

Usage of Colemanite in Transparent Wall Tile Glazes

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Boric oxide has an important place in glaze technology and is the second most important network-former after silica. Lower thermal expansion coefficient; higher chemical and mechanical durability; good glaze appearance are some of the benefits of boric oxide. In wall tile production; generally transparent frits with 1–7% boric oxide are used to obtain glossy transparent glaze. It can be said that boric acid is the fourth expensive raw material in frit production after zirconium, zinc oxide and potassium carbonate due to its high cost limits its usage in frit production. The aim of this study is to investigate colemanite ($\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$) mineral usage in transparent frit production instead of using boric acid. To achieve this aim, four different frit mixtures Std, K.1, K.2 and K.3 with 0 wt.%, 3 wt.%, 6.5 wt.% and 11.5 wt.% colemanite content were prepared respectively. For comparison of the thermal behavior of frits, hot stage microscope was used. It was observed that, all of the samples prepared with colemanite have lower sintering and softening temperatures than the standard recipe because of its high earth alkaline oxide content. The obtained glazes were characterized by X-ray diffraction, dilatometer, Harcourt and Autoclave tests.

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1. Introduction

As an element, boron is one of the indispensable industrial raw materials due to features such as its abilities of making a variety of compounds, absorption of neutrons and reduction the temperature of vitrification. Boron is widely used in aeronautics, nuclear applications, military vehicles, insulators, electronic communications industry, agriculture, glass industry, chemical detergent industry, ceramic and polymeric materials, nanotechnology, automotive and energy sector, metallurgy and construction [1]. World boron reserves are located mainly in Turkey (72%), followed by Russia (8%), United States (6.8%), Chile (3.5%) and China (3.2%) [2]. Recent studies have been focused on the use of boron minerals (boric acid, borax, colemanite, ulexite etc.) and wastes that were generated from the enrichment of these minerals in ceramic glaze compositions. Benefits of using B_2O_3 in glazes are improve in glaze appearance, chemical-mechanical durability, reduced coefficient of thermal expansion (CTE) [3]. Karasu and Gerede [4] have investigated the effect of concentration wastes of Etibor Kirka Borax Company in floor tile's composition up to a certain level. They have concluded that the concentration waste additions can be used until 13.5% without creating any defects on floor tile glaze. Gomez-Tena *et al.* [5] have studied the development of ceramic glaze by using a new synthetic borate raw material that turns boron into a glaze without this needing to be done in fritted form. Accordingly, they obtained a new synthetic raw material that can be used as a fluxing raw material in ceramic glazes and positive results in aesthetic and technical spec-

ifications for wall and floor tiles were carried out. Kartal and Gultekin [6] have investigated the effect of different boron raw materials to the melting behavior of glazes in their studies. They have reported that samples could be melt earlier by using borax and colemanite additions than by using boric acid. In the case of boric acid usage, the mixture melted at 1125°C and interacted with the substrate causing corrosion at 1150°C , but colemanite containing mixture melted at 1100°C . Yamik *et al.* [7] have investigated the effect of colemanite addition to industrial floor tile glaze recipes on the physical properties of glaze. They indicated that colemanite additions until to 6–8% did not create any problems in surface quality of floor tile glaze. Mazure and Levitsky [8] have evaluated the effect of colemanite addition to unfritted glazes in the rate of 3–6%. Results indicated that the temperature of formation of the liquid phase decreased from 1150°C to 1000°C and required physical-chemical properties that maintained for unfritted opacified glaze coating.

The production of boric acid is done by using boron raw materials (colemanite, tincal, ulexite) by the National Boron Board (Eti Mine) in Turkey. Sulfuric acid and hydrochloric acid are used in the production of boric acid. Colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) is still few-studied boron containing raw material, but reduces the sintering temperature and raw material cost [2]. A large amount of waste materials are produced during boron processing and enrichment operations. Considering the environmental impact, production costs and reduction of process temperatures, the frit-glaze compositions with colemanite will be beneficial by having a reduction in temperatures and costs of raw material compared to the usage of boric acid.

The aim of this study is to investigate the effect of colemanite additions on transparent wall tile glaze properties instead of usage of boric acid.

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2. Experimental

Raw materials used in frit and glaze preparation (kaolin, alumina, silica sand, zinc oxide, dolomite, calcite, K-carbonate, K-feldspar) were provided by Yurtbay Ceramic Factory (Turkey) and colemanite were received from Eti Mine (Turkey). The chemical compositions of raw materials are given in Table I. The trans-

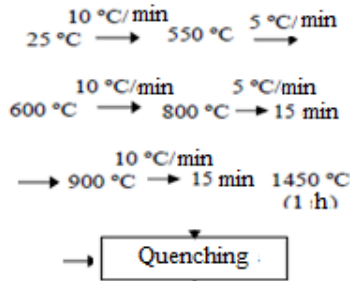


Fig. 1. Firing regime applied to frits.

parent frit which has been used by Yurtbay Ceramic Factory is accepted as a reference (STD). Thus, colemanite was added to standard transparent frit formulations from 3 to 11.5 wt.% instead of boric acid, also four recipes were prepared (Table II). The oxide composition ranges of prepared frits (wt.%) were given in Table III. The weighted batch materials, after thorough mixing were melted in an alumina crucible in an electric kiln (Protherm PLF 160/7) at a maximum tempera-

ture of 1450°C, for 1 h. according to firing regime given in Fig. 1. The fluid melt was quenched by pouring it into cold water to obtain the frit. The resulting frit was used to prepare a glaze, whose solid content comprised 92 wt.% frit and 8 wt.% kaolin and the necessary additives (0.1 wt.% carboxy methyl cellulose-CMC and 0.3 wt.% sodium tripolyphosphate-STPP) for wet application. Prepared glaze compositions were applied on a previously fired ceramic body, coated with an engobe. The glazed tiles were fast fired in a roller furnace under industrial conditions at 1120°C for 31 min. In order to find out the frit behavior under heat treatment was studied with a hot stage microscope (Misura 332 ODHT-HSM 1600/80). The following temperatures were determined as sintering, softening, sphere, half-sphere and melting. The hot stage microscope regime were performed in powder form using a heating rate of 50°C/min to 400°C then with 10°C/min. heating rate from 400°C to 140°C. The coefficient of thermal expansion of all frits was measured through an electronic dilatometer (Netzsch DIL 402 PC). After frit samples were fired at industrial wall tile regime, they were cut 5×5×50 mm in size, and using heating rate of 10°C/min to 60°C. In order to find out the phase transitions of the reference and colemanite-added glazed wall tiles after sintering, X-ray diffraction (XRD) analysis (Rigaku Rint 2000) was made on tile samples. Under the industrial conditions of Yurtbay Ceramic Factory standard Harcourt [9] and autoclave [10] tests were made to the glazed wall tiles.

Chemical analysis of raw materials [wt.%].

TABLE I

Raw materials	LOI*	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	BaO	ZnO	SrO	B ₂ O ₃
Boric acid	44.00	-	-	-	-	-	-	-	-	-	-	-	56.00
Alumina	1.00	0.30	98.21	0.08	-	0.40	-	-	-	-	-	-	-
Silica sand	0.20	97.89	0.95	0.25	0.31	0.05	0.03	0.10	0.22	-	-	-	-
Zinc oxide	-	-	-	-	-	-	-	-	-	-	100.0	-	-
Calcite	42.35	0.70	0.46	0.04	-	56.45	-	-	-	-	-	-	-
Potassium carbonate	32.00	-	-	-	-	-	-	-	68.00	-	-	-	-
Dolomite	44.63	0.57	-	0.23	-	37.51	16.80	0.09	-	0.17	-	-	-
Potassium feldspar	32.00	-	-	-	-	-	-	-	68.00	-	-	-	-
Colemanite	24.84	4.77	0.13	0.03	-	26.15	2.23	0.11	0.01	-	-	0.65	40.53
Kaolin	12.44	48.09	36.37	1.09	0.17	0.06	0.28	0.12	1.37	-	-	-	-

* L.O.I: Loss of ignition

3. Results and discussions

The detailed hot stage microscope results of the reference and colemanite-added frits are given in Table IV. When this table is examined, it is observed that the sintering, softening, sphere, half sphere and melting temperatures were a reduction in colemanite-added (K1-K3) frits compared to the reference frit (STD). This reduction was caused by augment of the content of earth alkaline oxide (CaO, MgO) and also SiO₂ within the colemanite mineral of K1-K3 frits. On the other hand, recent studies have been focused on the increase in Ca/Si ratio and on the other hand a decrease on the glass melting

temperature and sintering temperature and beneficial to crystallization of glass-ceramics are thoroughly displayed [11-13]. Especially CaO, as a typical network modifier caused the acceleration of the destruction of silicate network by breaking Si-O-Si bonds and creating non-bridging oxygen groups (Si-O-NBO) [13, 14]. Moreover, crystallization kinetics result shows that the increase in CaO/SiO₂ ratio up to 0.38 diminishes the activation energy of crystallization in studied glass-ceramic [13]. XRD patterns of glazed wall tiles were shown in Fig. 2. No crystalline phase was detected through the entire range of tiles due to transparent glaze. This situation was caused

Prepared frit recipes. TABLE II

Frit	Boric acid (wt.%)	Colemanite (wt.%)
STD	6.5	0
K1	3.5	3
K2	0	6.5
K3	0	11.5

The oxide composition of the studied frits [wt.%]. TABLE III

Oxide	Std	K1	K2	K3
Na ₂ O	0.44	0.44	0.44	0.45
K ₂ O	3.15	3.15	3.15	3.15
MgO	1.35	1.42	1.50	1.61
CaO	12.65	13.43	14.43	15.66
SiO ₂	52.45	52.59	52.76	53.00
Al ₂ O ₃	6.05	6.05	6.06	6.06
B ₂ O ₃	0.05	0.04	0.03	0.06
CaO/SiO ₂	0.24	0.25	0.27	0.28

by CaO/SiO₂ ratio, lower than 0.38 for crystallization.

Hot stage microscope analyses of frits [°C]. TABLE IV

Frits	*T _{Sint}	T _{Soft}	T _{Sph}	T _{H-Sph}	T _{Melt}
Std	906	1044	1196	1158	1250
K1	904	1044	1192	1130	1250
K2	890	1042	1160	1084	1188
K3	882	1044	1162	1086	1208

*T_{Sint} - sintering,

T_{Soft} - softening,

T_{Sph} - sphere,

T_{H-Sph} - half sphere,

T_{Melt} - melting temperatures.

The coefficient of thermal expansion values of frits at 400°C–500°C and 600°C were given in Table V. From the table V it can be seen that the coefficient of thermal expansion values were higher in K1-K3 than the standard. The glasses have high CTEs because they usually possess low glass transition and softening temperatures [15]. Moreover, the influence of earth alkaline-containing raw materials as sintering promoters on the vitrification of various compositions has already been studied in literature [16–19]. It is known that these oxides decrease the viscosity of glassy phase and hence cause bloating or deformation during sintering stage. Several models are currently available to estimate the CTE of glasses. Most of them are using the Eq. 1. where α_i is a proportionality factor, p_i is the weight fraction of the corresponding oxide and n is the total number of constituent oxides in the glass. The proportionality factor values of many oxides are given in many studies [20–22].

$$CTE = \sum_{i=1}^n \alpha_i p_i \quad (1)$$

When the amount of alkaline oxides and Al₂O₃ are

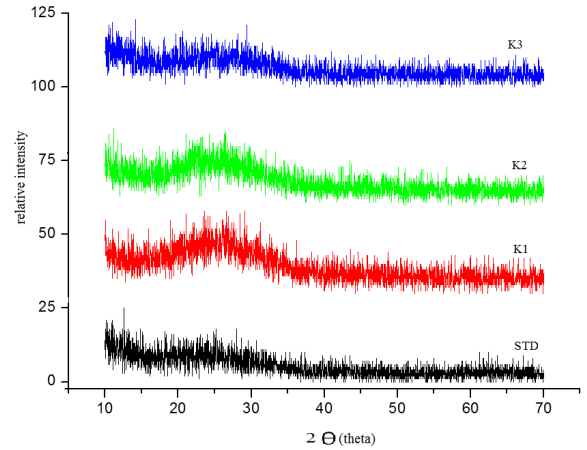


Fig. 2. XRD patterns of ceramic glazes.

constant relatively, the amount of CaO and SiO₂ are increased. The α_i of CaO and SiO₂, the coefficient of thermal expansion of studied glass-ceramic increased. Therefore the augment of the CTE was caused by especially CaO in the current study. All glazed tiles were produced without having any problem and glaze defects after firing. Harcourt results were conducted at 100, 125, 150, 175°C respectively and no crack occurrence was detected at these temperatures. In the autoclave test glazed tiles were hold in a furnace under the 6 atm pressure for 6 h and no crack formation was detected.

The coefficient of thermal expansion (CTE) of frits [$\times 10^{-7}/^\circ\text{C}$] TABLE V

Frits	400°C	500°C	600°C
Std	61.77	62.46	62.56
K1	62.11	62.84	63.05
K2	62.20	62.92	63.17
K3	64.98	65.78	65.89

4. Conclusions

In this study, the usage of colemanite as an alternative to boric acid was investigated for transparent frit production. Thermal analyses of the studied frits revealed that the usage of colemanite decreased the characteristic temperatures (T_{Sint} , T_{Soft} , T_{Sph} , $T_{\text{H-Sph}}$, T_{Melt}). Dilatometer analyses were also showed that the coefficient of thermal expansion was increased with increased the usage of colemanite. These thermal behaviors could be explained with higher CaO content of colemanite. When a network modifier, Ca²⁺ is inserted into glass structure, it can provoke the disruption of the glass network continuity by breaking some Si–O–Si bonds. Improved surfaces of glazed tiles can be attributed to the presence of colemanite and high earth alkaline content of colemanite. The experimental results demonstrated that a suitable combination of earth alkaline oxide provide a decrease in firing temperatures and the low raw material costs, however cole-

manite could be used in certain ratios instead of boric acid due to higher coefficient of thermal expansion.

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