

Kinetic study of the thermal dehydration of borogypsum

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Abstract

In Turkey, a large amount of borogypsum waste is discharged by the economically important boric acid industry. Calcination of this waste provides a promising technique not only for recovering an economic value but also for reducing its environmental impact. The aim of this work is to study the thermal behavior of borogypsum, which contains gypsum crystals, boron oxide and some impurities under nonisothermal conditions in air atmosphere by using thermogravimetry and differential thermal analysis techniques (TG–DTA). Experiments were carried out at temperatures ranging from ambient to 773 K at different heating rates. The temperatures of conversion from gypsum to hemihydrate and anhydrite states were determined. Various methods were used to analyze the TG and DTA data for determination of reaction kinetics. The activation energy and frequency factor were calculated for dehydration of borogypsum. Activation energy values of the main dehydration reaction of borogypsum were calculated to be approximately 95–114 kJ mol⁻¹.

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1. Introduction

About, 62% of the world's boron ores are found in the western part of Turkey. The hydrated boron minerals, which have a big potential in Turkey are the main materials for the chemical industry. Especially, colemanite, used in the production of boric acid (H₃BO₃), is very important from the economic point of view [1,2]. Over 120 million tons of borogypsum is produced as an industrial by-product of boric acid production at the factories of Bandırma Eti Holding in Turkey. Borogypsum is formed by reacting colemanite with sulphuric acid in the production of boric acid and is obtained by filtering the reaction mixture on the filter presses. The material mainly consists of gypsum, B₂O₃ and some impurities and causes various environmental and storage problems. The content of B₂O₃ in borogypsum obtained during the boric acid production increases up to 7%. It is a valuable industrial raw material for its B₂O₃ content. In contrast, B₂O₃ is dissolved by rain water and mixed with soil. High amount of

boron content, which has toxicological effect leads economic losses and also causes environmental pollution [3–5]. To reduce pollution and disposal of this industrial waste, several works have been carried out for the utilization for borogypsum as calcium sulfate dihydrate (gypsum) in cement production [6–12]. It has been reported that the mortar obtained from the cement with calcinated borogypsum gives better mechanical strength than cement prepared using natural gypsum and borogypsum. The addition of calcinated borogypsum to Portland cement clinker increases the compressive strength from 43.2 to 54.1 Nmm². Hence, the use of different forms of borogypsum in building industry as raw materials offers a potential alternative for utilization [12].

Also, the dehydration reaction of borogypsum has become an important process. Production of hemihydrate and anhydrite, which depends on the calcination temperatures due to different temperatures, leads to the formation of different structures. Therefore, kinetics of the dehydration reactions is an important factor in the design of calcination equipments.

The aim of this research is to determine the kinetic parameters by using TG–DTA techniques for the production of

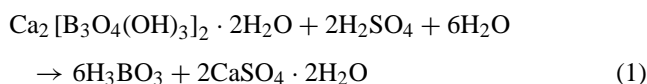
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hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) and anhydrite (CaSO_4) from borogypsum by the calcination process.

2. Material and methods

2.1. Material

Borogypsum used in the experiments was supplied by Eti Holding Bandırma Borax and Boric Acid Plants in Turkey. It is formed during the production of boric acid from colemanite, which is important borate ore. In the process, colemanite ($\text{Ca}_2[\text{B}_3\text{O}_4(\text{OH})_3]_2 \cdot 2\text{H}_2\text{O}$) is reacted with sulphuric acid (H_2SO_4) solution, and borogypsum is formed as a by-product in filter-press as follows;



Before the thermal experiments, borogypsum was dried in the oven at 105°C for 2 h, crushed and grounded by using mechanical methods. The particle sizes were not taken into account, since it has a crushable structure and completely sieved in a $-140 + 71 \mu\text{m}$. X-ray diffraction peaks are obtained by a Rigaku X-ray diffractometer using $\text{Cu K}\alpha$ radiation. Thermal analysis, to obtain the percentages of hemihydrate and anhydrite of the sample was performed in a SETARAM Labsys simultaneous TG–DTA instrument. Temperature calibration was achieved by using the ICTAC-recommended DTA standards. Sample mass was about 25 mg and different heating rates of 2, 5, 10 and 15 K min^{-1} up to 773 K were used under air flow of 100 ml min^{-1} in experiments. All data were obtained using covered sample crucibles due to content of colemanite in borogypsum. It is known that colemanite leads to explosive dehydroxylation at high temperatures due to its very porous structure [13]. This property of colemanite leads some samples to leap up from the crucibles. In the thermal experiments, alumina crucibles were covered to prevent the sample loss.

2.2. Kinetic theory for solids

Thermal analysis techniques are used in the evaluation of kinetic parameters of solid-state reactions in dehydration process [14,15]. A number of models have been developed to obtain the kinetic parameters from the thermogravimetric data for studying the mechanism of solid-state decomposition processes. In these works, the authors assumed first order reaction mechanism [14,16]. In this study, to determine the kinetic parameters for the dehydration of borogypsum, the first order ($n=1$) thermal decomposition model which proposed in earlier solid-state decomposition works was assumed.

The kinetic parameters, activation energy (E) and frequency factor (k_0) were calculated from the fraction of sample decomposed (χ) values by utilizing the mathematical equa-

tions of Coats–Redfern (CR) (Eqs. (2) and (3)) [17], Kissinger (KI) (Eq. (4)) [18], Doyle (DO) (Eq. (5)) [19].

The Coats–Redfern equation:

$$\text{For } n = 1 : \ln \left[\frac{-\ln(1 - \chi)}{T^2} \right] = \ln \frac{k_0 R}{\beta E} - \frac{E}{RT} \quad (2)$$

$$\text{For } n \neq 1 : \ln \left[\frac{1 - (1 - \chi)^{1-n}}{T^2(1 - n)} \right] = \ln \frac{k_0 R}{\beta E} - \frac{E}{RT} \quad (3)$$

The equation of Kissinger:

$$\ln \left(\frac{\beta}{T_m^2} \right) = \ln \left(\frac{k_0 R}{E} \right) - \frac{E}{RT_m} \quad (4)$$

The equation of Doyle:

$$\frac{d(\log \beta)}{d(1/T_m)} \approx -0.4567 \frac{E}{R} \quad (5)$$

The frequency factor, k_0 , may be determined by

$$\frac{\beta E}{RT_m^2} \exp \left(\frac{E}{RT_m} \right) = k_0 \quad (6)$$

where χ = fraction decomposed (%); T = temperature (K); k_0 = frequency factor (s^{-1}); R = gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); E = activation energy (J mol^{-1}); β = heating rate (K s^{-1}); T_m = temperature of the peak (K).

TG–DTA curves for borogypsum at various heating rates are presented in Figs. 2 and 3. Kinetic parameters were calculated from fraction of sample decomposed and temperature data with the help of the methods.

3. Results and discussion

X-ray diffraction pattern of the borogypsum is shown in Fig. 1, and the chemical composition of borogypsum is presented in Table 1. Both data confirm that borogypsum mainly consists of gypsum crystals, B_2O_3 and some impurities. Figs. 2 and 3 show TG and DTA curves of borogypsum obtained at heating rates of 2, 5, 10 and 15 K min^{-1} , respectively under air atmosphere. The dehydration patterns obtained under different heating rates were similar except for

Table 1
Chemical analysis of borogypsum

Constituents	Weight (%)
B_2O_3	7.00
SiO_2	7.74
Fe_2O_3	0.74
Al_2O_3	1.37
CaO	25.24
MgO	0.88
Na_2O	0.10
K_2O	0.79
SO_3	35.62
Cl^-	0.0042
Loss on ignition	20.91

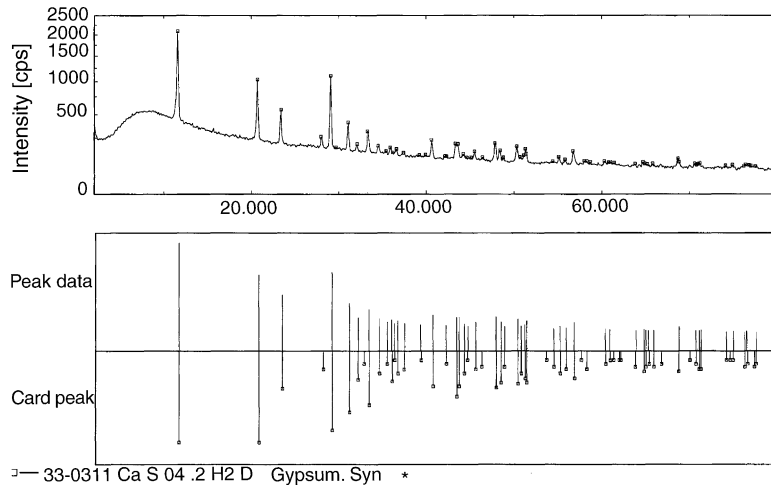


Fig. 1. X-ray pattern of borogypsum (−140 + 71 μm).

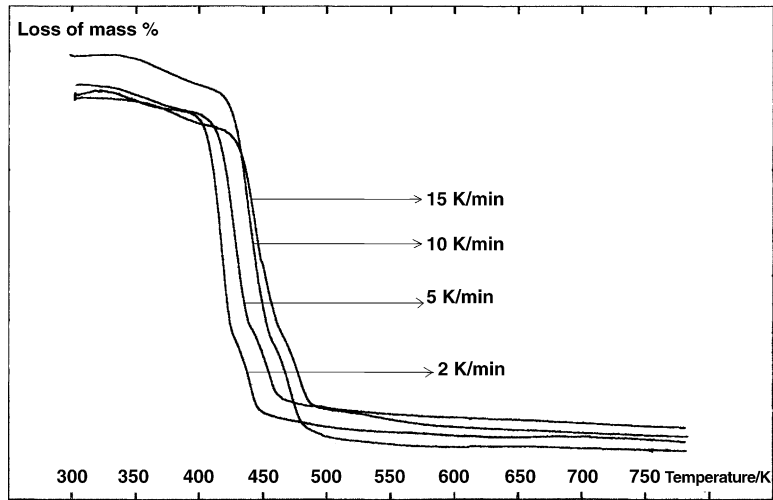


Fig. 2. TG curves for the dehydration of borogypsum carried out at different heating rates.

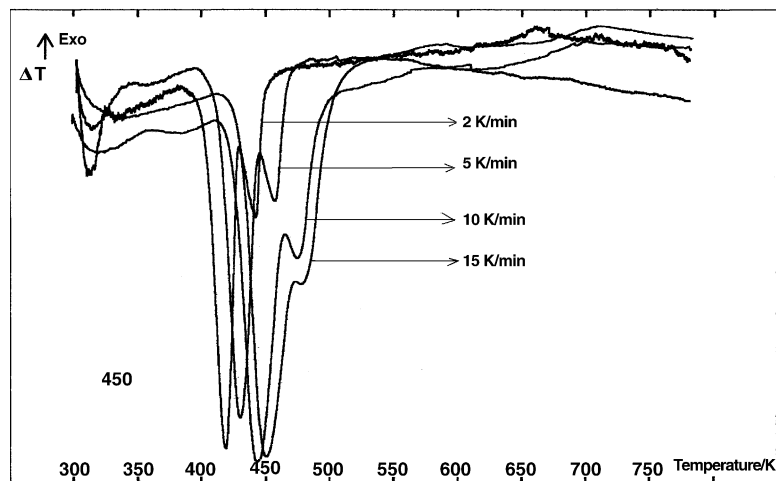


Fig. 3. DTA curves for the dehydration of borogypsum carried out at different heating rates.

the usual increase in the observed dehydration temperatures with increase in heating rate.

According to the DTA curves, based on two basic endothermic peaks, of this study dehydration of borogypsum occurs in two steps, which appears at approximately 418–450 and 441–475 K (Fig. 2). These curves consist of two reactions that are partially overlapping. Overlapping reactions are sometimes difficult to locate on the TG curve uncertain point where one reaction ends and the other starts. By using the DTA curve, an extrapolation procedure can be used to determine approximately where the second reaction begins. It can be seen from the DTA curves that minor reaction occur during near a major reaction when borogypsum is heated. Major reaction, which is shown as transformation to hemihydrate structure, occurs in the temperature range of 413–463 K (step 1). The first weight loss occurs in this region according to the TG curves corresponds to the loss of 3/2 moles of water. XRD pattern of the borogypsum after heating up to 463 K is shown in Fig. 4. The pattern shows the product formation as hemihydrate borogypsum. The second peak in DTA curves, which shows minor reaction, indicates the conversion of borogypsum from hemihydrate to anhydrite. This reaction occurs in the temperature range of 463–493 K (step 2). The observed second weight loss according to the TG curves corresponds to the loss of 1/2 moles of water crystallization. XRD pattern of the borogypsum after heating up to 493 K is shown in Fig. 5. The pattern demonstrates formation of soluble anhydrite or anhydrite III (hexagonal) with conversion of hemihydrate.

In addition to the two endothermic peaks, there is a visible small exothermic peak at 650 K in TG curves. This peak indicates transformation of soluble anhydrite (hexagonal) to insoluble anhydrite (orthorombik). Based on the TG data, the average weight loss measured for the four experiments carried out at different heating rates were found to be approximately 19.60%. This means that the mass loss, which occurred between the starting and the ending materials 19.60%. This is in accordance with the theoretical calcula-

Table 2
Temperatures of dehydration reactions for each steps

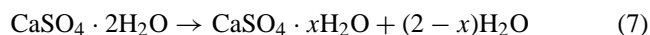
Rate of heating (K min ⁻¹)	Step 1			Step 2		
	T _i (K)	T _{m1} [*] (K)	T _f (K)	T _i (K)	T _{m2} [*] (K)	T _f (K)
2	400	418.59	430	430	441	448
5	405	429.84	440	440	457	463
10	410	440.00	461	461	473	479
15	416	449.82	465	465	475	489

*T_m: temperature at which maximum weight loss takes place in TG or peak temperature in DTA. T_i: initial temperature, T_f: final temperature. T_{m1} values were used in KI and DO methods for calculation of activation energy and frequency factor.

tions (20.93%). It can be observed that increase of the heating rate affects initial, final and peak temperatures (Table 2).

In the literature, there are a number of studies on gypsum and its conversion to hemihydrate and anhydrite states at different temperatures. In general, all the studies of the CaSO₄·2H₂O dehydration through DTA show the presence of two endothermic peaks. However, the dehydration temperatures have been quite varied. This difference might be explained by the influence of nature as well as by the different origins of the samples [20]. Although many studies about the decomposition of gypsum have been reported, we have not noticed any work about the kinetics of thermal decomposition of borogypsum.

The data obtained from the DTA–TG curves were used to calculate the activation energy of the dehydration steps. The conversion or fractions of sample decomposed was calculated as the ratio of the weight loss to the total weight loss by using computer programme of DTA–TG instruments on the basis of the following reactions:



where x is the mole fraction of water changing between 0 and 2. The conversion versus temperature graphs are drawn from TG data, as shown in Fig. 2. Borogypsum starts losing

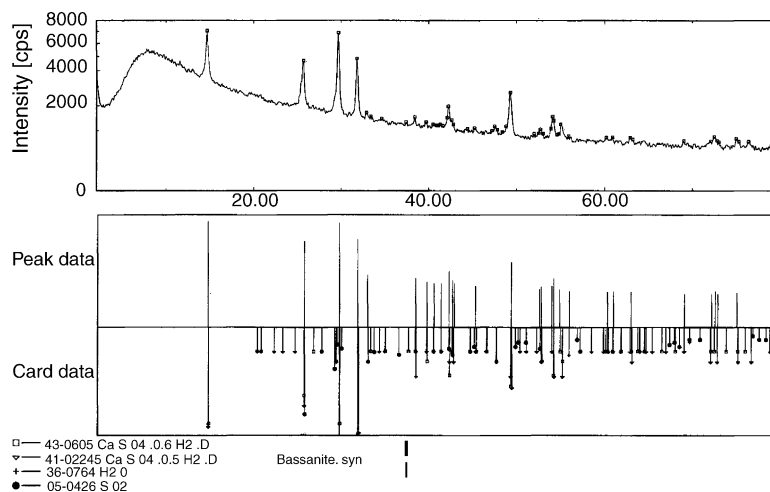


Fig. 4. X-ray diffractogram of hemihydrate structure for borogypsum.

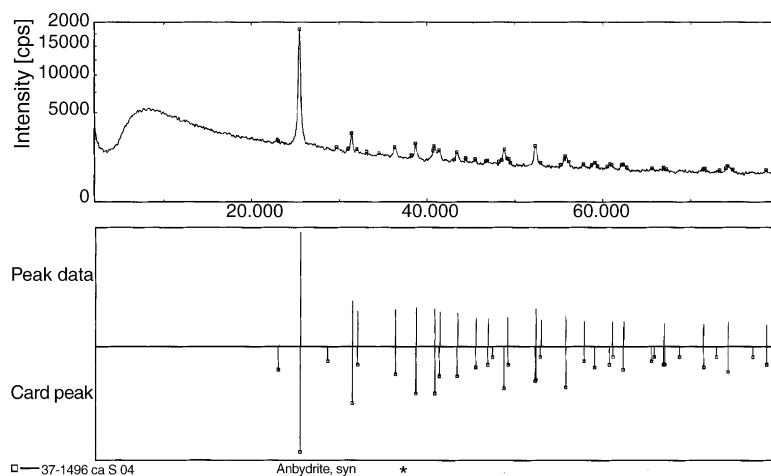


Fig. 5. X-ray diffractogram of anhydrite structure for borogypsum.

water approximately at 400 K, and weight loss is completed between 448 and 485 K. Table 3 shows the conversion at a given temperature for different heating rates. According to the Table 3, final temperatures of reaction or temperatures, which are fixed of mass loss have quite change depend on the heating rates. Table 3 shows values, which are used in calculation of kinetic parameters with CR method.

Kinetic parameters calculated for dehydration of borogypsum are given in Tables 4 and 5. According to the Coats–Redfern Method, the left side of Eq. (2) must be plotted versus $1/T$. Activation energy was calculated using the

slope of the line and the frequency factor was obtained from the intercept of the line. The method proposed by Kissinger utilizes DTA data. As indicated at Eq. (4), the $\ln(\beta/T_m^2 T_m^2)$ versus $1/T_m$ graph gives a straight line. The activation energy was calculated from the slope of the line, and the frequency factor is obtained from the intercept of the line. The approximation of Doyle uses Eq. (5), with DTA data. If the logarithm of heating rates is plotted against $1/T_m$, the slope will be equal to $-0.4567E/R$. From the slope the activation energy and the frequency factor are calculated from Eq. (5). Data obtained from TG curves at different heating rates are shown in Table 3

Table 3
Change of decomposed fractions at different heating rates with temperature during dehydration of borogypsum

2°C min^{-1}		5°C min^{-1}		$10^\circ\text{C min}^{-1}$		$15^\circ\text{C min}^{-1}$	
$T(\text{K}^{-1})$	χ (%)	$T(\text{K}^{-1})$	χ (%)	$T(\text{K}^{-1})$	χ (%)	$T(\text{K}^{-1})$	χ (%)
400.10	1.3747	405.06	1.841	410.07	1.741	416.02	1.8636
404.81	2.0257	407.57	2.0069	417.44	2.004	420.46	2.0089
408.28	3.0235	415.05	3.0124	426.15	3.0191	431.53	3.0081
410.59	4.0205	418.48	4.0366	430.04	4.0387	435.82	4.0082
412.41	5.0329	420.85	5.0160	432.75	5.0246	438.62	5.0215
414.01	6.0562	422.82	6.0241	434.91	6.0412	440.92	6.0137
415.45	7.0576	424.60	7.0650	436.80	7.0024	443.09	7.005
416.76	8.0227	426.17	8.0529	438.76	8.0377	445.19	8.0051
418.06	9.0324	427.77	9.0770	440.68	9.0116	447.48	9.0148
419.50	10.0648	429.38	10.0724	442.73	10.0005	451.40	10.0307
420.95	11.0417	430.98	11.0468	445.07	11.050	454.46	11.0325
422.63	12.0131	432.71	12.0042	447.57	12.0239	458.00	12.0203
425.15	13.0091	434.88	13.0039	450.48	13.0091	461.17	12.7016
430.86 ^a	14.0051 ^a	437.71	14.0229	450.61	13.0518	462.94	13.0046
435.64	15.0093	440.29 ^a	14.5147 ^a	456.67	14.4063	465.28 ^a	13.3514 ^a
439.60	16.0135	443.73	15.0032	461.41 ^a	15.0123 ^a	467.57	13.6615
443.56	17.0196	446.47	15.5085	466.98	16.0109	469.88	14.0144
448.08	17.5248	448.84	16.0096	469.42	16.5279	471.28	14.2429
		451.08	16.4904	471.54	17.0103	473.07	14.5941
		453.19	17.0025	473.84	17.5205	475.18	15.0197
		455.41	17.5213	476.19	18.0112	477.47	15.5022
		457.47	18.0038	479.52	18.5146	479.80	16.0023
		460.60	18.5015			482.50	16.5058
		463.08	18.6686			483.72	16.6967
						485.56	16.9586

^a Initial of step 2.

Table 4
Kinetic parameters evaluated from TG curves using Coats–Redfern (CR) method

Steps	E (J mol ⁻¹)	k_0 (s ⁻¹)	R^2	Heating rate β (K min ⁻¹)
Step 1	141188	1.28×10^{14}	0.9924	2
Step 2	19413	0.0142	0.9981	
Step 1	97823	4.15×10^8	0.9842	5
Step 2	14654	0.0065	0.9800	
Step 1	97864	3.65×10^8	0.9865	10
Step 2	16279	0.0174	0.9929	
Step 1	99469	5.59×10^8	0.9800	15
Step 2	16988	0.0272	0.9932	

R^2 : correlation coefficient.

Table 5
Kinetic parameters evaluated from DTA–TG curves using Kissinger (KI) and Doyle (DO) method

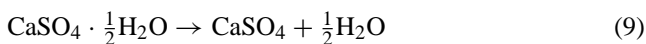
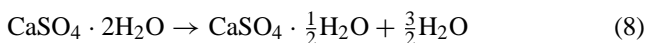
Parameters	KI	DO	CR ^a
E (J mol ⁻¹)	95004	97203	114143
k_0 (s ⁻¹)	1.68×10^9	3.49×10^8	3.65×10^8
R^2	0.9841	0.9864	0.9900

^a Supplementary total activation energy for two steps.

as a ratio of the mass loss at a given temperature. As it can be seen from the equations of KI and DO methods, peak temperatures (T_m) were used for the calculation of activation energy in step 1. It should be noticed that these methods can be used for only step 1 in order to mass loss of major reaction occurs in step 1. The amount of sample undergoing reaction in steps 1 and 2 is very similar for four experiments (Fig. 2) and has the same conversion. It is determined that CR method is a more suitable method for the calculation of kinetic parameters in each step than the KI and DO methods. Activation energy (E) and frequency factor (k_0), calculated for different heating rates by CR method, in Table 5 seem generally in good agreement.

4. Conclusions

The main point of this paper is the study of the thermal behaviour of the borogypsum and to calculation of kinetic parameters for dehydration reactions. Also, the effects of different heating rates on the course of dehydration are investigated. Based on the results of this work, the dehydration reaction is proposed to take place according to the following mechanism:



We noticed that the general state of dehydration does not change, although at a given temperature, the mass loss is same as proportional in different heating rates. On the other hand, the increase in the heating rate displaces the reaction towards high temperatures. Namely, a shift of the T_m val-

ues (T_m , the temperature of maximum rate of mass loss) towards higher temperatures take place as a result of increasing the heating rate. Kinetic parameters were deduced at each stage under nonisothermal conditions and are in good agreement for three models (Coats–Redfern, Kissinger, Doyle). Base on the calculation of CR, KI and DO methods, activation energy values for major dehydration reaction change between 95 and 114 kJ mol⁻¹ (step 1). However, the highest activation energy (141 kJ mol⁻¹) was obtained by the thermal experiment, which was carried out at the lowest heating rate.

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