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Utilization of Chromite Waste as Colorant in Single Fired Wall Tile Glaze Compositions

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Abstract

The present study focuses on the utilization of chromite waste after neutralization process as coloring agent for transparent and opaque wall tile glaze compositions. The neutralized processed chromite ore waste obtained from the Soda-Chrome Industries Inc. in Kazanlı (Mersin), a branch of Şişe-Cam Chemicals Group, was used in increasing amounts in ceramic wall tile glazes. 3-6% of chromite waste was used in opaque and transparent wall tile glaze recipes. The glaze compositions were applied as thin layers (0.5 mm) on engobed wall tile bodies and fired at 1200°C. After firing, no surface defects were observed on glazed surface. Glazes were charaterized by electron microscopy (SEM-EDX). The color obtained after glazing and firing was defined as CIE-$L^*a^*b^*$ parameters by using UV-Visible Spectrophotometer. Glazed samples were subjected to thermal shock test at 200°C and no evidence of crack and peeling were found between body and glaze coating. It has been observed that waste material has positive effects as a colorant in ceramic glazes at 1200°C.

Keywords : Chromite Waste, Waste utilization, Glaze, Colorant

Kromit Atığının Tek Pişirim Duvar Karosu Sırlarında Renklendirici Olarak Kullanılması

Öz

Bu çalışmada nötralizasyon işlemi sonrası elde edilen kromit atığının şeffaf ve opak duvar karosu sır kompozisyonlarında renklendirici olarak kullanılabilirliğine dikkat çekilmiştir. Nötralize edilmiş kromit cevheri atığı Kazanlı (Mersin)'da bulunan ve Şişecam Kimyasalları Grubuna bağlı Soda-Krom Fabrikaları'ndan elde edilmiş ve artan oranlarda şeffaf ve opak duvar karosu sır reçetelerinde %3-6 oranında kullanılmıştır. Sır kompozisyonları astarlı duvar karoları üzerine 0,5 mm kalınlığında uygulanmış ve 1200°C'de fırınlanmıştır. Pişirim sonrasında sırlı yüzeylerde herhangi bir hataya rastlanmamıştır. Sırların karakterizasyonu, Taramalı Elektron Mikroskobu (SEM-EDX) ile yapılmıştır. Sırlama ve pişirme işlemlerinden sonra sırlı yüzeylerde UV-Visible Spectrophotometer ile CIE-$L^*a^*b^*$ parametreleriyle ifade edilen renk değerleri elde edilmiştir. Sırlı örnekler 200°C'de ısıl şok testine tabi tutulmuş bünye-sır arasında, herhangi bir çatlama veya kavlama görülmemiştir. 1200°C'de atık malzemenin seramik sırlarını renklendirmede olumlu etkilere sahip olduğu gözlenmiştir.

Anahtar Kelimeler: Kromit atığı, Atık değerlendirme, Sır, Renklendirici

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1. INTRODUCTION

Industrial activities are generating huge amounts of inorganic and toxic waste materials and are not inherent to the production process due to technological developments in all over the world. Recycling and reuse are the best solution for waste utilization that become very important for today's community because of increase in production of wastes and their impact on the environment for living beings**.**

The ceramics sector can incorporate large amounts of waste materials without relevant process modifications, while taking advantage of the calorific value from waste combustion or incorporating the residue in the internal structure of materials, such that the residue forms part of these materials' matrix and becomes an inert element, Eliche Quesada et al. [1].

As stated in the literature, possibility of using a wide variety of inorganic wastes has become important aspect in the ceramic sector like as ceramic engobes [2-3], ceramic glazes [4-8], ceramic colorants or pigments [9-15], glass and glass-ceramics [16-18], bricks and roof tiles [19-27], and ceramic tiles [28-30].

According to Eppler et al. [31] and Bonolini et al., [32], obtaining a color in a vitreous matrix requires dispersion of a colored insoluble crystal or crystals which acted as pigments of the matrix. The color of the crystals is then imparted to the transparent matrix.

Different materials are widely used in production of colored glazes but direct use of solid wastes as a coloring agent is quite rare in Turkey. As a result of these aims, the solid waste of Soda-Chrome Industries was utilized in the transparent and opaque tile glazes. It was observed that, there was a wide color variety altering from grey to black in transparent glazes and violet in opaque glazes at 1200°C.

2. EXPERIMENTAL PROCEDURE

Wall tile glazes (transparent and opaque) and neutralized chromite waste were used in this study. Chromite waste obtained from Soda-Chrome Industries as a coloring agent. Transparent and opaque glazes obtained from Yurtbay Seramik Factory. The body and glaze compositions are not reported since they are still produced industrially. Glazes were colored by adding 3-6 wt% of the waste to the transparent and opaque glazes. Homogenous mixing was achieved by milling the materials constituting the slip, for 2 hours in a mill. This treatment gave a homogeneous mixture of the neutralized waste and glaze. The ground mixtures were then sieved through 63 μm mesh. A spraying method was used to apply the stained ceramic glazes to test tiles. The phase identification in the neutralized waste was performed by X-ray diffraction (XRD) method. XRD patterns were obtained using conventional powder diffraction technique with Ni-filtered Cu Kα radiation and X-ray scans were made between 2θ angles of 0° and 70°. The microstructure and chemical homogeneity of representative fired samples were studied by scanning electron microscopy (SEM) using a Leo-440 electron microscope.

The optical parameters of all the fired wall tiles were measured using Minolta CR-300 series chroma meter using the CIELab method. L * is the degree of lightness and darkness of the color in relation to the scale extending from white (L^*=100) to black (L^*=0). a^* is the scale extending from green (-a^*) to red (+a^*) axis and b^* is the scale extending from blue (-b^*) to yellow (+b^*) axis.

3. RESULTS AND DISCUSSIONS

The result of the chemical composition of the neutralized chromite waste is given in the Table 1. According to the Table 1, neutralized chromite waste consists mainly of iron oxide (~59%), also with chromium oxide (~21%).

Table 1. Chemical composition wt % of chromite waste

SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Cr_2O_3	SO_3	MnO	NiO	CoO	V_2O_5
2.24	0.01	1.49	58.96	1.28	8.70	1.85	0.04	20.52	0.19	0.48	0.19	0.09	0.81

The result of the XRD analysis of the chromite waste is shown in Figure 1. Chromite waste consists of chromite, magnetite, andradite (syn) and green rust.

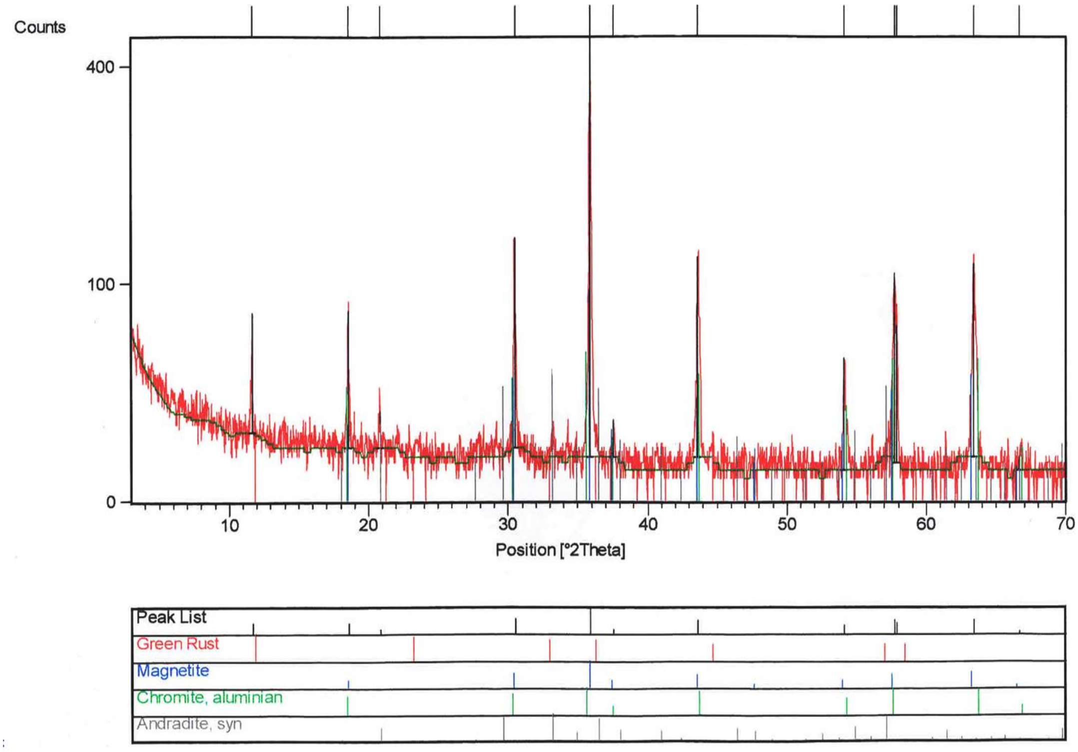

Figure 1. X-ray diffraction spectra of the chromite waste of soda chrome industry

The chemical composition is basically characterized by high amounts of Fe_2O_3, Cr_2O_3 and MgO. This waste material is extremely hazardous because it contains dangerous heavy metals such as Cr and Ni. Different amounts of chromite waste were ranged from 3% to 6% added into the transparent and opaque wall tile glaze compositions. These glaze compositions labeled as TG_1 (addition of 3% chromite waste to transparent glaze), TG_2 (addition of 6% chromite waste to transparent glaze), OG_1 (addition of 3% chromite waste to opaque glaze) and OG_2 (addition of 6% chromite waste to opaque glaze) respectively.

Figure 2 shows the surface appearance and color of the transparent and opaque wall tile glazes colored with the neutralized chromite waste applied on engobed single-fired wall tiles at 1200°C.

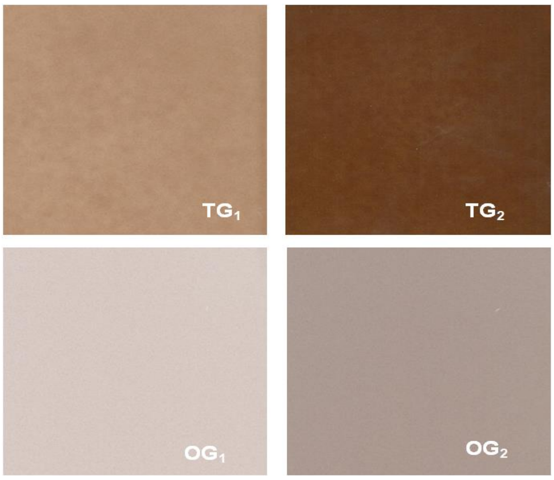

Figure 2. Surface appearance and color of the glazes prepared by neutralized chromite waste, fired at 1200°C; TG_1, TG_2, OG_1, OG_2

SEM micrographs and EDX patterns of TG_1 and OG_1 glazes were shown in Figure 3 and Figure 4. It could be seen that, large number of irregular shaped crystals disorderly distributed in glassy matrix. The chemical compositions of crystals (OG_1) and glassy matrix (TG_1) were analyzed by EDX. The crystals were rich in Si, Al, Na, Ca, Mg, Fe and Zn. The glassy matrix was rich in Si, Al, Cr, Na, Ca, Mg, Fe, Zn.

As the amount of waste increases in the coloring of ceramic glaze, color scale ranging from light brown to dark brown in transparent glazes and violet in opaque glazes at 1200°C. The chromite waste has reducing effect on whiteness. Transparent glaze matrix with 6% chromite waste (TG_2) showed intense brown coloration and opaque glaze matrix with 6% chromite waste (OG_2) showed intense violet coloration, as seen in Figure 2 and Table 2.

Under the lights of coloring parameters (L^*, a^* and b^*) of newly produced wall tile glazes with chromite waste it was concluded that higher waste contents caused decrease in whiteness.

Table 2. Optical parameters (L^*, a^*, b^*) of wall tile glazes

Glazes	L^*	a^*	b^*
TG_1	64	+12	+21
TG_2	32	+17	+28
OG_1	82	+5	+4
OG_2	65	+6	+7

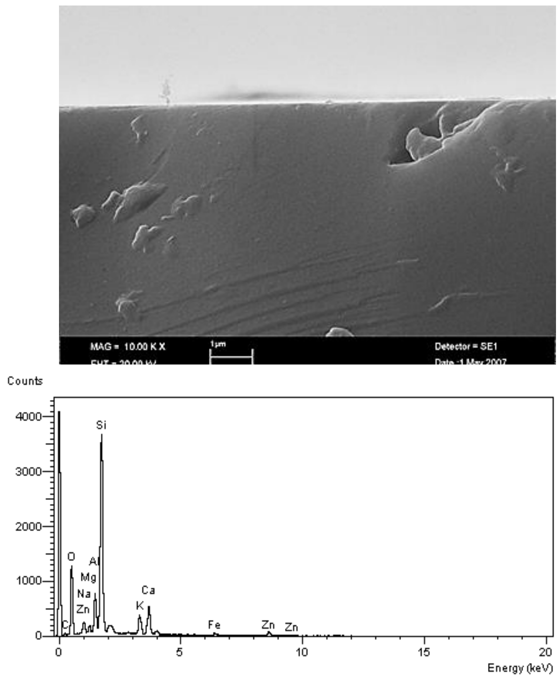

Figure 3. SEM micrograph of the TG_1 glaze and EDX pattern taken from the crystal occurrence

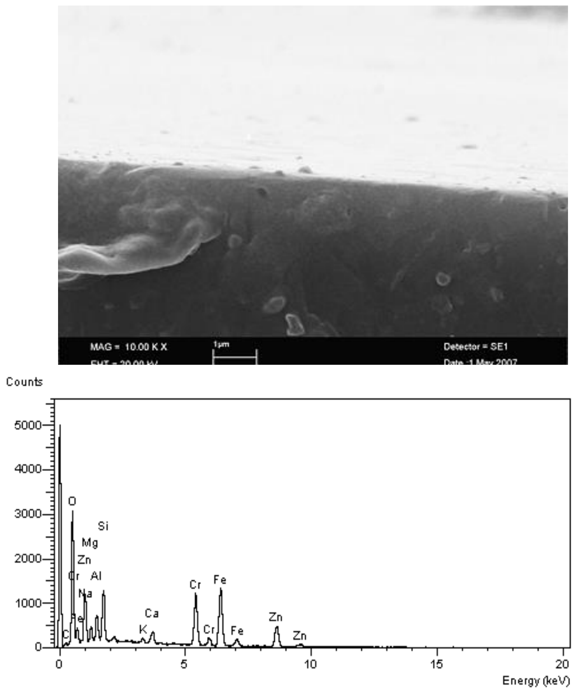

Figure 4. SEM micrograph of the OG_1 glaze and EDX pattern taken from the glassy matrix

4. CONCLUSIONS

This work showed that, it's possible to utilize chromite waste for coloring purposes and obtaining attractive textures for decorative purposes in different glaze compositions. The color change in transparent and opaque glazes is related with the phase transformation during firing, where the chromite ore waste reacts with the glaze composition with depending on firing temperature. Various shades of brown and violet were observed when neutralized chromite waste was added into the transparent and opaque glazes. The variation of shade is considered due to firing temperature, presence of different amounts of neutralized chromite waste and chemical composition of glazes. Glazed samples were subjected to thermal shock test at 200°C and no evidence of crack and peeling were found. Good adhesion was observed between the body and glaze coatings. As a result, the utilization of chromite waste as coloring agent in ceramic products will reduce environmental pollution.

5. ACKNOWLEDGEMENTS

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