Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 1715–1720

www.elsevier.com/locate/jeurceramsoc

Investigation of borax waste behaviour in tile production

S. Kurama[a,*], A. Kara[a], H. Kurama[b]

[a] Anadolu University, Department of Material Science and Engineering, Eskisehir, Turkey
[b] Osmangazi University, Department of Mining Engineering, Eskisehir, Turkey

Abstract

Although there are various studies published in the relevant literature on the use of borates in tile production, borax waste has been mainly used in place of feldspar and the results showed that borate migration to the surface was the commonly encountered problem. Previously, the same authors have investigated the possible use of dewatering sieve waste (TSW) of Etibor Kırka Borax Company (Turkey) in combination with a sanitaryware waste in commercial terracotta production in an attempt to achieve improved product properties. In the present study, the same borax waste (TSW) was preferred for use in a commercial wall tile formulation in proportions up to 20% as a partial substitution for Na-feldspar. A total of four formulations was prepared with 0.5, 1, 1.5 and 2 wt.% TSW incorporation and shaped by dry pressing. The obtained samples were single fast-fired at a peak temperature of 1170 °C for a total firing time of 30 min (from cold-to-cold) under industrial conditions. According to the results, the addition of TSW 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 as a co-flux in wall tile formulations.

Keywords: Borides; Traditional ceramics; Thermal properties; Microstructure

1. Introduction

The manufacture of ceramics dates back to about 24 000 B.C. Archeologists in Czech Republic have recently found figurines made of animal fat and bone mixed with ash and a fine clay-like material that were fired in kilns partially dug into the ground.[1] During the long history, ceramics industry has a reputation for being very conservative and resistant to changes in technology and formulation. Nowadays, this behaviour has, however, slightly changed due to the highly competitive and increasingly transparent markets.[2] The challenge for the ceramic industry is to reduce the cost of those materials whilst, at the same time, maintaining (or even improving) the quality and characteristics of the end product. Under this task, probably the most important drive is cost and, in particular, the cost of raw materials. Borates have been an essential ingredient in ceramic and enamel glazes for centuries, integral to affixing glazes or enamels, and enhancing their durability and luster. Borates now are gaining acceptance as an essential ingredient in ceramic tile bodies, allowing manufacturers to use a wider range of clays, heightening productivity and decreasing energy usage.[3–6]

There are two main world producers of borates, namely Eti Holding, based in Turkey, and Rio Tinto Borax with its main mine at Boron in California. These two companies control 75% of the borate market. The rest of the market is made up of half a dozen or so minor producers. Turkey holds 63% of the total boron deposition shares 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 consist of concentration and crystallization units and produce 800 000 tonnes concentrated tincal, 480 000 tonnes pentahydrate, 17 000 tonnes decahydrate and 60 000 tonnes anhydrite borax/year.[3–6]

Continuous accumulation of industrial waste, increasing environmental regulations, awareness and also depletion of natural resources have led to growing recognition of the need for extraction and manufacturing companies to seek for their waste management instead of establish routes such as landfill. Problems in the final disposal of waste, in particular, the public opposition of landfill facilities for waste is beginning to become a bottleneck to industrial activities.[7] Therefore, in recycling, it becomes of interest to develop economically viable refining technology. Development of technology becomes imperative for products with designs and facilitates the re-use of components and technology that enables recycling of waste despite the fact that such designs have minimal impact to

---

* Corresponding author. Tel.: +90 222 3213550x6372; fax: +90 222 323 9501.
E-mail address: skurama@anadolu.edu.tr (S. Kurama).

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.05.014

the environment. In a previous study by the same authors, borax waste (TSW), obtained from the crystallization unit of Etibor Kırka Borax Company, was investigated in terracotta production in an attempt to improve final product properties. It was found that increased presence of TSW as a co-fluxing material accelerated the vitrification process.[8]

Ceramic tiles are very common construction materials used in household and commercial facilities of all sizes. They are used on floors, walls and patios, both indoors and outdoors. There are approximately 22 ceramic tile manufacturing plants in Turkey, and in 2003, these plants produced nearly 190 million m^2 of tiles. About 84 million m^2 of this production was exported, which makes Turkey the fifth biggest exporter of the word.[9]

The aim of the present study is to extend the utilization TSW in wall tile production by replacing Na-feldspar in suitable amounts. The particular consideration was given to the change in the technological properties of the experimented formulations upon firing under industrial conditions. Phase and microstructural evolution were also examined. Glazing issue was, however, ignored.

2. Materials and methods

2.1. Raw materials

The solid waste (TSW) was collected from the upper part of the dewatering sieve of dissolution units of Etibor Kirka Borax Company (Turkey). Preparation of TSW prior to use in experimental compositions can be given as grinding and sieving. This process is described in detail in the previous study of the authors.[8] The main oxide constituents of the raw materials are presented in Table 1.

2.2. Processing and characterisation

First of all, relevant raw materials were obtained from a local tile company in order to formulate a standard mixture (designated as Std.). Then, representative experimental wall tile formulations were prepared by progressive incorporation of TSW in place of Na-feldspar in different amounts ranging from 0 to 2 wt.% (Table 2). The amounts mentioned were chosen so as to highlight the effects of TSW addition. These formulations were further designated as D5, D10, D15, and D20, respectively. The preparation of the formulations involved mixing in the relevant proportions and wet grinding in ball mills long enough until the residue on 63 μm sieve was reduced to 3.5–4.5%. The solid content of the slurries was aimed to be kept constant for all the formulations. To be more specific; the solid content and the weight volume of the experimental slurries were around 65 wt.% and 1670–1690 g/l, respectively. Furthermore, viscosity was adjusted to be about 18–20 s from 4 mm Ford cup. The obtained mixtures were first allowed to dry, 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 110 kg/cm^2. The shaped samples were dried at around 120 °C for 24 h. Finally, the representative tiles were single fast-fired in an industrial roller furnace at a peak temperature of 1170 °C for a total firing time of 30 min (from cold-to-cold).

Table 2
The composition of investigated formulations and their designations

Designation	Formulation (wt.%)				
	Std.	D5	D10	D15	D20
Clay	50	50	50	50	50
Quartz	11	11	11	11	11
Kaolin	19	19	19	19	19
Marble	10	10	10	10	10
Feldspar	10	9.5	9	8.5	8
TSW	–	0.5	1	1.5	2

The physico-mechanical properties of the representative samples were measured in accordance with the standard procedures.[10–12] On average, three specimens were used for each measurement. The vitrification behaviour of rectangular compacts of the representative tile bodies was studied using a double-beam non-contact optical dilatometer (Model: MISURA, Expert System Solutions, Italy). The measurements were conducted according to the corresponding industrial firing profile. In the literature, this equipment has been described to be effective for precise determination of the best firing profile for any porcelain composition since it solves the problem of electronic dilatometers where the slight pressure exerted by the mechanical contact of a small refractory bar on the sample above softening temperature modifies the measurement.[13]

The thermal expansion of the selected samples were also determined using a fully computer controlled Netzsch thermal dilatometer (Model: 402 EP) at a heating rate of 10 °C/min to 650 °C. 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^*

Table 1
Chemical composition of the raw materials (achieved using XRF)

Oxide (wt.%)	SiO_2	Al_2O_3	Na_2O	MgO	K_2O	CaO	TiO_2	Fe_2O_3	B_2O_3	LOI
Clay	63.43	23.22	0.58	0.18	1.53	0.77	–	3.07	–	7.15
Quartz	93.33	4.13	–	–	–	0.18	–	0.29	–	2.07
Kaolin	63.24	24.92	0.33	0.18	0.37	0.63	–	0.88	–	9.45
Marble	1.00	0.47	–	–	–	56.03	–	0.09	–	42.41
Feldspar	68.10	21.61	1.54	0.18	1.68	1.11	–	1.39	–	4.39
TSW	15.83	1.06	2.58	19.84	0.63	20.66	0.01	0.24	3.99	35.16

LOI is loss on ignition.

values with peak firing temperature was compared. Qualitative determination of major crystalline phases present in selected fired samples was achieved by X-ray diffraction (Rigaku, Rint 2000, Japan) on powdered samples. Microstructural observations were performed on polished surfaces of 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.

3. Results and discussion

3.1. Physical properties

The results of the evaluated physico-mechanical properties, namely linear firing shrinkage, water absorption, green and fired flexural strength, are presented in Fig. 1. As can be seen, the water absorption values of the fired products decrease slightly with increasing amount of TSW. As an expected consequence of this, there is a corresponding increase in the linear firing shrinkage values (Fig. 1a). This behaviour can mainly be explained by the fact that TSW acts a low temperature auxiliary flux, enhancing vitrification, due to strong fluxing action of its boron content. Use of boron compounds such as boric acid, hydroboracite and borax in floor and porcelain tile compositions has been previously investigated and reported that the presence of small quantities of boric oxide (B_2O_3) in the compositions increased the tile vitrification rate. It was further suggested that this advantage could be used to either reduce the peak firing temperature or lower tile soaking time at vitrification temperatures. On the other hand, it was also found that the nature of the boron-contributing raw material had a pronounced influence on suspension rheological behaviour.[14] In the preparation of TSW containing slurries studied in this study, an increase in viscosity with the further addition of TSW was also encountered. However, the problem was solved with slightly higher amount of electrolyte, namely sodium silicate addition. Referring back to the fluxing action of the TSW waste, it 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 magnesite and dolomite, as sintering promoters, on the vitrification behaviour of different compositions has already been studied by several authors. 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 as long as it was operated within defined limits of composition and firing regime.[15–19] Apart from the fluxing effect of the relevant oxides, considerable fine particle size distribution of the TSW waste is also believed to have played an important role in enhanced vitrification. According to the size distribution data obtained by laser diffraction in the previous study of the same authors, TSW waste has a mean particle size of around 0.74 μm.[8]

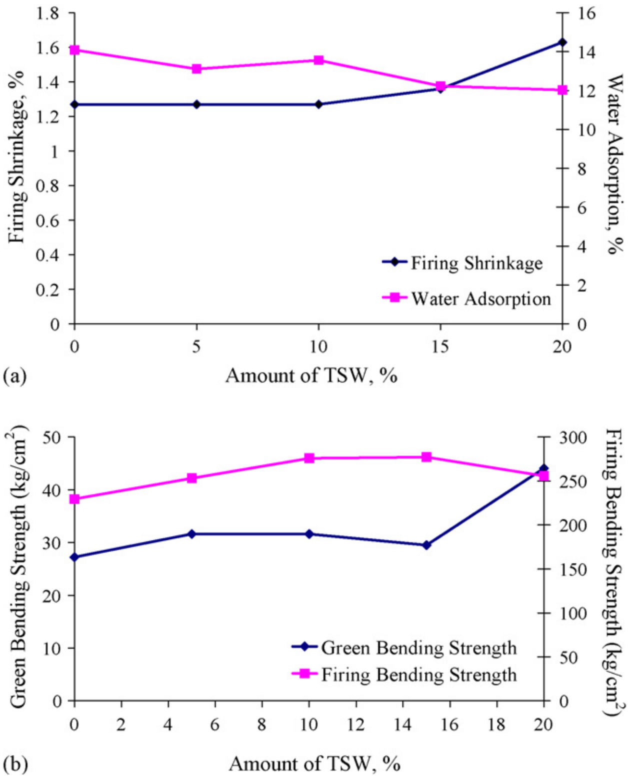

Fig. 1. Physical properties of the investigated formulations: (a) evolution of water adsorption and linear firing shrinkage in relation to TSW content; (b) evolution of green and firing bending strength in relation to TSW content.

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. 1a once again, the formulations that provided the lowest values of water absorption and the highest values of linear firing shrinkage are also expected to provide the maximum flexural strength values. Indeed, this assumption is mostly confirmed in Fig. 1b where the bending strength results of all the formulations are shown. It is also worth mentioning that higher amounts of TSW in place of the feldspar caused a considerable increase in the green strength values of the experimental formulations, which in turn decreases the risk of rupture during mechanical manipulation of the tile. Similar results were also reported in the literature and the increase in dry mechanical strength was explained by the fact that borates acts as a powerful inorganic binder in ceramic tile body compositions.[20]

3.2. Color measurements

The values of the chromatic coordinates of the studied formulations with increasing peak temperature are given in Table 3. It can be observed that L^* value decreases with increasing amount of TSW waste in the formulation. This can easily be explained

Table 3
The chromatic coordinates (L^*, a^*, b^*) of the investigated formulations

	Formulation				
	Std.	D5	D10	D15	D20
L^*	76.52	74.31	75.77	73.74	70.37
a^*	4.79	4.85	4.64	4.58	4.36
b^*	15.07	15.18	15.18	15.27	14.94
ΔE^*	–	2.21	0.77	3.00	6.17

ΔE^*, total color difference value.

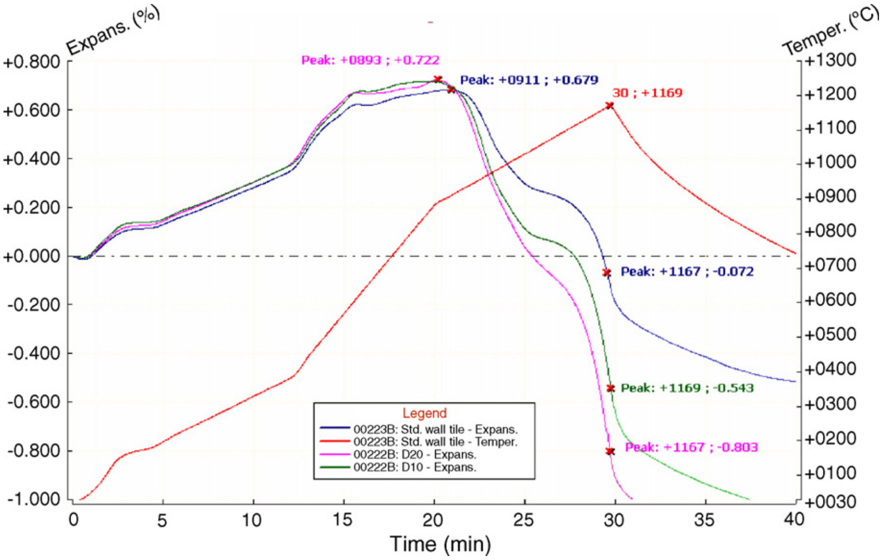

Fig. 2. Dilatometric linear firing shrinkage curve of the experimental wall tile bodies.

by the improved vitrification behaviour of the TSW modified formulations.

3.3. Thermal properties

Fig. 2 illustrates the shrinkage behaviour of the Std., D10 and D20 tile bodies obtained by using a double-beam optical dilatometer. All the representative curves were plotted with time on the *x*-axis and both temperature and sintering percentage on the *y*-axis. As can be seen from the figure, fastest sintering rate is obtained at the peak firing temperature of around 1170 °C for all the bodies involved but the main difference is the better sintering behaviour with the TSW addition.

Thermal expansion coefficient is an important property of a ceramic body. Reported in Table 4 are the results of linear thermal expansion values of the selected tile bodies for a specific temperature range. It is clear from the table that the thermal expansion of the TSW modified bodies is slightly lower than that of the standard wall tile body. This is expected since there appears to be higher amount of glassy phase in the TSW modified bodies thus dissolving more free quartz into the melt. This result is also in parallel with the measured physical properties of the relevant bodies given in Fig. 1.

3.4. Phase analysis

Fig. 3 presents the representative XRD spectra of Std., D10 and D20 samples where quartz, anorthite and mullite phases are easily detected. As known, most of the reactions taking place on firing of traditional tile bodies are kinetically governed processes that do not reach thermodynamic equilibrium, since the industrial firing cycles are as short as half an hour. This explains the common occurrence of residual quartz and feldspars that have not been entirely transformed in the fired bodies. As seen in Fig. 3, new crystalline phases, mainly anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$), and a small amount of mullite ($3Al_2O_3{\cdot}2SiO_2$) were formed all the investigated bodies. Anorthite development seems to be improving with the peak firing temperature. Apart from addition of free quartz, high dimensional stability required in fast-fired wall tile manufacture is commonly realised using various calcium containing materials in suitable amounts such as chalk, limestone, marble, wollastonite and dolomite. It has been reported that the presence of calcium carbonate ($CaCO_3$) modifies the reactions course and affects the formation of the liquid phase. During preheating, between 800 and 900 °C, the $CaCO_3$ decomposes to CaO accompanied by the evolution of CO_2 outside the structure of fired bodies. The CaO reacts with the amorphous phase (metakaolinite), which quickly diminishes at increasing firing temperature.

Table 4
Linear thermal expansion coefficients of the selected tile bodies

Formulation	CTE, $10^{-7}\,°C^{-1}$ (20–400 °C)
Std.	69.4
D10	67.8
D20	67.9

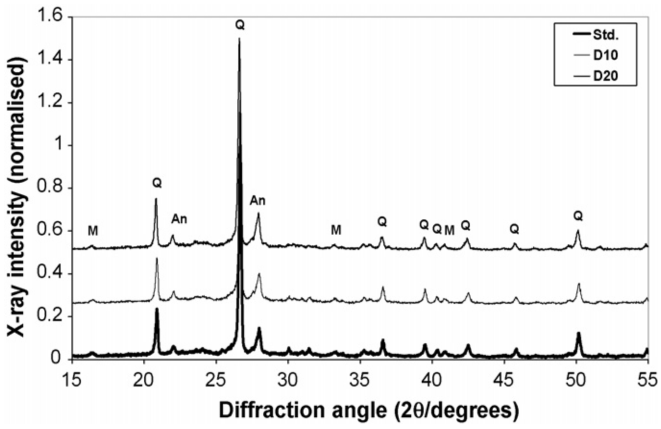

Fig. 3. Representative XRD spectra of the selected tile bodies.

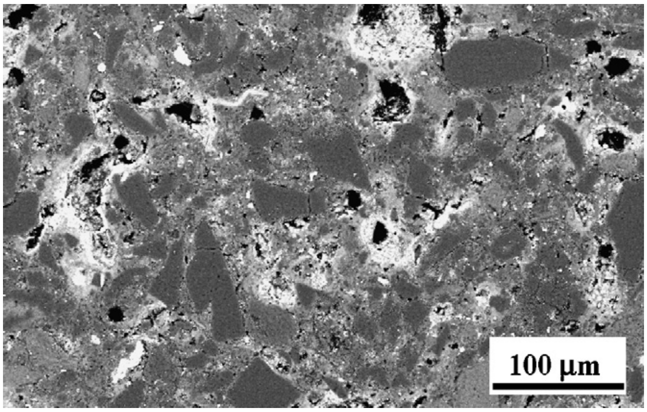

Fig. 4. Representative BE image of the Std. formulation.

Thus, the formation of crystalline phases, namely gehlenite as an intermediate phase and anorthite, occurs to a great extent at the expense of the metakaolinite. The series of reactions with the formation of small liquid phase volume, as expected, result in the body having high porosity.[21–23] Considering the mineralogical analysis of TSW; the presence of dolomite, tincalconite, montmorillonite and calcite minerals were detected in varying amounts by XRD in the previous study.[8] Under the circumstances, it is not surprising to see increased crystallinity of anorthite in the TSW containing bodies compared to the standard body. With regard to the influence of boric oxide originating from tincalconite; there was no clear indication of its effect on modifying the crystalline phases but it may have varied their proportions.

3.5. Microstructural analysis

Typical back-scattered images of the polished surfaces of the Std. and D20 formulations are illustrated in Figs. 4 and 5, respectively. Both images represent similar structures where the crystalline phases and pores are dispersed in a glassy matrix. Pores are easily distinguishable as dark areas. It is also evident that the sharp corners of the quartz grains, as grey areas, were somewhat rounded by surface tension forces and their partial solution into the glassy matrix during firing. In addition, the presence of microcracking around and within the large quartz grains due to the rapid displacive β to α phase transformation of quartz on cooling is visible on both images. The main perceptible difference between these images is the appearance of slightly improved vitrification of D20 formulation.

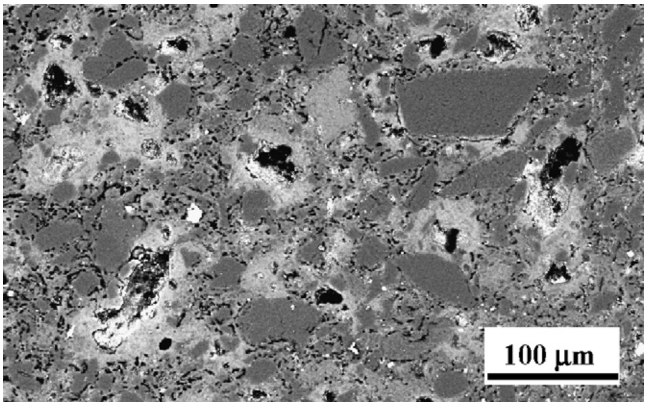

Fig. 5. Representative BE image of D20 formulation.

4. Conclusion

In this study, a series of wall tile formulations incorporated with dewatering sieve waste (TSW) of Etibor Kırka Borax Company (Turkey) up to 2 wt.% as a substitute for Na-feldspar was prepared and fired under industrial conditions. The results showed that the waste addition in a controlled manner improved the vitrification, and thus allowed to achieve better technological properties for the firing regime involved. It is also worth mentioning that valuable use of TSW in such a possible commercial application, with improved technological properties of the final product, can be mentioned as an added advantage. Further study is, however, needed on the industrial scale in order to establish the technical and economic feasibility of the study.

References

1. ACS, *About Ceramics*. American Ceramic Society, 2003.
2. P.S.E. CAVE. http://www.b2o3.com/montreal.doc.
3. Glendenning, M. D. and Lee, W. E., Microstructural development on crystallizing hot-pressed pellets of cordierite melt-derived glass containing B_2O_3 and P_2O_5. *J. Am. Ceram. Soc.*, 1996, **79**(3), 705–713.
4. Baele, S. M., Borate is an important ingredient in glass fiber manufacture. *Glass*, 1998, **75**(12), 420.
5. Mostofa, A. A., El-Maghraby, A., Naga, S. M. and Ibrahim, D. M., Role of borate frit as co-flux in tile bodies. *Br. Ceram. Trans.*, 2002, **101**, 120–123.
6. Austerberry, M., Using borates in brick and roofing tile. *Ceram. Indust.*, 2004, 31–37.
7. Iwasaki, I., Mineral processing technology and resources recycling. In *Proceedings of the Third International Conference on Materials Engineering for Resources ICMR'98*, 1998, pp. 243–248.
8. Kurama, S., Kara, A. and Kurama, H., The effect of boron waste in phase and microstructural development of a terracotta body during firing. *J. Eur. Ceram. Soc.*, 2005, **26**, 755–760.
9. Sezzi, G., World production and consumption of ceramic tiles. *Ceram. World Rev.*, 2004(58), 54–71.
10. *ISO 10545-2, Ceramic Tile Part 2, Determination of Dimension and Surface Quality*. Switzerland, 1995.
11. *ISO 10545-3, Ceramic Tile Part 3, Determination Water Adsorption, Apparent Porosity, Apparent Relative Density and Bulk Density*. Switzerland, 1995.
12. *ISO 10545-4, Ceramic Tile Part 4, Determination of Modulus of Rupture and Breaking Strength*. Switzerland, 1994.
13. Paganelli, M., Using the optical dilatometer. *Am. Ceram. Soc. Bull.*, 2002, **81**(11), 25–30.
14. Moreno, A., Garcia-Ten, J., Gozalbo, A., Simon, J., Cook, S. and Galindo, M., Using Boron as an Auxiliary Flux in Porcelain Tile Compositions. In: *Proceedings of the VI World Congress on Ceramic Tile Quality, Qualicer 2000, P.GI-77, Vol. I.* Castellon, Spain.
15. Mukhopadhyay, T. K., Das, M., Ghosh, S., Chakrabarti, S. and Ghatak, S., Microstructure and thermo mechanical properties of a talc doped stoneware composition containing illitic clay. *Ceram. Int.*, 2003, **29**, 587–597.
16. Dondi, M., Biasini, V., Guarini, G., Raimondo, M., Argnani, A. and Di Primio, S., The influence of magnesium silicates on technological behaviour of porcelain stoneware tiles. *Key Eng. Mater.*, 2002, **206–213**, 1795–1798.
17. Sandoval, F., Ibanez, A., Beltran, V., Pena, J. M. G. and Amoros, J. L., Dolomite marn for fast fired earthenware. *Interceram*, 1990, **39**(4–5), 38–40.

18. Grosjean, P., Fluxite: a functional raw material for large format earthenware tiles. *Ceram. Forum Int.*, 2005, **82**(1–2), E32–E38.
19. Chandra, N., Agnihotri, N., Bhasin, S. and Khan, A. F., Effect of addition of talc on the sintering characteristics of fly ash based ceramic tiles. *J. Eur. Ceram. Soc.*, 2005, **25**(1), 81–88.
20. http://www.borax.com.
21. Baran, B., Sarıkaya, Y., Alemdaroğlu, T. and Önal, M., The effect of boron containing frits on the anorthite formation temperature in kaolin–wollastonite mixtures. *J. Eur. Ceram. Soc.*, 2003, **23**, 2061–2066.
22. Sandoval, F. and Ibanez, A., Fast-firing wollastonite-based wall tile bodies. *Am. Ceram. Soc. Bull.*, 1999, **78**(3), 72–75.
23. Zanelli, C., Raimondo, M., Dondi, M., Guarini, G. and Tenorio Cavalcante, P. M., Sintering Mechanisms of Porcelain Stoneware Tiles. In: *Proceedings of the VIII World Congress on Ceramic Tile Quality, Qualicer 2004. Vol. I, P.GI.-247*. Castellon, Spain.