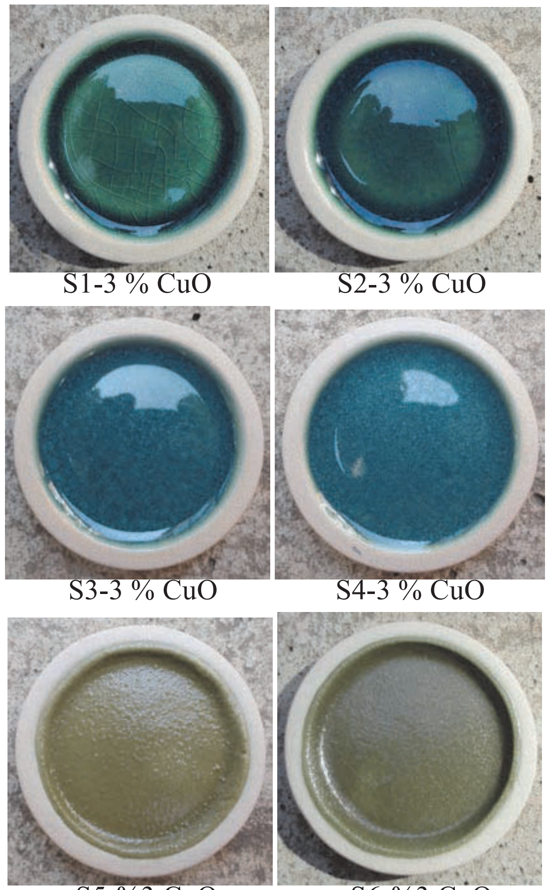


Figure 7. The colors of cupper oxide added glazes.

Table 5. The optical parameters of the glazes with perlite and CuO

Recipe No	3 % CuO added glazes		
	L*	a*	b*
S1-3 % CuO	42.46	-10.43	5.37
S2-3 % CuO	37.35	-5.83	-2.72
S3-3 % CuO	42.05	-7.67	-1.64
S4-3 % CuO	43.16	-9.41	-1.50
S5-3 % CuO	41.29	-0.09	10.58
S6-3 % CuO	46.54	0.67	16.52

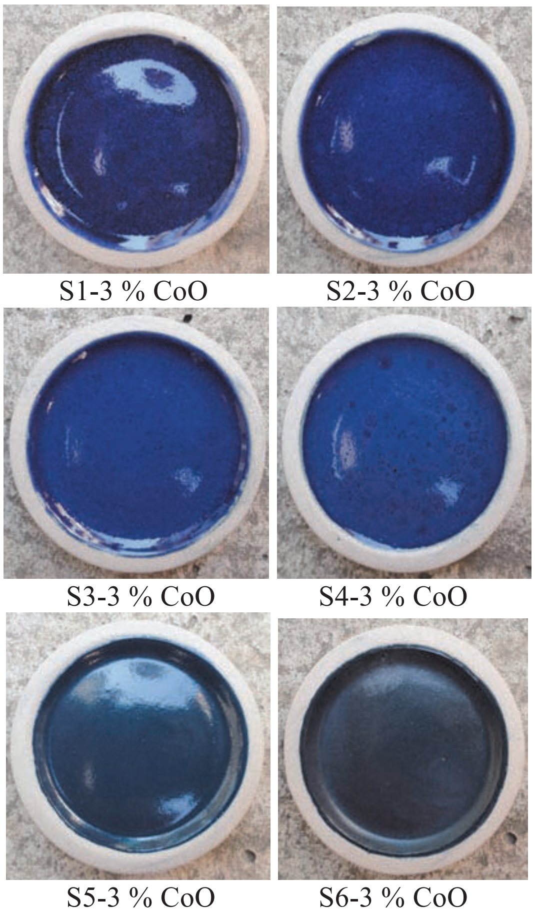


Figure 8. The colors of cobalt oxide added glazes

Table 6. The optical parameters of the glazes with perlite and CoO

Recipe No	3 % CoO added glazes		
	L*	a*	b*
S1-3 % CoO	27.35	7.39	-19.08
S2-3 % CoO	28.37	7.29	-21.29
S3-3 % CoO	31.48	5.44	-19.58
S4-3 % CoO	33.31	4.65	-18.70
S5-3 % CoO	31.21	-2.45	-5.50
S6-3 % CoO	33.24	-1.75	-2.23

4. DISCUSSION

Varying colors and surface textures were obtained by using perlite originated in Kütahya, instead of ulexite, sodium feldspar and potassium feldspar (by using perlite in equivalent amounts of the prescribed quantities of raw materials) in the alkaline and boron added standard stoneware glazes. Although there is no colorant addition in the transparent glazes, perlite concentrations more than 30 % resulted in dark buff-colored surfaces. In case of copper and cobalt oxide additions into perlite, significant differences are observed in the glaze color. Although, when cobalt oxide concentration is fixed while perlite is used instead of the entire amount of the melting agent prescribed, a matte dark blue colored black was obtained after firing at 1160 ^oC. If perlite is used as melting agent in the glazes, iron level in perlite plays an effective role leading to these colors. This study indicated that perlite can be utilized in the raw stoneware glazes both as colorant and melting agent. It is also suggested that perlite with high alkaline content can be used in various body and glaze recipes with using its advantages of coloring effects to create works in artistic sense.

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