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CHARACTERIZATION OF ESPEY COLEMANITE AND VARIATION OF ITS PHYSICAL PROPERTIES WITH TEMPERATURE

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Abstract: It is important to characterize boron containing minerals because of their uses in a wide range of applications. The purpose of this study is to characterize Espey colemanite by mineralogical, petrographical and thermal means and to investigate the variation of its physical properties with temperature (up to 600 °C). Colemanite, having a non-porous crystalline structure, was found to consist of 35.8% B₂O₃ and 30.5% SiO₂. The thermal decomposition of colemanite occurred within the temperature range of 300–600 °C. It was found that calcination, a thermal treatment method, influenced the physical properties of colemanite. The highest surface area, 131.9 m²/g, was obtained at 500 °C. The physical properties were found to have high statistical relation.

Keywords: colemanite, boron mineral, characteristic property, physical property, temperature

Introduction

Turkey is the largest producer of natural borates worldwide. Boron reserves are highly concentrated in Turkey, which accounts for around 70% of the world total (Roskill, 2010). The Turkish borate deposits occur in western Anatolia in five main districts; Bigadic, Kestelek, Sultançayiri, Emet, and Kirka (Palmer and Helvacı, 1995). The borates in Turkey are tincal, colemanite and ulexite. Colemanite reserves have the largest share (73.9%) compared to tincal (24.5%) and ulexite (1.6%) (Eti Mine, 2008). Colemanite (calcium borate, Ca₂B₆O₁₁·5H₂O) and tincal (sodium borate, Na₂B₄O₇·10H₂O) are the most widely-used boron minerals. B₂O₃ wt. percentages of the minerals are 50.8% and 36.5%, respectively. Nearly 10% of the natural borates are consumed as it is; whereas the rest is used to produce refined products. Turkey is the world's major source of colemanite, although USA is also a significant source (Roskill, 2010).

Boron compounds and minerals find applications in many products in a variety of industries. The main consumption areas of borates are glass, ceramics, soap and detergents, and agriculture. Borates are used in industrial applications primarily because they are safe to handle and their natural functions impart a wide range of performance, cost, and environmental health and safety advantageous in various products (Freedonia, 2010).

Colemanite is an industrially important mineral, which is mostly used in textile type fiberglass, glass and ceramic industries and metallurgy. Colemanite is also used in detergent and cosmetic industries and for production of boric acid by reacting with sulfuric acid. When used in textile type fiberglass industry, colemanite drops the melting temperature of the mixture, provides low viscosity at the melting temperature, prevents crystallization and positively affects the chemical and physical properties of final glass product. Colemanite reduces the melting point in glass industry and it is resistant to thermal shocks. In formulation of ceramic and enamel glazes, it provides a stable structure, homogeneous melting and low segregation. Since it is a solvent for almost all metal oxides, it is used as a fluxing agent in the metallurgy industry (Eti Mine, 2014). As seen, the most important factor that determines the potential application of colemanite is that it decreases the melting point during production.

In literature, there are studies that characterize colemanite. The location and geological map of the Emet Borate Mine is presented by Colak et al., (2000), together with the mineralogical composition of Hisarcik and Espey Colemanites. Christ et al., (1958) studied the crystalline structure of colemanite. It was reported that colemanite contains infinite chains linked together laterally by ionic bonds through Ca^{2+} ions to form sheets parallel to [010]. The sheets, in turn, are linked together through a system of hydrogen bonds involving the hydroxyl groups of the chains and water molecules. Burns and Hawthorn (1993) investigated the hydrogen bonds of colemanite as these bonds control many of the physical and chemical properties of the mineral. Frost et al., (2013) studied the infrared and Raman spectroscopic characterization of colemanite. It was stated that the basic structure of colemanite contains endless chains of interlocking $\text{BO}_2(\text{OH})$ triangles and $\text{BO}_3(\text{OH})$ tetrahedrons with the calcium, water and extra hydroxide units interspersed between these chains. Thermal analysis of hydrated borates, including colemanite, was studied by Waclawska (1998). It was stated that the thermal decomposition of hydrated borates comprises two stages: formation of free water molecules and removal of these towards the outside of the solid matrix. Other studies investigate the use of colemanite as a raw material mainly during boric acid production (Cakal, 2004; Cakal et al., 2006) or additive (Celik, 2010; Celik et al., 2014).

The main aim of this work is to evaluate the influence of temperature on the physical properties of the Espey Colemanite, Emet, Kutahya, Turkey. The characteristic properties of this mineral are also determined.

Materials and methods

Colemanite was supplied by the Espey Mine, Eti Mine Works, Emet, Turkey. Colemanite, having 1-3 mm particle size, was used in this study after being pulverized to 0.5 mm. The characteristic properties of the colemanite were determined by performing petrographic analysis, X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM) analysis, energy dispersive X-ray spectroscopy (EDS) analysis, thermo-gravimetric/differential thermal (TG-DTA) analysis and loss on ignition measurements.

The colemanite samples having 35.4% B_2O_3 were calcinated according to the Turkish patent TR-2007/03372, describing the calcination of tincal, sodium borate mineral. The colemanite samples were calcinated in closed vessels in a laboratory furnace at temperatures 100–600 °C. The calcination process duration was 2 hours. The vessels only have an outlet for water vapor. After the calcination process at 600 °C, colemanite mineral having 45% B_2O_3 was obtained. To find out some of the important physical properties of colemanite at ambient temperature and temperatures up to 600 °C, surface area, specific gravity, bulk density, porosity, water absorption and compactness ratio analyses were carried out on five different samples. Calcination is known to affect these parameters significantly. Analyses were performed at Mining Technical Research Institute (MTA), Ankara, Turkey, Middle East Technical University (METU) Chemical Engineering and Mining Engineering Departments, Ankara, Turkey and Cukurova University Mining Engineering Department, Adana, Turkey.

Petrographic analysis was done by an Olympus BH-2 microscope. For the petrographic investigation, 0.02 mm thick slices of colemanite were prepared. Chemical analysis of the 105 °C dried samples was performed by using Siemens SRS 300 X-ray Fluorescence Spectrometer (XRF) instrument. XRD of the powdered samples was carried by using Rigaku XRD Geigerflex equipped with Cu X-ray tube. XRD patterns were recorded from $20^\circ < 2\theta < 60^\circ$ with step of 0.02° . Images and elemental composition of the samples were obtained by SEM instrument using FEI Quanta 400 MK2 equipped with EDAX Genesis XM 4i detector. Proportional elemental distribution was found by EDS analyzer. The amount of weight loss of the colemanite samples were determined by TG-DTA using TG/DTA 6300 S11 EXSTAR 6000. The measurements were performed up to 1000 °C under air flow using uniform heating rate of 20 °C/min. The sample holder was cylindrical-shaped platinum crucible having a diameter of 6 mm and height of 10 mm.

BET (Brunauer, Emmett and Teller) surface area measurements were performed using Nova Instruments Quantochrome 2200. To determine the bulk densities, the samples were ground, sieved through 16 mesh sieves (1 mm sieve opening) and impurities were removed. The bulk density analyses were done according to the TS 3529 (1980) and ASTM C127-42 (2003) standards. Specific gravities were determined by means of a pycnometer in accordance with TS 1114 EN 13055-1 (2004) standards.

Porosity measurements were performed using a Autopore IV 9220 mercury porosimeter. Before the mentioned analyses, the samples were put into the furnace at the preset temperature for two hours.

Water absorption properties of the particles were found according to the TS 1114 EN 13055-1 and ASTM C 127-42 standards. The compactness ratio was determined in accordance with the ASTM C127-42 and ASTM C128-57 (2003) standards while the loss on ignition analysis of colemanite according to the TS 1114 EN 13055-1 standards.

Results and discussion

Mineralogical and petrographical analysis of *Espey colemanite*

The chemical analysis performed by XRF and mass loss on ignition analyses are given in Table 1. It can be seen there, that colemanite consisted of 35.8% B_2O_3 and 30.5% SiO_2 . The values in Table 1 are the average of 5 different samples.

Table 1. Chemical analysis of colemanite samples (%)

Element	Content (%)
B_2O_3	35.8±1.2
SiO_2	30.5±2.1
Al_2O_3	12.2±0.8
CaO	8.6±1.2
Fe_2O_3	1.2±0.2
MgO + SrO	3.1±0.2
Other	8.3±2.1
Loss on ignition	4.95±0.2

As a result of the XRD analysis, Fig. 1, the major component of the boron samples (80–85%) were found to be colemanite. The other components were smectite and illite (10%). There were also trace amounts of chlorite and mica. Colak et al. (2000) investigated the mineralogical composition of *Espey colemanite* by XRD and found out that *Espey colemanite* has calcite, quartz, K-rich feldspar, cahnite, plagioclase, smectite, illite, chlorite, kaolinite and clay. As known, the composition of the colemanite mineral may differ from sample to sample as it is a heterogeneous mineral. The samples were subjected to the XRD analysis. Colak et al. (2000) also studied colemanite obtained from the upper limestones, to the bottom of the open pit mines. When the XRD peaks of the samples in Colak et al., (2000)'s study were examined, it was seen that samples had a high clay (saponite) content. In this study, before the colemanite samples were supplied by the Eti Mine Works, they were subjected to a standard processing and milling including screening and washing. That is why the samples had a low clay content. Thus, the peak intensity of the colemanite in the XRD analysis was higher. Besides, Yildiz (2004), obtained a similar XRD result for Emet

colemanite having about 83 wt% purity, which was also subjected to a standard processing and milling.

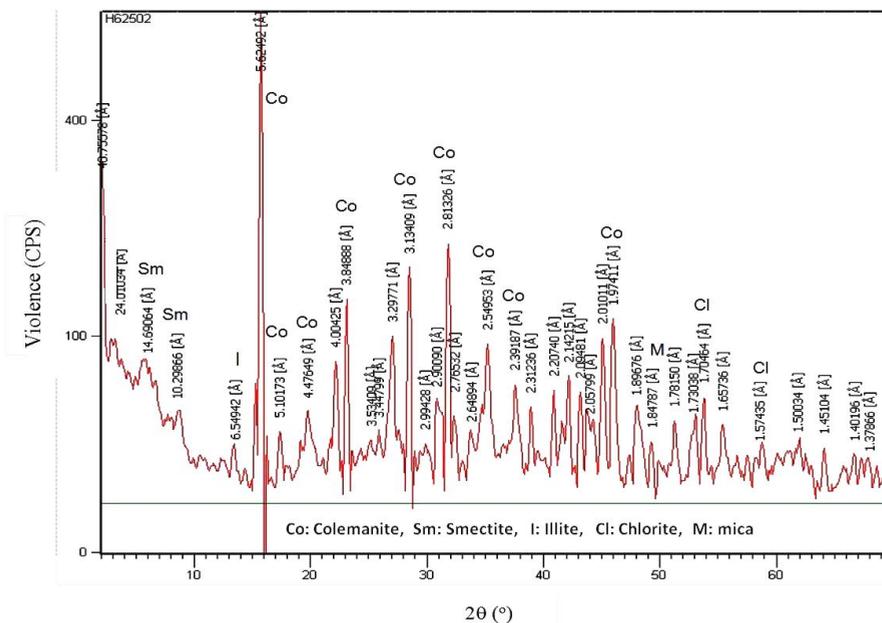


Fig. 1. XRD analysis of Espesey colemanite

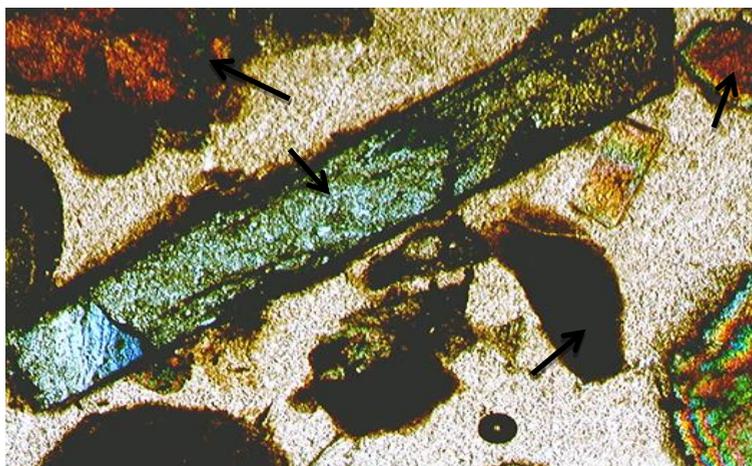


Fig. 2. Microphotograph of Espesey colemanite

In general, sodium and calcium borates are formed under near-surface conditions as a result of volcanic activity and are associated with continental sediments and volcanic rocks (Roskill, 2010). Palmer and Helvacı (1995) reported that although there are differences between the different districts, borates are all generally enclosed within

limestones and clays and are interbedded with layers of volcanic ash, limestone, marl, and clays. From the petrographic investigation (Fig. 2) it was observed that the boron samples were colemanite. There was also iron together with quartz, chlorite, feldspar, mica and illite minerals.

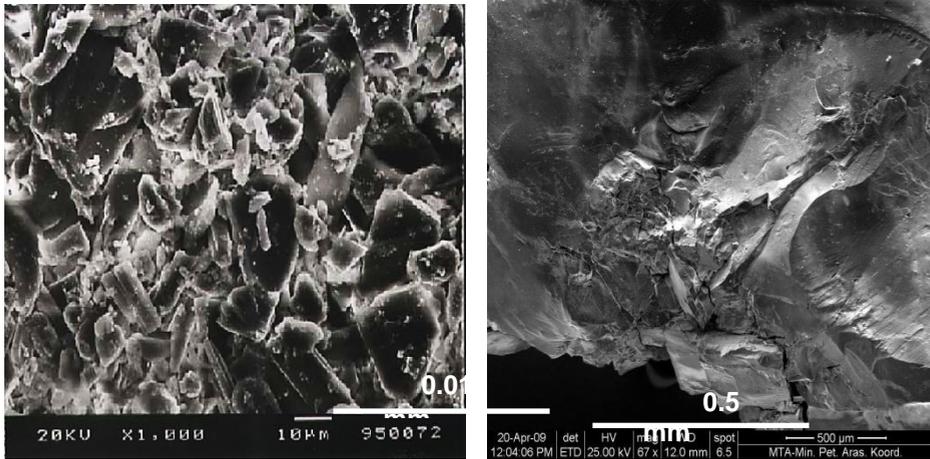


Fig. 3. SEM images of Espey colemanite

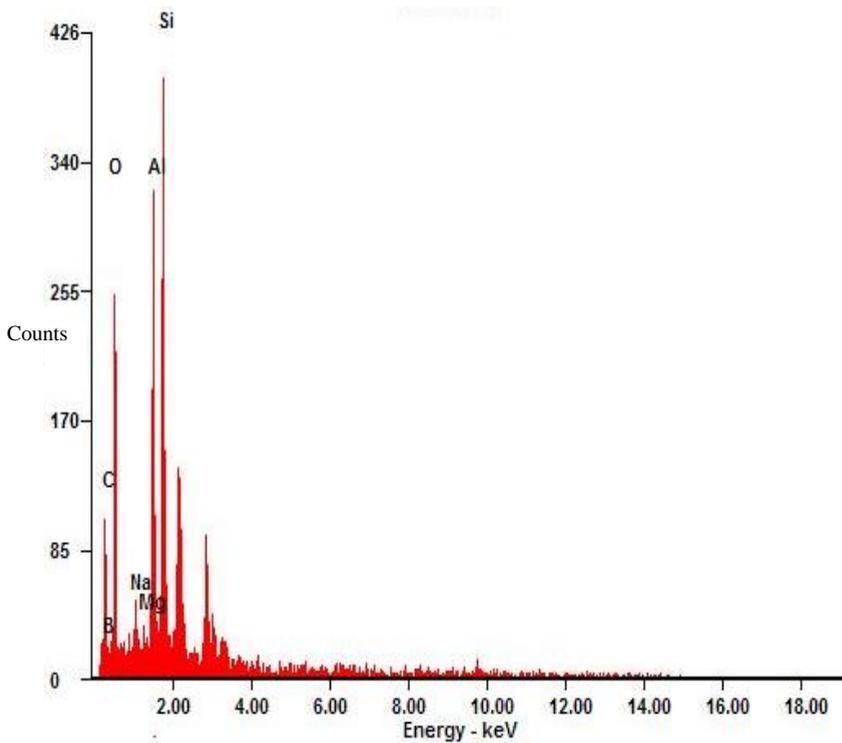


Fig. 4. EDS analysis of Espey colemanite

As seen from the SEM images (Fig. 3) colemanite has a non-porous crystalline structure and the accompanying clays are smectite and illite. A proportional distribution of the elements, determined by the EDS analysis (Fig. 4) showed that there are 35.4% boron and 27.6% silicon within the colemanite samples. Besides a high content of Si, B, O, C and Al, the colemanite samples also have trace amounts of Mg, Ca, Fe and Na.

Thermal analysis of Espey colemanite

From the TGA analysis (Fig. 5) it was seen that the decomposition of colemanite begins with the removal of water molecules. First, colemanite loses 1.8% of its weight up to 350 °C. The thermal decomposition of colemanite occurs within 300-450 °C as examined from DTA curve. A distinct inflection is seen at 307 °C. It means that the thermal dissociation of colemanite begins with the removal of the OH groups, which form water molecules. Next, the bonds of molecular water with borate rings become broken. This can be judged from the endothermic peak at 389 °C. Next, the removal of water proceeds rapidly as observed from the TG curve. The remaining water escapes slowly up to 600 °C. At temperatures between 350 and 600 °C, colemanite loses 35.7% of its weight. At 600 °C, the completion of the reaction occurs. A similar TG/DTA curve was also obtained by Waclawska (1998).

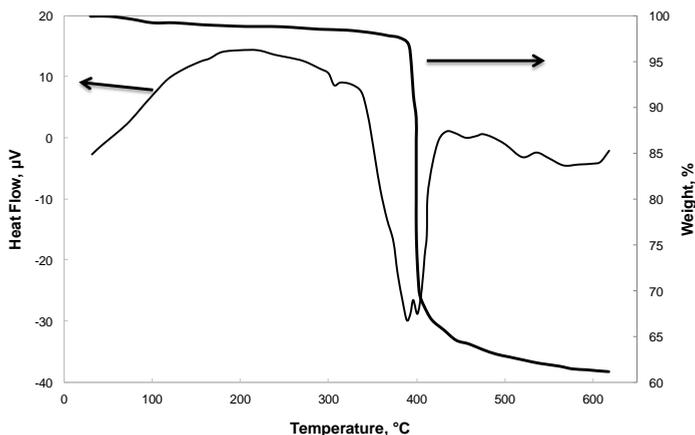


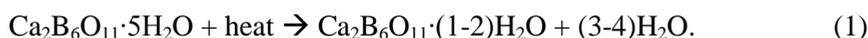
Fig. 5. TG-DTA curves of Espey colemanite (heating rate 20 °C/min)

Variation of physical properties of Espey colemanite with temperature

Surface area, bulk density, specific gravity, porosity, water absorption and compactness ratio values of colemanite were determined at different temperatures and are given in Table 2.

As seen from Table 2, the surface area and porosity of colemanite increases with temperature. The highest surface area (131.9 m²/g) is at 500 °C and porosity (52%) at

400 °C. The surface area and porosity do not change considerably above that temperature. Bulk density, specific gravity compactness ratio and water absorption values decrease depends on the temperature. Colemanite has a density of 2.37 g/cm³ and bulk density of 1150 kg/m³ at 100 °C. These values decreased to 2.25 and 690 kg/m³ at 500 °C, respectively. The water absorption and compactness ratio of colemanite decreased from 27.85% to 15.45% and 0.49% to 0.31% at 500 °C, respectively. With the increase of temperature, the water content in the colemanite structure decreases, leading to increased surface area and porosity of the colemanite sample. The release of water can be explained with Eq.1:



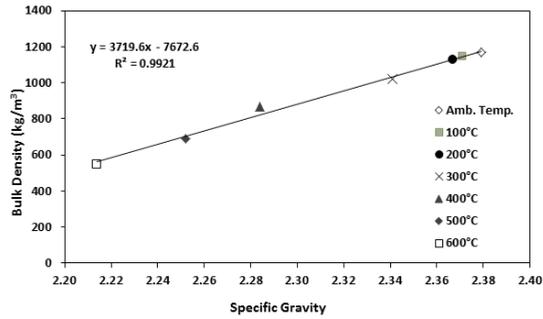
As the mass of colemanite was decreased with temperature, the bulk density, which is mass per volume, also decreased together with density. The compactness ratio, which is 1-void ratio, also decreased with the increase of void ratio. The thermal treatment of other borate minerals, namely tincal (Yilmaz, 2014) and ulexite (Sener et al., 2000) was also studied. It was also found that porosity of the borate minerals increased with calcination process up to 600 °C. The increase of porosity was attributed to the formation of microcracks throughout the structure during the removal of water.

Table 2. Physical properties of *Espey colemanite* at different temperatures

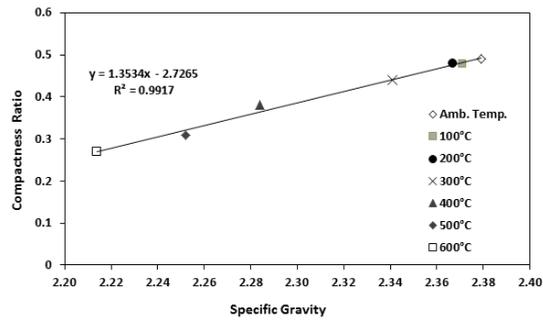
Temperature (°C)	Surface area (m ² /g)	Bulk density (kg/m ³)	Specific gravity	Porosity (%)	Water absorption (%)	Compactness ratio
Ambient	27.6±1.9	1170±110	2.38±0.05	18±1	27.85±0.05	0.49±0.09
100	29.3±1.5	1150±80	2.37±0.09	21±2	26.15±0.04	0.48±0.08
200	34.2±5.1	1130±10	2.37±0.03	28±1	25.28±0.07	0.48±0.11
300	77.0±8.2	1020±60	2.34±0.15	49±2	24.33±0.12	0.44±0.07
400	117.4±5.4	870±50	2.28±0.08	52±4	19.62±0.07	0.38±0.10
500	131.9±13.5	690±40	2.25±0.14	50±2	15.45±0.05	0.31±0.05
600	128.7±15.8	550±40	2.21±0.09	48±3	12.55±0.04	0.27±0.08

Comparison of characteristic properties of *Espey colemanite*

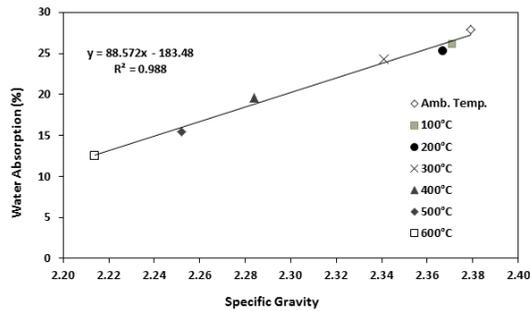
When the characteristic properties of colemanite were examined, it was observed that chemical, petrographic, XRD, SEM and EDS analyses results support each other. Besides, significant statistical relations exist between the physical properties of the colemanite; especially between specific gravity and bulk density ($R^2 = 0.9921$) (Fig. 6(a)), specific gravity and water absorption ($R^2 = 0.988$) (Fig. 6(b)), specific gravity and compactness ratio ($R^2 = 0.9917$) (Fig. 6(c)) and specific gravity and surface area ($R^2 = 0.9076$) (Fig. 6(d)). It can also be seen that although there exists sets of relationships between the physical properties of the colemanite, they also decrease with temperature, except surface area and porosity.



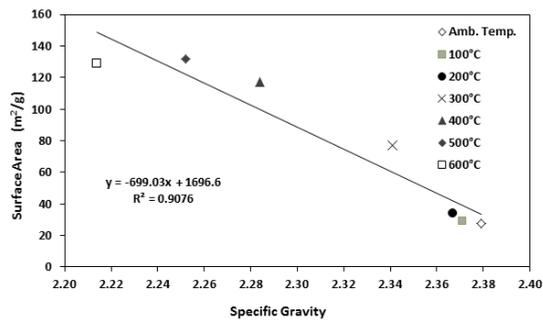
a)



b)



c)



d)

Fig. 6. Relationship between specific gravity and (a) bulk density, (b) water absorption, (c) compactness ratio, (d) surface area. R2 min for a core

Conclusions

In this study, the thermal and physical properties of colemanite were determined. Colemanite consists of 35.8% B₂O₃ and 30.5% SiO₂. The petrographic observations confirmed that the boron sample was colemanite. There was also some iron minerals together with quartz, chlorite, feldspar, mica and illite minerals. SEM images of colemanite showed a non-porous crystalline structure and the clays that accompany it are smectite and illite. The EDS analysis showed the presence of 35.4% boron and 27.6% silicon within the colemanite samples. A weight loss of 1.8% at 350 °C, and 35.7% between 350 and 600 °C was found from the TG-DTA analysis. There existed a sharp endothermic peak at 389 °C. Although specific gravity, bulk density, water absorption, compactness ratio and surface area of colemanite differ at different temperatures, they were found to have high statistical relation. In addition, the surface area and porosity values increased up to 500 °C and 400 °C, respectively and then, decreased slightly.

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