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# Dehydration kinetics of howlite, ulexite, and tunellite using thermogravimetric data

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## Abstract

In this study, some boron mineral samples (howlite, ulexite and tunellite) have been analysed by DTA and TG methods. The thermochemical reactions of these boron compounds have been studied. The dehydration kinetic parameters for howlite, ulexite and tunellite were activation energies: 65.0, 39.5 and 50.4 kJ $\mathrm{mol}^{-1}$; the pre-exponential factors: $50.8\times10^5$, $6.60\times10^5$, $32.4\times10^5$ $\mathrm{s}^{-1}$ and rate constants: 70.1, 113.1 and 82.3 $\mathrm{s}^{-1}$, respectively, at a constant heating rate of 10 K $\mathrm{min}^{-1}$. The average particle size was 200 μm for all samples. The order of dehydration reactions ($n$) was accepted as first order.

## 1. Introduction

Nearly 62% of the total boron reserves of the world are in Turkey which has rich boron resources, and a boron industry has been developing continuously. There are large boron reserves in Western Anatolia, Turkey. In recent years, boron industry has developed quickly in Turkey. Depending on this parallel development, investigations into boron minerals has continuously developed by Turkish researches [1–6].

Howlite, ulexite and tunellite have the formulae $Ca_2B_5SiH_5O_{14}$, $NaCaB_5H_{16}O_{17}$ and $SrB_6H_8O_{14}$, respectively, and are important boron minerals. At present, they are used in the production of fire-resistive chemical substances, insulators, and glass [7]. The theoretical compositions of howlite, ulexite and tunellite are 28.66% CaO, 15.34% $SiO_2$, 44.49% $B_2O_3$, 11.51%; 11.74% $Na_2O$, 21.21% CaO, 12.50% $B_2O_3$, 54.55% $H_2O$ and 26.94% SrO, 54.32% $B_2O_3$, 18.74% $H_2O$, respectively. The dehydration of the hydrated minerals are important in the production of boron compounds.

The dehydration of hydrated boron minerals has been investigated [8,9] for a long time. This has generally been based on slow dehydration and thermogravimetric methods. In a study carried out by Gülensoy [10], the dehydration of pandermite, colemanite and howlite minerals was investigated in a temperature range of 520–820 K over 5 h. Davies et al. [11] compared the leaching behaviour of colemanite minerals calcined by flash and slow calcination methods, and found that the minerals calcined by flash method at 870 K for <1 s could be leached more effectively than minerals calcined by slow methods at 670 K for 13 h.

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## 2. Experimental

The boron minerals used in this study were supplied as followed: howlite Sağir Köyü-Damyan-Sindirgi in Balikesir; ulexite Kirka in Eskişehir and tunellite Göcenoluk-Kirka-Seyitgazi in Eskişehir (Turkey). Chemical compositions were performed by XRD and analytical methods are given in Table 1.

A Schimadzu DTA-TGA system was used for the measurements of TGA and DTA as heat flow against temperature. In the thermal analyses $Al_2O_3$ was used as reference in air.

The initial mass and particle size of the samples used in the measurements were about 100 mg and 200 μm, respectively. The experiments were carried out from ambient temperature to 1100 K with a programmed heating rate of 10 K $min^{-1}$ or 0.17 K $s^{-1}$. Pure $N_2$ and a mixture containing 15% by vol. $CO_2$ and 85% by vol. dry air were used as gaseous atmospheres. The flow rate of gases was maintained at a constant rate of 40 $cm^3$ $min^{-1}$ throughout the measurements. Dehydration TG curves were traced by using a chart speed of 2.5 mm $min^{-1}$.

### 2.1. Theory

In recent years, thermogravimetric (TG) methods have been widely used to study the kinetics of various solid-state decomposition reactions. Dynamic TG has been widely applied to the study of various solid-state processes [12]. The shape of the thermogravimetric curves is a function of the reaction kinetics and, hence, the information obtained from these curves is useful in evaluating the kinetic parameters.

Several computation methods have been presented in the literature which utilize non-isothermal TG data to obtain kinetic information [13].

Generally, the rate of mass loss for a decomposition reaction is described by the Eq. (1),

$$(\mathrm{d}X/\mathrm{d}t) = kf(W) \tag{1}$$

$$X = (W_0 - W)/W_0 \tag{2}$$

$$k = A\exp(-E/RT) \tag{3}$$

$$T = T_0 + bt \text{ or } t = (T - T_0)/b \tag{4}$$

where $X$ is the degree of dehydration or conversion, $W_0$ the initial weight (g), $W$ the remaining weight (g), $t$ the time (s), $k$ the reaction rate constant ($s^{-1}$), $f(W)$ a function depending on the reaction mechanism, $A$ and $E$ the pre-exponential factor ($s^{-1}$) and apparent activation energy (kJ $mol^{-1}$), respectively; $R$ is the gas constant (kJ $mol^{-1}$ $K^{-1}$), $T$ the absolute temperature (K), $b$ the linear heating rate (K $s^{-1}$) and $T_0$ the initial reaction temperature (K). By combining the above expressions one can obtain the general non-isothermal kinetic equation,

$$(\mathrm{d}X)/(\mathrm{d}T) = (A/b)\ \exp\ (-E/RT) \tag{5}$$

$X$ is the fractional weight loss. The simple $n$th order kinetic equation, describing the rate of weight loss of the sample, is taken from Refs. [14–16]:

$$(-1/W_0)(\mathrm{d}W/\mathrm{d}t) = k\ \exp\ (-E/RT)f(W)^n \tag{6}$$

Assuming that

$$f(W)^n = [(W_0 - W)/(W_0)]^n \tag{7}$$

then the logarithmic form for the Eq. (6) at any specific heating rate is:

Table 1
Chemical compositions of howlite, ulexite and tunellite, wt%

| *Mineral* | $Na_2O$ | CaO | SrO | $B_2O_3$ | $SiO_2$ | $H_2O$ | Impurity |
|---|---|---|---|---|---|---|---|
| *Howlite* | | | | | | | |
| Experimental | — | 28.61 | — | 44.03 | 15.19 | 11.60 | 0.57 |
| Theoretical | — | 28.66 | — | 44.48 | 15.35 | 11.51 | |
| *Ulexite* | | | | | | | |
| Experimental | 7.24 | 13.67 | — | 42.44 | — | 35.42 | 1.23 |
| Theoretical | 11.74 | 21.21 | — | 12.50 | — | 54.55 | |
| *Tunellite* | | | | | | | |
| Experimental | — | — | 27.02 | 53.93 | — | 18.80 | 0.25 |
| Theoretical | — | — | 26.94 | 54.32 | — | 18.74 | |

$$\ln[(-1/W_0)(\mathrm{d}W/\mathrm{d}t)] = -(E/RT) + \ln k[(W_0 - W)/(W_0)]^n \qquad (8)$$

assuming that:

$$\ln k[(W_0 - W)/W_0)] = n\ln[(W_0 - W)/(W_0)] + \ln k \qquad (9)$$

The reaction rate constant ($k$) and the order of reaction ($n$) can be calculated from Eq. (9). The combined form of the above equations is:

$$\ln[(-1/W_0)(\mathrm{d}W/\mathrm{d}T)] = -(E/RT) + n\ln[(W_0 - W)/(W_0)] + \ln(A/b) \qquad (10)$$

If $n$=1 the following equation must be used

$$\ln[(-1/W_0)(\mathrm{d}W/\mathrm{d}T)] = -(E/RT) + \ln[(W_0 - W)/(W_0)] + \ln(A/b) \qquad (11)$$

Thus, if drawing a plot of either ln [$(-1/W_0)$ ($\mathrm{d}W/\mathrm{d}T$)] vs. ($1/T$) should result in a straight line of slope $-(E/R)$.

There are various models developed to obtain the kinetic parameters from the thermogravimetric data [17]. In this study to determine the kinetic parameters for the dehydration of howlite, ulexite and tunellite the first order ($n$=1) thermal decomposition model proposed in earlier studies [12,13] was assumed. This method was used to determine the conversion and temperature differences between $\Delta X$ and $\Delta T$ to approximate initial and final conversion levels. It also made use of the average temperature to calculate the pre-exponential factor, $A$. Finally, the rate of reaction constant, $k$, was calculated using $A$ and $E$ values in the Arrhenius equation

$$k = A\mathrm{e}^{(-E/RT)} \qquad (12)$$

## 3. Results and discussion

TGA diagrams for howlite, ulexite and tunellite are given in Fig. 1.

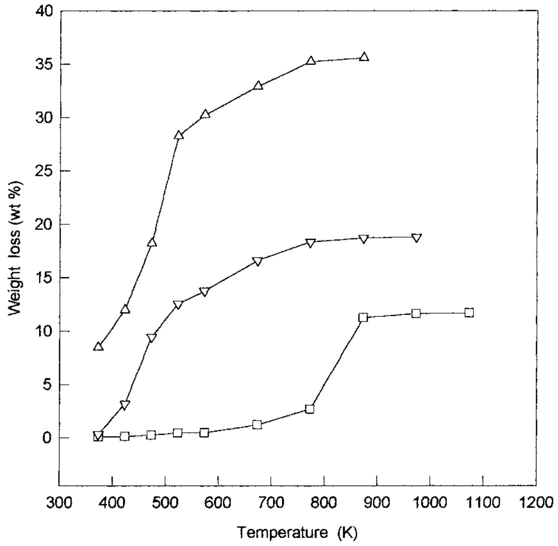

Fig. 1. Weight loss vs. temperature curves for howlite, ulexite and tunelite. □: howlite, △: ulexite, ▽: tunellite.

### 3.1. Analyses of DTA and TGA

In the DTA diagram of howlite, there were two basic endothermic peaks which appeared at 794 and 825 K. From the TGA diagram, the dehydration of howlite began approximately at 373 K, and the dehydration was slow up to 785 K, after this temperature the dehydration continued at a high rate up to 850 K, above 920 K there was no appreciable weight loss.

In the DTA diagram of ulexite, there were two basic endothermic peak which appears at 430 and 460 K. The peak observed at 487 K was larger than the other. According to TGA diagram, the dehydration of ulexite begins ≈275 K, and the dehydration temperature is high up to 505 K, after this temperature the dehydration continues at a quite low rate up to 805 K, above this temperature almost there is no weight loss.

In the DTA diagram for tunellite, there were four basic endothermic peaks which appeared at 417, 456, 509, and 715 K. The peaks observed at 456 and 509 K were larger than the others. According to TGA diagram, the dehydration of tunellite begins ≈373 K, and the dehydration is quite high from 420 to 500 K, after this temperature the dehydration continues at a considerable rate up to 710 K, after this temperature the rate of dehydration increased and then above 820 K almost there is no weight loss.

### 3.2. Dehydration reactions

The conversion was calculated as the ratio of the weight loss to the total weight loss, on the basis of the

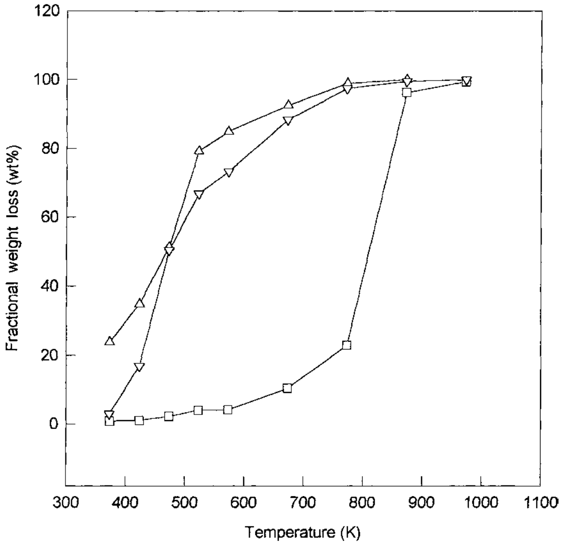

Fig. 2. Fractional weight loss vs. temperature curves for howlite, ulexite and tunellite. □: howlite, △: ulexite, ▽: tunellite.

Table 2
Kinetic parameters for dehydration of howlite, ulexite, and tunellite samples

| Parameter | Howlite | Ulexite | Tunellite |
|---|---|---|---|
| $\Delta X$ [a] | 0.9231 | 0.7268 | 0.7893 |
| $T_1$ (K) [b] | 523 | 373 | 423 |
| $T_2$ (K) [c] | 873 | 723 | 723 |
| $\Delta T$ (K) | 350 | 350 | 300 |
| $\ln\Delta X$ | −0.080 | −0.319 | −0.237 |
| $-\ln(\Delta X/\Delta T)$ ($K^{-1}$) | 5.938 | 6.177 | 5.940 |
| Slope | −7813 | −4752 | −6061 |
| $E$ (kJ $mol^{-1}$) | 65.0 | 39.5 | 50.4 |
| $A$ ($s^{-1}$) | $50.8\times10^5$ | $6.60\times10^5$ | $32.4\times10^5$ |
| $k$ ($s^{-1}$) | 70.1 | 113.1 | 82.3 |

[a] $d\left(\frac{W}{W_0}\right)$ instead of $\Delta X$ and $dT$ instead of $\Delta T$ were used.

[b] Initial dehydration temperature. Linear heating rate ($b$) 0.17 K $s^{-1}$.

[c] Final dehydration temperature. Linear heating rate ($b$) 0.17 K $s^{-1}$.

following reactions

$$\underset{\text{Howlite}}{4CaO\cdot 5B_2O_3\cdot 2SiO_2\cdot 5H_2O} \rightarrow 4CaO\cdot 5B_2O_3\cdot 2SiO_2\cdot xH_2O + (5-x)H_2O \quad (13)$$

$$\underset{\text{Ulexite}}{Na_2O\cdot 2CaO\cdot 5B_2O_3\cdot 16H_2O} \rightarrow Na_2O\cdot 2CaO\cdot 5B_2O_3\cdot xH_2O + (16-x)H_2O \quad (14)$$

$$\underset{\text{Tunellite}}{SrO\cdot 3B_3O_3\cdot 4H_2O} \rightarrow SrO\cdot 3B_3O_3\cdot xH_2O + (4-x)H_2O \quad (15)$$

where $x$ is the moles of water changing between 0 and 5, 16 or 4. The conversion versus temperature graphs were constructed from the TGA data, as shown in Fig. 2.

### 3.3. Kinetic analysis

The kinetic parameters for dehydration of howlite, ulexite, and tunellite samples are given in Table 2. The dehydration kinetic parameters for howlite, ulexite and tunellite are activation energies: 65.0, 39.5 and 50.4 kJ $mol^{-1}$; the pre-exponential factors: $50.8\times10^5$, $6.60\times10^5$, $32.4\times10^5$ $s^{-1}$ and rate constant values: 70.1, 113.1 and 82.3 $s^{-1}$, respectively, by using a constant heating rate of 0.17 K $s^{-1}$.

If the dehydration is carried out with slow heating rate the theoretical weight loss is obtained in a very long period compared with the flash dehydration used in this study. In view of these results, it is obvious that a certain weight loss is reached in a much shorter time in the flash dehydration than in the slow dehydration method. While in the slow dehydration method of ulexite the complete weight loss is approximately at 750 K for 5 h, the temperature to reach to the complete dehydration with the flash dehydration is too high because of its nature. But the residence time is very short in the flash dehydration, hence this method turns out to be more advantageous.

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