

# Utilization of Bigadiç Boron Works Waste Clay in Wall Tile Production

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The investigations on the use of the alternative raw materials have been always popular in the ceramic tile production. Manufacturers have been interested in this subject for both increasing product quality and decreasing production costs. In this research the Bigadiç boron works waste clay was utilized as an alternative raw material. Boron works waste clay was characterized by chemical and X-ray diffraction analyses. Ceramic characteristics were determined from pressed bodies, using four elevated firing temperatures (1040, 1060, 1080, and 1100 °C) for samples with 5, 10, 15, and 20 wt% boron works waste clay additions to a commercial wall-tile batch. The physical properties of the fired tiles were evaluated in terms of water absorption, linear shrinkage, and flexural strength. Microstructural observations were performed by scanning electron microscopy analyses. Based on the technological characteristics of the resulting ceramic material, the results were discussed.

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## 1. Introduction

The growing consumption and the increase of industrial production cause exhaustion of the natural resources. On the other hand, industrial production wastes or sub-products are steadily growing and leading to environmental problems. Ceramic materials such as floor and wall tiles consist of clays with a very wide-ranging overall composition. Because of this, clay containing wastes in considerable percentages can be used to produce these materials [1–3]. In addition, studies on the utilization of waste materials and producing new products have gained great importance [4–8].

Turkey has about 800 million tons of boron reserves, which consist of 70% of the world boron reserves. The borate deposits of Turkey occur in western Anatolia, south of the Sea of Marmara, within an area roughly 300 km east–west by 150 km north–south. The main borate districts are Bigadiç, Kestelek, Sultançayır, Emet, and Kırka. The Bigadiç borate deposits are among the largest colemanite and ulexite deposits in the world. The high-grade colemanite and ulexite ores are adequate to supply the world's B needs for many years. During the processing of boron ores, concentrator wastes occur and these wastes are stored in tailing dams [9–13].

Ceramic wall tiles are highly porous ceramic materials. They are multicomponent systems that contain mainly clay, silica, feldspar, and carbonates [14–17] while approximately 50% of the wall tile body composition is composed of clay. Demand for clay in the ceramics industry has been growing steadily. Almost all of the clay extracted from the large deposits in the Söğüt and Istanbul

regions of Turkey (1,500,000 ton/year) is used for wall tiles, floor tiles and sanitaryware by domestic industries. As a result, reserves of white-firing clays are running out. Thus, manufacturers are seeking alternative, less expensive raw materials [2].

The aim of this research is to characterize the Bigadiç waste clay (BWC) and to utilize BWC as a ceramic raw material in the wall-tile production. This study also will minimise the environmental impact of BWC disposal.

## 2. Material and methods

The waste clay investigated in this work was obtained from Eti Maden Bigadiç Boron Works, which is located in Balıkesir, Turkey. The waste clay was characterized by chemical and X-ray diffraction (XRD) analyses. The chemical composition of the waste clay was analyzed by atomic absorption spectroscopy (GBC).  $B_2O_3$  component was determined by titrimetric method at Eti Maden laboratories. The phases present in the sample were identified by XRD using a Rigaku Model diffractometer with monochromatic  $Cu K_\alpha$  radiation.

Preparation and testing of the samples were done on a laboratory scale. Wall-tile compositions were formed using commercial raw materials (Istanbul and Söğüt clays, kaolinite, calcite, albite, and quartz), with BWC used in place of the Istanbul clay at varying proportions (Table I).

In order to enlighten the physical properties pellet samples were used. To produce pellet samples, each composition was dried and ground separately. The ground agglomerates were then humidified up to 6 wt% water. The humid powders were pressed under  $150 \text{ kg/cm}^2$  pressure to obtain  $100 \times 50 \times 6 \text{ mm}^3$  prismatic samples. The shaped samples were dried at 120 °C for 24 h and fired at 1040, 1060, 1080, and 1100 °C using a laboratory kiln (Nabertherm LH 15/14). Fired samples were used to

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TABLE I

Weight percent compositions of the wall-tile samples  $R_i$ .

Material	R0	R1	R2	R3	R4
BWC	0	5	10	15	20
Istanbul clay	20	15	10	5	0
Söğüt clay	30	30	30	30	30
kaolinite	15	15	15	15	15
quartz	15	15	15	15	15
albite	10	10	10	10	10
calcite	10	10	10	10	10

characterize the physical properties of the materials according to TS EN ISO 10545-3 and TS EN ISO 10545-4 norms [18, 19]. The microstructures of the fired samples were analyzed by a scanning electron microscope, SEM (JEOL-JSM 6060). The colours of the fired bodies were analysed and classified in terms of the  $L$ ,  $a$ , and  $b$  parameters using a 3NH NH-310 model reflectance.

### 3. Results and discussion

Table 2 lists the chemical compositions of BWC. The main characteristic of the clay is its high MgO, CaO, and  $B_2O_3$  content, and its low  $Fe_2O_3$  content. XRD analysis showed that BWC powder sample contains ulexite, smectite, illite, quartz, calcite and magnesite phases (Fig. 1).

TABLE II

Chemical analysis results [wt%] of the clay samples.

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	LOI
29.05	2.63	0.26	14.57	17.16	1.02	0.12	0.03	9.61	25.20

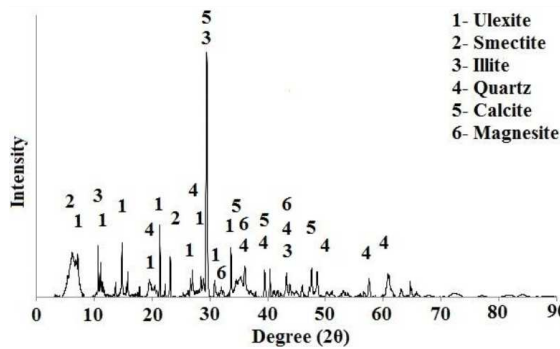


Fig. 1. XRD analysis of BWC powder.

A typical wall-tile composition (R0) and typical firing temperature (1080 °C) were selected for the tests. In this composition, we replaced Istanbul clay with BWC, and prepared tiles with various compositions (Table I). Tables III and IV list the water absorption and linear shrinkage values of the fired wall-tile bodies at different firing conditions, respectively.

TABLE III

Water absorption values of the prepared wall tile batches fired at different temperatures.

Temperature [°C]	R0	R1	R2	R3	R4
1040	11.62	12.56	17.36	20.95	20.99
1060	11.37	12.02	17.35	20.13	17.67
1080	11.70	12.15	16.84	16.23	10.86
1100	11.43	11.47	15.14	6.30	0.63

TABLE IV

Linear shrinkage values [%] of the prepared wall tile batches fired at different temperatures.

Temperature [°C]	R0	R1	R2	R3	R4
1040	-0.23	-0.06	0.23	1.00	1.37
1060	-0.17	0.18	0.43	0.89	0.03
1080	0.29	0.11	0.43	-0.49	-3.49
1100	-0.03	-0.17	-0.23	-4.77	-8.46

The water absorption values tended to decrease with increasing temperature. For batches fired at a given temperature, water absorption values decreased with increasing BWC content. R1 composition showed optimum water absorption and contraction (according to R0 values) values that were obtained at a temperature 20 °C below the typical firing temperature (1080 °C) of wall tiles, representing a saving in energy costs.

Cracks were observed for the samples having larger values than those for R1 composition. As a result, bending strength tests were performed for R0 and R1 bodies. The bending strengths of the bodies increased with increasing firing temperature (Table V). At a typical firing temperature of 1080 °C, R0 had strength of 18.9 MPa; R1 reached a similar value at 1060 °C.

TABLE V

Bending strength values for the selected wall-tile batches.

Temperature [°C]	R0 [MPa]	R1 [MPa]
1040	15.8	16.1
1060	16.4	18.3
1080	18.9	19.9
1100	21.4	21.7

Colour measurements along the chromatic coordinates show that  $L$  values increased while  $a$  and  $b$  values decreased with increasing temperature and BWC content ( $L$  value indicates the lightness scale where 0 is black; 100 is white,  $a$  value indicates the red-green scale where positive values are red; negative values are green and 0 is neutral,  $b$  value indicates the blue yellow scale where positive values are yellow; negative values are blue and 0 is neutral). It is reasonable to think that high CaO content caused whitening effect. As a result  $L$  values increased with increasing BWC content and temperature.

Figures 2 and 3 show the microstructures of the ceramic bodies fired at elevated temperatures. The SEM

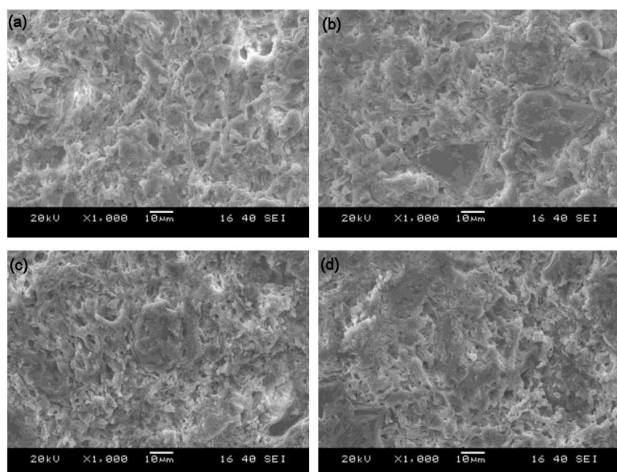


Fig. 2. SEM images of RO samples fired at (a) 1040 °C, (b) 1060 °C, (c) 1080 °C, (d) 1100 °C.

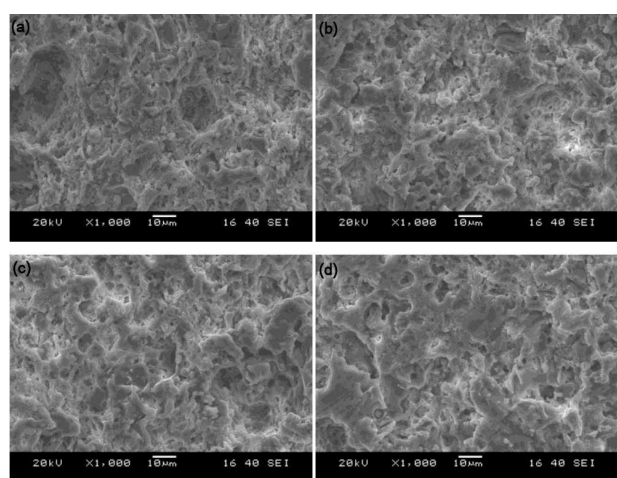


Fig. 3. SEM images of R1 samples fired at (a) 1040 °C, (b) 1060 °C, (c) 1080 °C, (d) 1100 °C.

images show the progression of densification with increasing firing temperatures. The particles tend to approach and the porosity reduces as the temperature increases. It is reasonable to think that microstructures of R0 and R1 samples fired at same temperatures show similarities. This result is also compatible with the physical test results.

#### 4. Conclusions

In this study, the characteristics of BWC and its usage in wall-tile production were investigated. From the results obtained, the following conclusions can be drawn.

The predominant oxides in BWC are SiO<sub>2</sub>, MgO, CaO and B<sub>2</sub>O<sub>3</sub>. Ulexite, smectite, illite, quartz, calcite, and magnesite are found as the main phases. The results showed that it was possible to use 5 wt% BWC to produce wall-tile ceramics. It was observed that R1 batch that

was fired at 1060 °C and R0 that was fired at 1080 °C (the typical firing temperature) had similar physical properties. This result was taken as an indication of cost decrease for a firing energy. The results of colour measurements showed that R1 showed higher colour values than R0 due to CaO content of BWC. SEM micrographs, taken at increasing firing temperatures, show the reduction of porosity and the progression of enhanced densification with increasing temperature. It is expected that this study will help to improve the knowledge about BWC and contribute correct assessment of the deposits.

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