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Utilization of Bandırma Colemanite Enrichment Wastes in the Production of Transparent Frits

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Abstract:
Turkey has approximately 73% of total world boron reserves and each year due to the increased production capacity of the mines operated by Eti Mine Co. the amount of the mining wastes also increases correspondingly. The disposal of wastes cause an economic loss, bringing technical and environmental issues with itself. In the present study, Bandırma colemanite enrichment wastes were employed as a raw material into the production of transparent frits. The wastes were used in the frit compositions as a source of B_2O_3, instead of boric acid (H_3BO_3) provided a sharp reduction of boric acid consumption. The modified frit compositions were applied on tile bodies, and then fired under industrial sintering conditions. Produced frits were characterized in terms of optical, mineralogical and microstructural properties. The results showed that waste-added-frits were similar to the standard frit and also the glazes containing the waste-added-frits showed similar properties with the standard glaze, can be employed in production.

Keywords: Colemanite - Boron - Waste - Transparent Frit - Tile.
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1. Introduction

Turkey is the leading boron producer of the world with total production over 2 Mt of boron concentrates and 1.78 Mt boron chemical products. Estimated production in 2014 was around 0.8 Mt B_2O_3 [1].

Boric acid, borax, borax hydrates and sodium perborates are the boron products possessing commercial value, boron compounds are used as a key additive over one hundred industries [2]. Boric acid (H_3BO_3) is one of most preferred boron related commercial chemical with increasing consumption rate. It was reported that in 2015 total boric acid production was over 9,667,000 t gross [1].

State owned Eti Mine is the sole domestic mining company of Turkey, performs its operations in five mines and seven enrichment plants. A mass mining and production of borate minerals are also leading to a mass extractive waste still containing high amount of valuable B_2O_3. The barrier in front of industrial utilization is thought to be the operational difficulties. B-containing wastes have been already proposed to be utilized in ceramic industry and in glass ceramics production [3-5] yet still there has been no industrial utilization.

Frit is a glass-ceramic structured material mostly containing high amorphous phase. In frit production, the raw material composition is prepared and fired above 1400˚C followed by quenching in water in order to form an amorphous structure containing ceramic crystal nucleuses. The glassy particles are milled to an expected particle size and dissolved in water based solutions before application. Frits play an important and irreplaceable role in the production of enamels and ceramic glazes; the purpose of the use of frit and the pre-fusion of frit is that the glass phase rendering soluble surfaces insoluable [4-6] enabling long service life, decorative sustainability while providing functional properties thanks to adjustable glass-ceramic structure.

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Usage of B_2O_3 in frits, indirectly in glazes, has numerous technical and visual appearance benefits providing them a unique place ceramic industry. The main reason is that the B_2O_3 is a flux, but in numerous circumstances it is acting different from other fluxes (alkalines, alkaline earths, etc.). B_2O_3 does not increase the thermal expansion coefficient unlike the other fluxes, and very effective network former after silicon. B_2O_3 increases glaze structure's chemical and mechanical durability, providing long range thermal processability, also, in literature some research claims that certain amounts of B_2O_3 (12%) increases scratch resistance of the glaze [7]. B_2O_3 usage also improves the surface quality of the glazes with same characteristics making them demanding in glass industry.

Due to the high and pure amount of B_2O_3, boric acid is the mostly used B_2O_3 source in the production of frits, as in the case of other B_2O_3 using industries. Concerning the amount of the boron enrichment wastes present in Turkey, and the percentage amount of B_2O_3 in these wastes, it is likely to utilize the wastes as a B_2O_3 source instead of boric acid. Bandırma colemanite enrichment wastes contain high B_2O_3 amount (16-31%) and minerals which are also a part of the frit composition.

Bandırma colemanite enrichment wastes were employed as a B_2O_3 source in the production of transparent frits. The addition of colemanite wastes into the composition was done under constant circumstances with using Seger ratios while respecting the standard composition. The manufactured frits were used to yield glazed slips. Prepared glazes were applied on the tile surfaces and necessary characterizations were performed.

In the present study, the main partner of the research is one of the leading ceramic producer of Europe; Eczacibasi Group together with Yildiz Technical University. The study was supported by National Boron Research Institute of Turkey (BOREN) aiming to overcome operational difficulties both from boron mines and industry in order to utilize boron containing mining wastes in ceramic production.

2. Experimental Procedure

Starting the study, chemical analysis was applied to all colemanite wastes obtained from Bandırma enrichment plants (Eti Mine Boron Company) and the wastes were code as A5 and A6. The composition of the wastes was given in Table 1. The metal oxide content of the A5 and A6 wastes are the most suitable options to be used as a B_2O_3 source in transparent frit production.

Table 1. Chemical compositions of Bandırma colemanite enrichment wastes.

	Bandırma colemanite wastes (wt %)	
Oxides	A5	A6
B_2O_3	29.52	31.12
Na_2O	0.91	0.82
MgO	0.82	0.60
Al_2O_3	0.11	0.63
SiO_2	0.39	1.28
P_2O_5	0.01	0.01
SO_3	0.56	0.77
K_2O	-	0.04
CaO	52.75	33.42
Fe_2O_3	0.14	0.14
Cr_2O_3	-	0.04
SnO_2	-	0.34
***L.O.I.**	14.80	30,80
Total	100.00	100,00

*L.O.I. : Loss of Ignition

In order to utilize A5 and A6 wastes in transparent frit production, new composition were developed with a condition of keeping the oxide ratios constant. Oxide ratios of the standard frit composition, which will be named as TF1, was calculated and the Seger table of the TF1 was formed. Concerning the condition of keeping the oxide ratios constant, new compositions were developed depending on the TF1 Seger table. Then, oxide ratios of the new compositions were calculated and their Seger tables were formed (Table 2). Forming of the Seger tables was done by grouping oxides as R_2O (Na_2O, K_2O), RO (CaO, ZnO), R_2O_3 (B_2O_3, Al_2O_3, Fe_2O_3), RO_2 (SiO_2) and the ratio (SiO_2/Al_2O_3).

Table 2. Seger tables of the TF1, TF1-A5, TF1-A6, TF1-A6-2 frits.

Oxides	TF1	TF1-A5	TF1-A6	TF1-A6-2
R_2O (Na_2O, K_2O)	6,230	6,500	5,000	6,320
RO (CaO, ZnO)	11,070	11,250	10,350	10,090
R_2O_3 (B_2O_3, Al_2O_3, Fe_2O_3)	21,240	20,920	22,290	21,750
RO_2 (SiO_2)	61,460	61,350	62,370	61,830
SiO_2/Al_2O_3	11,611	11,550	11,210	11,380
Total B_2O_3	0,918	0,877	1,090	0,991
*B_2O_3 (BW)	0	0,120	0,470	0,420

*B_2O_3 (BW): Boron trioxide derived from colemanite wastes.

The comparison of Seger tables of TF1 and new compositions, it can clearly be seen that the values are actually very similar. To achieve this similarity, calcite (CaO) was totally removed from the composition because of the high CaO content of the wastes. However, a quantity of boric acid was not removed from the transparent frit composition. Because wastes are not suitable enough to become

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the only B_2O_3 source for the transparent frit because of their high CaO content. New compositions were named similar to standard frit composition, the difference is that the names of the new compositions also included the employed wastes code and numbers were used to point out the second composition developed by using the same waste, for example TF1-A6-2.

Newly developed compositions were used to produce transparent frit as the Figure 1. All the frit raw materials were dried in oven (Nüve FN 400) at 100°C for 24 hours and weighing was carried out depending on the composition and they were blended. Then, prepared transparent frit blends were put in porcelain Al_2O_3 crucibles and the melting process is carried out for one hour with a peak temperature of 1450°C in a laboratory type furnace (Protherm, TR). The molten is quenched by pouring into water at room temperature; the produced frits were dried in drying oven (Nüve FN 400) at 100°C.

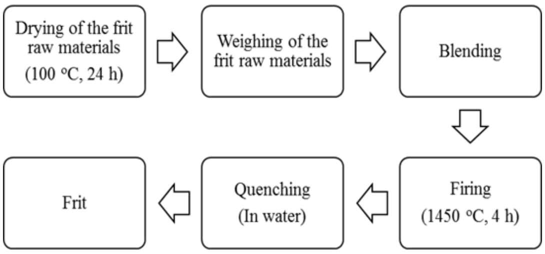

Figure 1. Production process flow chart of transparent frits.

TF1-A5, TF1-A6 and TF1-A6-2 were used in the production of the glaze in comparison with TF1. The production flow of the glaze is given in Figure 2. 92 gr of TF1, 8 gr kaolin, 0,1 gr carboxy methyl cellulose (CMC), 0,4 gr sodium tri polyphosphate (STPP) and 35 ml water were mixed and grinded in ball mill (Ceramic Instruments Rapid Mills Moduler System SD Series) for 14 minutes. Then the grinded mix was put through 45 μm sieve and the obtained suspension is called as "glaze suspension". Prepared glaze suspensions were applied on sintered wall tiles by the method of drawing then left for drying at 100°C. After drying, the tiles were fired in industrial furnaces at 1145°C for 36 minutes and the final layer on the tile surface is called as "glaze".

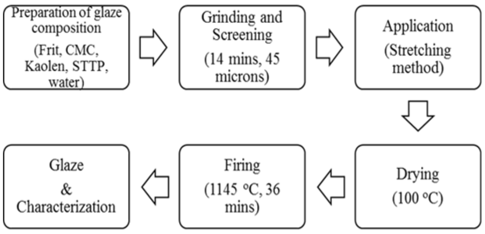

Figure 2. Production process flow chart of glazes.

3. Results and Discussion

3.1. Chemical Analysis:

In order to obtain the chemical composition of the frits, X-ray fluorescence spectroscopy (XRF) and energy-dispersive X-ray spectroscopy (XRD) were used. Settled voltage and current values for Ca and K elements are 40 kV and 75 mA, values for Cl, S, P, Si, Al, Mg, Na, F and B elements are 30 kV and 100 mA.

3.2. Mineralogical Analysis:

In order to obtain the mineralogical structure of the glazes, X-ray diffraction analysis was applied. Analysis were applied by the "Rigaku Rint 2000" XRD with a 40 kV acceleration voltage and 30 mA current. Specimens were inspected form 10° to 70° with a scanning velocity of 2°/min.

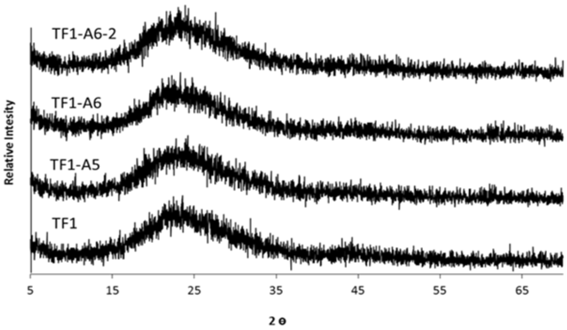

Figure 3. XRD patterns (results of mineralogical analysis) of TF1, TF1-A5, TF1-A6, TF1-A6-2.

In Figure 3 XRD patterns of the TF1, TF1-A5, TF1-A6 and TF1-A6-2 glazes are given. There were no clue of a crystal phase in the patterns, an amorphous structure.

3.3. Microstructure Analysis:

Before the analysis, glazes were coated with gold (Au) and Palladium (Pd) alloy in order show conductive property. For the SEM/EDX analysis, 20 kV acceleration voltage was used for 9.5 and 10 mm working distances.

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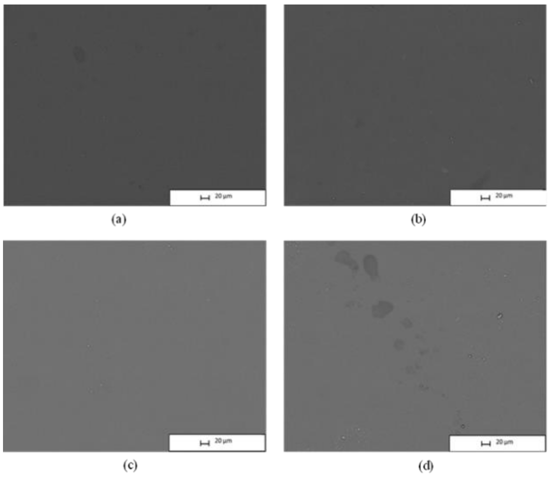

Figure 4. SEM images taken from the surface of (a) TF1, (b) TF1-A5, (c) TF1-A6, (d) TF1-A6-2.

In Fig. 4 SEM images taken from the surface of TF1, TF1-A5, TF1-A6, TF1-A6-2 glazes are given. There were no clue of a crystal structure and this images also proves the amorphous structure which is obtained from XRD results.

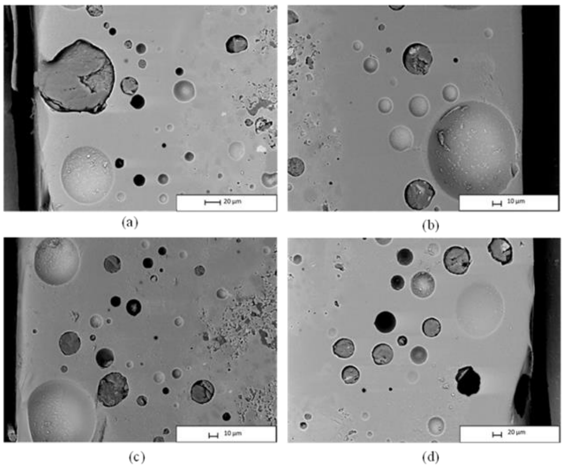

Figure 5. SEM images taken from the cross-section of (a) TF1, (b) TF1-A5, (c) TF1-A6, (d) TF1-A6-2.

In Figure 5 SEM images taken from the cross-section of TF1, TF1-A5, TF1-A6, TF1-A6-2 glazes are given. Images showed that the porous structure which are present in the standard TF1 glaze are also present in the TF1-A5, TF1-A6 and TF1-A6-2 glazes.

3.4. Physical Analysis:

Color analysis (L, a, b color values) of the specimens were carried out by “X-rite” color checker. Surface roughness of the specimens was obtained by “Ceramic Instruments KR 100” roughness analyzer and the brightness values were obtained by “Konica Minolta Multi Gloss 268 Plus” gloss meter.

As a result of the color, surface roughness and brightness analysis, Table 3 is formed. Whiteness of the glazes derived from frits including wastes are increased and this caused a small decrease in transparency of the glazes. The brightness of the new glazes are very close with the standard glaze but the surface roughness of the new glazes were slightly increased, most significant increase was seen at TF1-A6-2 glaze.

Table 3. Color, brightness and roughness values of glazes including the developed frits.

FRIT	COLOR			BRIGHTNESS			ROUGHNESS
	L	a	b	20 °	60 °	80 °	µm
TF1	69,3	4,41	12,49	21	56,1	71,7	1,67
TF1-A5	70,61	4,03	11	27,1	58,3	73,5	2,82
TF1-A6	72,38	3,84	10,53	21	55,4	74,7	2,05
TF1-A6-2	73,31	4,67	11,98	22,5	56,1	71,7	3,18

3.5. Thermal Analysis:

In order to observe the sintering behaviours of the specimens “ODHT-HSM 1600/50 Misura 3.32” heat microscope was used. Temperatures of sintering, softening, sphere, half sphere and melting temperatures were obtained by going up to 400^{o}C with 30^{o}C/minute and 1400^{o}C with 10^{o}C/minute.

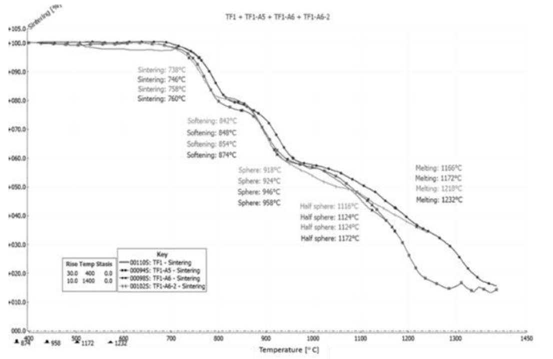

Figure 6. Result of thermal analysis applied to frits by using heat microscope.

Sintering curves (Figure 6) of the frits developed with wastes is very similar to the standard frits. Sintering, softening, sphere, half sphere and melting temperatures of all compositions are very close to each other (Table 4).

Table 4. Results of the thermal analysis applied to developed frits.

FRIT	Sintering Temperature °C	Softening Temperature °C	Sphere Temperature °C	Half Sphere Temperature °C	Melting Temperature °C
TF1	758	854	924	1124	1166
TF1-A5	746	848	946	1124	1172
TF1-A6	760	874	958	1172	1232
TF1-A6-2	738	842	918	1116	1218

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4. Conclusions

In this study, it has been shown that Bandırma colemanite enrichment wastes can clearly be used as a source of B_2O_3 along with the boric acid in the production of transparent frits. Despite the high amounts of CaO present in the composition of wastes, they can succesfully support a quantity of boric acid as a B_2O_3 source if the necessary arrangements are made on the frit compositions. This study proves that recycling of the colemanite enrichment wastes and decreasing the costs by using them instead of certain amounts of boric acid is possible.

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