Evaluation of borax solid wastes in production of frits suitable for fast single-fired wall tile opaque glass–ceramic glazes[†]

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Abstract. Zircon (zirconium silicate, ZrSiO_4) is the main opacifier of glossy, opaque, white-coloured, frit-based wall tile glazes. However, zirconia containing frits employed in the preparation of these glazes raise the production cost limiting zircon usage as a raw material at an industrial scale. Therefore, there have been several searches on seeking for alternative frit compositions with lower or without zirconia content. Consequently, positive outcomes were recently reported. With the present study, 1.5–5% of borax concentrator waste replaced certain level of acid boric for B_2O_3 content in a low zircon containing frit recipe. It is confirmed that waste contribution did not distort the surface properties of the fast single-fired wall tile opaque glazes. Zircon was found to be the main crystal phase of the glazes in laboratory trials. Industrial applications revealed that shorter firing cycles lead to zircon and petedunnite ($\text{CaZnSi}_2\text{O}_6$) formation in the CW-4 glaze.

Keywords. Borax solid wastes; evaluation; wall tiles; glass–ceramic glazes; fast single-firing.

1. Introduction

Frits are the indispensable constituents of most industrial glazes which mature at the temperatures below 1150°C (Taylor and Bull 1986). The opacity of the traditional wall tile opaque glazes usually originates through hardening of glass matrix by adding high amounts of zirconia containing frits into their batches (Yekta *et al* 2006). Nowadays, researchers point out that certain types of glass–ceramic layers can be alternatively employed as tile coatings lowering the use of zirconia containing expensive opaque frits. One of the best methods to obtain an opaque glaze surface is to induce a crystal phase in the coating, whose refractive index significantly differs from that of the glassy matrix. The opacity of such a coating is determined by the diffusion, refraction and reflection of light through the layer which contains emerging crystals, and the degree of opacity mainly depends on the size and quantity of crystals (Taylor and Bull 1986; Yekta *et al* 2006).

The development of glazes not possessing expensive or toxic components is of special interest (Moreva and Levitskii 2006). When compared to raw glazes fritted ones decrease melting temperatures and consequently, the

glaze maturation time is narrowed, smooth and bright surfaces can easily be formed. The bright and transparent glaze appearances can be changed with the opacification supplied by one or more crystal phases and zirconium compounds are the most effective ones in that term. In recent years, high prices of some raw materials led to searches directed on seeking new alternatives to reduce the production cost. Previously done studies (Pekkan *et al* 2007, 2008a–d, 2009a, b) pointed out that the amount of zircon could be decreased and even completely eliminated in frit recipes.

Some ceramics have been manufactured by using suitable wastes as a raw material to reduce the production cost. In addition, there has recently been much interest in providing a market for a product, in which wastes were evaluated, thereby reducing the volume of waste that must ultimately be disposed off (Chiang *et al* 1994). For instance, borax solid wastes have been re-cycled in the manufacture of glass–ceramics suitable for glaze applications. Acid boric is the main B_2O_3 resource of frit recipes. In the glazes, B_2O_3 reduces the softening and melting temperatures, lowers surface tension and improves their mechanical and thermal properties. Moreover, it influences the aesthetic characteristics of the coating. Therefore, supplying B_2O_3 through a suitable waste is of economical, technical and environmental importance. There have been some researches conducted on the evaluation of borax solid wastes in single fast-fired floor and porcelain tile glazes, in which certain oxides were brought up to an optimum level through the wastes (Karasu *et al* 2006a–d;

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Table 1. Compositional details of studied frits (in moles).

Frits	Al ₂ O ₃ /SiO ₂	Al ₂ O ₃ /*ΣR ₂ O	Al ₂ O ₃ /**ΣRO	Al ₂ O ₃ /B ₂ O ₃	CaO/MgO	ZrO ₂	ZnO
HZG	0.06	1.73	0.14	3.25	2.58	<i>x</i>	<i>y</i>
LZG	0.04	0.38	0.08	0.38	2.19	<i>x</i> – 0.01	<i>y</i> – 0.24
CW1-4	0.04	0.38	0.08	0.38	2.19	<i>x</i> – 0.01	<i>y</i> – 0.24

*Na₂O + K₂O; **CaO + MgO + ZnO.

Table 2. Composition of the base LZG frit.

Components	Content (mol %)
R ₂ O (R: Na, K)	4.67
RO (R: Ca, Mg, Sr, Zn)	21.78
R ₂ O ₃ (R: B, Al, *Fe)	9.43
RO ₂ (R: Si, Zr, *Ti)	64.12
Total	100.00

*Fe₂O₃ and TiO₂ come from some raw materials and their amounts are negligible.

Kaya *et al* 2008). In the current work, borax concentrator wastes were incorporated into the newly synthesized, low zircon and ZnO containing frit recipes, from which fast single-fired wall tile opaque glass–ceramic glazes were developed.

2. Experimental

The frits were developed in the Na₂O–K₂O–MgO–CaO–SrO–ZnO–Al₂O₃–B₂O₃–ZrO₂–SiO₂ glass–ceramic system. In the previously done study 25% reduction of both zircon and zinc oxide in the frit batch (LZG) was achieved with respect to the industrially used commercial frit (HZG) containing 6–10% ZrO₂ and 6–10% ZnO for glossy white opaque wall tile glaze (table 1). Request for certain boric oxide content in the LZG frit with low zirconia (4.5–7.5%) and ZnO (4.5–7.5%) taken as a reference for the present study (table 2) was fulfilled with Eti Maden Kirka Boron Company borax concentrator wastes (CW), chemical composition of which is indicated in table 3. 1.5–5% of CW was added into the LZG frit and the new frit recipes were named as CW 1–4 (table 4).

The weighed and thoroughly mixed batches were melted in alumina crucibles in a laboratory type, electrically-heated furnace (Protherm PLF 160/7) at 1450°C for 1 h. The melt was then quenched by pouring into cold water to obtain frits under laboratory working conditions.

The glass transition and the crystallization temperatures of the studied frits were determined with a differential thermal analyser (DTA, Netzsch STA 409 PC) on samples ground to a grain size of <63 µm with a heating rate of 10°C/min up to 1140°C.

In order to prepare glazes suitable amounts of frit, kaolin, carboxyl methyl cellulose (CMC), sodium triphosphate (STPP) and water were mixed in a ball

mill for 50 min. The slurries were applied onto industrial pre-engobed green wall tile bodies. After drying, fast single-firing took place in a laboratory type roller furnace (Nannetti Faenza ER 30) with peak temperatures resembling those industrially employed for this type of product. Under the lights of the results obtained from laboratory firing, CW 4 frit-based glaze, which was found to be the most successful one, was selected. For the industrial trial, first, frit of CW-4 was produced under laboratory conditions and then, glaze preparation and industrial firing were conducted. The optical parameters *L** [(–) black and white (+)], *a** [(–) green and red (+)], and *b** [(–) blue and yellow (+)] (Henkes *et al* 1996) of all the fired tiles were measured using a Minolta CR-300 series chromameter. Gloss was determined with a gloss-meter (Minolta Gloss 268) with 60° light incident angle on the glaze surface. XRD analyses were made by a Rigaku Rint 2000 series diffractometer with CuK_α radiation at 40 kV and 30 mA and, the scanning velocity of 2°/min. XRD patterns were taken from the fired glazed tile surfaces to identify the crystal phases formed. In order to study the effect of glaze composition on the formation, size, and distribution of the opacifying crystal phases, the samples analysed with XRD were also subjected to the investigations by scanning electron microscopes [SEM (Zeiss EVO 50 EP and Zeiss SUPRA 50 VP at 20 kV)] attached to EDX.

3. Results and discussion

ZrO₂ and ZnO contents were lowered in the frit recipes by only modifying the original frit chemical composition with no other nucleating agent incorporated for opacification. ZrO₂ (*x* mole) and ZnO (*y* mole) contents in the commercially available HZG glaze were decreased and finally, it was found that successful frit recipes could be produced by *x* – 0.01 and *y* – 0.24 values (table 1). Decreasing ZrO₂ level at a constant ZnO content results in pinhole problem in the HZG glaze. Pinhole can be explained by the migration of small gaseous bubbles due to dissociation of carbonates, from the interior of the glaze layer toward its surface forming small craters, which do not have time enough to be filled by viscous flow of melted glaze, accordingly, more or less perceptible pinholes remained after cooling (Levitskii and Mazura 2005). If the glaze is such a kind covering the substrate at

Table 3. Chemical composition of the borax concentrator waste (CW) used in the study (in wt. %).

SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SrO	B ₂ O ₃	*L.I.
19.97	2.44	0.05	0.50	11.37	13.75	7.50	2.34	1.06	14.30	26.72

*L.I.: losses on ignition.

Table 4. Acid boric and CW contents of the studied frits (in wt %).

Frits	Acid boric	Concentrator waste (CW)
LZG	x	–
CW-1	$x - 2.5$	2.5
CW-2	$x - 5$	5
CW-3	$x - 3$	3
CW-4	$x - 1.5$	1.5

Table 5. Colour (L^* , a^* , b^*) and gloss (60°) values of the selected glazes.

Glazes	L^*	a^*	b^*	Gloss (60°)
HZG-based	92.67	–0.12	2.06	89.8
LZG-based (reference)	92.81	–0.36	2.27	88.2
CW 1-based	89.10	0.42	2.55	77.1
CW 2-based	89.33	0.18	2.73	81.7
CW 3-based	90.31	–0.30	2.52	70.8
CW 4-based	91.17	–0.62	1.36	85.6

a quite lower temperature then, there will be insufficient time for gases to escape (Eppler and Eppler 2000). In addition to ZrO₂ decrement, presence of R₂O (Na₂O and K₂O) oxides strongly influences the maturation temperature in fast single-fired glossy opaque glazes. In order to increase this temperature and get rid of pinholes, both Al₂O₃ content and CaO/MgO ratio were increased. However, higher Al₂O₃ levels result in surface defects as a consequence of high surface tension (Taylor and Bull 1986; Sorli *et al* 2004; Kawamura *et al* 2005). The glaze should have a suitable surface tension to minimize crawling of the coating away from the edges or any holes that are present on firing. In terms of gloss, whiteness and surface quality of the opaque glazes, increasing boric oxide in the composition has a positive effect (Levitskii *et al* 1998; Djambazov and Damgaliev 2000). When compared to the HZG glaze, Al₂O₃/B₂O₃ ratio was declined in the LZG by incorporating B₂O₃ to the system. In this glaze, optimum Al₂O₃/B₂O₃ ratio was determined as 0.38 and the surface quality of the glaze was improved. ZnO content decreased as $y - 0.24$ mole (20%) without changing the Al₂O₃/SiO₂ ratio. In that glaze ZrO₂ level was diminished by $x - 0.01$ mol (21%) by keeping the Al₂O₃/SiO₂ and CaO/MgO ratios constant compared to that of the HZG glaze.

Lowering ZnO content in a zirconia containing opaque glaze diminishes the whiteness because ZnO contributes to the enhancement of colour development and increases the brightness as well as improving the glaze surface quality (Djambazov and Damgaliev 2000; Kawamura *et al* 2005; Levitskii and Mazura 2005). These indispensable contributions of ZnO in opaque glazes were fulfilled with the presence of B₂O₃ and Al₂O₃ in the current study.

The comparison of L^* , a^* , b^* and gloss values was made with those of the standard wall tile covered by LZG-based opaque white glaze with low levels of ZrO₂ and ZnO (table 5).

Borax concentrator waste can be used up to 5 wt.% in the frit recipes by keeping the original Seger formula of the LZG constant. Thanks to this amount of waste, there was no need for Na-feldspar use in frit recipes studied.

The LZG frit was prepared in a box type industrial melting furnace and LZG-based glaze was industrially fast single-fired. However, the newly synthesized CW 1–4 frit recipes were prepared in the laboratory and their firings were conducted in the laboratory type roller furnace with the parameters industrially applied at 1140°C for a total firing time of 55 min. *In situ* applications were made for the CW-4 based glaze. Since industrial firing conditions have been changed during that time period, the reference LZG and CW-4 based glazes have been fired at 1140°C for 37 min. Such an important time reduction in firing cycle did not affect the glaze properties. The colour (L^* , a^* , b^*) values of CW-4 based glaze then became 91.20, –0.28 and 1.91, respectively. The gloss value was measured as 90.8. These results revealed that CW-4 glaze is stable under different firing conditions and cycles.

Figure 1 shows the DTA traces of the studied frits. Although they exhibited exothermic effects, it was determined that they have different crystallization peak intensities due to the compositional changes made. T_g values of the HZG and LZG frits were measured as 718 and 713°C, respectively. The HZG frit exhibited two shallow exothermic peaks at 873 and 953°C. The former one should belong to the calcium aluminium silicate (Ca₃Al₆Si₂O₁₆) formation while the latter one to that of zircon (ZrSiO₄) whose devitrification was reported to happen at about 900–950°C (Amoros *et al* 1994; Escardino *et al* 1996, 2000; Taylor 2001; Quinteiro *et al* 2002). The LZG one demonstrated had an intense exothermic peak at 951°C. The glass transition temperature, T_g , of CW 1 with 2.5% waste incorporation into its starting batch and CW 3 with 3% waste are 725 and 720°C, respectively. They have higher T_g and broad exothermic

peaks indicating relatively low crystallization rates in them. The other studied and reference frits present a similar thermal behaviour in terms of T_g and show an exothermic peak at about 950°C, referring to the zircon crystallization.

When 10.3–22.4% of total boric oxide content in the LZG frit composition was replaced by boric oxide coming from CW, L^* , a^* , b^* values of the glazes did not fluctuate significantly (table 5). The CW 4-based glaze has the highest whiteness value (L^*) amongst the others derived from the LZG frit. Although all the glazes present similar whiteness, their gloss values are lower than that of the standard LZG-based one (table 5). The colour values

of the glazes, in frits of which waste was evaluated, can be said alike in comparison with high level of zirconia and ZnO containing HZG-based opaque glaze. According to the previous experiences it is thought that compared to the LZG-based one the decrement in gloss values of the CW 1-4-based glazes might be arising because of varying cooling conditions of the laboratory type roller furnace.

Figure 2 exhibits the XRD patterns of the phases present in the studied glazes. The HZG-based glaze experiences both calcium aluminium silicate ($\text{Ca}_3\text{Al}_6\text{Si}_2\text{O}_{16}$) and zircon (ZrSiO_4) crystallizations. Apart from this, zircon is seen to be the main crystalline phase in all the other glazes fired under laboratory conditions. Although the submission of concentrator waste into frit batch did not change the type of crystal phase, it is observed that zircon peak intensities differed. The CW 2-based glaze has the highest level of waste incorporation (5%) in its

Figure 1. DTA curves of the HZG, LZG, CW1, CW2, CW3 and CW4 frits.

Figure 2. X-ray diffraction spectra of the HZG, LZG, CW1, CW2, CW3 and CW4 frit-based glazes.

Figure 3. SEM micrographs of the HZG-based glaze showing the general **a.** and detailed **b.** microstructural views.

Figure 4. EDX patterns taken from the HZG-based glaze inhibiting occurrence of **a.** zircon and **b.** calcium aluminosilicate.

Figure 5. SEM micrographs of the LZG-based reference glaze showing **a.** general and **b.** detailed microstructural views.

frit batch and presents intense zircon peaks. The XRD results of the glazes obtained from the studied frits agreed with the DTA data confirming both calcium aluminium

silicate and zircon crystallizations. It was determined that, during industrial fast single-firing of CW 4-based glaze, petedunnite ($\text{CaZnSi}_2\text{O}_6$) also occurred besides

Figure 6. EDX patterns taken from the LZG-based glaze inhibiting the **a.** zircon occurrence and **b.** the elemental constitutions of the glassy phase.

Figure 7. SEM micrographs of the CW1-based glaze showing **a.** general and **b.** detailed microstructural views.

Figure 8. EDX patterns taken from the CW1-based glaze inhibiting **a.** zircon occurrence and **b.** the elemental constitutions of the glassy phase.

Figure 9. SEM micrographs of the CW2-based glaze presenting **a.** general and **b.** detailed microstructural views.

Figure 10. EDX patterns taken from the CW2-based glaze depicting **a.** zircon occurrence and **b.** elemental constituents of the glassy phase.

Figure 11. SEM micrographs of the CW3-based glaze exhibiting **a.** general and **b.** detailed microstructural views.

zircon crystallization leading to the thought that its formation is favoured by shorter firing cycles.

The general microstructural views of the HZG-based glaze and the crystals formed are depicted in figures 3

and 4. The acicular white crystals with different sizes belong to zircon and grey irregular-shaped ones to calcium aluminium silicate. The microstructure of the reference LZG-based glaze is indicated in figure 5. The

Figure 12. EDX patterns taken from the CW3-based glaze representing **a.** zircon occurrence and **b.** elemental constitutions of the glassy phase.

Figure 13. SEM micrographs of the CW4-based glaze showing **a.** general and **b.** detailed microstructural views.

Figure 14. EDX patterns taken from the CW4 glaze inhibiting **a.** zircon occurrence and **b.** elemental constitutions of the glassy phase.

acicular crystals originated from its frit belong to zircon (figure 6). These crystals are generally dispersed in the glassy matrix and they are approximately 2 μm or smaller in size.

The general and detailed microstructural views of newly developed glazes are presented in figures 7, 9, 11 and 13. According to EDX studies, the acicular and round-shaped white crystals immersed in the glassy

Figure 15. SEM micrographs of the industrially fired CW4-based glaze showing a. general and b. microstructural views.

Figure 16. EDX patterns taken from the CW4-based glaze indicating a. petedunite and b. zircon occurrence.

matrix belong to zircon (figures 8, 10, 12, and 14). Generally, zircon crystals were found to be dispersed in a glassy matrix that exhibited immiscible-liquid-phase separation. In the studied glazes, crystal-free areas can also be observed, owing to zircon crystallization preferentially occurring from the surface of the original frit particles inwards (Levitskii *et al* 1998). The devitrification of zirconium silicate crystals gives rise to a homogenous microstructure in the CW 1, 2 and 4-based glazes. However, the CW 3-based one represents a heterogeneous microstructure with localized needle-shaped zircon crystals in the glassy matrix (figure 11). It is thought that this heterogeneous microstructure may explain the lower gloss value of the CW 3-based glaze when compared to the others. In such sense, the CW 4-based one (figures 13 and 14) has the highest gloss value (see table 5). Industrially fired CW-4 based glaze at 1140°C for 37 min has a homogenous microstructure. In the relatively short firing cycle, zircon and petedunnite crystals are identified (fig-

ures 15 and 16). The amount of light reflected, and therefore, the opacity is dependent on both the number and the refraction index of the particles present in the glassy matrix (Karasu *et al* 2001). Zircon crystals were seen to have a tendency to become aligned through the surface of the glaze, and their elongation sizes may lead to a loss of opacity (Castilone *et al* 1999). SEM and EDX analyses revealed that the opacity of the LZG and CW 1-4-based glazes was achieved as a result of zircon crystallization and the concentrator waste usage in frit recipes is appropriate up to a certain level (5%) for the Na₂O–K₂O–MgO–CaO–SrO–ZnO–Al₂O₃–B₂O₃–ZrO₂–SiO₂ glass–ceramic glaze system.

4. Conclusions

Differing amounts of borax concentrator waste (1.5–5%) replaced certain level of acid boric in the frit recipes for B₂O₃ content and the final glaze surface properties were

found to be similar to those of the industrially produced standard LZG-based glaze with lower zirconia (4.5–7.5%) and ZnO (4.5–7.5%) contents. Zircon crystals originated from the frits during laboratory fast single-firing of the glazed wall tiles at 1140°C for 55 min. Industrial trials indicated that firing conditions influence the type of crystals in the glaze. Zircon and petedunnite were the main crystals of the glaze observed as a result of shorter firing time (37 min). Industrial application of the CW-4 based glaze confirmed that the glaze opacity, colour and gloss properties are stable under different firing conditions and cycles. Although the CW-4 frit batch which contains 1.5% concentrator waste gave better results in terms of glossiness and surface smoothness of the final fast single-fired opaque wall tile glazes, the others, in which the waste level was increased up to 5%, could also be evaluated. It was determined that the borax wastes of Kirka region of Türkiye can be re-cycled in this type of glazes with the complete replacement of Na-feldspar in their frit batches without consequently causing any kind of glaze defects.

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