

## The use of tincal calcination plant waste as an additive in ceramic wall tile production

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The aim of the present study is to extend the utilization of tincal calcination plant waste (TCW) of Kirka Borax Company (KBC) in wall tile production by replacing marble in suitable amounts. It is worthy mentioning that the TCW has been neither tested for tile production nor characterized for academically, yet until today. First of all, the characteristic features of TCW were determined by some analyses techniques such as quantitative XRD analysis, XRF and DTA-TGA analyses. Then, representative experimental wall tile formulations were prepared by progressive incorporation of TCW in wall tile recipes. A total of four formulations was prepared with 2, 4, 6 and 9 wt.% TCW incorporation and shaped by dry pressing. The representative tiles were single fast-fired in an industrial roller furnace at a peak temperature of 1150 °C for a total firing time of 38 min. The physico-mechanical properties namely linear firing shrinkage, water absorption, fired flexural strength of the representative samples were measured in accordance with the standard procedures. According to the results, the addition of TCW appeared to improve liquid phase development with better physical properties compared to those of standard composition for the firing regime involved. The results indicated a prospect for using the waste in wall tile formulations up to 4 wt%.

**Key words:** Boron waste, Wall tile, Ceramic raw materials, Tincalconite.

### Introduction

Not only rapid depletion of natural ceramic resources but also rapid growth of the Turkish ceramic covering tile industry has led research activities to find alternative raw materials with low cost within last years in Turkey. The boron waste [1-10] and coal fired power station waste [10-13] have gained considerable interest as alternative ceramic materials in Turkey. Increasing environmental regulations is also considered to be important matters.

Turkey has the largest reserves of boron minerals with 69.7% (in terms of  $B_2O_3$  content) of the total boron reserves of the world. ETİ Mine Works General Management, a state owned company is the sole producer of boron minerals in Turkey and it is the biggest borate producer of the world, producing 39.6% of the world borate production. The principal borate minerals of Turkey are borax (tincal) ( $Na_2B_4O_7 \cdot 10H_2O$ ), ulexite ( $NaCaB_5O_9 \cdot 8H_2O$ ) and colemanite ( $Ca_2B_6O_{11} \cdot 5H_2O$ ) which are refined into pure chemical compounds [14]. Run-of mine boron ores are enriched by selective crushing, attrition scrubbing and classifying. Concentrates are either directly marketed or treated to produce pure chemical refined products like borax decahydrate, borax pentahydrate, anhydrous borax, boric acid, sodium perborate in boron derivatives plant. In addition to these boron products, the calcinated tincal is produced from run-of mine tincal ore at Kirka Borax Company (KBC) with capacity of 5000 tonnes/year [15].

During these processes, different types of solid boron-containing wastes are formed and rejected in tailing dams next to the boron plant. This raises substantial environmental concerns in fear of boron leaching and subsequent soil and groundwater pollution. In particular, the dissolved boron compounds form several complexes with the heavy metals (Pb, Cu, Co, Ni, Cd, etc.), which are more toxic than their metals [16]. Nowadays, as much as 400.000-450.000 tpy waste is produced as a result of refined boron production facilities whereas 5000 tpy waste is occurred from tincal calcination plant at KBC [17].

In this study, an attempt was made to test the possibility of recycling TCW in ceramic wall tile production in industrial scale. Several wall tile compositions were formulated using varying proportions of the TCW by replacing marble. The TCW was characterized with respect to its chemical composition, mineral phase presents, and thermo gravimetric analysis (DTA-TGA). The physical and mechanical properties, as well as the thermal behaviour and the microstructure of the final wall tile products were also studied.

### Materials and Methods

#### Raw materials

The solid waste (TCW) was collected from the waste pouring area of tincal calcination plant of Kirka Borax Company located in Kirka Town (Seyitgazi County) of Eskisehir Province, Turkey. The TCW has been neither tested for tile production nor characterized for academic purposes. Thus, to investigate the suitability of this

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waste for manufacturing tile bodies is of interest from an academic and technological viewpoint. At the calcination plant, the raw tincal ore is subjected to calcination in rolling furnace at 350–400 °C with about 30 min. Then, TCW is separated from calcined tincal product by means of pneumatic separation. Other raw materials used for representative wall tile formulations were supplied from UMPAS Ceramic Factory in Usak, Turkey.

### Characterization and industrial tests

First of all, the characteristics features of TCW were determined by some analyses techniques. Quantitative determination of major crystalline phases present in TCW sample was achieved by X-ray diffraction (XRD) method. The XRD patterns were obtained with a Rigaku Rint-2200 diffractometer operating at tube voltage and current 40 kV and 30 mA, respectively using monochromatic Cu-K $\alpha$ 1 radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Diffraction patterns were recorded between 5 and 70 ° 2 $\theta$  with scanning rate of 2 °/min. Quantification of different phases was carried out by using the computer program MAUD 1.9 [18]. The chemical composition of TCW was determined by X-ray fluorescence spectrometer (Rigaku ZSX Primus) while B<sub>2</sub>O<sub>3</sub>% content was determined by wet chemical analysis method. A differential calorimeter apparatus Netzsch STA 409 under air atmosphere was used for differential thermal analysis-thermo gravimetric analysis (DTA-TGA) to determine the thermal behavior of the wastes with increasing temperature. The temperature was increased from room temperature to 1200 °C at a rate of 10 °C/min, kept at this maximum temperature for 10 min. A combination of wet sieve screening for the fraction > 63  $\mu\text{m}$  and X-ray sedimentation technique for the fraction < 63  $\mu\text{m}$  was used. For the sieve screening, 100 g samples dispersed in deionised water were disaggregated by using 0.1% sodium hexametaphosphate. For the X-ray sedimentation analysis, the < 63  $\mu\text{m}$  fraction (about 3 g) was disaggregated using 0.5% sodium hexametaphosphate, agitated mechanically and disaggregated ultrasonically. The size analysis was performed with the Mikromeritics SediGraph 5120 particle size analyzer, size range 0.1–300  $\mu\text{m}$ .

For representative wall tile recipes, the raw TCW sample was dried firstly at 105 °C, and crushed for homogenization. Then, experimental wall tile formulations (total 600 grams) were prepared by progressive incorporation of TCW (2, 4, 6 and 9 wt.%) in wall tile recipes (see Table 1). The mixtures were ground using a jet mill with 1% Na<sub>2</sub>SiO<sub>3</sub> addition and sieved < 180  $\mu\text{m}$ , the oversize fraction was recorded. After the measurement of the mass per liter with the pycnometer (100 cm<sup>3</sup>) and viscosity by the Ford-cup (100 cm<sup>3</sup>) of the < 180  $\mu\text{m}$  fraction, the sample was dried at 105 °C. It was ground to fine powder in a porcelain mortar and pestled with gentle vertical crushing movement for 30 min. The fine powder was humidified (6 mass%

**Table 1.** Composition of investigated formulations and their designations.

	STD	R1	R2	R3	R4
TCW	–	2.0	4.0	6.0	9.0
Marble	9.0	7.0	5.0	3.0	–
Clay 1	27.0	27.0	27.0	27.0	27.0
Clay 2	10.0	10.0	10.0	10.0	10.0
Kaolin	16.0	16.0	16.0	16.0	16.0
Pegmatite	38.0	38.0	38.0	38.0	38.0
Total	100.0	100.0	100.0	100.0	100.0

moisture content), homogenized and pressed at 250 kg/cm<sup>2</sup> by the Gabbrielli Titan, Italy mark press giving rectangular (84 × 20 × 7 mm<sup>3</sup>) for bending strength determination and cylinders specimens (Ø50 mm) for determination of shrinkage and water absorption rate. The firing step was carried out in commercially kiln at UMPAS Ceramic Factory within firing cycle of total 38 min (cold-to-cold). The specimens were maintained at 1150 °C for 8 min. The physico-mechanical properties namely linear firing shrinkage, water absorption, fired bending strength (Nannetti Faenza, Italy mark fleximeter) of the representative samples were measured in accordance with the standard procedures.

The bending strength was carried out by using the three-point bending test and calculated by  $3FL/2bh^2$  in which F = breaking load (kg), L = distance between supports (mm), b = sample width (mm) and h = sample thickness (mm). The dimensions of the pressed specimens were measured before and after firing to determine the firing shrinkage by  $100(L_d - L_f)/L_d$ , where  $L_d$  = the length of the dried specimen and  $L_f$  = the length of the fired specimen. The water absorption values were determined by the routine procedure involving measuring mass differences between the as-fired and water saturated samples (immersed in boiling water for 2 h, cooling for 3 h and sweeping of their surface with a wet towel). The presenting results were the average of 10 tested specimens. The determination of water absorption and bending strength were carried out following the Turkish Standards [19] and [20], respectively. Microstructural observations were performed on polished surfaces of selected fired samples using a scanning electron microscope (SEM-Camsan S4 Series, UK) in back-scattered (BE) electron imaging after sputtering with a thin layer of gold-palladium alloy in order to prevent charging, attached with an Oxford Instruments 7430 energy dispersive X-ray (EDX) spectrometer.

## Results and Discussion

### Mineralogical and chemical analysis

Fig. 1 shows the X-ray diffraction patterns of the tincal calcination plant waste (TCW) sample, whereas the result for the quantitative mineralogical analysis of

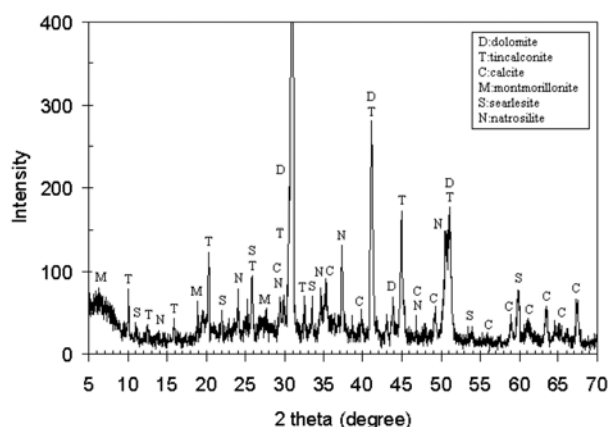


Fig. 1. X-ray diffraction pattern of TCW.

Table 2. Mineral content of the TCW (mass%) estimated by the computer program MAUD 1.9.

Main crystalline phases	Dolomite	Tincalconite
	67.08 ± 0.71	26.50 ± 0.69
Minor crystalline phases	Montmorillonite	Searlesite
	1.71 ± 0.12	1.97 ± 0.31
	Calcite	Natrosilite
	1.93 ± 0.15	0.80 ± 0.17

TCW is presented in Table 2. In terms of mineralogy, the following phases were identified for TCW: dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) and tincalconite ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ ), typically form as a dehydration product of tincal, as the major crystalline phases at 67.08 wt.% and 26.50 wt.% respectively; montmorillonite, calcite ( $\text{CaCO}_3$ ), searlesite ( $\text{NaBSi}_2\text{O}_5(\text{OH})_2$ ) and natrosilite ( $\text{Na}_2\text{Si}_2\text{O}_5$ ) as the minor phases.

The chemical analysis of TCW and other raw materials used for formulation of wall tile bodies are reported in Table 3. When chemical analysis of the TCW is examined it is seen that this waste contains a large amount of fluxing oxides ( $\text{B}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$ ) at about 19 wt% and alkaline-earth oxides such as  $\text{MgO}$  and  $\text{CaO}$  at about 36 wt.% indicated the presence of carbonates especially dolomite in agreement with the quantitative XRD analysis (Table 2). The high loss on ignition (27.82%) was due to the significant

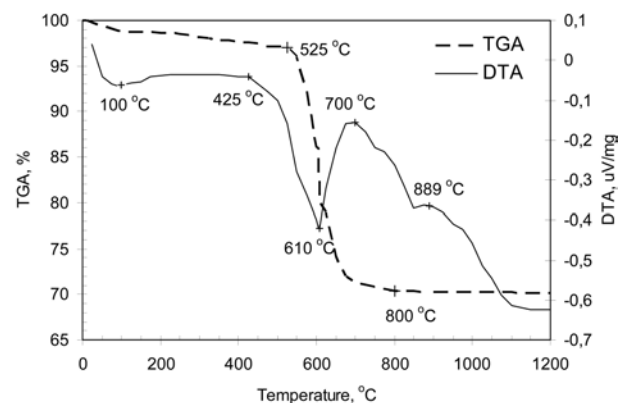


Fig. 2. DTA-TGA analyses of the TCW.

content of dolomite and tincalconite supported the XRD analysis.

### Thermal analysis (DTA-TGA)

A significant endothermic peak at 100 °C (Fig. 2) can be attributed to the removal of adsorbed and interlayer water of the TCW (dehydration). Any reaction was not observed until 425 °C. The reason for this was that the organic matter had been already decomposed in the raw tincal ore at the calcination plant. The mass loss was about 3% until 525 °C. The strong endothermic peak centered at 610 °C could be attributed to the breakdown of calcite and dolomite and gradually dehydroxylation of tincalconite to anhydrous borax ( $\text{Na}_2\text{B}_4\text{O}_7$ ). It was mentioned as parallel to this work that the dehydroxylation of tincalconite to anhydrous borax taken place approximately at 520-550 °C [21]. The associated to this endothermic peak, the mass loss of the TCW was about 27%. The endothermic decline observed 700-850 °C is thought to be due to the tincalconite melting. The small exothermic peak at 889 °C is due to the formation of new crystalline phase.

### Particle size analysis

Apart from the fluxing effect of the relevant oxides, considerable fine particle size distribution of the TCW is also believed to have played an important role in enhanced vitrification. According to the size distribution data, TCW has a mean particle size of around 3 µm,

Table 3. Chemical composition of TCW and the raw materials used for commercially.

Oxide (wt.%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	TiO <sub>2</sub>	SrO	LOI*
TCW	14.63	1.07	0.31	10.95	17.65	18.42	7.05	0.61	0.42	—	1.06	27.82
Clay1	60.79	23.82	2.07	—	0.19	0.97	0.21	2.14	0.21	1.23	—	7.88
Clay2	53.08	25.55	3.97	—	0.57	0.76	0.45	2.66	0.16	1.01	—	10.91
Kaolin	65.82	18.78	0.77	—	1.13	1.16	1.08	5.33	0.77	0.28	—	5.46
Marble	0.78	1.92	0.07	—	54.21	0.75	0.24	0.15	—	—	—	44.62
Pegmatite	72.30	14.53	0.80	—	1.23	0.86	5.46	1.60	0.10	0.25	—	4.46

\*LOI is loss on ignition at 1000 °C.

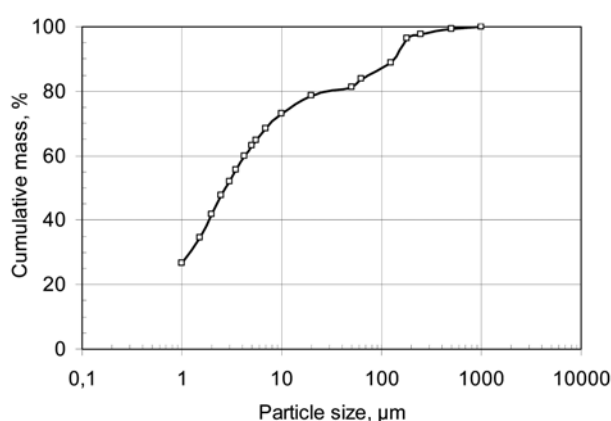


Fig. 3. Particle size distribution of the TCW.

Table 4. Technological properties of the recipes.

	STD	R1	R2	R3	R4
Rheological properties					
Weight volume, g/l	1710	1685	1670	1660	1640
Time of flow, s	25	53	n.m	n.m	n.m
Sieve residue on 180 μm, %	4.0	4.11	4.38	4.54	4.72
Firing properties					
Water absorption, %	14.78	13.27	12.51	10.02	6.41
Firing shrinkage, %	0.82	1.56	2.04	1.89	1.54
Firing strength, kg/cm <sup>2</sup>	195	218	247	233	210

\*n.m: not to be measured.

while d<sub>80</sub> size is around 50 μm (Fig. 3). It is obvious that the fine size distribution feature of the TCW makes them usable in the as-received form without any further size reduction.

### Industrial tests

Various physical and mechanical properties of the recipes obtained from progressive incorporation of TCW in the standard wall tile composition were listed in Table 4. As can be seen, the mass per liter of the recipes decrease with increasing amount of the TCW in tile formulations mainly due to high density of marble (2.711 g/cm<sup>3</sup>) as compared with dolomite (2.876 g/cm<sup>3</sup>) and tincalconite (1.894 g/cm<sup>3</sup>) [22]. It was recognized that in the preparation of TCW containing slurries studied in this study, an increase in viscosity with the further addition of TCW was also encountered. It was not to be measured for > 2 wt.% TCW addition. It can be seen from Table 4 that the increase in viscosity influenced the grindability of the formulations, and increased the sieve residue on 180 μm.

All recipes had almost the same drying shrinkage of about 0.2%. A value of drying shrinkage between 0 and 0.5% is required to avoid microcracks around sand grains [23].

The water absorption ( $W_a$ ) is the parameter according to Turkish Standards [24], and it defines the class to

which the tile products belong. The bodies (STD, R1, R2 and R3) showed values corresponding to class BIII ( $W_a > 10$  individual maximum 9), whereas R4 to class BII<sub>b</sub> ( $6 < W_a \leq 10$  individual maximum 3.3). The water absorption values of the fired products decrease slightly with increasing amount of TCW. As an expected consequence of this, there is a corresponding increase in the linear firing shrinkage values up to 4 wt.% TCW addition. This behaviour can mainly be explained by the fact that TCW acts a low temperature auxiliary flux, enhancing vitrification, due to strong fluxing action of its boron content.

When Table 4 is examined, it is seen that the fired strength of the bodies were increased gradually up to 4 wt.% TCW content. This result can be explained by relatively higher occurrence of glassy phase due to the existence of fluxing oxides such as B<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O. This reduces the porosity by closing up the pores and therefore, causes more compact microstructure than the standard body. The TCW has a considerably higher content of alkaline-earth elements (MgO and CaO) compared to the other raw materials (Table 3). The influence of MgO containing raw materials, such as magnesite and dolomite, as sintering promoters, on the vitrification behaviour of different compositions has already been studied. It has been pointed out that the concurrent presence of alkaline and alkaline-earth elements promoted the development of a less viscous liquid phase which improved the densification kinetics [25-27]. On the other hand, when the TCW added to the recipes further amount (> 4 wt.%), firing strength of the bodies influenced negatively.

XRD analysis was carried out in order to determine the phase changes in reference body (STD) and R2 body with 4 wt.% TCW content sintered at 1150 °C. Comparison of the XRD results of STD and R2 recipes is exhibited in Fig. 4. The addition of TCW in the wall tile body mixture had no significant change in the phase formation at 1150 °C, being qualitatively the same as for STD. When Fig. 4 is examined, it is seen that the main phases in the STD and R2 wall tile body are quartz (SiO<sub>2</sub>), anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) and albite (NaAlSi<sub>3</sub>O<sub>8</sub>).

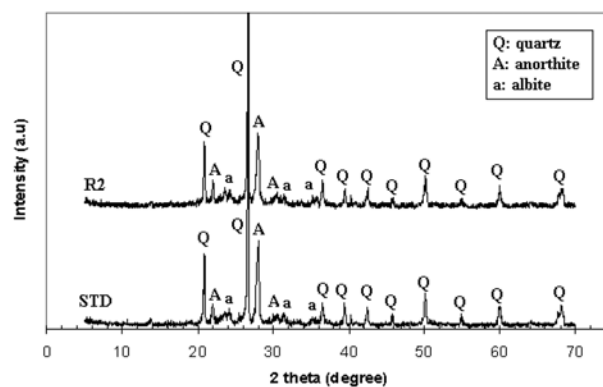
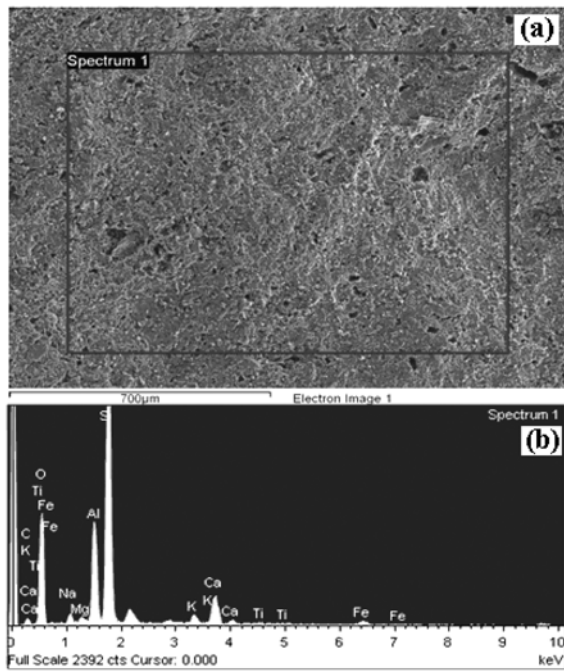
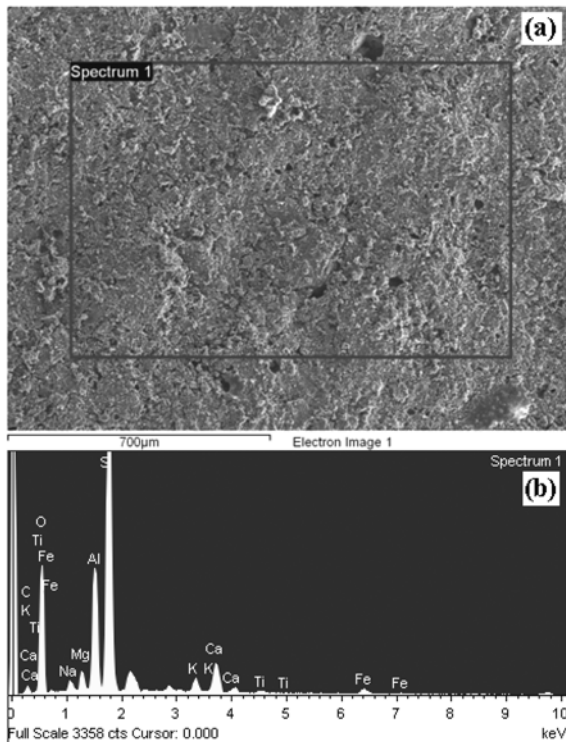


Fig. 4. X-ray diffraction patterns of STD and R2 bodies fired at 1150 °C.



**Fig. 5.** SEM backscattered electron image of STD wall tile body (a) and EDX spectrum obtained from the selected area (b).



**Fig. 6.** SEM backscattered electron image of waste-added wall tile body (R2) (a) and EDX spectrum obtained from the selected area (b).

### Microstructural analysis

The changes in the microstructure of the standard (STD) (Fig. 5) and waste-added wall tile (R2) (Fig. 6) bodies after sintering at 1150 °C at factory conditions were investigated by using characterization techniques

such as scanning electron microscopy (SEM) and an energy dispersive X-ray (EDX) spectrometer. In these images, the areas with a higher concentration of elements with a higher atomic number, such as iron and titanium, appear to be brighter than the rest of the sample [28] supports the EDX spectrums. Both images represent similar structures where the crystalline phases and pores are dispersed in a glassy matrix. As can be seen from Fig. 5, a larger amount of porosity, represented by dark areas, exists within the structure when compared with R2 body (Fig. 6). The main perceptible difference between these images is the appearance of slightly improved vitrification of R2 formulation. From the SEM investigation of the R2 formulation fired at the same temperature, the extent of vitrification with addition of boron waste can be easily observed (Fig. 6). With the substitution of the marble by TCW, the R2 composition contained progressively more of the fluxing oxides, therefore viscosity decreased and the rate of densification increased. This caused having better physical properties to R2 composition like lower water absorption and higher firing strength values than STD body as seen from Table 4. The area EDX analysis revealed that the both of the fired bodies contain Si, Al, Mg, Na, K, Ca, Fe, Ti and O elements (Fig. 5-6 b). These results are in good agreement with the chemical analysis of the raw materials and the waste used in the present research and XRD results of STD and R2 body with 4 wt.% TCW content sintered at 1150 °C (Fig. 4).

### Conclusions

In this study, a series of wall tile formulations incorporated with tincal calcination plant waste (TCW) of Kirka Borax Company (Turkey) up to 9 wt.% as a substitute for marble was prepared and fired under industrial conditions. It was demonstrated that it is possible to utilize TCW as alternative raw material resources for the production of the wall tile up to 4 wt.% TCW content in the body (R2 recipe). With the R2 recipe firing strength increased about 27%, and water absorption value decreased about 15% when compared with the standard composition (STD). It was believed that the concurrent presence of alkaline and alkaline-earth elements promoted the development of a less viscous liquid phase which improved the densification kinetics of R2 composition. Although the increasing problem in viscosity with the addition of TCW was defined; it was seen that this problem could be solved with slightly higher amount of electrolyte addition to grinding operation. At industrial condition the problem can be solved with separate dry grinding of the waste from other wall tile raw material. As a result, the utilization of TCW for tile production will result in the reduction of manufacturing costs in the ceramic industry. In addition, because the wastes

will be consumed, it will also have an environmental advantage.

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