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Valorisation of boron mining wastes in the production of wall and floor tiles

Bugra Cicek [a,b,*], Emirhan Karadagli [a,b], Fatma Duman [c]

[a] Department of Metallurgy and Material Science Engineering, Yildiz Technical University, Esenler, Istanbul, Turkey
[b] Boron Based Materials and Advanced Chemicals Research and Application Center, Koc University, Sarıyer, Istanbul, Turkey
[c] Eczacibasi Building Products Company, VitrA Innovation Center, Bozuyuk, Bilecik, Turkey

HIGHLIGHTS

- The boron mining wastes can be used as a raw material in ceramic tile production.
- The B_2O_3 content in mining wastes provide lower sintering temperatures in conventional tile production.
- CaO present at wastes can lead reduction or removal of CaO rich raw materials.
- The potential environmental risks caused by mining waste disposal areas can be eliminated.

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ABSTRACT

A huge volume of boron mining wastes is generated in boron producing countries every year, necessitating the need to find a viable valorisation solution urgently. Their potential in the production of ceramic tiles to curb energy consumption in the ceramics manufacture has been investigated. The 5–6 wt% waste-containing ceramic tile formulations proposed had a boron oxide (B_2O_3) content in the range from 1 to 33 wt%. Owing to the fluxing ability of B_2O_3, the sintering temperature of the developed wall tile ceramics decreased down 70 °C–1050 °C, sintering temperature of the developed floor tile ceramics decreased down to 1130 °C, 65 °C lower compared to benchmarked commercial ceramics. The mechanical, chemical and physical properties of the new compositions were comparable to those of typical commercial products. The developed wall tiles had a water absorption of 19.39% and 20.46 N/mm^2 strength providing the requirements of TS EN ISO 10545 standard, where floor tiles had a 0.49% water absorption and 38.43 N/mm^2 strength. There is considerable scope to incorporate boron mining waste in the production of more sustainable ceramics at industrial scales.

1. Introduction

Annual production of boron concentrates and chemicals exceed 2 Mt and 1.78 Mt, respectively in Turkey [1–3]. In 2014, the total production of boron oxide (B_2O_3) was estimated to be around 0.8 Mt [2]. Mining and boron enrichment facilities are primarily located in the North West Anatolian region, where major ceramic production plants are also located. Despite the large volumes of boron-rich wastes generated from the production of borates and several proposals for their use in various applications [4–12], viable and resource-efficient solutions are yet to be implemented.

Considering the high B_2O_3 content (16–31%) in boron wastes, their use in the production of ceramic tiles is considered to be a promising valorisation option. B_2O_3 is not only an effective glass-former, but it also serves as a fluxing agent without causing an increase in the thermal expansion coefficient of ceramic products, unlike other fluxes (alkalis and alkaline earth metals). It also helps accelerate the vitrification process [16] and hence, curb energy consumption in ceramic production.

In 2015, 12.355 million m^2 of ceramic tiles were produced globally with 2.6% being produced in Turkey [12]. Different types of ceramics can be produced having various physical and chemical properties for use in a broad range of applications. Hence, ceramic tiles are used primarily as complimentary construction materials in applications where durability and beauty are of major importance. However, the market growth rate for ceramic tiles increases along with environmental responsibility for the industry, pushing

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* Corresponding author at: Faculty of Metallurgical and Chemical Engineering, Yıldız Technical University, Esenler, Istanbul, Turkey.
E-mail address: Bcicek@yildiz.edu.tr (B. Cicek).

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researchers and producers to develop sustainable strategies such as waste valorisation to enable energy efficiency.

Sintering is the most energy-intensive stage of the ceramic tile production process taking place at elevated temperatures varying from 900 °C to 1450 °C [13]. There have been numerous studies on decreasing the energy consumption in tile production, but most of them focus on the optimisation of the production efficiency rather than the sintering process itself [14,15].

In the present study, modified compositions for wall and floor tiles containing boron wastes were developed. Introduction of the wastes was done respecting the Seger formations of the standard composition in order to minimise differences in both rheological and mechanical properties. Finally, the effects of the microstructural and phase evolution on the physical and mechanical properties of waste-containing ceramics were investigated [17].

2. Experimental procedure

Six different boron waste samples, denoted as A1, A2, A3, A4, A5 and A6, were used throughout this study. The samples A1, A2, A3, A4 were obtained directly from mine extraction facilities, while A5 and A6 were obtained from borate enrichment plants. The chemical compositions of these wastes as well as of the standard wall and floor tiles, denoted as WT-STD and FT-STD, respectively, were obtained by X-ray fluorescence (XRF) analysis (see Tables 1 and 2).

2.1. Preparation of floor ceramic tiles

Based on XRF analysis results for the FT-STD products, it was found that the samples had high contents of SiO_2 and Al_2O_3 but low contents of CaO and MgO. Given that all boron wastes were rich in CaO and MgO, the addition of boron wastes to ceramic formulations was kept to small amounts to maintain expected rheological properties. As a result, the modified formulations had the same total alkaline earth metal amount and oxide ratios comparable to those of the standard floor tile composition.

Twenty one different new floor tile formulations were developed with varying amounts of boron wastes, while keeping the ratio of the oxide identical to those of the benchmark composition. Given the low CaO and MgO contents of the FT-STD composition, the maximum amount of boron waste introduced into the new formulations was 8.05 wt%.

To prepare floor ceramic tiles, all the raw materials were first dried in an oven (Nüve FN 400) at 100 °C for 24 h. Then, dry powder mixtures of 500 g were weighed and blended, followed by the addition of water and deflocculants to obtain a slurry. The slurry was ball milled (Ceramic Instruments Rapid Mills-Moduler System SD Series) using alumina balls to obtain a powder with a particle size of less than 45 μm. The compositions with the expected particle size were turned into suspensions to obtain a ceramic slurry. The density of the slurry was measured by a pycnometer (TQC VF2097) and was compared against the standard value for ceramic tiles (1648–1782 gr/lt). The acquired slurry was, then, subjected to a rheological study involving the addition of deflocculants until the slurry had the desired viscosity and thixotropic characteristics. After each consecutive addition of deflocculants (0.1, 0.2 mg), the slurry was thoroughly homogenised at 700 rpm for 3 min using a mixer (IKA RW 20 Digital). After each mixing step, the viscosity was measured using a viscometer (Brookfield Dial Reading). This process continued until a viscosity within the range of 4.5–6.0 Poise was attained. The optimum amount of deflocculant for every composition was calculated according to equation (Eq. (1)).

Table 2
Chemical compositions of standard floor and wall ceramic tiles.

Oxide	FT-STD Wt.%	WT-STD Wt.%
SiO_2	63.58	56.42
Al_2O_3	19.48	17.99
Fe_2O_3	1.72	1.84
B_2O_3	0.00	0.00
TiO_2	0.60	0.75
CaO	1.60	8.57
MgO	2.14	0.42
Na_2O	0.00	0.74
K_2O	3.00	2.70

*L.O.I: Loss on ignition.

$$\frac{\text{Total Added Deflocculant Amount}}{\text{Total Solid Amount}} \times 100 = \text{Optimum Deflocculant Amount}\,\% \tag{1}$$

2.2. Preparation of wall ceramic tiles

Based on the XRF results for WT-STD, it was found that the CaO content was higher than that of FT-STD. This explains the high porosity (16–20%) of WT-STD tiles. This level of porosity results in lightweight and durable ceramic products facilitating the absorption of adhesives. Hence, in this case, the maximum amount of boron waste that was added was 5.64%.

The preparation of wall tile formulations was similar to that described above for floor tiles, mimicking commercial processes. However, in this case, the concentration of solids in the ceramic slurry was between 63 and 66% and the desired viscosity values

Table 1
Chemical compositions of boron-rich mining wastes.

Oxide (wt.%)	A1	A2	A3	A4	A5	A6
SiO_2	10.25	19.81	16.98	17.13	0.39	1.28
Al_2O_3	0.34	0.72	0.57	0.31	0.11	0.63
Fe_2O_3	0.19	0.33	0.24	0.31	0.13	0.13
B_2O_3	20.41	18.41	21.20	16.37	29.52	31.11
CaO	34.18	25.34	23.31	31.28	52.75	33.41
MgO	3.70	8.96	8.82	7.32	0.80	0.60
K_2O	0.04	0.13	0.12	0.17	0	0.03
Na_2O	0.17	0.57	1.34	0	0.81	0.90
P_2O_5	0	0.04	0.01	0.03	0.01	0.01
SnO_2	0	0	0	0	0	0.338
Cr_2O_3	0	0	0	0	0	0.03
BaO	0	0.23	0	0	0	0
*L.O.I.	30.17	24.11	24.97	25.43	14.68	30.74

*L.O.I.: Loss on ignition.