Characterization of porcelain tile bodies with colemanite waste added as a new sintering agent

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This research investigated the possible use of high boron oxide (B₂O₃) bearing solid waste, obtained during the enrichment of colemanite mineral (Ca₅B₂O₇·5H₂O), as an alternative sintering agent to Na-feldspar (NaAlSi₃O₈) in porcelain tile production. The chemical composition, mineralogical properties and behaviour under the heat treatment of solid colemanite waste were characterized in detail by the use of inductive coupled plasma (ICP), X-ray diffraction (XRD) and differential thermal analysis (DTA) / thermo-gravimetric analysis (TG). Physical-mechanical properties of standard and waste-added porcelain tile bodies obtained by sintering at 1210 °C (under factory conditions) such as green strength, dry strength, fired strength and water absorption were determined as a function of waste replacement for Na-feldspar. The sintering behaviour of waste-added porcelain tile bodies under fast firing conditions was also determined by an optical dilatometer and compared with that of standard porcelain tiles. The phases obtained in standard and waste-added porcelain tile bodies after sintering were determined by XRD analysis. The effect of these phases on microstructure and the relationships between physical-mechanical properties and the microstructure were also investigated through a scanning electron microscope (SEM) and energy dispersive X-ray (EDX) spectrometry. After detailed phase studies and microstructural analysis together with the characterization of behaviour under heat treatment, it was discovered that colemanite waste had a high fluxing character and decreased the sintering temperature when used in porcelain tile recipes to replace Na-feldspar. It was also determined that factories using colemanite waste should work at lower sintering temperatures in order to obtain better physical-mechanical properties for porcelain tiles and to reduce energy costs.

Key words: Characterization, Colemanite wastes, Sintering agent, Porcelain tiles.

Introduction

Porcelain tiles were first developed by a leading Italian porcelain tile producer, Fiandre, in 1980. Recently the production and the utilization of porcelain tiles have increased. The US national standards describes porcelain tiles as dense, smooth, non-absorbent (water absorption is equal to or less than 0.5%) and highly resistant to stains. These unique properties have considerably increased the use of porcelain tiles both in the interior and exterior decoration of buildings. Moreover, it is expected that porcelain tiles will completely replace the use of traditional ceramic floor tiles in a very short time owing to their greater physical-mechanical properties and decorative quality [1]. Currently porcelain tiles are regarded as the best quality product the ceramic tile industry has ever developed. The production process is almost similar to that of traditional ceramic tiles. Porcelain tiles are obtained as a dense material comprised of a larger amount of glassy phase with quartz and mullite crystals after being sintered at 1210 °C or 1215 °C [2]. However, there are some technical and economic difficulties associated with the production of porcelain tiles owing to the necessities for high purity raw materials and a larger amount of glassy phase in the bodies in order to obtain very low water absorption values in their microstructural design, compared to traditional floor and wall tiles. These necessities have made the investigation of alternative raw materials inevitable and there have been numerous researches on alternative raw materials to be used in porcelain tile production [3-12]. Research has shown that alternative sintering materials should not only have the appropriate chemical and mineralogical compositions but also interact appropriately with the other constituents in the body in terms of thermal character and microstructural phase transformation property at the sintering stage which are determined by characterization techniques such as an optical dilatometer, a scanning electron microscope (SEM) and energy dispersive X-ray (EDX) spectrometry [13-16]. Therefore, physical, chemical, thermal, crystallographic and microstructural characterization techniques are of great importance in porcelain tile production in almost every stage of their manufacture.

Boron oxide-bearing minerals can technologically be considered as important alternative raw materials since they have a glass-forming character and have been used in the ceramic industry to reduce the melting point of the glass phase [17] such as in the production of frits, glass-
ceramics and cordierite ceramics. On the other hand, the only economical way to supply boron oxide-bearing raw materials to the industry is to use the wastes obtained during the production of boron products. After a detailed review of the related literature it was observed that most of the research on the use of boron wastes in the ceramic industry were concentrated on the wastes containing tincal (Na\(_4\)CaB\(_6\)O\(_{11}\)·5H\(_2\)O) whereas colemanite mineral-containing wastes (Ca\(_2\)B\(_4\)O\(_7\)·5H\(_2\)O) were mainly studied for possible use in the cement industry [31-34].

Borates are generally known as natural materials containing B\(_2\)O\(_3\) and they have been used by the industry for centuries. Boron does not occur in nature as a free element; instead it occurs in nature as minerals associated with clay and other impurities. There are over 200 naturally occurring boron containing minerals but the most commercially important and frequently traded minerals are tincal (Na\(_4\)B\(_3\)O\(_7\)·10H\(_2\)O), colemanite (Ca\(_2\)B\(_4\)O\(_7\)·5H\(_2\)O), ulexite (NaCaB\(_2\)O\(_7\)·8H\(_2\)O) and kernite (Na\(_4\)B\(_3\)O\(_7\)·4H\(_2\)O). These ores can be refined into pure chemical compounds of commercial importance such as boric acid (H\(_3\)BO\(_3\)), anhydrous boric acid (B\(_2\)O\(_3\)), anhydrous borax (Na\(_3\)B\(_4\)O\(_5\)), borax pentahydrate (Na\(_3\)B\(_4\)O\(_5\)·5H\(_2\)O), borax decahydrate (Na\(_3\)B\(_4\)O\(_5\)·10H\(_2\)O) and sodium perborate (Na\(_3\)B\(_4\)O\(_5\)·5H\(_2\)O).

World boron reserves are located mainly in Turkey (72%), the United States (6.8%), Russia (8%), Chile (3.5%) and China (3.2%). The main users of boron products are in the United States (6.8%), Russia (8%), Chile (3.5%) and China (3.2%). The main users of boron compounds are in the insulation fibre, textile fibre, borosilicate glass, detergent and ceramic industries. The agricultural applications of boron compounds have also increased. In recent years, however, the attention has been focused on the possible use of a boron compound as a fuel cell. Boron mining and processing activities have been carried out by the National Boron Board (Eti Mine) in Turkey as a monopoly by law. Eti Mine produces concentrated and refined products of tincal, colemanite and ulexite in Turkey. Boron chemical production was planned to reach 1,063 million tonnes in 2007 by the Eti Mine [35].

A large amount of waste is produced during both mining and boron processing operations. Most boron compounds are easily dissolved in water which may result in severe environmental pollution when rains dissolve and carry these wastes to underground or surface water reservoirs. The new EU standard for drinking water is a maximum 1 mg per litre and prolonged utilization of boron of more than 2 ppm has been prohibited for plant irrigation [36].

It is, therefore, very important to make use of the waste for both protecting the environment and providing a valuable financial resource.

The Emet Colemanite Mine of National Boron Board of Turkey (Eti Mine) located in Emet Town of Kütahya Province was established in 1958. It produces concentrated colemanite by processing the ore excavated from “Espey” and “Hisarcık” districts. It also produces boric acid in its recently constructed plant with a production capacity of 100,000 tonnes/year [35].

The colemanite waste used in this research was taken from the concentrator plant of Hisarcık district. The ores which come from the mine are charged to an ore container after passing a grizzly of 600 mm in the concentrator. The ore is then fed to a 75 mm screen and (-75) mm ores are separated as (-75 + 25) mm and (-25) mm fraction *groups*. The (-25) mm fraction is regarded as “tailing” and is directly sent to the waste area. The (-75 + 25) mm fraction is sent to a log washer to remove its clay particles. While the overflow is sent to the tailing pond, the underflow is screened to separate the ores into the fractions of (-75 + 25) mm, (-25 + 3) mm and (-3) mm. The (-3) mm size group is again sent to the tailing pond, the (-25 + 3) mm fraction is called the “low grade concentrate” while the (-75 + 25) mm fraction is hand sorted to improve its grade. The (+75) mm fraction from the first screen is crushed to 100 mm by a combination of jaw crusher and toothed roll crusher. The (-100) mm fraction is washed in a trommel and then sized. The (-100 + 25) mm fraction is upgraded by hand sorting while the (-25 + 3) mm is accepted as concentrate. The (-3) mm fraction is pumped into a hydrocyclone to remove the (-0.2) mm fraction as overflow. The (-3 + 0.2) mm fraction is fed to a mechanical classifier whose overflow is sent to the tailing pond and the underflow is washed in an attrition scrubber and pumped into a hydrocyclone. All clay materials are washed and discharged (-0.2) mm; the remaining part is called the “fine concentrate” [37].

According to the Technical Office of Emet Colemanite Mine, the amount of ore processed and the total waste production were 610,000 tonnes and 329,983 tonnes, respectively in 2007 at the Hisarcık Concentrator. The amount of (-25 + 3) mm and (-3) mm wastes in their total were 290,385 tonnes and 39,598 tonnes, respectively.

The aim of this research is to show that colemanite mineral-bearing wastes are suitable for use in ceramic tile production with factory conditions (without changing any process parameters) as an alternative sintering agent to replace Na-feldspar by using appropriate characterization techniques. If this aim is made possible, then the ceramic industry will benefit by having a new and cheaper raw material in ceramic tile production and the boron industry will gain both by marketing and reducing the stockpiling of the wastes which is costly and an environmentally risky operation.

Experimental Studies

The raw materials and the characterization techniques used

In order to prepare porcelain tile recipes, Na-feldspar, K-feldspar and 3 different clays and siliceous (quartz) sand were used as the starting raw materials. Chemical analysis of the raw materials was made using a Spektro X-Lab 2000 X-ray fluorescent (XRF) instrument. The chemical analysis of colemanite waste was made using a Perkin Elmer Optima 3000 inductive coupled plasma (ICP) instrument since it contained boron oxides.

The results of semi-quantitative chemical analysis of the
raw materials used in the present research and colemanite solid waste are given in Table 1. The phase analysis of colemanite waste was made by X-ray diffractometers (Rigaku Miniflex ZD13113 and Rigaku Rint 2000 series) using CuKα X-rays (λ = 1.54056 Å) in the range 5-70° at a rate of 1°/minute in order to find out the mineral content of the material. Fig. 1 shows the result of the XRD analysis of the colemanite waste.

The thermal behaviour of colemanite waste was investigated through an Inseis Thermowage L81 differential thermo-gravimetric analysis instrument at a rate of 10 °C minute⁻¹ up to 600 °C. The thermal behaviour of the waste with increasing temperature was determined using the DTA and TG curves obtained and presented in Fig. 2.

Production method, the tests and the characterization techniques applied

New tile recipes which enable colemanite waste to be used as a replacement of Na-feldspar as the sintering agent and the rational analysis of these recipes are given in Table 2. R1, R2, R3, R4 and R5 coded porcelain tile recipes comprised of 65% solid ratio were ground by a wet technique through a porcelain ball mill using sodium tripolifosphate (Na₅P₃O₁₀) at a rate of 0.3% for reological arrangement. The suspensions placed on a porcelain tray were then fully dried at 105 ± 5 °C in a drier. The dried material was then ground and humidified at 5-6% before being granulized by passing them through a 63 µm screen. In order to provide humidity homogenization of the granules, the samples were kept in sealed plastic bags for 24 hours. The prepared granules were then shaped in steel moulds at a pressure of 150 kg/cm² using a uniaxial hydraulic hand press. The shaped samples were kept at room temperature for 2 hours and then dried at 85 °C for 22 hours in order not to cause any fracturing. Sintering operations were carried out at 1210 °C in a large scale single firing and roller type oven for 34 minutes as a fast firing.

| Table 1. Semi-quantitative analysis of colemanite waste and the raw materials (weight %) |
|---------------------------------|----------------|--------------|--------------|------------|------------|-------------|----------------|
| Oxides                  | Clay-1 | Clay-2 | Clay-3 | Na-Feldspar | K-Feldspar | Silica Sand | Colemanite Waste |
| SiO₂                   | 8.58   | 62.75  | 60.65  | 67.41      | 73.44      | 91.36       | 23.03          |
| Al₂O₃                  | 1.17   | 23.24  | 26.28  | 20.65      | 17.66      | 5.42        | 7.22           |
| Fe₂O₃                  | 0.50   | 2.25   | 0.95   | 0.24       | 0.54       | 0.30        | 3.11           |
| TiO₂                   | 0.07   | 1.22   | 1.34   | 0.30       | 0.10       | 0.21        | 0.25           |
| CaO                    | 3.74   | 0.12   | 0.24   | 0.39       | 0.11       | 0.05        | 14.98          |
| MgO                    | 39.80  | 0.73   | 0.85   | 0.19       | 0.19       | 0.03        | 7.37           |
| Na₂O                   | 0.72   | 0.40   | 0.68   | 6.55       | 3.22       | 0.10        | 0.06           |
| K₂O                    | 0.11   | 2.44   | 2.34   | 3.62       | 4.24       | 1.08        | 2.10           |
| B₂O₃                   |        |        |        |            |            | 0.45        | 0.50           |
| *LOI                   | 45.31  | 6.85   | 6.94   | 0.45       | 0.50       | 1.45        | 20.98          |
| TOTAL                  | 100    | 100    | 100    | 100        | 100        | 100         | 100            |

*Loss of Ignition

| Table 2. Rational analysis of the recipes used (weight %) |
|---------------------------------|----------------|--------------|--------------|------------|----------------|
| Rational analysis | R1 | R2 | R3 | R4 | R5 |
| (weight %)          | (weight %)   | (weight %)  | (weight %)  | (weight %) |
| Na-feldspar         | 32.1         | 27.1        | 22.1        | 17.1       | 12.1          |
| Colemanite waste    | -            | 5.0         | 10.0        | 15.0       | 20.0          |
| K-feldspar          | 10.0         | 10.0        | 10.0        | 10.0       | 10.0          |
| Silica sand         | 9.0          | 9.0         | 9.0         | 9.0        | 9.0           |
| Clay-1              | 1.7          | 1.7         | 1.7         | 1.7        | 1.7           |
| Clay-2              | 22.1         | 22.1        | 22.1        | 22.1       | 22.1          |
| Clay-3              | 25.1         | 25.1        | 25.1        | 25.1       | 25.1          |
| TOTAL               | 100.0        | 100.0       | 100.0       | 100.0      | 100.0         |
Characterization of porcelain tile bodies with colemanite waste added as a new sintering agent

Physical and mechanical properties of the raw and fired porcelain tiles were determined according to standard methods [38-39]. For each test, 3 samples were used in order to provide better representation of the material. The sintering behaviour and sintering transitional temperatures during sintering of porcelain tile bodies and colemanite waste-added tiles were determined by a Misura 332-OHT-HSM 1600/80 optical dilatometer which would be a guide to understand the sintering behaviour of colemanite waste-added tile compositions in fast firing porcelain tile production conditions. In order to find out the phase transformations of the standard and the colemanite waste-added porcelain tile bodies after sintering, X-ray diffraction (XRD) analysis was made on powder samples by Rigaku Miniflex ZD13113 and Rigaku Rint 2000 instruments. Microstructural analysis was also made in order to examine the changes in the microstructure of standard porcelain tile bodies and colemanite waste-blended tiles after sintering.

The surfaces of the porcelain tile bodies which were prepared through conventional sample preparation methods (cutting, mounting, polishing and etching) were coated with a thin gold layer by an Agar sputter coater instrument, (cutting, mounting, polishing and etching) were coated with a thin gold layer by an Agar sputter coater instrument, in order to prevent charging with a thin gold layer by an Agar sputter coater instrument, during microstructural analysis. Microstructural analysis was undertaken by a Zeiss Supra 50 VP scanning electron microscope (SEM) attached with an Oxford Instruments 600 energy dispersive X-ray (EDX) spectrometer. Backscattered electron (BSE) and secondary electron (SE) imaging techniques were used in the SEM.

**Results and Discussion**

**Characterization of colemanite solid waste**

When chemical analysis of the colemanite waste is examined, it is seen that the waste contains a large amount of fluxing oxides (B$_2$O$_3$, K$_2$O, Na$_2$O and Fe$_2$O$_3$) and earthy alkali oxides such as MgO and CaO which play an important role in the vitrification behaviour and ease liquid phase occurrence during sintering (Table 1). According to the XRD analysis of the colemanite waste, natronite-15A [Na$_2$Fe$_2$Si$_4$O$_{10}$(OH)$_2$·4H$_2$O], muscovite [KAl$_2$Si$_3$AlO$_{10}$ (OH)$_2$], colemanite [Ca$_3$B$_2$O$_6$·5H$_2$O], quartz [SiO$_2$], and calcite [Ca(CO$_3$)$_2$] phases were present (Fig. 1). This shows the conformity of the XRD results with the chemical analysis results.

When the thermal behaviour of the waste was examined, an endothermic peak was seen at 70.8°C owing to the loss of physically bonded water in the DTA curve (Fig. 2). The DTA curve applied to the colemanite waste shows great similarity with the DTA curve of a pure colemanite mineral [40]. Hence, it is proven that the waste contains colemanite mineral which is the source of boric oxide.

After the XRD and DTA/TG analysis, it was understood that the colemanite-bearing waste could be used as a replacement for feldspar which is used in the composition of porcelain tile products as a sintering agent. The chemical composition of the rich oxide content is not the only criteria for a material to be used in porcelain tile production; the possible reactions of the alternative raw material with the other body constituents during firing and sintering behaviour are important. Therefore, these properties were also investigated.

**Characterization of porcelain tile recipes**

The sintering behaviour in fast firing production conditions of standard (R1) and colemanite waste-added porcelain tile bodies (R1, R2, R3, R4 and R5) were examined through an optical dilatometer to show whether they were suitable raw materials (Fig. 3). When the optical dilatometer curve of the R1 porcelain tile body is examined, expansion owing to the polymorphic phase transformation of quartz at 500-600°C [41] can be seen. This expansion reaches a value of 0.968% with an increase of temperature up to 951°C. The reason for this expansion can be explained by the existence of clay minerals in the starting raw materials [42]. Due to the sintering at 951°C, the body started to contract and the value of contraction increased up to 1207°C. This point (1207°C) is the maximum temperature of sintering for the standard tile composition. The maximum sintering temperature applied in the factory in which the experiments were carried out was 1210°C. Under this circumstance, it can be said that standard tile body recipes were regarded to be correctly applied at the factory. In other words, the standard tile body production temperature correlated well with the results of the optical dilatometer.

![Fig. 3. Comparison of optical dilatometer results for reference (R1) and colemanite waste-added porcelain tile recipes (R2, R3, R4, and R5).](image-url)
When the optical dilatometer curve of the R2 porcelain tile body was examined (Fig. 3), it was seen that the expansion reached a value of 1.44% up to 446 °C depending on the waste addition. The reason can be explained by the removal of the chemically bonded 5 molecules of water in the colemanite mineral \((\text{Ca}_2\text{B}_6\text{O}_{11}\cdot5\text{H}_2\text{O})\) within the waste with an increase in temperature (Fig. 2). Above this point, the expansion reached a value of 1.7% at 876 °C owing to the polymorphic phase transformation of quartz [41], the removal of crystal water in the clay minerals in the waste material [42] and decomposition of calcite [43]. The starting point for sintering was reduced to 876 °C from 951 °C by the addition of waste material to the standard tile composition (R1). In other words, the starting temperature for sintering was reduced by 75 °C owing to the existence of fluxing oxides such as \(\text{B}_2\text{O}_3\), \(\text{Na}_2\text{O}\), \(\text{K}_2\text{O}\) and \(\text{Fe}_2\text{O}_3\) which eased the vitrification by reducing the viscosity of the liquid phase during sintering [43].

The contraction in the R2 tile bodies continued from 876 °C to 1163 °C, and 1163 °C was determined as the maximum sintering temperature for the R2 body. This temperature is 44 °C lower than the maximum sintering temperature of the R1 body (1207 °C). This is an expected result considering the addition of boron oxide bearing waste which causes a reduction in the sintering temperature. The other observation was that some deformation occurred in the body above the sintering temperature. Since the fluxing oxides (especially boron oxide coming from the waste material) reduce the viscosity of the liquid phase during sintering, working with temperatures above the sintering point causes deformation in the body called “bloating” [44].

The maximum sintering temperature applied in the factory in which the experiments were carried out was 1210 °C. Therefore, this temperature was rather a high temperature for the R2 bodies and the bodies after sintering were found to be bloated or deformed (Fig. 3). In order to find out the effect of sintering temperature on the bodies of the R2 composition, the bloating behaviour of the bodies at maximum sintering temperatures of 1160 °C, 1170 °C and 1180 °C were investigated. When Fig. 4 is examined, it is clearly seen that the body was bloated at 1180 °C, contracted (shrank) by 4.91% but was not bloated at 1170 °C and contracted (shrank) by 5.47% but was not bloated at 1160 °C. From these results, it can be said that 1160 °C is the optimum sintering temperature for the R2 body since it yields a maximum shrinkage value of 5.47%.

When the R3 bodies were examined (Fig. 3) an expansion of 2.84% was observed up to 449 °C owing to the decomposition of colemanite mineral. This is a very high value compared to those of the R1 and R2 bodies. The starting temperature for sintering was observed to be 835 °C. The shrinkage between 835 °C and 1134 °C proved that the optimum sintering temperature was 1134 °C. The bodies suffered bloating when temperatures above this were applied. There was a 76 °C temperature difference between the maximum sintering temperature applied in the factory (1210 °C) and the maximum sintering temperatures of the R3 bodies (1134 °C). Therefore, the R3 bodies were found to be more bloated compared to the R1 and R2 bodies.

When the R4 coded porcelain tile recipes were examined, it was seen that the bodies had an expansion of 2.99% up to 439 °C. The starting temperature for sintering was observed to be 813 °C. Since the shrinkage continued from 813 °C to 918 °C, the maximum sintering temperature was regarded as 918 °C. The bodies were subjected to excessive bloating owing to the existence of fluxing oxides in the colemanite bearing waste above 1050 °C (Fig. 3).

When the R5 coded porcelain tile recipes were examined, it was seen that the bodies had an expansion of 3.71% up to 444 °C. The starting temperature for sintering was observed to be 786 °C. Since the shrinkage continued from 786 °C to 915 °C, the maximum sintering temperature was regarded as 915 °C (Fig. 3).

A foamy or bubble type of structure was observed in the bodies owing to the bloating effect at temperatures above 1050 °C (Fig. 5) because there was not enough time in the factory’s fast firing conditions for the decomposition of the colemanite mineral \((\text{Ca}_2\text{B}_6\text{O}_{11}\cdot5\text{H}_2\text{O})\) in the waste-added bodies at the temperature range of 350-450 °C.

![Fig. 4. Comparison of optical dilatometer results for 5% (by weight) colemanite waste-added body (R2) at 1160 °C, 1170 °C, and 1180 °C temperatures.](image)

![Fig. 5. SEM secondary electron images of colemanite waste additions to R2 (a), R3 (b), R4 (c), and R5 (d) porcelain tile bodies.](image)
The changes in the microstructure of the standard (R1) and colemanite-added porcelain tile bodies after sintering at 1210°C (factory conditions) were investigated using characterization techniques such as scanning electron microscopy (SEM) and an energy dispersive X-ray (EDX) spectrometer. When the R1 standard porcelain tile body was investigated by backscattered electron (BSE) imaging, it was seen that it had a homogeneous matrix and a very low porosity (Fig. 7. a). In this image, dark grey sections show matrix phase and black sections show the porosity. In order to determine the phase/ phases of the grains and the chemical composition of the matrix phase, area and point energy dispersive X-ray (EDX) spectrometer analysis were employed (Fig. 7. b and 7. c). The area EDX analysis

**Characterization of sintered porcelain tile bodies: phase analysis**

XRD analysis was carried out in order to examine the phase formations of the R2, R3, R4 and R5 coded porcelain tile recipes which were obtained by the replacement of Na-feldspar by colemanite-bearing waste in comparison to the standard R1 porcelain tile after sintering at 1210 °C. The result of the XRD analysis of the standard and colemanite waste-added porcelain tile bodies are summarized in Fig. 6. It is seen that the main phases were quartz (SiO$_2$) and mullite (3Al$_2$O$_3$·2SiO$_2$) in the standard porcelain tile bodies (R1). When the R2 body was investigated, no new phase formation was observed after Na-feldspar in the standard R1 porcelain tile body was replaced by colemanite-bearing waste. The only change was the lower intensity of the mullite phase compared to the R1 body. In other words, waste addition lowered the amount of mullite in the standard porcelain body. This result was explained by dissolution of the mullite in the low viscosity liquid phase created by B$_2$O$_3$ and other high fluxing oxides within the colemanite waste [46].

In the R3, R4 and R5 coded bodies, the mullite phase was not observed and the intensity of the quartz phase was lowered. This was explained by dissolution of quartz and mullite phases in the excessive glassy phase caused by the increased amount of colemanite waste in the bodies. Moreover, the cristoballite phase was observed in the R4 and R5 bodies as a new phase formation which was not present in the R1 bodies. These bodies (R4 and R5) had large deformations owing to the bloating effect of the excessive glassy phase (Fig. 3). The cristoballite phase after sintering was thought to have occurred in the cooling stage by the introduction of excessive SiO$_2$ found in the waste material [41].

**Microstructural characterization and its relationship with the physical-mechanical properties**

Therefore, it was believed that sudden gas removal caused the deformation of the waste-added bodies.

<table>
<thead>
<tr>
<th>Recipe Codes</th>
<th>Green Strength (N/mm$^2$)</th>
<th>Dry Strength (N/mm$^2$)</th>
<th>Fired Strength (N/mm$^2$)</th>
<th>Water Absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>0.71</td>
<td>2.28</td>
<td>32.28</td>
<td>0.10</td>
</tr>
<tr>
<td>R2</td>
<td>0.74</td>
<td>2.60</td>
<td>20.24</td>
<td>1.44</td>
</tr>
<tr>
<td>R3</td>
<td>0.76</td>
<td>2.66</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>R4</td>
<td>0.81</td>
<td>2.72</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>R5</td>
<td>0.86</td>
<td>3.22</td>
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* could not be measured owing to the deformation and bloating effect occurred.

**Physical-mechanical properties**

The result of the tests applied (green strength, dry strength, fired strength and water absorption) to the R1, R2, R3, R4 and R5 coded porcelain tile bodies are summarized in Table 3. In general, dry shrinkage, green strength and dry strength values of unsintered bodies with a waste addition were found to be higher than those of standard porcelain tile bodies. The reason for this result can be explained by the removal of water physically absorbed to the high plasticity clays such as natronite-15A [Na$_2$Fe$_2$Si$_4$O$_{10}$(OH)$_4$·4H$_2$O] during drying and the action of the muscovite [KAl$_2$Si$_3$AlO$_{10}$(OH)$_2$] type of minerals with the organic binder in the unsintered porcelain tile bodies with waste [45].

After sintering, it was observed that the R2 coded bodies showed lower fired strength and higher water absorption compared to the standard (R1) porcelain tile bodies. The reason for the lower fired strength could be explained by the fact that the existence of high fluxing oxides in the R2 composition caused the bodies to be deformed owing to the bloating effect (Fig. 3) which was a result of the lowered liquid viscosity at a sintering temperature of 1210 °C. The reason for the high water absorption, on the other hand, can be explained by the high porosity caused by the bloating effect of fluxing oxides within the R2 bodies (Fig. 5. a).

Measurements of fired strength and water absorption values of the R3, R4 and R5 bodies were not made owing to the excessive deformation and bloating effect in these bodies (Fig. 3).
revealed that the body contains Si, Al, Mg, Na, K, Fe and O elements (Fig. 7.b). These results are in good agreement with the chemical analysis of the raw materials and the waste used in the present research and proved that impurities did not go into the composition of R1 during porcelain tile production. Point EDX analysis showed that the Si and O elements were present in the investigated grain which corresponded to the quartz phase in the standard porcelain tile body (Fig. 7.c). This finding supported the result of XRD analysis made on the standard porcelain tile body (Fig. 7.a). These results are in good agreement with the findings of previous studies [13-15, 46].

When Fig. 5 a, b, c and d corresponding to R2, R3, R4 and R5 porcelain tile bodies, respectively, are examined and compared to the R1 standard porcelain body given in Fig. 7a, it can be seen that there are many pores in the microstructure of the R2, R3, R4 and R5 porcelain tile bodies and it is obvious that these pores affect the physical-mechanical properties negatively. The pores were created by the gas bubbles that occurred by the removal of B2O3 after sintering and the weight loss of colemanite waste (39.76%) between 350 °C and 400 °C (Fig. 2). The gas bubbles created at 350-400 °C were caused by the loss and removal of 5 molecules of water during the decomposition of colemanite (Ca3B2O6 · 5H2O) [41].

There is not enough time during sintering and enough space in the green body after forming at the stage of fast firing and high press forming in porcelain tile production for the removal of a weight loss of 39.76% from the system. Therefore, the gases for the removal of crystal water at 350-400 °C were not accomplished and these were kept in the body and held to higher temperatures for removal.

The transferred gases and the removal of the B2O3 from the system at the sintering stage were the main reasons for the high porosity of the bodies (Fig. 5 a, b, c and d).

In colemanite waste-added bodies, sodium oxide (Na2O) was replaced by boron oxide (B2O3) and some K2O, Na2O, CaO and Fe2O3 also entered to the system. All these oxides have high fluxing ability [43] and cause (especially boric oxide) bloating of the body [44]. Point EDX analysis applied to the close vicinity of a gas bubble remained in an R2 body after sintering supported this idea through a high CaO and Fe2O3 content (Fig. 8 a, b). Therefore, it can be said that the sintering temperature of 1210 °C is rather a high temperature for bodies with colemanite waste and causes bloating of the bodies which in turn creates higher porosity. Microstructural images (Fig. 5 a, b, c and d), the DTA curve of the colemanite waste (Fig. 2) and the optical dilatometer results of colemanite waste-added bodies (Fig. 3), all proved the reasons of high porosity in the bodies.

The homogeneous matrix after sintering as well as the quartz (SiO2) and mullite phases (3Al2O3·2SiO2) in the body as determined by SEM-EDX and XRD analysis, respectively, were thought to be the main reason for the high fired strength of the R1 bodies [46]. The reason for very low water absorption of R1 bodies (0.10%), on the other hand, was explained by the existence of glassy matrix having minimum visible porosity which occurred by the filling of the pores with a low viscosity glassy phase during the sintering stage through the Na2O and K2O provided by Na and K-feldspars within the standard recipe [44].

In fact, the glassy matrix and very few pores of the standard porcelain tile body can be noticed when the microstructure in Fig. 7(a) is examined and compared to the colemanite waste-added bodies (Fig. 5a, b, c and d). The reason for a lower fired strength and higher water absorption values of colemanite waste-added porcelain tile bodies (R2) compared to the standard tile bodies (R1) was explained by the occurrence of a higher porosity in the microstructure owing to the severe decomposition reactions of colemanite mineral at 350-400 °C during sintering. Moreover, these intensive reactions of the R2 porcelain tile body could also be observed from both the expansion (1.44%) in the optical dilatometer curve (Fig. 3) and from the gas bubbles seen in the microstructural analysis (Fig. 5a).

As is well known, any increase in body porosity usually results in a decrease in the body strength [47].
Conclusions

In this research, colemanite mineral (Ca$_3$B$_2$O$_7$·5H$_2$O) containing waste was used in porcelain tile production without changing any process parameters in the factory conditions as an alternative sintering agent to replace Na-feldspar (Na$_2$SiO$_3$·6SiO$_2$) in the standard tile recipe. The chemical composition, mineralogical properties and behaviour under the heat treatment of solid colemanite waste were characterized in detail by the use of inductive coupled plasma (ICP), X-ray diffraction (XRD) and differential thermal analysis (DTA) / thermo-gravimetric analysis (TG), respectively. After detailed characterization studies, it was found that colemanite-bearing waste could be used in porcelain tile production as an alternative fluxing agent to Na-feldspar since it contains:

- a high amount of fluxing oxides such as B$_2$O$_3$, K$_2$O, Na$_2$O and Fe$_2$O$_3$,
- MgO and CaO which ease the occurrence of liquid phase and play an important role in the vitrification behaviour,
- natronite-15A [Na$_3$Fe$_2$Si$_2$O$_9$(OH)$_2$·4H$_2$O], muscovite [KAl$_3$Si$_4$O$_10$(OH)$_2$], quartz [SiO$_2$] and calcite [Ca (CO$_3$)$_2$] phases which have various roles in ceramic tile materials.

For each recipe, the effect of waste addition on the sintering behaviour was investigated through optical dilatometer analysis. In the R2 recipe, even a small amount of waste addition in place of Na-feldspar resulted in a 75°C decrease in the sintering start point. This result showed that a colemanite waste addition to porcelain tile bodies as an alternative sintering agent had an important potential. As the amount of waste additions increased (R3, R4 and R5 recipes), the starting temperatures of sintering were considerably reduced compared to that of the standard recipe (R1), however, the physical-mechanical properties were then found to be outside the required standards. The reason for these results were explained by the application of rather high sintering temperatures (1200°C) and inadequate time left for the decomposition of colemanite mineral in the factory conditions, as clearly explained by the optical dilatometer analysis. These results were also investigated through scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis on the sintered bodies. On the other hand, XRD analysis on the sintered bodies showed that the waste material should be considered as an alternative sintering raw material in porcelain tile production since the quartz (SiO$_2$) and mullite (3Al$_2$O$_3$·2SiO$_2$) phases in the standard tile bodies were conserved with the waste addition without changing the sintering temperature employed in the factories.

As a conclusion, it can be said that the use of colemanite waste is advantageous for the porcelain tile industry since it reduces the sintering temperature and raw material cost. In addition this will also be beneficial for the boron production plants in reducing the stockpiling problems related to the waste material and may provide some economic gains in marketing these previously unused wastes.

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