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The effect of boron waste in phase and microstructural development of a terracotta body during firing

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Abstract

In the present study, a dewatering sieve waste (TSW) of Etibor Kırka Borax company (Turkey) was employed in different amounts in order to develop an experimental terracotta floor tile body composition in combination with a feldspathic waste provided from a local sanitaryware plant and a ball clay. Several formulations were prepared and shaped by dry pressing under laboratory conditions. The obtained samples were fired at selected peak temperatures (1050, 1100 and 1150 °C) to establish their optimum firing temperatures. Some technological properties of the resultant products, namely linear firing shrinkage, water absorption and breaking strength were determined as a function of increasing TSW content in place of the sanitaryware waste at these temperatures. The phase content of the starting raw materials and that of the fired compositions was determined by XRD. The relevant polished surfaces of selected fired samples were also examined using SEM. According to the results, increased presence of TSW compared to the standard mixture of clay and the sanitaryware waste, as a co-fluxing material, in the experimental terracotta body considerably accelerated the vitrification process. The overall results indicated a prospect for using the TSW as a raw material in mixtures with both clay and sanitaryware waste for the production of a terracotta floor tile body.

Keywords: Firing; Mechanical properties; Borax waste

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1. Introduction

Both manufacturers and customers in traditional ceramic industry like any other industrial activity require high quality products with low cost. Environmental protection and energy saving are also considered to be important matters. Therefore, in addition to finding alternative raw materials, recycling wastes as a possible replacement has gained considerable interest within last years. Turkey holds 63% of the total boron reserves of the world with 640 million tonnes. Boron ores in Turkey are colemanite, ulexite and tincal. Etibor Kırka Borax Company is the biggest borax producer in Turkey. This plant consists of concentration and crystallization units and produces 800,000 tonnes of concentrated tincal; 480,000 tonnes of pentahydrate; 17,000 tonnes of decahydrate and 60,000 tonnes of anhydrous borax per year. Borax is firstly separated from contaminants (mainly clay minerals) by simple washing–screening-scrubbing concentration methods then undergoes the crystallization unit. At this stage the concentrated tincal having about <3 mm particle size is fed to the stirrer reactor containing water heated to 368–373 K. After the treatment, the undissolved part of the tincal, called as dewatering sieve waste (TSW), is discharged as land filling. For a ton borax production, 500 kg of TSW is obtained. The amount of waste material, obtained from the beneficiation plant, has being progressively increased due the lower recycling rate of the produced waste material. Therefore, its disposal currently poses a serious problem.

Borates are valued constituents of the glass-making batch, offering both process and product advantages. They have also been key ingredients in the ceramic industries, such as cordierite ceramics, glass ceramics and frits. In such applications borates reduce the melting point of the glass and act as an important glass builder.[1,2] According to the relevant literature, there are various studies involving employment of borates and borax wastes in ceramic and cement industry.[3–11]

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Table 1
Chemical composition of the raw materials

Oxide (wt%)	SiO_2	Al_2O_3	Na_2O	MgO	K_2O	CaO	TiO_2	Fe_2O_3	ZrO_2	ZnO	B_2O_3	L.O.I.
Clay[a]	70.36	22.92	0.50	0.48	1.88	0.32	1.64	1.90	–	–	–	–
Scrap[a]	71.20	19.32	0.88	0.17	1.62	2.27	1.00	1.07	1.81	0.66	–	–
TSW[b]	15.83	1.06	2.58	19.84	0.63	20.66	0.01	0.24	–	–	3.99	34.75

[a] Achieved on the polished surfaces of the samples fired at 1100 °C semi-quantitatively using EDX.

[b] Achieved using XRF.

Recently, coal combustion fly ash and sanitaryware waste have been employed in an attempt to develop an experimental terracotta floor tile body. As a result, it has been demonstrated that both wastes helped the vitrification of the body at lower firing temperatures.[12,13]

The present study was achieved in order to obtain an experimental terracotta floor tile body with improved physico-mechanical properties and lower production cost using TSW in various amounts. A particular consideration was given to the phase and microstructural evolution of the experimented formulations upon firing at different temperatures and its correlation with the physico-mechanical properties.

2. Experimental procedure

2.1. Raw materials

The TSW sample was collected from the upper part of the dewatering sieve of dissolution units of Etibor Kırka Borax Company. Prior to use it in several formulations, a representative lot of 5 kg was separated, crushed and ground. Grinding was performed step by step by using a laboratory ceramic ball mill. Two hundred grams of waste material were dry milled for 2 h then sieved; the >149 μm size fractions of each step were collected and reload in a mill until all the samples would pass below in 149 μm. The plastic clay and feldispathic waste materials were obtained from a local terracotta producer and a local sanitaryware plant, respectively. The main oxide constituents of the raw materials are given in Table 1. The particle size distributions of the raw materials were measured by Malvern 2000 Mastersizer Laser Diffraction Particle Size Analyser as surface distribution (Table 2).

2.2. Processing and characterisation

Representative terracotta floor tile formulations were prepared by progressive incorporation of TSW in place of sanitaryware in different amounts (Table 3). The amounts mentioned were chosen so as to highlight the effects of TSW addition. These formulations were designated as std, B5, B10, B20, B30 and B40, respectively. As it can be seen from Table 3, the std formulation used as reference consisted of 60 wt% clay and 40 wt% sanitaryware waste. The preparation of the formulations involved mixing in the relevant proportions and dry grinding in ball mills to pass a 500 μm sieve. The obtained mixtures were then humidified (4–5 wt% moisture content) and sieved to pass through 1 mm screen in order to obtain suitable powders for pressing. Rectangular samples of dimensions 110 mm × 55 mm × 6 mm were uniaxially pressed at 160 kg/cm^2. The shaped samples were dried at 110–120 °C for 24 h. Firings were achieved in an electric laboratory kiln at a heating rate of 2 °C/h to the selected peak temperatures (1050, 1100 and 1150 °C) for 60 min in air.

Table 2
Particle size distributions of the raw materials

Cumulative values (μm)[a]	Clay	Sanitaryware waste	TSW
D (10)	1.53	1.66	0.39
D (50)	5.32	7.82	0.74
D (90)	21.1	41.0	2.27

[a] Measured as surface distribution.

Table 3
The composition of investigated formulations and their designations

Designation	Formulation (wt%)					
	std	B5	B10	B20	B30	B40
Clay	60	60	60	60	60	60
Sanitaryware waste	40	38	36	32	28	24
TSW	–	2	4	8	12	16

The physico-mechanical properties of the representative samples were measured in accordance with the standard procedures.[14–16] On average, three specimens were used for each measurement. Qualitative determination of major crystalline phases present in selected green and fired samples was achieved by X-ray diffraction (Rigaku, Rint 2000, Japan) on powdered samples. Microstructural observations were performed on polished surfaces of selected fired samples using a scanning electron microscope (SEM-Camscan S4 Series, UK) in back-scattered (BE) electron imaging after sputtering with a thin layer of gold-palladium alloy in order to prevent charging. The thermal analysis of TSW was determined by using simultaneous differential thermal and thermogravimetric analysis (DTA-TG/Linseis Thermowaage L81) with alumina crucible and a heating rate of 10 °C/min. Furthermore, the fired bodies were subjected to color measurements using a UV–vis spectrophotometer (Minolta 3600d) and the change in chromatic coordinates of L^*, a^*, b^* values with peak firing temperature was compared.

3. Results and discussion

3.1. Thermal and physical properties

DTA-TG curves for TSW are presented in Fig. 1. In the DTA curve, there are four basic endothermic peaks. The first one is observed in the range from 50 to 100 °C, with a peak at 77.3 °C; the second from 100 to 160 °C (peak at 141.1 °C); the third from 160 to 190 °C (peak at 179.2 °C). These effects correspond to weight losses due to the elimination of water in tincalconite and montmorillonite. The last endothermic peak at 621.9 °C represents the decomposition of dolomite.

The results of the evaluated physico-mechanical properties, namely, firing shrinkage, water absorption, and breaking strength are presented in Fig. 2. As it can be seen, the water absorption values of the fired products decrease considerably with both increasing amount of TSW and peak firing temperature (Fig. 2a). As an expected consequence of this, there is a corresponding increase in the linear firing shrinkage values (Fig. 2b). This behaviour can mainly be explained by two reasons: firstly, TSW acts as a co-flux, enhancing vitrification, due to strong fluxing action of its boron content. Secondly, TSW has a considerably higher content of alkaline-earth elements (MgO and CaO) compared to the other raw materials (Table 1). Particularly, the influence of MgO-containing raw materials, such as talc, magnesite, dolomite and chlorite, as sintering promoters, on the vitrification behaviour of different compositions has already been studied by several authors.[17–19] It has been reported that the concurrent presence of alkaline and alkaline-earth elements promoted the development of a less viscous liquid phase which improved the densification kinetics. Furthermore, importance of particle physics on kinetics and reaction paths during firing has already been stressed.[20] It has been suggested that increasing the number of contacts between particles of different mineralogical species enhances the probability that desired reactions occur. Thus, it is believed that substitution of the sanitaryware waste with much finer TSW has also played an important role in enhanced vitrification.

It is known that bulk density or porosity is a property with a strong influence on mechanical strength of traditional ceramic bodies. With reference to Fig. 2a and b once again, it is expected that the formulations that provided the lowest values of water absorption and the highest values of linear firing shrinkage at the relevant firing temperatures be also expected to provide the maximum flexural strength values. Indeed, this assumption is confirmed in Fig. 2c where the bending strength results of all the formulations at three firing temperatures are shown. Both higher amounts of TSW in place of the sanitaryware waste and higher peak firing temperature caused an increase in the strength values.

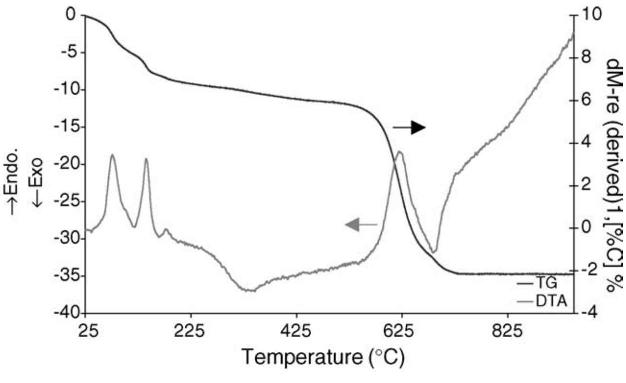

Fig. 1. Simultaneous DTA-TGA curves of TSW.

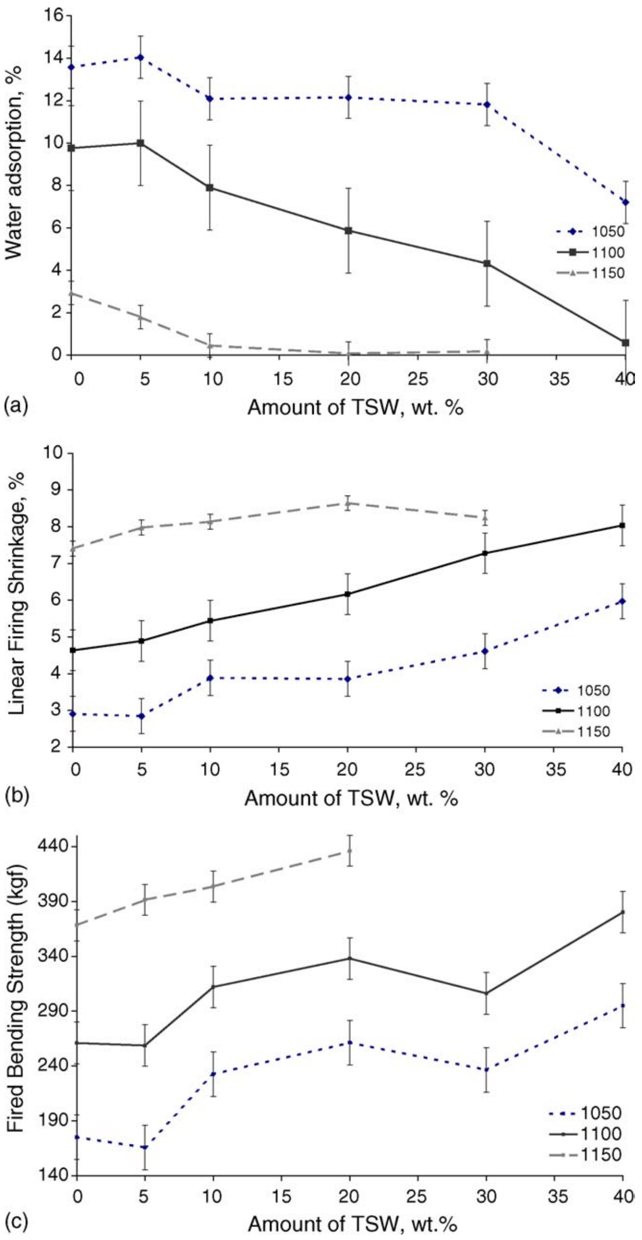

Fig. 2. Physical properties of the investigated formulations. (a) Variation in water adsorption in relation to TSW content. (b) Variation in linear firing shrinkage in relation to TSW content. (c) Variation in fired bending strength in relation to TSW content.

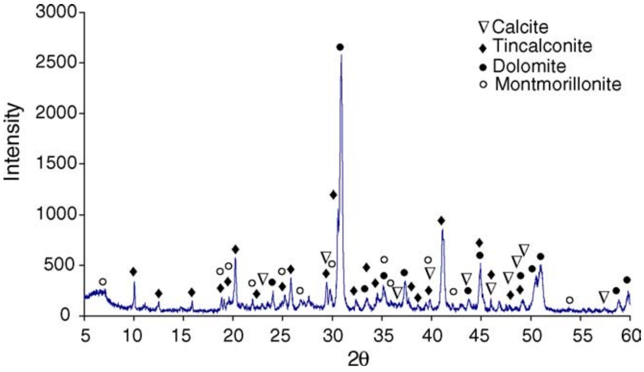

Fig. 3. Representative XRD spectrum as-received TSW.

3.2. Phase analysis

Fig. 3 gives the representative XRD spectrum of TSW where the presence of dolomite, tincalconite, montmorillonite and calcite minerals is easily detected. The main crystalline phases in the green body disappear during firing and are replaced by new phases. Fig. 4 illustrates the representative XRD spectra of the std, B20 and B40 formulations fired at 1100 °C. From these spectra, it can be concluded that quartz is the main crystalline phase, being to a large extent an unreacted residue of the initial amount quartz present in the bodies. It is worth mentioning that the presence of zircon points of the possible contamination of the sanitaryware waste with the glaze during production process in the plant. Apart from the residual phases, mullite appears to be the main crystalline phase formed during firing. The amorphous phase is believed to increase in a regular way for the compositions with increasing amount of TSW.

3.3. Microstructural analysis

Fig. 5 is a typical back-scattered image of the polished surface of the std formulation fired at 1100 °C. In this image, 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. As can be seen, a large amount of porosity, represented by dark areas, exists within the structure. The large variety of pore sizes, their irregular shape, and the presence of particles with sharp edges can be taken as characteristics of the initial stages of vitrification.

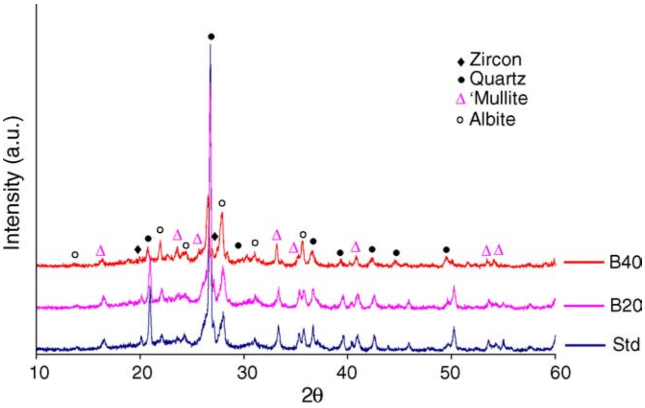

Fig. 4. Representative XRD spectra of the selected formulations fired at 1100 °C.

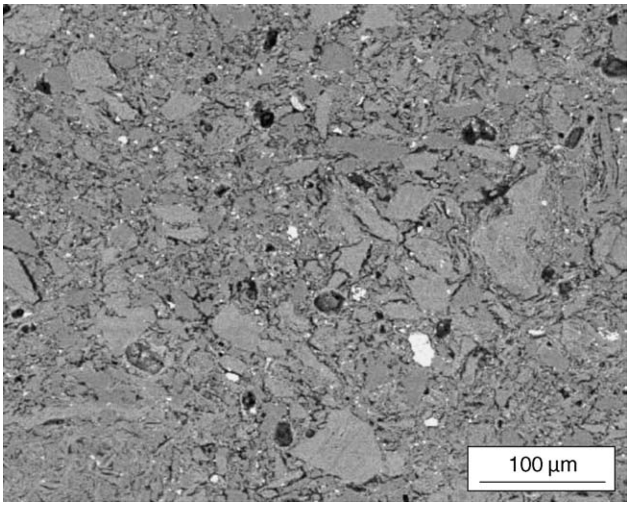

Fig. 5. A representative back-scattered SEM image of the std formulation fired at 1100 °C.

From the SEM investigation of the B40 formulation fired at the same temperature, the extent of vitrification with increasing amount of TSW can be easily observed (Fig. 6). At higher temperatures, liquid phase becomes progressively less viscous and is able to eliminate larger pores. The number of small pores thus decreases, while the larger pores become more isolated and start acquiring a rounded shape. In addition, the sharp corners of the quartz grains were also rounded by surface tension forces and their partial solution into the glassy matrix during firing. Apart from the effect of

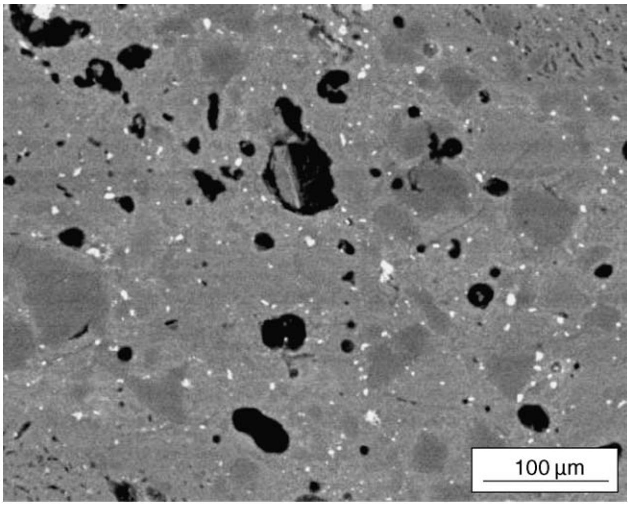

Fig. 6. A representative back-scattered SEM image of the B40 formulation fired at 1100 °C.

Table 4
The color values (L^* a^* b^*) of the investigated formulations

Firing conditions (temperature/soaking time)		Formulation					
		std	B5	B10	B20	B30	B40
1050 °C/1 h	L^*	82.89	84.89	82.84	81.82	79.98	75.09
	a^*	5.19	4.79	5.4	5.7	6.08	7.26
	b^*	16.15	16.76	8.18	20.28	19.79	21.33
	ΔE^*		2.12	2.04	4.29	4.74	9.59
1100 °C/1 h	L^*	80.34	81.01	78.94	77.42	74.16	67.26
	a^*	5.65	5.95	6.39	6.77	6.64	6.1
	b^*	19.39	21.33	22.16	24.09	22.47	21.28
	ΔE^*		2.08	3.19	5.65	6.98	13.23
1150 °C/1 h	L^*	72.93	73.19	69.74	63.36	60.76	–
	a^*	6.63	7.09	6.03	4.19	4.64	–
	b^*	22.99	25.16	23.19	20	19.12	–
	ΔE^*		2.24	3.25	10.32	12.92	–

ΔE^*: total color difference value.

temperature, with the substitution of the sanitaryware waste by TSW, the composition contains progressively more of the fluxing oxides, therefore viscosity decreases and the rate of densification increases.

3.4. Color measurements

The values of the chromatic coordinates of the studied formulations with increasing peak temperature are given in Table 4. The L^*-value (lightness) decreases as all the compositions approach vitrification at higher temperatures. This can be attributed to increased intensity of color-forming oxides, such as Fe_2O_3 and TiO_2 at such temperatures, particularly present both in the clay and the sanitaryware waste (Table 1). It is also to be noted that the decrease in L^* is more for the TSW-containing formulations, where it is expected to be a higher amount of glassy phase. Indeed, it has been shown in the relevant literature that reducing the quantity of these oxides in a standard porcelain tile composition raises the degree of whiteness in the fired product; in other words, the L^* co-ordinate increases and the b^* co-ordinate (yellowness) decreases. However, it is worth mentioning that at the same chromophore impurities content, the final whiteness of a vitrified body also depends on the nature and proportion of the phases developed during firing.[21]

4. Conclusions

In view of the pre-industrial findings, the progressive inclusion of TSW waste as a substitution of the sanitaryware waste on the physico-mechanical properties and microstructural development of several experimental terracotta floor tile formulations fired at different peak temperatures was reported. It was found that the addition of TSW improved the vitrification at all the firing temperatures involved. Although the highest bending strength and the lowest water adsorption (436 kgf and 0.1%, respectively) were observed for the composition designated as B20 fired at 1150 °C, the bending strength value of 380 kgf and the water adsorption value 0.6% at 1100 °C can also be taken as acceptable values for the same formulation. Improved physical and mechanical properties can be attributed to the presence of boron and high alkaline-earth oxides content of the TSW waste. As emphasized earlier, these oxides promote vitrification by causing development of less viscous liquid phase at the peak firing temperature.

Based on the XRD data, mullite was found to be the main crystalline phase formed during firing. Although there does not appear to be any considerable differences detected between the TSW containing formulations in terms of crystalline phase content, a gradual increase in the amount of amorphous phase is noticeable in parallel with both the increase in the amount of TSW incorporation and peak firing temperature.

To sum up, a potential seems to be present for the utilisation of TSW in combination with a sanitaryware waste and a ball clay in order to obtain low porosity, dense terracotta floor tiles. In addition, valuable use of these waste materials in such a possible commercial application, with all the positive effects both on the processing, such as the possibility of lowering the firing temperature to save energy, and the improved technological properties of the product can be mentioned as added advantages. An in-depth study is, however, needed on the industrial scale in order to establish the technical and economic feasibility of the study. Furthermore, however the TSW is in solid form and is not classified as a hazardous waste; it would still need to be disposed of in a specific site or controlled landfill. Disposal of the waste at a controlled landfill is costly. For that reason the use of this waste in terracotta formulations a possible alternative to the disposal is attractive. The benefit of this usage is that it is an economically viable method for the recycling of TSW that might otherwise have little or no value.

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