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# Changes in the structure of ulexite on heating

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## Abstract

On heating, hydrated boron minerals, colemanite and ulexite lose their water of crystallisation while undergoing various mineralogical and structural changes.

In this study, the nature and mechanisms of the thermal reactions of ulexite have been determined by TG, DTG and DTA. The changes in the structure have been investigated by XRD, SEM, and Hg-porosimetry. Thermal decomposition of ulexite occurred within the temperature range 60–500°C with two dehydration stages proceeded by two dehydroxylation stages. The structure was first transformed into $NaCaB_5O_6(OH)_6{\cdot}3H_2O$ within 60–180°C, then into $NaCaB_5O_6(OH)_6{\cdot}H_2O$ within 151–260°C. Amorphisation took place along with dehydroxylation. The structure was first transformed into a multi-domain heterogeneous matrix consisting of $NaCaB_5O_6(OH)_6{\cdot}H_2O$ and an amorphous phase to X-ray during the first stage of dehydroxylation within 180–260°C. Then remaining hydroxyl groups removed between 260 and 500°C. The sample has become completely X-ray amorphous. During the gradual liberation of water vapour, the structure developed numerous microcracks and had exfoliated without decrepitating. The microcracks increased the degree of porosity and the structure became more easy to grind. Furthermore, the amorphous structure recrystallised as $NaCaB_5O_9$ at 636°C and transformed into $CaB_2O_4$. Any remaining $NaB_3O_5$ after 855°C was amorphous. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Ulexite; Thermal reaction; Dehydration; Dehydroxylation; Porosity; Grindability

## 1. Introduction

Turkey has the largest boron reserves in the world with over 60% share. Most of the mined boron mineral, tincal, colemanite and ulexite, are exported in the form of raw materials and Turkey is the most important source of borates supplement [1]. The extra weight of water and other impurities in the raw materials increase transportation and energy cost for producing anhydrous borates. Therefore, the demand for raw hydrated borates has declined in recent years. This has forced the producers to produce the dehydrated borates and boron products.

When boron minerals are heated, internal thermal reactions occur. The mineral first looses its water of crystallisation followed either by the production of amorphous material or recrystallises into new phases. The structure has undergone significant changes. Colemanite decrepitates due to sudden release of confined water vapour within micropores during this thermal treatment. While, ulexite does not decrepitate. Instead it only exfoliates due to gradual removing of water vapour and the structure becomes amorphous with numerous microcracks and interstices. This product is weak and easily ground to a powder [2,3].

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The aim of this study is to determine the nature and mechanism of the thermal reactions which occurred in ulexite ($NaCaB_5O_9{\cdot}8H_2O$, i.e. hydrated sodium calcium borate) during heat treatment, to examine the mineralogical and structural changes which accompany the thermal reactions and to determine the effect of heat treatment on the degree of porosity of the ulexite.

## 2. Materials and methods

Ulexite samples used throughout the study were prepared from the ulexite concentrates taken from Balikesir Bigadiç mine of Etibank. Hand picked coarse crystals were cleaned by dipping in water and washing to remove some of the impurities such as dispersed clay minerals.

Cleaned and air dried samples were crushed and ground by a jaw and a roll crusher, respectively, and then screened through the 1.168 and 0.600 mm sieves. The (1.168–0.600 mm) sized samples were kept in nylon bags for the subsequent experiments.

Chemical analysis of the ground samples was carried out and their purity was found to be about 96% on the basis of $B_2O_3$ content (Table 1). The chemical analysis for $B_2O_3$ content was achieved by volumetric titration based upon the Institute of Turkish Standard method (TSI 2481), [4]. Other elemental analysis was performed using atomic emission spectroscopy and flame photometry. All reagents and chemicals used throughout the study were of analytical grade.

Conventional thermo-gravimetric (TG), differential thermogravimetric (DTG) and differential thermal analyses (DTA) were performed on the samples to determine the amount of $H_2O$ removed, the temperature of decomposition and the nature and mechanism of thermal decomposition and reconstitution reactions. A Thermal Science TG 1500 thermogravimetric analyzer equipped with a microbalance system was used in the TG and DTG analyses. DTA analysis was carried out using a Rigaku Thermoflex TG 8110 model differential thermal analyzer. All the experiments were performed in a rhodium–platinum crucible under $N_2$ to sweep out accumulated water vapour produced during the calcination of the sample. Experiments were carried out at heating rate of 10°C $min^{-1}$. In the DTA study, platinum crucible, Rh–Pt thermocouple and $Al_2O_3$ were used as inert material.

Table 1
The chemical analysis of ulexite samples

| Element | % |
|---|---|
| $B_2O_3$ | 41.17 |
| CaO | 18.80[a] |
| $Na_2O$ | 7.50 |
| $SiO_2$ | 0.85 |
| MgO | 0.22 |
| $K_2O$ | 0.02 |
| $Fe_2O_3$ | 0.09 |
| $Al_2O_3 + TiO_2$ | 0.85 |
| Loss on ignition at 800°C | 33.83 |

[a] CaO content exceeds the theoretical value of ulexite (13.8) due to the most probably presence of Ca-bearing impurities such as colemanite, calcite and gypsum in the ulexite concentrate.

The calcination test was performed in a Heraeus brand muffle furnace equipped with time-proportioning temperature control system that provides ±0.8%/°C sensitivity from the set point of temperature. In the procedure, the furnace was first set to the desired temperature with an empty crucible and the experiment started on introducing the sample into the preheated crucible. At the end of each experiment, the calcined sample was allowed to cool down to room temperature in a desiccator. A cylindrical porcelen crucible with a volume of 340 $cm^3$ was used for the treatment of all samples.

In the identification of crystalline structure of the phases, X-ray diffraction analysis (XRD) was carried out, using a Philips model PW 1840 and a Rigaku Miniflex X-ray diffractometers with Ni filtered Cu K$\alpha$ radiation.

Surface characterisation was performed using a scanning electron microscopy (SEM) using a Leitz model AMR 1000 scanning electron microscope.

Specific surface area and pore volume measurements were performed using a Micromeritics 9310 Pore Sizer brand Hg-porosimeter for determining size distribution of the pores created during thermal treatment at various temperatures.

## 3. Results and discussion

### 3.1. Thermal decomposition of ulexite

The TG and DTG analyses showed that thermal decomposition of ulexite began at about 60°C and

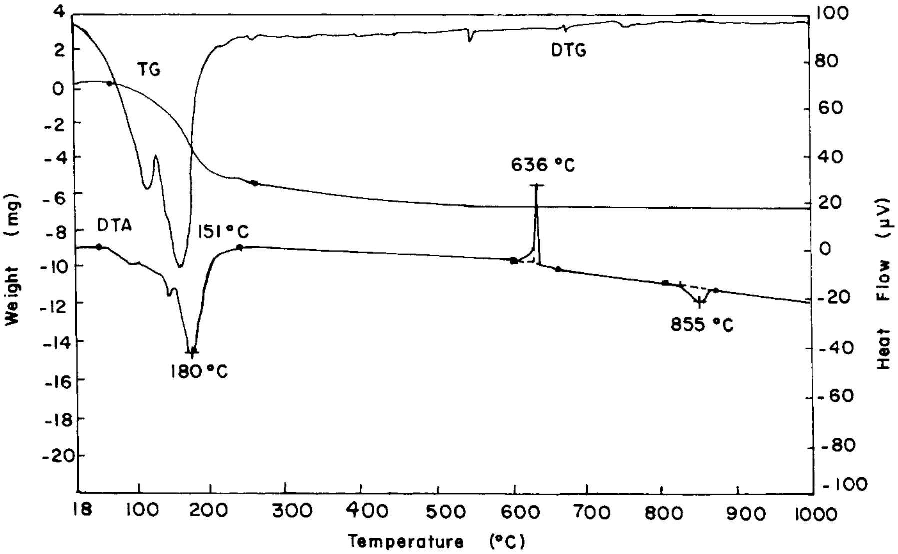


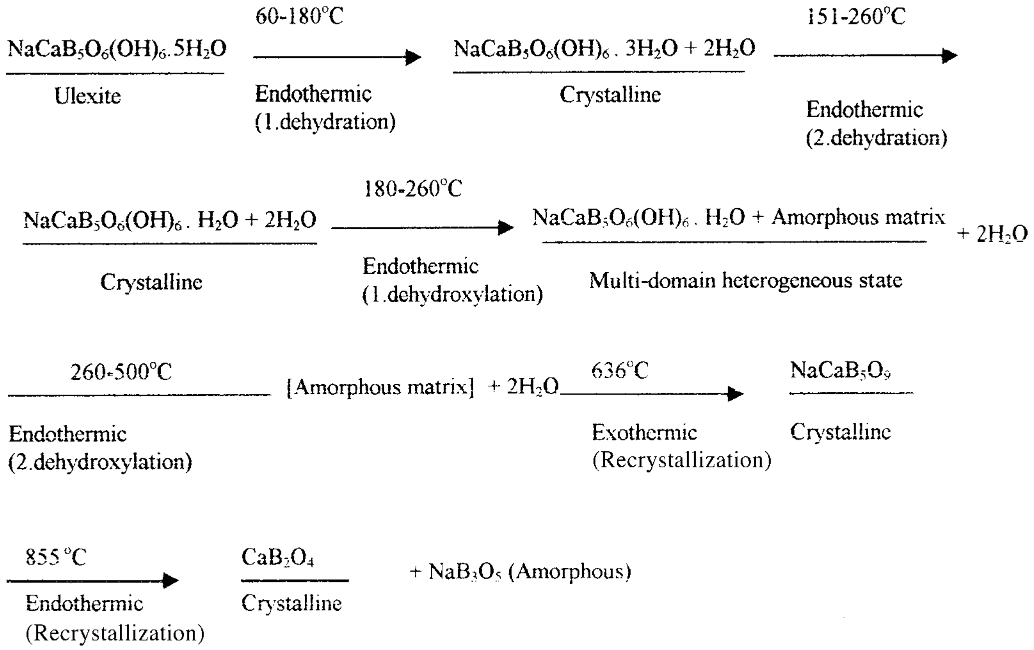
Fig. 1. TG, DTG and DTA curves of ulexite.

proceeded up to 240°C. Two partly overlapping DTG peaks are observed at around 150 and 180°C, corresponding weight looses of 8 and 17%, respectively. The reaction stopped at 240°C.

The change in weight continued up to about 500°C by which time 35% of the weight had been lost (see Fig. 1).

The results of DTA analysis showed that there were three distinct reactions. The first occurred within the temperature range 60–240°C and were accompanied by two partly overlapping endotherms (Fig. 1). This was consistent with the DTG analysis. An exothermic reaction was observed in the range 600–640°C with a maximum at 636°C. The third reaction is endothermic and occurs in the region 800–880°C.

The decomposition of ulexite has begun with two stage dehydration, exhibiting three endothermic DTA peaks (Fig. 1). In the first stage of dehydration, 1.5 mol of $H_2O$ have been removed at 118°C. This first phase was identified as $NaCaB_5O_6(OH)_6{\cdot}3H_2O$ as indexed by the ASTM standard of 38–206. The second stage occurred within 118–260°C giving two endothermic peaks at 144 and 152°C where 0.5 and 2.5 mol of $H_2O$ have been removed by two stage dehydration. This phase was identified as $NaCaB_5O_6(OH)_6{\cdot}H_2O$ as indexed by ASTM standard of 38–207. The reaction then proceeded up to 500°C with multi-stage decomposition (two stage dehydration and two stage dehydroxylation reactions) giving two distinct endothermic DTA peaks at 151 and 180°C [5,6]. The first stage of dehydroxylation reaction took place within 180–260°C. The OH groups were split from the free $H_2O$ molecules from polyhedra retaining small amounts of OH groups in the polyhedra. From the view of strength of bonds in the framework, the OH groups are more strongly bonded with $Na^+$ than $Ca^{2+}$ cations [7] so that the bonds between $Ca^{2+}$ and OH groups are first broken selectively during the first stage of dehydroxylation (150–260°C). On the other hand, the Na-coordinated OH groups can be removed during the second stage of dehydroxylation within wide range of temperatures as 260–500°C. During the dehydroxylation, amorphisation has been observed above 160°C and the structure was found completely amorphous at 260°C. At 500°C, a new crystalline phase was observed. It was identified as $NaCaB_5O_9$ as indexed by ASTM standard of 37–827. This structure was also present at 600 and 700°C calcined ulexite. The XRD pattern of ulexite calcined at 850°C shows the presence of a new crystalline phase beside $NaCaB_5O_9$. This was identified as $CaB_2O_4$ as indexed by ASTM standard of 32–0155. After 850°C, sodium bearing component of $NaCaB_5O_9$ most probably remained in amorphous state as $NaB_3O_5$. According to the results derived from DTA and XRD examinations, the overall thermal reactions occurred in the structure of ulexite during the heat treatment are given as follows:



$$\underset{\text{Ulexite}}{\underline{NaCaB_5O_6(OH)_6.5H_2O}} \xrightarrow[\text{Endothermic (1.dehydration)}]{60\text{-}180^\circ C} \underset{\text{Crystalline}}{\underline{NaCaB_5O_6(OH)_6.3H_2O + 2H_2O}} \xrightarrow[\text{Endothermic (2.dehydration)}]{151\text{-}260^\circ C}$$

$$\underset{\text{Crystalline}}{\underline{NaCaB_5O_6(OH)_6.H_2O + 2H_2O}} \xrightarrow[\text{Endothermic (1.dehydroxylation)}]{180\text{-}260^\circ C} \underset{\text{Multi-domain heterogeneous state}}{\underline{NaCaB_5O_6(OH)_6.H_2O + \text{Amorphous matrix}}} + 2H_2O$$

$$\xrightarrow[\text{Endothermic (2.dehydroxylation)}]{260\text{-}500^\circ C} [\text{Amorphous matrix}] + 2H_2O \xrightarrow[\text{Exothermic (Recrystallization)}]{636^\circ C} \underset{\text{Crystalline}}{\underline{NaCaB_5O_9}}$$

$$\xrightarrow[\text{Endothermic (Recrystallization)}]{855^\circ C} \underset{\text{Crystalline}}{\underline{CaB_2O_4}} + NaB_3O_5 \text{ (Amorphous)}$$

These results contradicted with the previous investigators [7]. It was noted that the structure has crystallized into $NaCaBO_3$ while $B_2O_3$ has remained in amorphous state after calcination at 700°C.

### *3.2. Structural changes in ulexite by heat treatment*

SEM investigations showed that the original sample appeared to be composed of well crystallized parallel fibrous crystal aggregates throughout the matrix. The cleaved planes are present between these individual crystals (see Fig. 2). Sample calcined at 120°C contained the well crystallized aggregates, but cleaved along planes and some crystals are broken laterally. The structure is less compact and porous. On calcination at 180°C, the crystals of the aggregates disintegrated both longitudinally along the cleavage planes and laterally along the crystal itself and became much more loose, permeable and porous. In the sample calcined at 240°C, individual ulexite crystals have partially disappeared, whilst many partings, microcracks and interstices have formed. In the calcination at 320°C, individual ulexite crystals have mostly disappeared. Aggregates were disturbed and too many large partings, microcracks and interstices were produced. The cavities between aggregates were much more extended than that of material calcined at 240°C. The structure has become more permeable, exfoliated and porous (Fig. 3a). After calcination at 600°C, the previous structure has completely disappeared and a new phase has appeared (Fig. 3b). According to XRD analysis, this structure corresponds to $NaCaB_5O_9$ where an exothermic DTA peak was

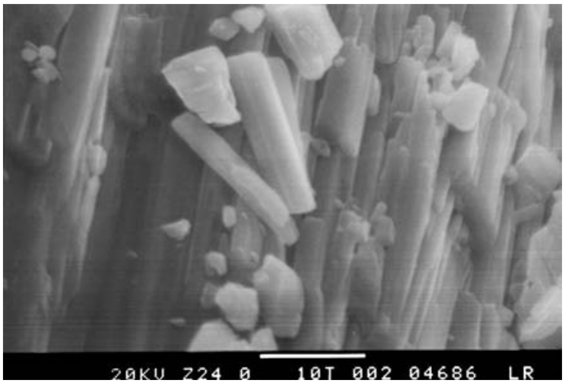


Fig. 2. SEM micrograph of original ulexite (5000×).

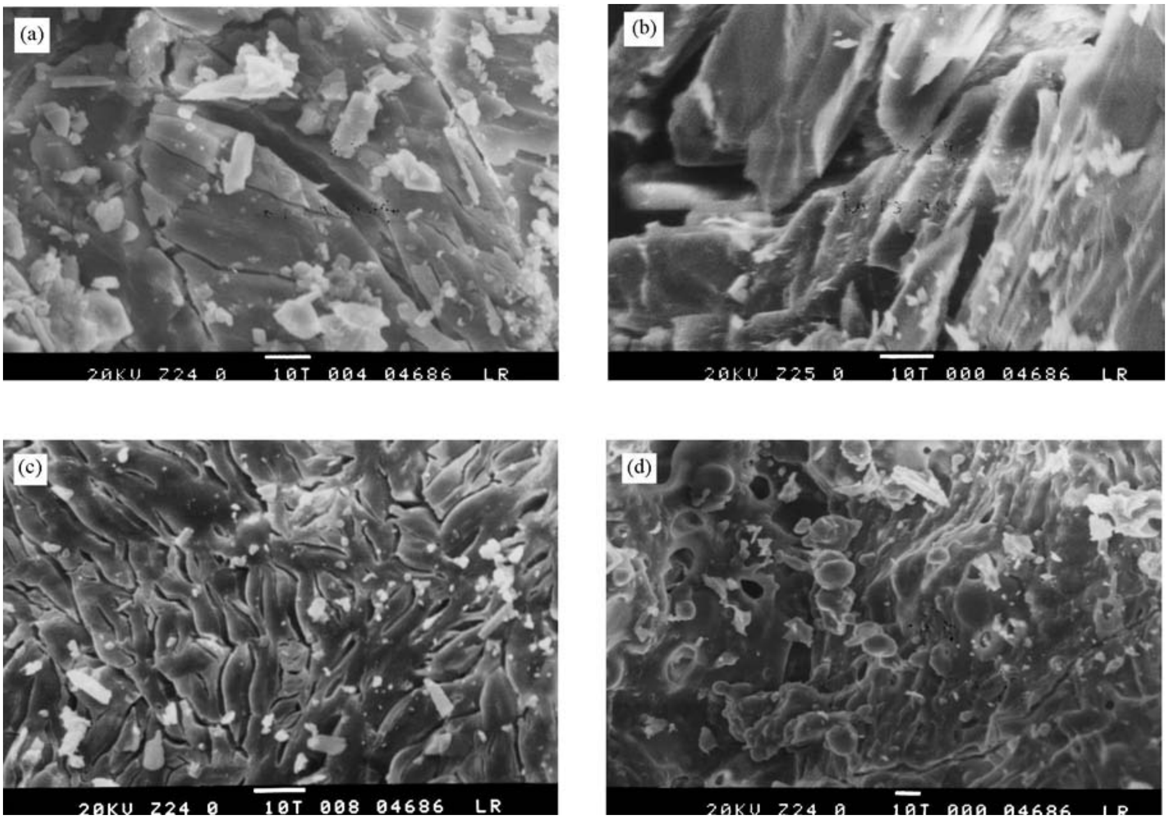


Fig. 3. SEM micrographs of calcined ulexite: (a) calcinet at 240°C (2000×); (b) calcined at 320°C (2000×); (c) calcined at 600°C (2000×); (d) calcined at 850°C (1000×).

observed (at 636°C). The cavities along the cracks and parting have been reduced and folded. The structure has reniform (kidney-like) texture due to the rebuilding and shrinkage of the aggregates during recrystallization. The structure seems to be less permeable and porous (Fig. 3c). After calcination at 850°C, the structure has been transformed into sponge type texture containing both open and closed spherical pores by fusion of whole structure (Fig. 3d).

The effect of heat treatment on porosity and pore size distribution in the structure of ulexite was investigated for original and calcined samples at 240, 320, 600 and 850°C. The overall comparative results with respect to total intrusion pore volume, total specific pore area, median pore diameter (with respect to both volume and area) apparent and true densities and degree of porosity are given in Table 2. It can be seen that heat treatment has resulted in a significant increase in intrusion pore volume of ulexite from 0.0608 to 0.4455 ml/g up to 600°C, then decrease to 0.3685 ml/g at 850°C. So, porosity (determined by calculation using total intrusion pore volume) also increased from 10.67 to 45.00% and slightly decreased to 37.95% at 850°C. The created pores actually seemed as interstices and microcracks instead of spherical shaped pores, except at 850°C (Fig. 3d). The increase in degree of porosity also improved the grindability of ulexite. The work index of original ulexite has been decreased from 7.11 to 5.5 kWh/sh-t (Kilo watt hour per short-ton) at 200°C and then decreased to 4.5 kWh/sh-t at 380°C. In addition, apparent density decreased from 1.7513 to 1.10103 g/ml related with increase in degree of porosity. On the other hand, true density of the sample was almost constant up to 600°C but decreased at about 850°C which might be due to enclosed pores formed during shrinkage due to partial melting of the structure. Heat treatment also affected

Table 2
Total intrusion pore volume, specific pore area, median pore diameter (with respect to volume and area), apparent and true densities and percent porosity values of original and calcined ulexite

| Property | Original ulexite | Ulexite sample calcined at | | | |
|---|---|---|---|---|---|
| | | 240°C | 320°C | 600°C | 850°C |
| ∑ Instrusion pore volume (ml/g) | 0.0608 | 0.1655 | 0.1574 | 0.4455 | 0.3685 |
| ∑ Specific pore area ($m^2$/g) | 2.7213 | 2.7733 | 6.3364 | 0.2162 | 3.1306 |
| Median pore diameter (volume) (μm) | 91.3958 | 2.0582 | 1.2556 | 14.1122 | 17.6230 |
| Median pore diameter (area) (μm) | 0.0085 | 0.0211 | 0.0091 | 4.5069 | 0.0082 |
| Apparent density (g/ml) | 1.7531 | 1.4230 | 1.4936 | 1.0103 | 1.0180 |
| True density (g/ml) | 1.9623 | 1.8615 | 1.9529 | 1.8371 | 1.6289 |
| Porosity (%) | 10.65 | 23.56 | 23.52 | 45.00 | 37.95 |

size distribution of the pores in the structure of ulexite. Median diameter of the pores was found to decrease from 91.3958 to 1.2556 μm at 320°C and then increased to 17.623 μm at 850°C. The increase can be attributed to the formation of microcracks throughout the structure during the removal of water. The increase may be due to the enlargement and folding of the pores during recrystallization.

## 4. Conclusions

Under heat treatment, ulexite loses its water of cryztallization while undergoing various mineralogical and structural changes.

Thermal decomposition of ulexite occurred within the temperature range 60–500°C with a two-stage dehydration proceeded with a two-stage dehydroxylation. With dehydroxylation, the samples became amorphous with the gradual liberation of water vapour, the structure develops numerous microcracks and exfoliates without decrepitating.

The microcracks increased the porosity. The changes increased the degree of discontinuity within the structure and made the material more easy to grind.

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