

# Dehydroxylation Reaction Kinetic Mechanism of İnderite Mineral

Mehmet Burcin Piskin<sup>1+</sup> and Halit Eren Figen

<sup>1</sup> Yildiz Technical University, Department of Bioengineering

<sup>2</sup> Yildiz Technical University, Department of Chemical Engineering

**Abstract.** Dehydroxylation kinetic of Kirka inderite mineral is investigated based on thermogravimetry analysis (TGA) and fourteen different solid-state mechanisms are applied to determine of dehydroxylation kinetic mechanism. Dehydroxylation experiments were carried out at five different heating rates of 2, 5, 10, 15 and 20°C/min in pure nitrogen atmosphere to obtain the thermal curves under non-isothermal conditions. It is found that random nucleation is the most probable mechanism of dehydroxylation of inderite mineral.

**Keywords:** Dehydroxylation, inderite mineral, kinetic mechanism, thermogravimetry

## 1. Introduction

The magnesium borates ( $x\text{MgO}\cdot y\text{B}_2\text{O}_3\cdot z\text{H}_2\text{O}$ ) are important boron minerals for various application areas because of magnesium and boron contents. In general, they are used as catalyst for the conversion of hydrocarbons, as the luminescent materials for use in fluorescent discharge lamps, as the cathode ray tube screens and X-ray screens, as the electro conductive treating agent and as a reinforcing material for plastics. Especially, they have greater importance in superconductor magnesium diboride ( $\text{MgB}_2$ ) production [1]. Not only inderite and also kurnakovite and inderborite have been first time found in Turkey at Kırka deposits. Turkey has 73% of world's boron mineral reserves based on 851 million tons of  $\text{B}_2\text{O}_3$  content in the western part. Inderite is found in Kırka borate deposits in Eskisehir providence with borax, ulexite, colemanite, tunellite, meyerhofferite, inyonite, kurnakovite, and inderborite minerals [2]. It is necessary to determine the kinetic mechanism of dehydroxylation in order to predict its stability and transformation. These properties will affect inderite usability in different applications.

There is not available apparent published research concerning the kinetic mechanism of inderite dehydroxylation. There are some published works concerning only dehydration kinetics.  $\Delta H$  and  $E_a$  parameters of some Mg-containing borates as macallisterite ( $\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 7.5\text{H}_2\text{O}$ ), inderite ( $2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 15\text{H}_2\text{O}$ ) and kurnakovite ( $2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 15\text{H}_2\text{O}$ ) had been determined by using a DSC thermal analyzer. Kinetic parameters for dehydration reaction are calculated by Kissinger and the simple Ozawa method [3, 4]. According to the non-isothermal kinetic theory, thermal decomposition of a solid can be express by the following function. Also, Coats-Redfern, Arrhenius, Ozawa, Kissinger, and Doyle non-isothermal kinetic models were used to calculate the dynamic kinetic parameters for dehydration reaction of Mg-borate mineral, inderite (Kırka/Turkey) based on thermogravimetric analysis, derivative thermogravimetric analysis and differential thermal analysis [5].

Thermal analysis techniques are used in the evaluation of kinetic parameters of solid-state reactions in the dehydroxylation process.



<sup>+</sup> Corresponding author. Tel.: + 0902123834756; fax: +0902123834744  
E-mail address: mpiskin@yildiz.edu.tr

$$g(\alpha) = k.t \quad (2) \quad \alpha = \frac{(W_0 - W_t)}{(W_0 - W_\alpha)} \quad (3) \quad \ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \left[ \frac{k_0}{\beta E_a} \right] - \frac{E_a}{RT} \quad (4)$$

$\ln[g(\alpha)/T^2]$  function for each mechanism are calculated and plotted against to the  $1/T$ . It is evaluated to determine the linearity of the function and the equation giving the best fitting of results indicates the most probable mechanism of the reaction.  $E_a$  and  $k_0$  can be calculated from the intercept and slope of straight line, respectively [6].

The  $E_a$  and  $k_0$  is related with  $g(\alpha)$  mechanism function which is listed in Table 1. Urbanovici was suggested a new general equation (5) in order to describe kinetics of solid state reaction and particularly the kinetics of heterogeneous decompositions [7]. This differential equation can be expressed as;

$$\frac{d\alpha}{dt} = k \cdot (1 - \alpha)^q \cdot \left[ \frac{1 - (1 - \alpha)^{1-q}}{(1 - q)^y} \right] \quad (5)$$

Table 1: Various reaction mechanism of solid thermal decomposition

Kinetic mechanism	$g(\alpha)$	Observation
Power law ( $P_m$ )	$\alpha^{1/m}$	$m = 1, 2, 3, 4$
Avrami-Erofeev ( $A_n$ )	$[-\ln(1 - \alpha)]^{1/n}$	$n = 3/2, 2, 3, 4$
$n^{\text{th}}$ - Order Reaction ( $F_n$ )	$[1 - (1 - \alpha)^{1-n}] / (1 - n)$	$g(\alpha) = -\ln(1 - \alpha)$ ( $n = 1$ )
One-dimensional diffusion ( $D_1$ )	$\alpha^2$	-
Two-dimensional diffusion ( $D_2$ )	$\alpha + (1 - \alpha)\ln(1 - \alpha)$	-
Three-dimensional diffusion ( $D_3$ )	$[1 - (1 - \alpha)^{1/3}]^2$	-
Ginstling-Brounshtein ( $D_4$ )	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$	-

In the present study, the dehydroxylation kinetic mechanism was analyzed according to the Coats-Redfern method using fourteen of solid-state kinetic equation. TGA were performed at 2, 5, 10, 15 and 20°C/min heating rate under non-isothermal conditions. It was found that the nucleation mechanism ( $F_{3/2}$ ,  $A_2$ ,  $A_3$ ,  $A_4$ ) were the best of fourteen mechanism which describe the experimental data. In the present study, the dehydroxylation kinetic mechanism was analyzed according to the Coats-Redfern method using fourteen of solid-state kinetic equation. TGA were performed at 2, 5, 10, 15 and 20°C/min heating rate under non-isothermal conditions. It was found that the nucleation mechanism ( $F_{3/2}$ ,  $A_2$ ,  $A_3$ ,  $A_4$ ) were the best of fourteen mechanism which describe the experimental data.

## 2. Experimental

The inderite mineral used in the study was provided from the region of Kırka, Eskisehir in Turkey. After cleaning the mineral manually from visible impurities, it was ground and sieved with ASTM standard sieves to achieved uniformed size.

TGA were performed at 2, 5, 10, 15 and 20°C/min heating rate at pure  $N_2$  flow rate of 200 ml/min in the temperature range of 30-800°C with a sample size of ~10 mg by Perkin Elmer Diamond TG\DTA. The instrument was calibrated by means of the melting points of indium (156.6 °C) and tin (231.9 °C) as the standard substances under the same conditions with the sample. Obtained TG curves at different heating rates are given in Fig.1a. The thermal curves of the dehydroxylation regions were converted into kinetic curves by plotting the fractional conversion ( $\alpha$ ) against to the absolute temperature ( $T$ ) as shown in Fig.1b. The dehydroxylation kinetic mechanism was analyzed according to the Coats - Redfern method (eq. 4) using fourteen of solid-state kinetic equation which are listed in Table 1.

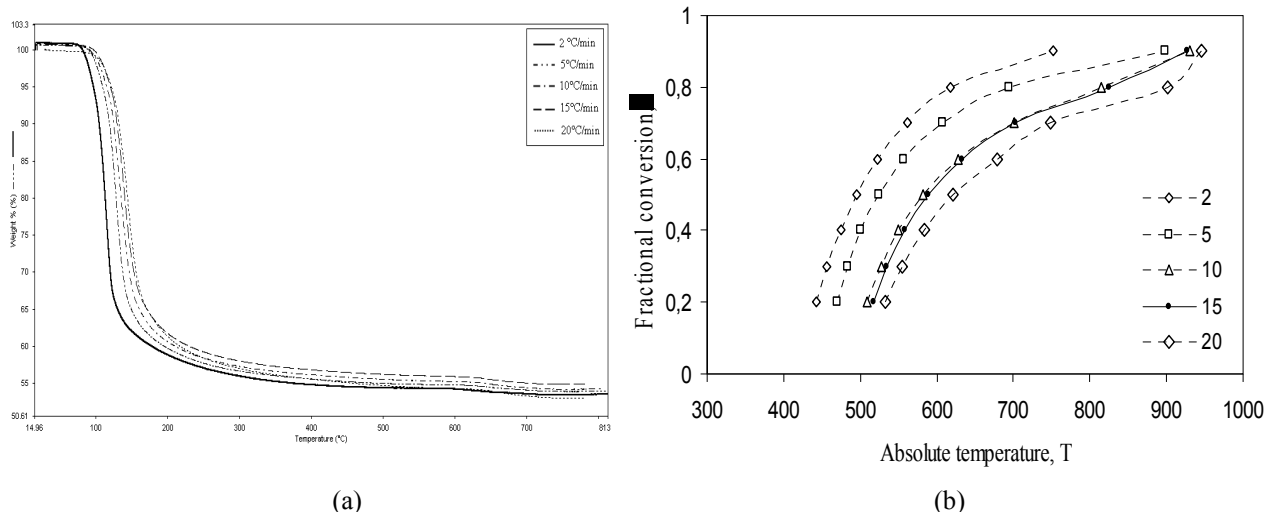


Fig. 1: Thermal analysis results (a) TG curves; (b) Kinetic curves of dehydroxylation reaction

### 3. Results and Discussions

#### 3.1. Thermal Properties

The series of TG curves of inderite at different heating rates are given in Fig.1a. Analysis of these curves estimate the mass loss can be associated with the dehydroxylation reactions are given in below with temperature range. It is observed that all off the characteristic temperature values on the TG curves are increased while increasing heating rate from 2 to 20 °C/min (Table 2).

Table 2: Mass loss of dehydroxylation steps at different heating rates

$\beta$ (°C/min)	2	5	10	15	20
$T_i$ (°C)	122.01	140.52	150.36	157.36	160.15
$(T_f)$ (°C)	700.15	734.83	759.51	760.84	766.87
m (%)	15.04	13.94	13.74	13.23	15.05
Average	$T_i: 146 \pm 19$		$T_f: 744 \pm 34$		$m\% = 14 \pm 0.1$

#### 3.2. Dehydroxylation Kinetic Mechanism

Fig.2a shows the correlation coefficients ( $R^2$ ) values of Power-Law kinetic model of inderite mineral. Kinetic mechanism for  $n=1$  was investigated and the  $R^2$  values for this kinetic mechanism were determined as 0.1144, 0.0428, 0.00001, 0.0032, 0.0439 for 2, 5, 10, 15 and 20 °C/min heating rates, respectively.

Fig. Fig.2b shows the  $R^2$  values of  $n^{\text{th}}$ -order reaction kinetic mechanism of inderite mineral. In the  $n^{\text{th}}$ -order reaction kinetic mechanism, reaction rate was determined based on random nucleation, one nucleus on each molecule. The results indicated that maximum linearity of the function was obtained for  $n=3/2$  at all the heating rates. The  $R^2$  values for this kinetic mechanism were determined as 0.8693, 0.7158, 0.8234, 0.7574, 0.8234 for 2, 5, 10 15 and 20 °C/min heating rates, respectively.

Fig.2c shows the  $R^2$  values of diffusion kinetic mechanism of inderite mineral. In  $D_1$  mechanism, reaction rate is determined based on one-dimensional diffusion, in  $D_2$  reaction rate is determined based on two-dimensional diffusion and cylindrical symmetry, in  $D_3$  reaction rate is determined based on three-dimensional diffusion, spherical symmetry, Jander's equation. In  $D_4$  reaction rate is determined based on three-dimensional diffusion, spherical symmetry, Ginstling and Brounstein's equations. The results indicated that maximum linearity of the function was obtained at  $D_3$  mechanism for each heating rates. The correlation coefficients for this kinetic mechanism were determined as 0.7882, 0.6532, 0.7313, 0.7268 and 0.7942 for 2, 5, 10, 15 and 20°C/min heating rates, respectively.

Fig.2d shows the  $R^2$  values of Avrami-Erofeev kinetic model of inderite mineral. Kinetic mechanism for  $n=3/2, 2, 3$  and 4 is investigated and maximum linearity of the function was obtained for  $n=4$  at all the

heating rates. The correlation coefficients for this kinetic mechanism were determined as 0.8962, 0.8432, 0.8751, 0.8682 and 0.9031 for 2, 5, 10, 15 and 20 °C/min heating rates, respectively. Results indicated that the dehydroxylation of inderite mineral follows the solid phase mechanism  $F_{3/2}$ ,  $A_2$ ,  $A_3$ ,  $A_4$ . The values of kinetic parameters of dehydroxylation for the possible solid phase mechanism are listed in Table 3.

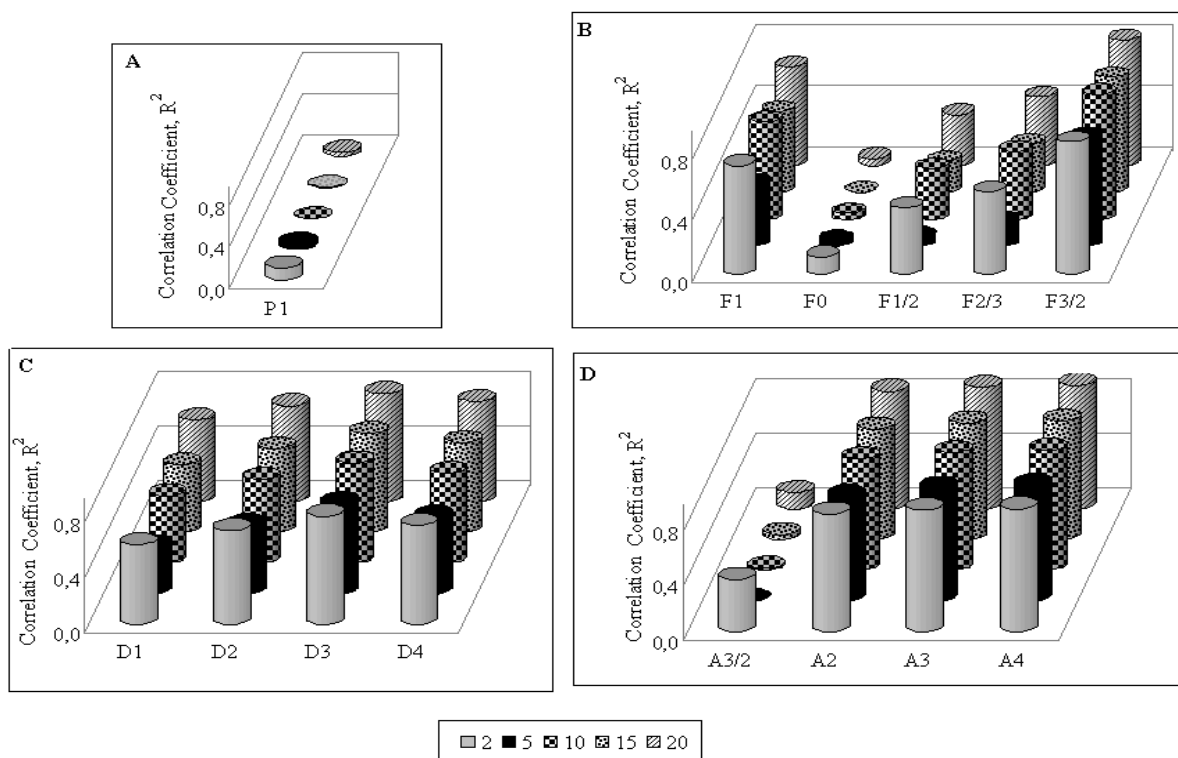


Fig. 2: Kinetic Mechanism -  $R^2$  value, (A) power-law, (B)  $n^{\text{th}}$ -order reaction, (C) diffusion, (D) Avrami-Erofeev

Table 3: Kinetic parameters of the dehydroxylation reaction of inderite mineral

Mechanism	$F_{3/2}$		$A_2$	
Heating rate (°C/min)	Ea (kJmol <sup>-1</sup> )	$k_0$ (min <sup>-1</sup> )	Ea (kJmol <sup>-1</sup> )	$k_0$ (min <sup>-1</sup> )
2	15.13	0.41	29.14	11.68
5	9.98	0.16	21.33	2.30
10	12.77	0.33	24.38	4.52
15	11.62	0.45	25.60	8.42
20	12.77	0.65	28.09	13.60
Mechanism	$A_3$		$A_4$	
Heating rate (°C/min)	Ea (kJmol <sup>-1</sup> )	$k_0$ (min <sup>-1</sup> )	Ea (kJmol <sup>-1</sup> )	$k_0$ (min <sup>-1</sup> )
2	48.44	12.39*10 <sup>2</sup>	67.73	11.06*10 <sup>4</sup>
5	37.32	95.83	53.31	32.53*10 <sup>2</sup>
10	42.20	18.17*10 <sup>1</sup>	60.02	60.02*10 <sup>2</sup>
15	44.08	36.86*10 <sup>1</sup>	62.55	13.31*10 <sup>3</sup>
20	47.94	63.42*10 <sup>1</sup>	67.78	24.51*10 <sup>3</sup>

## 4. Conclusions

The results obtained from investigations on dehydroxylation kinetic mechanism from a set of experimental data at different heating rates lead to following conclusion:

- 1) The dehydroxylation of inderite mineral continued at a very low rate in a wide temperature range up to 767 °C after dehydration step. Release of hydroxyl group (OH<sup>-</sup>) from polyanion structure is occurred at dehydroxylation stage.
- 2) Investigating the different fourteen kinetic mechanisms, it is found that dehydroxylation kinetic mechanism obeyed random nucleation mechanism (F<sub>3/2</sub>, A<sub>2</sub>, A<sub>3</sub>, A<sub>4</sub>) for each heating rate.
- 3) It is found that random nucleation is the most probable mechanism of dehydroxylation of inderite mineral.

## 5. Acknowledgments

The authors would like to thank for the financial sport of Turkish Republic Prime Ministry - State Planning Organization (Project No: 23-DPT-07-01-02) is gratefully acknowledged.

## 6. References

- [1] E.M. Elssfah, A. Elsanousi, J. Zhang, H.S. Song and C. Tang. Synthesis of Magnesiumborate Nanorods Mater. Lett., 2007, 61: 43-58.
- [2] O. Baysal. New Hydrous Magnesium-Borate Minerals in Turkey: Kurnakovite, Inderite, Inderborite. Mineral Research and Exploration Bulletins, 1973, 89: 93-103.
- [3] Y. Ximing, S. Zuwei and T. Yuanjun. DSC studies on the kinetics of decomposition of some Mg-containing borates under normal pressure. Thermochim. Acta., 1991, 191: 1-11.
- [4] Y. Ximing, S. Zuwei and T. Yuanjun. DSC studies on the kinetics of decomposition of some Mg-containing borates under high pressures. Thermochim. Acta., 1991, 191: 13-20.
- [5] A.K.Figen, M.S.Yilmaz and S.Piskin. Structural characterization and dehydration kinetics of Kırka inderite mineral: Application of non-isothermal models. Mater Charact. 2010, 61: 640 – 647.
- [6] E. Urbanovici, C. Popescu, E. Segal. Improved iterative version of the Coats-Redfern method to evaluate Non-isothermal kinetic parameters. J. Therm. Anal. Cal., 1999, 58: 683-700.
- [7] E. Urbanovici and E. Segal. General kinetic equation for solid state reactions. J. Therm. Anal. Cal., 1999, 55: 919-924.