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A thermodynamic analysis of the decrepitation process

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Abstract

The decrepitation properties of the two typical boron minerals colemanite and ulexite reveal that, whereas colemanite undergoes decrepitation, ulexite shows no sign of significant fragmentation upon heating. This process enables separation of colemanite from ulexite at temperatures above 400°C. A thermodynamic evaluation of 14 boron minerals has shown that only colemanite exhibits decrepitation. A mechanism involving the temperature differential at the onset of dehydration and decomposition and the resultant enthalpy change is proposed as being responsible for this intriguing phenomenon.

Keywords: Boron mineral; Calcination; Colemanite; Decrepitation; Thermodynamics

1. Introduction

Despite over 150 boron minerals' having been identified, only about a dozen of them are found in commercial deposits and fewer than half of these are considered as ores [1]. The boron minerals of greatest commercial importance are borax ($Na_2B_4O_7 \cdot 10H_2O$), colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$), ulexite ($NaCaB_5O_9 \cdot 8H_2O$) and kernite ($Na_2B_4O_7 \cdot 4H_2O$). A majority of boron minerals is found in the hydrated form. Colemanite and ulexite are frequently found together, and their separation by surface based processes such as flotation is difficult owing to similarities in their surface properties.

Hydrated boron minerals undergo a reduction in their original weight upon heating because the water molecules are driven off. Thermal treatment of boron minerals also results in some structural modifications owing to the formation of

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micropores and the resultant expansion of the crystal matrix through development of uneven stresses. Such internal stresses subsequently produce fractures and in turn fragmentation of the crystals. When heated to decomposition temperature, some minerals, such as colemanite, decrepitate to a fine powder. A similar phenomenon may also occur upon cooling. This phenomenon is called decrepitation. In the case of colemanite, visible decrepitation appears to start with the loss of the first water molecule. However, one should distinguish between decrepitation and calcination of volatile minerals, e.g. barite and calcite, where the original mineral is converted into its oxide form.

The decrepitation and calcination properties of colemanite ore have been studied to some extent [2–5]. The fragmentation behavior of colemanite and ulexite upon decrepitation has recently been studied [6]. To our knowledge, most colemanites, including Turkish colemanite samples from the three different boron deposits and Californian colemanites [2], show spontaneous decrepitation. Preliminary studies indicated that, although most boron minerals exhibit various degrees of hydration, only colemanite appears to undergo decrepitation. No plausible reason has been afforded to explain this phenomenon.

The objective of this study was therefore to analyze the thermal properties of fourteen hydrated boron minerals and to identify the mechanism of the decrepitation phenomenon for boron minerals.

2. Experimental

2.1. Materials

Colemanite and ulexite crystals of highest purity, hand picked from the Bigadic boron deposit, Turkey, were subjected to crushing followed by sizing. The samples obtained had an assay purity of $>98\%$.

2.2. Methods

Decrepitation tests were conducted in a Heraeus muffle furnace. The tests were carried out in a 600 cm^3 (10 cm $\times$ 15 cm $\times$ 4 cm) steel box with a lid. The sample box was first brought to the desired test temperature; a 50 g sample was immediately placed in the box, which was then returned to the furnace to start the experiment. At the end of each experiment, the sample box was taken out and weighed immediately to determine the water loss. Screen analysis was then performed on each sample, followed by chemical and microscopic analysis, if necessary.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) as reported by Piskin [7] was conducted by the methods given by Wendlandt [8] and Duval [9]. TG was used to determine the dehydration pattern of boron minerals, the loss of water molecules as a function of temperature and, in conjunction with DTA data, to identify phase transformations. A Linseis model L81 thermogravime-

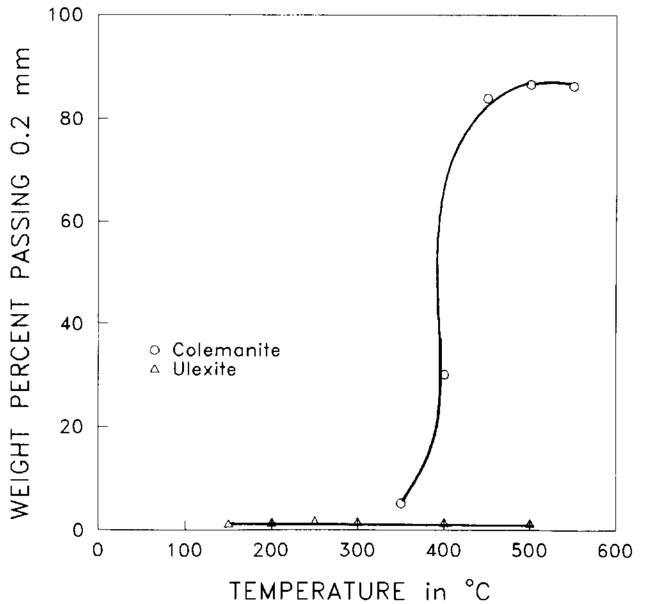


Fig. 1. Decrepitation behavior of colemanite and ulexite as a function of temperature as measured by percentage passing a 0.2 mm screen.

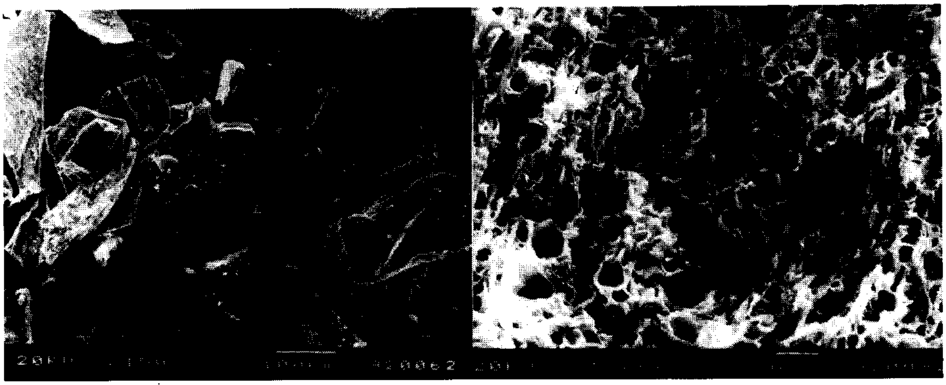
ter with capability to work in both horizontal and vertical directions was used. A heating rate of 10°C min^{-1} and a Pt/PtRh10% thermocouple were used.

DTA measurements were carried out with Linseis L62 equipment using the methods described by Mackenzie [10]. Alumina was used as a reference material. Platinum crucibles with 100 mg capacity were employed in the measurements and a thermocouple made of Pt/PtRh10% was used.

3. Results and discussion

Decrepitation studies were carried out based on the optimum conditions established previously [6]. For colemanite these are a reaction temperature of 500°C and a reaction time of 15 min. A screen size of 0.2 mm was used to measure the performance of the decrepitation process. Unlike colemanite, ulexite exhibited maximum fragmentation at 250°C with a 15 min reaction time. However, ulexite did not undergo decrepitation in its real sense but fragmented because of the handling processes such as heating and screening.

Fig. 1 illustrates the effect of temperature on the fragmentation of 1.68 mm × 1.00 mm portions of colemanite and ulexite as measured by the percentage passing a 0.2 mm screen size. The screen size of 0.2 mm was found to be convenient for measuring the ability of boron minerals to decrepitate [6]. It is evident from Fig. 1 that ulexite indeed does not undergo decrepitation at any of the temperatures studied.



(a) (b)

Fig. 2. Scanning electron micrographs of colemanite: (a) before decrepitation; (b) after decrepitation (500°C, 15 min).

Visual examination coupled with the fragmentation patterns revealed that colemanite decrepitates to a fine powder whereas ulexite does not undergo decrepitation. Scanning electron microscope (SEM) images were taken under different conditions to identify further the structure and morphology of the heat treated colemanite and ulexite. Colemanite was found to show a porous structure following heat treatment (Figs. 2(a) and 2(b)); the porosity increased with increase in temperature and reaction time. In contrast to this, a typical micrograph of a ulexite sample after heat treatment, illustrated in Figs. 3(a) and 3(b), revealed no apparent structural change before and after "decrepitation" except the deposition of fragmented fines on the heat treated ulexite. This further confirms that ulexite does not decrepitate. X-ray diffraction analysis of the ulexite samples upon heat treatment is reported to reveal an amorphous structure [11]. The shrinkage observed on heating ulexite (Fig. 3(b)) is consistent with this finding.

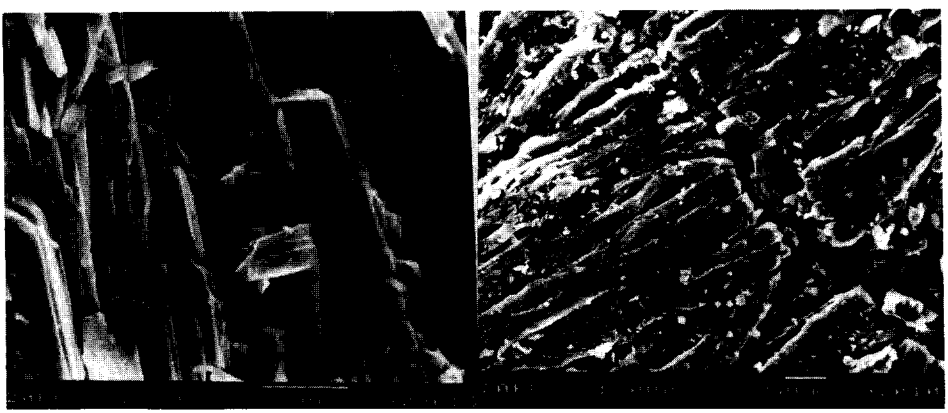
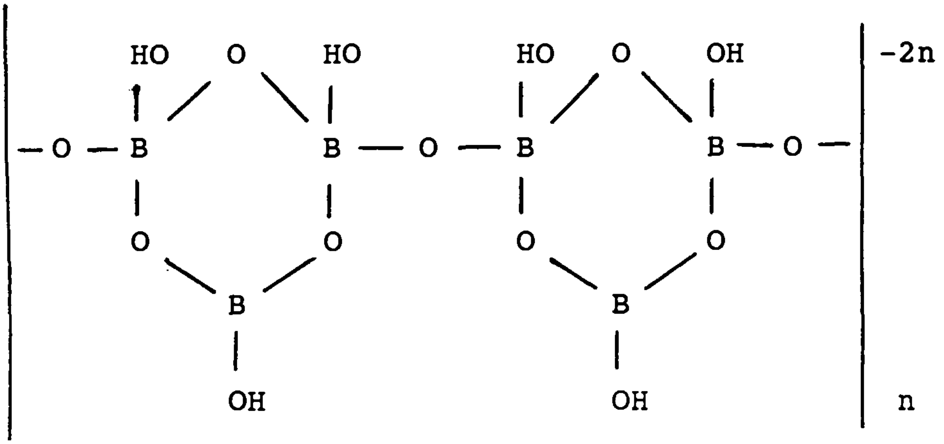
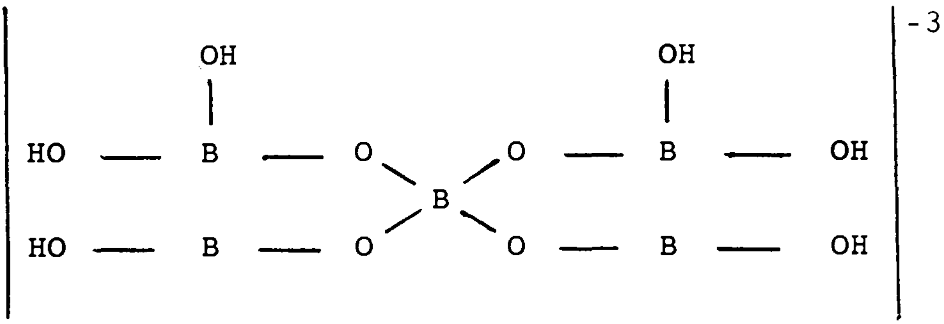


Fig. 3. Scanning electron micrographs of ulexite: (a) before heat treatment; (b) after heat treatment (250°C, 15 min).



(a)



(b)

Fig. 4. The basic structural unit for boron minerals: (a) colemanite; (b) ulexite.

3.1. Decrepitation mechanism of boron minerals

The structure and crystal-chemical classification of hydrated borates has been studied in detail [12–14]. The basic structural unit for colemanite and ulexite is shown in Fig. 4. All borates are composed of fundamental building blocks (FBB) which lead to different types of polyanions. The structural formula of ulexite is depicted as $NaCa[B_3O_4(OH)_3] \cdot H_2O$ [12,13,15]. The pentaborate FBB is found isolated and fully hydrated in the structure of ulexite [16]. Colemanite consists of $Ca[B_3O_4(OH)_3] \cdot H_2O$. The structure of colemanite is represented as $[B_3O_4(OH)_3]$, which is equivalent to

$$n[B_3O_3OH)_5]^{2-} = [B_3O_4(OH)_3]_n^{2n-} + nH_2O \quad (1)$$

The FBB structucture of colemanite is in the form of repeating triborate units. Hydrated boron minerals exhibit hexagonal, monoclinic and triclinic crystal structures. However, there is no correlation between the crystal structure of a mineral

Table 1
Dehydration data for colemanite [7]

Water loss/mol	Temperature/°C	Type of water loss
1	327	**
2	338	**
3	345	***
4	363	***
5	412	***

** Free crystal water. *** Release of water molecules within the polyanions in the form of $(OH)^{-1}$.

and the tendency of the mineral to undergo decrepitation. Therefore a thermodynamic analysis was carried out to clarify the reason why only colemanite is conducive to decrepitation.

The dehydration data for colemanite and ulexite obtained by Piskin [7] using TG analysis are presented in Tables 1 and 2. It is evident that the temperature of onset of dehydration for colemanite is 262°C and the first water molecule is lost only at 327°C, which coincides approximately with the onset of decrepitation. In contrast to this, the onset tempaerature of dehydration for ulexite is 59°C and the loss of the first water molecule occurs at 105°C. This reveals that colemanite loses its five water molecules in a narrow temperature range. Ulexite, on the other hand, loses its water gradually over a much wider temperature range. The rapid water loss causes the crystal matrix of colemanite to expand suddenly owing to the development of uneven stresses. Such internal stresses subsequently produce fractures and in turn fragmentation of the crystals.

The enthalpy values obtained by DTA analysis are presented in Table 3. Examination of Table 3, based on the evaluation of 14 hydrated boron minerals reported by Piskin [7], reveals that colemanite has the highest enthalpy value prior to dehydration among all the hydrated boron minerals studied. Interestingly, colemanite also exhibits the highest dehydration temperature. More interestingly,

Table 2
Dehydration data for ulexite [7]

Water loss/mol	Temperature/°C	Type of water loss
1	105	* + **
2	137	**
3	162	**
4	178	**
5	185	**
6	196	***
7	267	***
8	449	***

* Capillary water. ** Free crystal water. *** Release of water molecules within the polyanion in the form of $(OH)^{-1}$.

Table 3
Dehydration and decomposition temperatures of 14 boron minerals together with their enthalpy values prior to dehydration

Mineral	Formula	Crystal structure	T_1	T_2	ΔT	ΔH
Kernite	$Na_2B_4O_7 \cdot 4H_2O$	Monoclinic	63	445	382	14.80
Tincalconite	$Na_2B_4O_7 \cdot 5H_2O$	Hexagonal	39	200	161	5.60
Probertite	$NaCaB_5O_9 \cdot 5H_2O$	Monoclinic	57	422	365	14.80
Ulexite	$NaCaB_5O_9 \cdot 8H_2O$	Triclinic	59	449	390	27.04
Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$	Monoclinic	262	412	150	149.52
Pandermite	$Ca_4B_{10}O_{19} \cdot 7H_2O$	Triclinic	196	550	354	110.77
Hydroboracite	$CaMgB_6O_{11} \cdot 6H_2O$	Monoclinic	170	800	154	62.99
Meyerhofferite	$Ca_2B_6O_{11} \cdot 7H_2O$	Triclinic	67	221	393	31.60
Inyoite	$Ca_2B_6O_{11} \cdot 13H_2O$	Monoclinic	57	450	393	14.80
Kurnakovite	$Mg_2B_6O_{11} \cdot 15H_2O$	Monoclinic	61	403	342	14.21
Inderite	$Mg_2B_6O_{11} \cdot 15H_2O$	Triclinic	47	420	373	19.06
Veatchite	$Sr_4B_{22}O_{37} \cdot 7H_2O$	Monoclinic	36	624	588	5.52
Tunellite	$SrB_6O_{10} \cdot 4H_2O$	Monoclinic	57	625	568	17.68
Howlite	$Ca_4B_{10}O_{23}Si_2 \cdot 5H_2O$	Monoclinic	87	610	523	23.70

Key: T_1, temperature at onset of dehydration in °C; T_2, decomposition temperature in °C; $\Delta T = T_2 - T_1$; ΔH, enthalpy prior to dehydration in J mol^{-1} g^{-1} (calculated from 25°C to T_1).

the temperature difference ΔT between the onset of dehydration and decomposition is the lowest for colemanite, as seen in Table 3. Although the ΔT values of other minerals such as meyerhofferite and tincalkonite are close to that of colemanite, these minerals are not eligible for decrepitation because their enthalpy values are lower than that of colemanite. In addition, meyerhofferite and tincalconite cannot decrepitate, as the temperature for onset of dehydration for both minerals is low, viz. 67°C and 39°C, respectively. Correspondingly, the decomposition temperatures, namely 221°C and 200°C, are not sufficient for inducing decrepitation. Only hydroboracite appears to behave abnormally in that it exhibits a high ΔH value despite a high ΔT value. To our knowledge, this interpretation based on the thermodynamic data is reported for the first time in the literature.

4. Conclusions

1. Colemanite undergoes the decrepitation process, but ulexite does not decrepitate in a real sense but becomes friable when subject to processes such as heating and handling.

2. The scanning electron micrographs indicate that colemanite turns into a porous material upon decrepitation, whereas ulexite shows no significant structural change except shrinkage in appearance. Ulexite exhibits shrinkage with increasing temperature and acquires an amorphous structure.

3. Examination of the thermal properties of 14 hydrated boron minerals reveals that only colemanite is capable of decrepitation. The mechanism of decrepitation for colemanite is ascribed to the temperature differential between the onsets of

dehydration and decomposition together with the enthalpy of colemanite prior to dehydration. This mechanism is believed to be reported for the first time in the literature.

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