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INVESTIGATION OF STRUCTURAL CHEMISTRY OF THERMAL PROCESSES APPLIED FOR IMPROVEMENT OF GRINDABILITY OF ULEXITE

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In this investigation, mechanism of the thermal processes and effect of the mineralogical and structural modifications on the grindability of ulexite were investigated. The mechanism of the thermal reactions were examined by thermo-analytical methods including TGA and DTA. The mineralogical and structural modifications were investigated by XRD and SEM techniques, respectively. The results indicated that ulexite thermally decomposes within 60-500°C. The structure was first transformed into $\text{NaCaB}_5\text{O}_6(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ and then $\text{NaCaB}_5\text{O}_6(\text{OH})_6 \cdot \text{H}_2\text{O}$ and finally became as completely X-ray amorphous phase accompanied with the thermal processes in the sequence of two-stage dehydration and two-stage dehydroxylation reactions resulting in two endothermic DTA peaks at 151°C and 180°C. Further treatment caused two-stage recrystallization processes resulting in an exothermic DTA peak at 636°C and an endothermic peak at 855°C. The changes in the grindability of ulexite were determined in terms of work index by the Hardgrove Grindability Test. The results showed that work index of ulexite was found as 7.11 kWh/shton and decreased to 3.5 kWh/shton level within 200-280°C for 60 minutes. Further heating lead to 8.49 kWh/shton at 640°C for 60 minutes.

Keywords: ulexite, thermal reaction, thermal decomposition, grindability

INTRODUCTION

Ulexite is Na-Ca hydrated borate consisting of both OH species and water of crystallization. Under heat treatment, some thermal reactions take place. The mineral

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ulexite ($\text{NaCaB}_3\text{O}_9 \cdot 8\text{H}_2\text{O}$) first gradually removes its water of crystallization and then either becomes amorphous or recrystallizes into newly formed crystalline phase while the structure undergoes significant structural changes. It only exfoliates due to gradual removing of water vapor within inducing the structure as amorphous state having numerous numbers of microcracks and interstices throughout the structure. This makes the structure weak and easily grindable (Şener, 1991; Şener and Özbayoğlu, 1995). There is a strong relationship between heat treatment and grindability of minerals. The change in chemical and mineralogical composition, degree of discontinuity due to heating may cause to decrease strength of the structure in such a way that the chemical bonds are broken and the structure is more disordered (Şener 1997; Şener and Özbayoğlu 1999).

In this study, the nature and mechanisms of thermal reactions accompanied with the mineralogical and structural changes in the structure of ulexite during heat treatment were examined and effect of the structural chemistry of the thermal processes on grindability of ulexite were investigated.

MATERIALS AND METHODS

Ulexite samples used throughout the study were prepared from the ulexite concentrates taken from Balıkesir-Bigadiç Mine of Etibank. Hand picked coarse crystals were cleaned by dipping them in water and then washing to remove dispersed clay minerals. The cleaned and air dried samples were crushed, ground and screened, and $-1.168+0.600$ mm sized samples kept for the subsequent experiments. The purity of the sample was found to be around 96% on the basis of B_2O_3 content. The chemical analysis of the sample is given in Table 1.

Conventional thermo-gravimetric (TG), differential thermo-gravimetric (DTG) and differential thermal analyses (DTA) were performed to determine amount of H_2O removed, temperature, nature and mechanism of thermal decomposition and reconstitution reactions. The Thermal Science brand TG1500 model thermo-gravimetric analyzer equipped with a microbalance system was used in the TG and DTG analyses. The Rigaku brand Thermoflex TG8110 model differential thermal analyzer was used in the DTA analysis. All the experiments were performed in a Rh-Pt crucible with the heating rate of $10^\circ\text{C}/\text{min}$ under the flow of N_2 to sweep out accumulated water vapor produced during the decomposition.

The calcination tests were performed in a Heraeus brand muffle furnace equipped with time proportioning temperature control system that provides $\pm 0.8\text{ }^\circ\text{C}$ sensitivity from the set point of temperature. In the procedure, the furnace was first set to the desired temperature with the empty porcelain crucible in cylindrical shape with the volume of 340 cm^3 and then the experiment was started right after 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.

Table 1. The Chemical Analysis of Ulexite Sample

Chemical Compounds, %	Ulexite
B ₂ O ₃	41.17
CaO	18.80 *
Na ₂ O	7.50
SiO ₂	0.85
MgO	0.22
K ₂ O	0.02
Fe ₂ O ₃	0.09
Al ₂ O ₃ +TiO ₂	0.85
Loss of ignition at 800°C	33.83

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

Mineralogical and structural changes and the identification of crystalline structure of the phases were carried out by X-ray diffraction analysis (XRD). In the analyses, Philips PW 1840 and Rigaku Miniflex brand X-ray powder diffractometers with Ni filtered CuK_α radiation were used. The surface characterization were performed by Leitz brand AMR 1000 model scanning electron microscope (SEM).

The changes in the grindability were evaluated with respect to work index, W_i. The standard Hardgrove grindability test was employed with Neco brand Hardgrove machine in accordance to ASTM D 409-93a, 1971.

RESULTS AND DISCUSSIONS

The temperature of decomposition, nature and mechanism of the thermal reactions occurred in the structure of ulexite are given in Figure 1. As seen in the figure, three distinct reactions were observed. The first reaction was due to the thermal decomposition of ulexite and occurred in two stages dehydration and two stage dehydroxylation reactions within 60-500°C. The dehydration reactions occurred within 60-260°C resulting in two overlapped endothermic DTA peaks at 151 and 180°C. The first stage of the dehydration reaction proceeded up to 180°C with a new crystalline phase [NaCaB₅O₆(OH)₆3H₂O] formation and the corresponding weight loss was about 8% (two moles of H₂O). The second stage of the dehydration reaction began at 151°C, then proceed up to 260°C (as being overlapped with the first stage of

the dehydration reaction within 151-180°C). The corresponding weight loss was about 17% (four moles of H₂O) at 180°C. A new crystalline phase which was identified as [NaCaB₅O₆(OH)₆H₂O] was produced. The mineralogical transformation within 120-260°C is given in Figure 2.

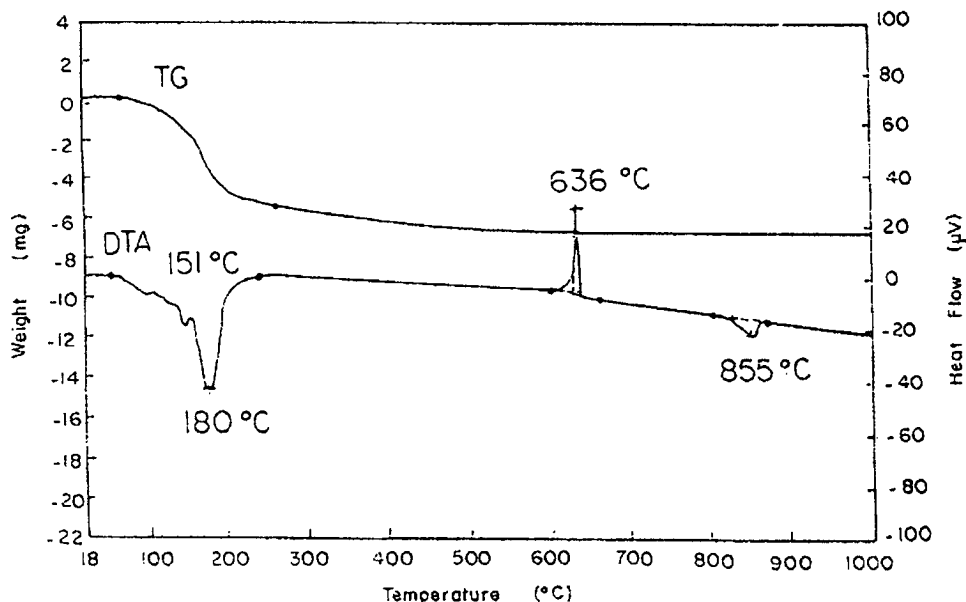


Fig. 1. TG and DTA curves of ulexite

The first stage of the dehydroxylation reaction took place within 180-260°C (as being overlapped with the second stage of the dehydration reaction) during which 26% weight loss (corresponds to 6 moles of H₂O; 5 moles by removing water of crystallization and 1 mole by splitting the OH groups) was obtained. The remaining 2 moles of water was gradually removed from the structure in a continuous way during the second stage of the dehydroxylation up to 500°C. The reaction did not give any peak but negative heat flow was observed along DTA curve up to 600°C, as seen in Figure 1. During the reaction, the structure was transformed into a completely X-ray amorphous state.

The gradual liberation of water vapour during the dehydration and dehydroxylation reactions has caused the structure having numerous numbers of microcracks and has exfoliated without decrepitating. The structural modifications were observed in the SEM microphotographs of ulexite calcined at 240°C given in Figure 3.

The second reaction in the DTA curve in Figure 1, was reconstitution reaction which was observed within 600-640°C giving an exothermic peak at 636°C. The

amorphous structure has been recrystallized as NaCaB_5O_9 (Şener 1997). The structural modification was observed in the SEM microphotographs of ulexite calcined at 600°C given in Figure 4. As seen in the figure, the cavities along the microcracks and partings was reduced and folded and so the structure was transformed into reniform (kidney-like shape) texture due to rebuilding and shrinkage of the aggregates during the recrystallization.

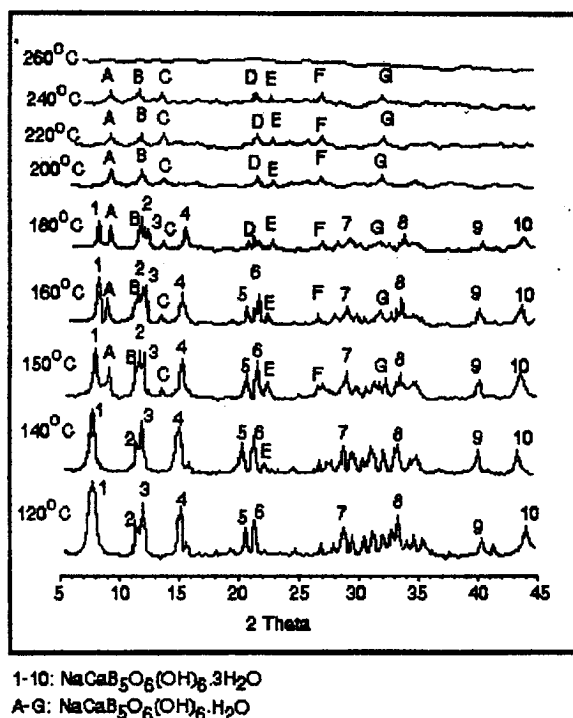


Fig. 2. Comparative results of the XRD patterns of ulexite calcined at 120 – 260°C

The third reaction in the DTA curve was again reconstitution reaction giving an endothermic peak at 855°C . The crystal NaCaB_5O_9 has been transformed into CaB_2O_4 remaining NaB_3O_5 in amorphous (Şener 1997). The SEM microphotographs of ulexite calcined at 850°C given in Figure 5 showed that the structure was in spongy texture containing open and closed pores due to partial fusion of the structure.

According to the results derived from the DTA and XRD examinations, the overall thermal reactions occurred in the structure of ulexite is given in equation (1).

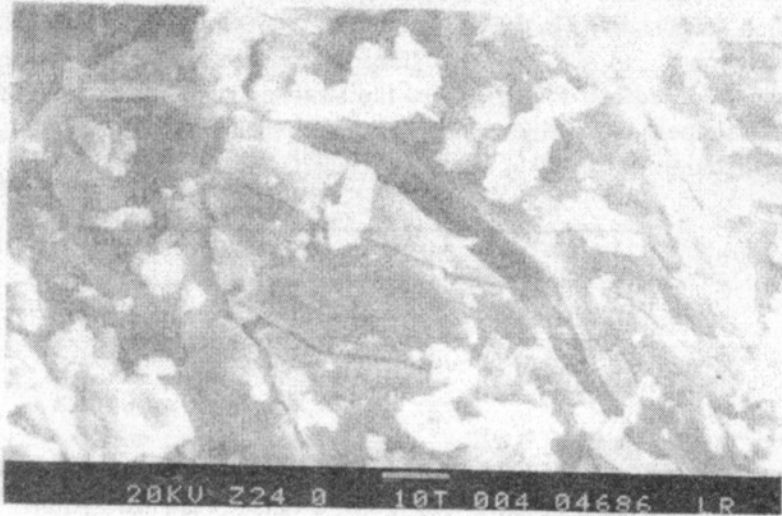


Fig. 3. Microphotograph of the SEM image of ulexite calcined at 240°C (2000x)

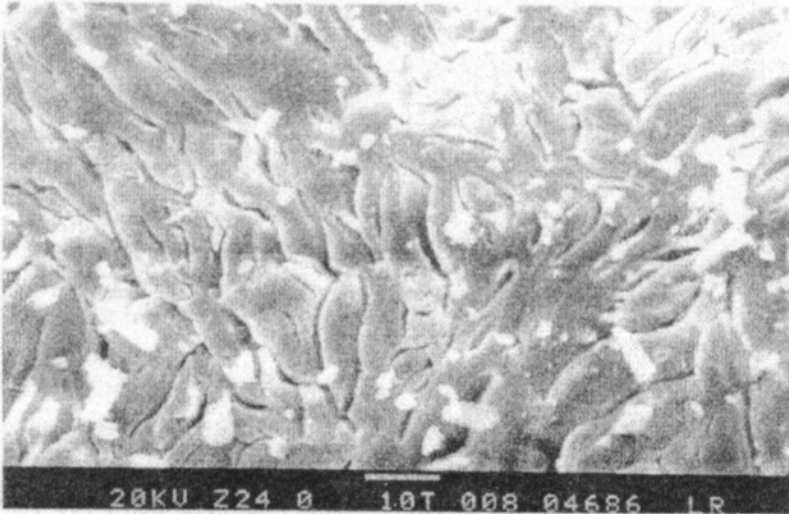


Fig. 4. Microphotograph of the SEM image of ulexite calcined at 600°C (2000x)

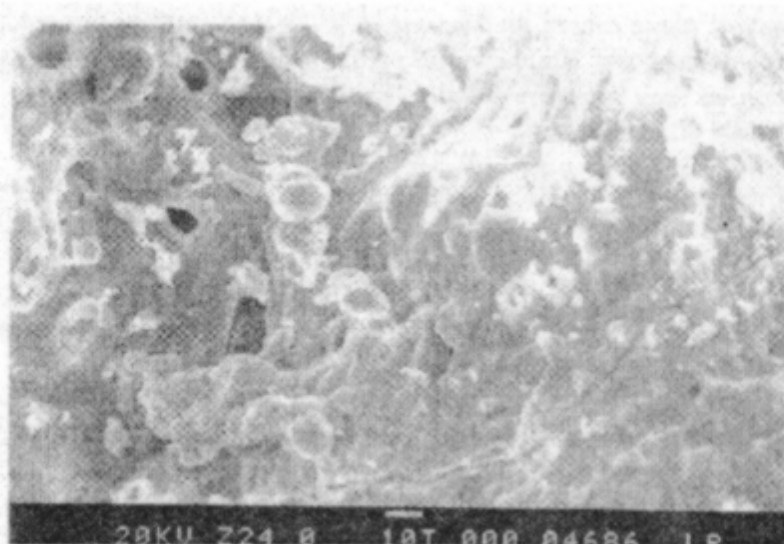
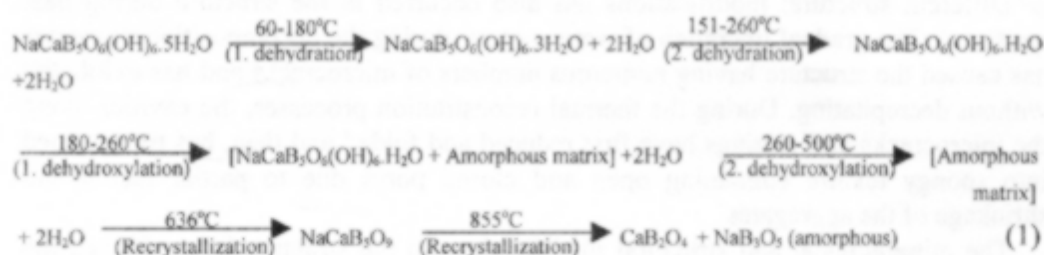


Fig. 5. Microphotograph of the SEM image of ulexite calcined at 850°C (1000x)



The effect of heat treatment on grindability of ulexite was measured in respect to work index (W_i). W_i of the uncalcined ulexite sample was found as 7.11 kWh/shton. The W_i of ulexite sharply decreased to 3.8 kWh/shton at 200°C and 3.5 kWh/shton at 280°C and reached to the minimum value of 3.45 kWh/shton at 320°C thereafter it sharply increased to 8.49 kWh/shton at 640°C.

The decrease in W_i was attributed to the mineralogical and structural changes in the structure. The gradual liberation of the produced water vapour due to heat treatment caused the structure to transform into chemically more disordered crystalline and amorphous phases and to form numerous microcracks and interstices throughout the structure (see Figure 3). This caused to increase the degree of discontinuity and porosity of the structure and makes it easily grindable. The reconstitution of the amorphous phase and the transformation of the structure into structurally more

ordered crystalline phase caused the increase in W_i . It was attributed to reducing and folding the microcracks and, shrinkage and partial fusion of the aggregates during the recrystallization, as seen in Figure 4 and 5. This gained the structure higher strength and made it hardly grindable.

CONCLUSIONS

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

Thermal decomposition of ulexite has occurred within 60-500°C with two-stage dehydration proceeded by two-stage dehydroxylation reactions. Crystal structure has been transformed first into multi-domain heterogeneous matrix containing both crystalline and amorphous phases and then into completely X-ray amorphous state. Amorphization process has taken place along with dehydroxylation reaction.

Thermal reconstitution of the amorphous phase has taken place above 600°C. The amorphous structure has been first recrystallized as NaCaB_5O_9 at 636°C and then it has been transformed into CaB_2O_4 remaining NaB_3O_5 in amorphous at 855°C.

Different structural modifications has also occurred in the structure during heat treatment. The gradual liberation of water vapour during the decomposition processes has caused the structure having numerous numbers of microcracks and has exfoliated without decrepitating. During the thermal reconstitution processes, the cavities along the microcracks and partings have first reduced and folded and then, has transformed into spongy texture containing open and closed pores due to partial fusion and shrinkage of the aggregates.

The mineralogical and structural modifications in the structure have affected the work index of ulexite. The heat treatment within 200-360°C improved the grindability.

REFERENCES

- ŞENER S. (1991), *Beneficiation of Balıkesir-Bigadiç ulexite concentrate by calcination*, M.Sc. Thesis, METU, Ankara, Turkey.
- ŞENER S. (1997), *Determination of mechanisms of thermal reactions in the structure of ulexite and its use in the separation of ulexite from colemanite*, Ph.D. Thesis, METU, Ankara, Turkey.
- ŞENER S. , ÖZBAYOĞLU G. (1995), *Separation of ulexite from colemanite by calcination*, Minerals Engineering, 8:6, 697-704.
- ŞENER S. ÖZBAYOĞLU G. (1999). *Effect of structural changes on grindability of some boron minerals*. SME Annual Meeting. 99-13, Denver, Colorado.

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W pracy badano mechanizmy procesów termicznych i wpływu przemian mineralogicznych i strukturalnych na rozdrobialność ulexytu. Badania mechanizmów reakcji prowadzono metodą analizy termicznej w tym TGA i DTA, a zmiany mineralogiczne i strukturalne za pomocą technik XRD i SEM. Wyniki wskazują, że ulexyt ulega termicznemu rozkładowi w zakresie 60-500°C. Najpierw powstaje $\text{NaCaB}_5\text{O}_6(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ a potem $\text{NaCaB}_5\text{O}_6(\text{OH})_6 \cdot \text{H}_2\text{O}$ ostatecznie stając się amorficzny. Towarzyszą temu procesy termiczne, kolejno, dwustopniowe odwodnienie i dwustopniowa dehydroksylacja powodujące dwa endotermiczne piki na krzywej DTA przy 151°C i 180°C. Dalsze ogrzewanie powoduje dwustopniową rekrytalizację powodującą egzotermiczny pik przy 636°C oraz endotermiczny pik przy 855°C. Zmiany rozdrabialności ulexytu określono za pomocą testu rozdrabialności Hardgrove'a. Stwierdzono, że indeks rozdrabialności ulexytu wynosi 7.11 KWh/krótką tonę i maleje do 3.5 KWh/krótką tonę dla próbek wygrzewanych w zakresie 200-280°C przez 60 minut. Dalsze ogrzewanie w temp. 640°C przez 60 minut podnosi wartość indeksu do wartości 8.49 KWh/krótką tonę.