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Flash dehydration of ulexite and investigation of dehydration kinetics from thermogravimetric data

Hürriyet Erşahan [a,*], Mehmet Tunç [b], Ahmet Ekmekyapar [a], Sinan Yapıcı [a]

[a] *Atatürk University, Engineering Faculty, Chemical Engineering Department, 25240 Erzurum, Turkey*
[b] *Atatürk University, Institute of Science, 25240 Erzurum, Turkey*

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Abstract

The flash dehydration of a ulexite mineral in an entrained flow reactor was investigated. Flash dehydration experiments were carried out in the range 400–700°C with material of particle size $-425+300$ μm. The weight loss at 700°C dehydration temperature was measured as 22%. A thermal gravimetric method was used to obtain the activation energy and rate constants for the dehydration of ulexite. The activation energy was in the range 48.2–53 kJ mol^{-1} for different particle sizes. The rate constants for different particle sizes were found to vary between 1.8×10^{-4} and 1.35 s^{-1} in the temperature range 110–530°C.

Keywords: Dehydration; DTA; Kinetics; TGA; Ulexite

1. Notation

$E/(\mathrm{kJ\ mol^{-1}})$	Activation energy for the thermal dehydration of ulexite
$E_1(x)$	Exponential integral in Eq. (4)
$k/\mathrm{s^{-1}}$	First-order rate constant for thermal dehydration of ulexite
$k_0/\mathrm{s^{-1}}$	Preexponential factor for the thermal dehydration of ulexite
$m/(\mathrm{K\ s^{-1}})$	Heating rate
$R/(\mathrm{kJ\ mol^{-1}\ K^{-1}})$	Gas constant

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* Corresponding author. Address: Atatürk Üniversitesi Mühendislik Fakültesi, 25240 Erzurum, Turkey; fax 90-442-2187141.

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$T_{1/2}$	Temperature at 50% conversion (Fig. 4)
$\Delta T/\mathrm{K}$	Temperature difference defined in Fig. 3
x	$= E/RT_{1/2}$
x_C	Conversion of ulexite
ξ	$\equiv \Delta T/T_{1/2}$

2. Introduction

Ulexite, which has the formula $Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot nH_2O$, is an important commercial boron mineral. At present, it is commonly used for the production of fire-resistant chemical substances, insulators and fiberglass [1]. In Turkey, an important portion of the ulexite reserves, together with colemanite and other boron minerals, is to be found in the Bigadiç region [1,2].

Most boron minerals, such as ulexite, tincal, colemanite and pandermite, include water. The dehydration of the hydrated minerals is an important stage of preparation before processes for the production of boron compounds.

If the calcination/dehydration processes of minerals are reviewed, it can be seen that these processes have been carried out in two modes. The first mode is slow calcination/dehydration, and the second is the flash (rapid) calcination/dehydration. In the slow methods applied for many years the heating rate is low, $1-10°\mathrm{C\ min^{-1}}$. The residence time of the material subjected to the process is long, in the order of a few hours. In the flash methods, the material is subjected to calcination/dehydration for a very short time and is taken out of the system very quickly. In this method the heating rate is in the range $10^3-10^5 °\mathrm{C\ s^{-1}}$, and the residence time of the solids is in the order of milliseconds to seconds [3]. The flash calcination/dehydration method has the advantage of providing important and useful physical and chemical changes, which may facilitate the subsequent processes, besides having the advantage of a very short process time [4].

The dehydration of hydrated boron minerals has been investigated by some researchers over a long period. These researches have generally been based on the slow dehydration and thermogravimetric methods. In work carried out by Gülensoy [5], the dehydration of pandermite, colemanite and hawlite minerals was investigated in the temperature range 150-550°C over 5 h. In a study of tunellite [6], the dehydration of the mineral by the static and dynamic methods was investigated. Gülensoy and Savcı [7] worked on the dehydration of ulexite, pandermite and colemanite minerals by the static method in the range 50-700°C. These researchers recorded that the dehydration of these minerals was almost complete at 500°C. In a study on the dehydration of terugit mineral by static and dynamic methods [8], it was found that the weight loss was rapid up to 200°C, very slow between 200 and 300°C, and dehydration was complete at 500°C. In work in which the dehydration of ulexite was investigated [9], it was reported that the dehydration was almost complete at 500°C and that the weight loss was negligible above this temperature.

In research carried out by Tuğtepe and Sanıgök [10], the thermogravimetric dehydration of ulexite was investigated at heating rates of 30 and 60°C h^{-1}. In work performed by Stoch and Waclawska [11], the thermal decomposition of ulexite was investigated using TGA, DTG and DTA. In DTA measurements, three endothermic peaks were observed at temperatures of 118, 152 and 181°C.

Davies et al. [12] compared the leaching behaviour of colemanite minerals calcined by flash and slow calcination methods. They found that the minerals calcined by the flash method at 600°C for less than 1 s could be leached more effectively than minerals calcined by the slow method at 400°C for 13 h.

In the light of the above literature review, it is obvious that research on the flash dehydration of the boron minerals is very sparse. In the present study, the flash dehydration of ulexite has been investigated. For this purpose, the mineral was dehydrated in an entrained flow reactor in the temperature range 400–700°C. In addition, the dehydration kinetics of ulexite were investigated employing TGA and DTA measurements.

3. Experimental

3.1. Material

The ulexite mineral used in this study was obtained from the reserves around Eskişehir–Kırka. The chemical analysis performed by X-ray diffraction (XRD) and analytical methods is reported in Table 1. The particle size of the mineral used in the flash dehydration experiments was $-425+300\ \mu m$.

A Schimadzu DTA–TGA system was used for the TGA and DTA measurements. The TGA and DTA curves are given in Fig. 1.

3.2. Flash dehydration

The entrained flow reactor used in the present study is used commonly in the flash calcination of solids as well as in dehydration [4,13]. A feature of this system is the use of a primary gas flow, which can carry the solids into the reactor, and a preheated secondary gas flow which carries the solids through the reactor. The secondary gas flow rate is higher than that of the primary gas.

The entrained flow flash dehydration system used in this study is shown in Fig. 2. The system consisted mainly of a reactor, an oven, a preheater and a temperature

Table 1
Chemical analysis of ulexite

Component	Wt%	Component	Wt%
CaO	13.67	H_2O	35.42
B_2O_3	42.44	Impurity	1.23
Na_2O	7.24		

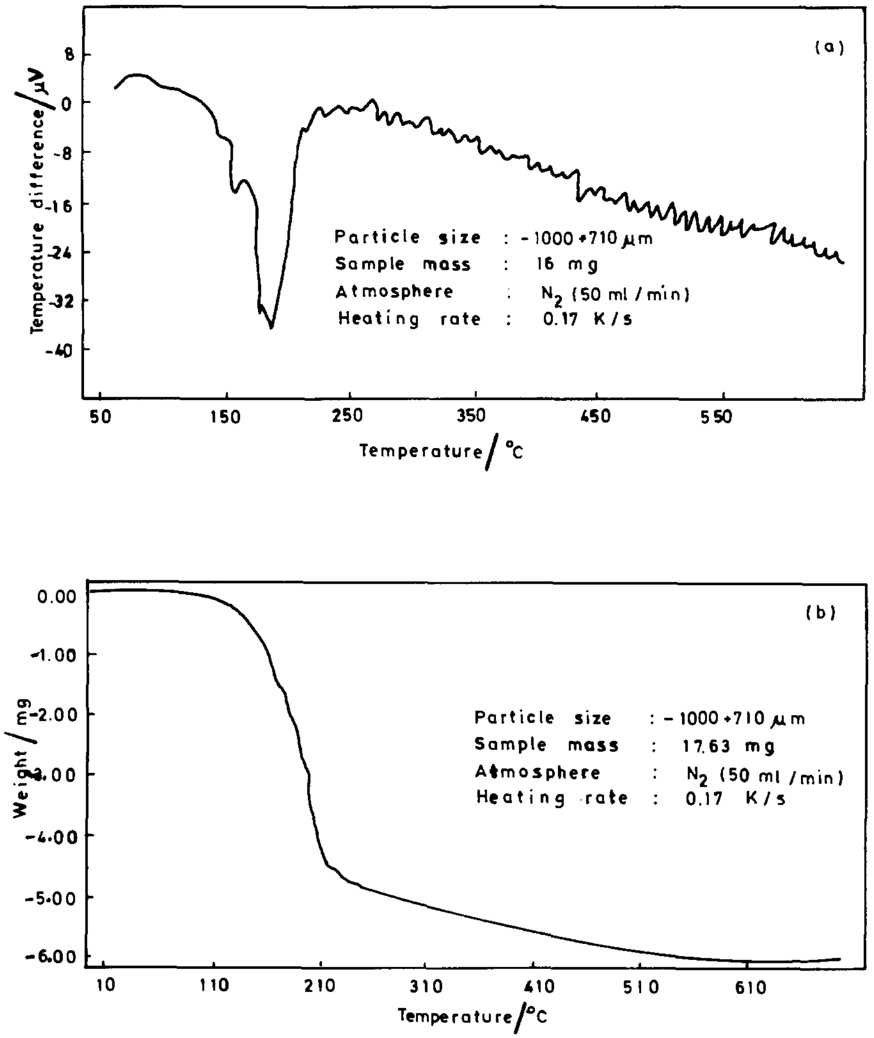

Fig. 1. (a) DTA and (b) TGA diagrams of ulexite.

control unit. The reactor, of ID 2 cm and made of stainless steel, was placed vertically in the oven. The total length of the reactor was 82.5 cm and the heated length was 60 cm. The heating was performed electrically with a resistance wire coiled around a ceramic tube. The reactor temperature was measured in the centre of the reactor with a Ni–Cr thermocouple, and the temperature was controlled by the control unit.

The ulexite was fed into the reactor with the primary gas by means of a mini fluidized bed at a rate of 0.5 g min^{-1}. The secondary gas was supplied to the reactor from the top after preheating to the reactor temperature. The dehydrated solid was passed through a water-cooled jacket outside the heating region of the reactor to

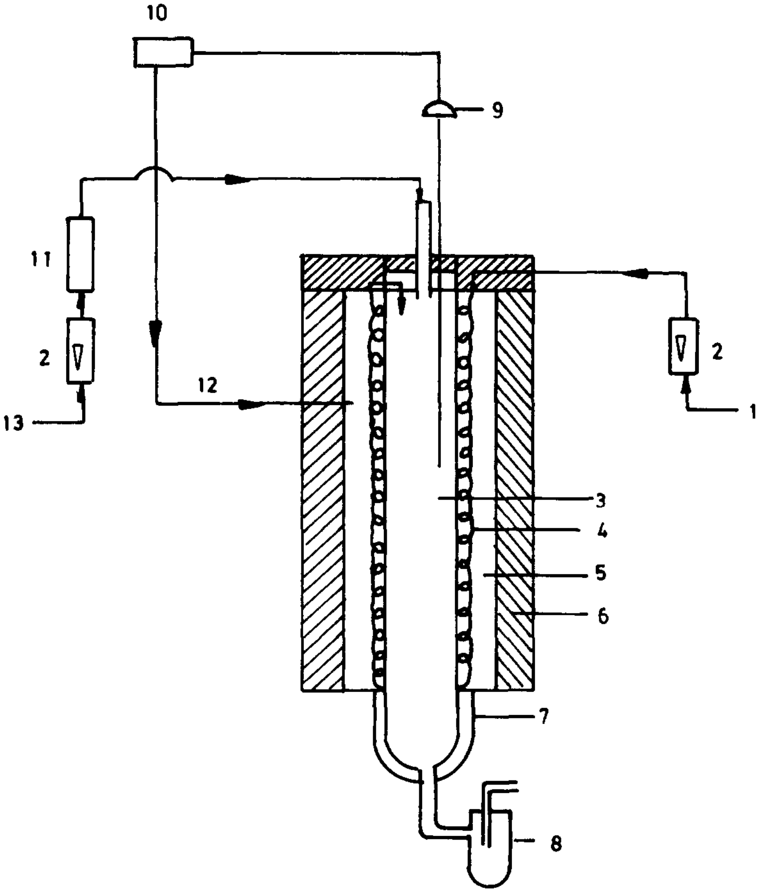

Fig. 2. Schematic diagram of the flash dehydration system. 1, N_2 gas (secondary flow); 2, rotameter; 3, reactor; 4, preheater; 5, oven; 6, insulation; 7, water-cooled jacket; 8, cyclone; 9, thermocouple; 10, temperature control unit; 11, fluidized bed; 12, current supply; 13, N_2 gas (primary flow).

stop dehydration, and then into a cyclone to separate gas and solid. After weighing the solid collected in the cyclone the weight loss was calculated.

Nitrogen was used as primary and secondary gas. The experimental flow conditions and gas Reynolds numbers employed in the study are given in Table 2. In all the experiments the flow rates of the primary and secondary gases were kept constant. The flow rate of primary gas was kept to the minimum value able to carry the solid into the reactor. As seen from Table 2, the experiments were carried out under laminar flow conditions. The reason for working under laminar flow conditons in the entrained flow systems is to avoid radial movement of the solid in the reactor owing to turbulence [14,15].

The dehydration experiments were performed in the temperature range 400–700°C. For technical reasons no study was performed above 700°C.

Table 2
Gas flow conditions and gas Reynolds numbers

	Reactor temperature/°C					
	400	500	550	600	650	700
N_2 flow rate/(l $\min^{-1}$) at 20°C and 1 atm						
Primary	0.79	0.79	0.79	0.79	0.79	0.79
Secondary	3.50	3.50	3.50	3.50	3.50	3.50
Total gas velocity/(cm s^{-1}), at reactor temperature	52	60	64	68	72	76
Residence time/s, at reactor temperature	1.15	1.00	0.93	0.88	0.83	0.79
Gas Reynolds number at reactor temperature	159	145	140	134	130	122

4. Results and discussion

4.1. Thermogravimetric measurements and interpretation of TGA data

As seen from the DTA diagram in Fig. 1(a), there are two basic endothermic peaks which appears at 157 and 187°C. The peak observed at 187°C is larger than the other. According to the TGA diagram given in Fig. 1(b), the dehydration of ulexite begins at $\approx$100°C and the dehydration rate is high up to 230°C; above this temperature the dehydration continues at a quite low rate up to 530°C, and above this temperature there is almost no weight loss.

Various models have been developed to obtain kinetic parameters using thermogravimetric data [16–19]. In this study to determine the kinetic parameters for the dehydration of ulexite, the first order thermal decomposition model proposed by Suzuki et al. [19] was used. In the literature, some further work applying this model is reported [19,20].

This method, which requires the temperature $T_{1/2}$ and the temperature difference ΔT at 50% conversion, was used to evaluate the preexponential factor k_0, and the activation energy E. For this purpose, a conversion vs. temperature graph was constructed from the TGA data, as shown in Fig. 3. The conversion was calculated as the ratio of the weight loss at any dehydration temperature to the total weight loss, on the basis of the following reaction

$$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O \rightarrow Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot nH_2O \qquad (1)$$

where n is the number of moles of water between 0 and 16.

The temperature $T_{1/2}$ and the temperature difference at 50% conversion were found to be 468 and 87.5 K, respectively, as shown in Fig. 3. According to the

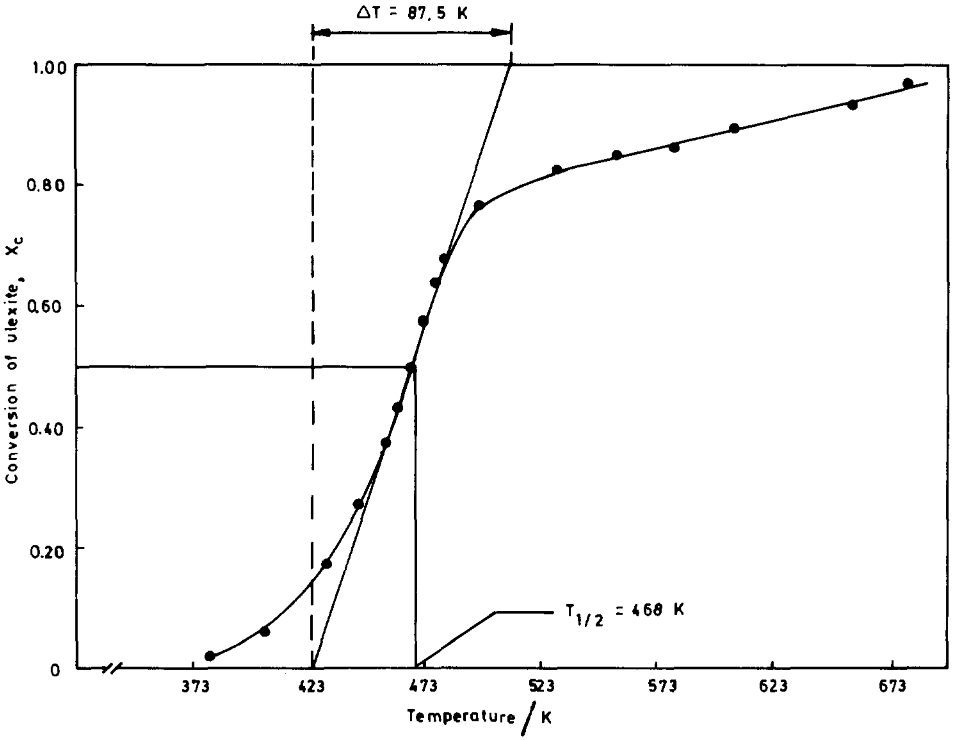

Fig. 3. Conversion–temperature curve of ulexite obtained from TGA data.

Suzuki method

$$\xi \equiv \frac{\Delta T}{T_{1/2}} = \frac{2}{\ln 2}\psi(E/RT_{1/2}) \tag{2}$$

$$\psi(E/RT_{1/2}) = 1 - [x, \mathrm{e}^{x}, E_1(x)] \tag{3}$$

where

$$E_1(x) = \int_x^{\infty} [\mathrm{e}^{-x}/x]\mathrm{d}x \tag{4}$$

and

$$x = (E/RT_{1/2}) \tag{5}$$

In order to calculate the activation energy E, ξ is obtained from the experimentally determined $T_{1/2}$ and ΔT. The term $\psi(E/RT_{1/2})$ is then calculated from Eq. (2). The term x is found from a plot of $\psi(x)$ vs. x as given by Suzuki et al. [19], and finally the activation energy is calculated from Eq. (5). The preexponential factor k_0, is obtained as

$$k_0 = \frac{2m}{\Delta T}\mathrm{e}^{(E/RT_{1/2})} \tag{6}$$

Table 3
Kinetic parameters for the dehydration of ulexite

Particle size/μm	Heating rate/(K s^{-1})	$T_{1/2}$/K	ΔT/K	E/(kJ mol^{-1})	k_0/s^{-1}
−300 + 250	0.17	475	97.5	48.2	707
−710 + 600	0.17	465	82.0	53.1	3879
−1000 + 710	0.17	468	87.5	53.0	3150

	Dehydration temp./°C											
	110			210			350			530		
Particle size/μm	−1000 +710	−710 +600	−300 +250	−1000 +710	−710 +600	−300 +250	−1000 +710	−710 +600	−300 +250	−1000 +710	−710 +600	−300 +250
$k \times 10^4$/s^{-1}	1.8	2.1	1.8	57	69	42	1100	1400	600	11200	13500	5000

where m is the heating rate. Finally, the rate constant k is calculated using k_0 and E values in the Arrhenius equation

$$k = k_0 \, e^{(-E/RT)} \tag{7}$$

The values of k_0, E and k for different particle sizes are given in Table 3. As may be seen from this table, the particle size of the ulexite has no significant effect on the activation energy. The rate constant for particles of $-710 + 600$ μm is greater than that for the other particles at all temperatures owing to the higher preexponential factor for these particles.

4.2. Flash dehydration results

The weight loss results obtained from the flash dehydration of ulexite with a particle size of $-425 + 300$ μm in the temperature range 400–700°C are given in Fig. 4. As may be seen from this figure, the weight loss increases continuously with temperature.

The residence time of solids in an entrained flow reactor is generally calculated using particle velocity models, or the particle velocity can be accepted as being

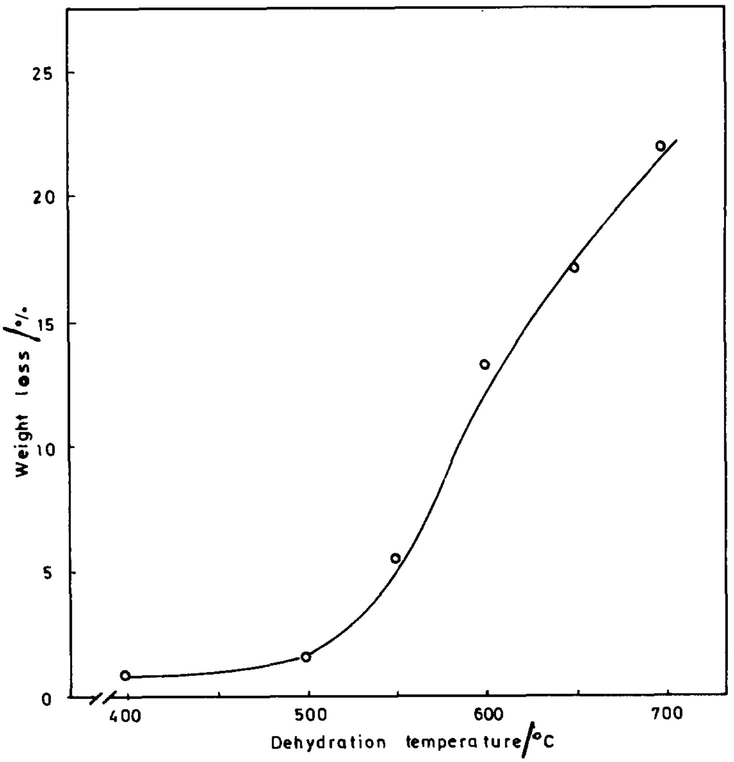

Fig. 4. Effect of flash dehydration temperature on weight loss.

equal to the gas velocity [21]. In the literature some other studies using the second method are present [4,21,22]. In this work, as the particle size is quite small, particle velocity can be taken as being equal to the gas velocity, ignoring the other factors affecting the particles. Therefore, taking into consideraton the gas flow rates in Table 3, it is found that the residence time of the particles is between 0.79 and 1.15 s.

As is seen from Fig. 4, a weight loss of 22% is obtained at 700°C, which is the highest temperature obtainable in the system. As is known, in the complete dehydration of ulexite the theoretical weight loss is 35.5%. If one looks at the dehydration studies on ulexite carried out at a slow heating rate, the so-called static method, the 35.5% weight loss is obtained over a very long period compared with the time for flash dehydration. For instance, in two publications [7,23], the weight loss of ulexite was found to be $\approx 35\%$ at 500°C during 5 h. In the light of these findings it is obvious that a certain weight loss is reached in a much shorter time in the flash dehydration than in the classical dehydration method. Whereas in the classical dehydration method the weight loss is complete at $\approx 500°C$, the temperature required to reach complete dehydration with flash dehydration is too high because of the nature of the method. But, as mentioned before, the residence time is very short in the flash dehydration, making this method advantageous. Davies et al. [12] worked on the calcination of colemanite and emphasized the advantage of flash calcination over slow calcination, which continues for hours; they also pointed out that flash calcination can be more economical than slow calcination from the viewpoint of energy.

5. Conclusions

In this study, the flash dehydration of ulexite and the dehydration kinetics from TGA data were investigated. It can be noted that flash dehydration has more advantages than the slow process, as the process time is very short. A weight loss of 22% was reached at 700°C in a process time of several seconds.

From the TGA data, the activation energy for the dehydration of ulexite of different particle sizes was found to range from 48.2 to 53 kJ mol^{-1}, and the rate constants were found to vary between 1.8×10^{-4} and 1.35 s^{-1} in the temperature range 100–530°C.

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