Microwave Dehydration Behaviour of Inderite and Comparison with Thermal Analyses Methods

Iklim N. Ozdogan[1*], Yasemen T. Aksoy[1], F. Tugce Senberber[1], A. Seyhun Kıpçak[1], Mehmet B. Pişkin[b], Emek Moroydor Derun[1]

[1]Department of Chemical Engineering,
Faculty of Chemistry and Metallurgical, Yildiz Technical University,
Istanbul, Turkey
iklim.ozdogan@ytu.edu.tr
[2]Department of Bioengineering,
Faculty of Chemistry and Metallurgical, Yildiz Technical University,
Istanbul, Turkey
*Corresponding author

Abstract

Dehydration is called as the water removal from hydrated structure. Dehydration behavior is important for the usage areas and transportation of minerals. Magnesium borates can be used as additive materials in areas such as in the production of superconducting materials, in the composition of detergents, due to the content of boron in the friction-reducing additives in oils and insulating coating compositions due to their good mechanic and thermal properties. In this study, dehydration behavior of Inderite ($Mg(B_3O_3(OH)_5).5H_2O$) was experimented by both using microwave energy different and thermal analyses techniques. In microwave dehydration, power level was selected as 600W. Mass loss and drying rates were determined. In thermal dehydration, hydrated mineral was applied to thermal analysis (TG-DTG). Structural changes of hydrated and dehydrated samples were characterized using the techniques of XRD and FT-IR. XRD results show that crystallinity of sample may decrease in microwave dehydration. According to FT-IR results, characteristic band values of water disappeared at the end of the dehydration.

Keywords-microwave; dehydration; thermal analysis; inderite

1 Introduction

Metal borates are the compounds which involve the combinations of boron with other metal elements; and can be classified according to the metal atom such as sodium borates, calcium borates, magnesium borates and etc. The main features of magnesium borates are heat resistance, corrosion resistance and having high elasticity coefficient. Magnesium borates can be found in hydrated or dehydrated forms. Admontite ($MgB_6O_{10}\cdot 7H_2O$), Mcallisterite ($Mg_2[B_6O_7(OH)_6]_2\cdot 9H_2O$), Aksaite ($MgB_6O_7(OH)_6\cdot 2H_2O$), Pinnoite ($MgB_2O(OH)_6$), Inderite ($MgB_3O_3(OH)_5\cdot 5H_2O$) are the some examples of hydrated magnesium borate minerals in nature. Inderite mineral has the appearance of white, colorless and transparent. Its crystals are in the monoclinic system and its hardness is 3. Inderite reserves are found in Turkey, USA, Argentina, Russia, China and Kazakhstan [1–5].

Thermal behavior of mineral generally determined with the techniques of Thermal Gravimetric Analysis (TGA), Differential Thermal Gravimetric Analysis (DTG) and Differential Thermal Analysis (DTA). Dehydration of boron minerals could be explained by two steps. Firstly, crystal water removed from the structure. The second step is called dehydroxilation which is removal hydroxyl groups on a compound as water molecules. Dehydration behaviors for different kinds of metal borates were studied in literature; and the thermal parameters were calculated [5, 6].

Microwave energy is the nonionizing electromagnetic radiation with frequencies in the range of 300 MHz to 300 GHz. It is used in the applications of communication, cooking food, tempering and thawing, mineral synthesis and curing of wood and rubber products. There are some studies about dehydration process of some kinds of foods and minerals using microwave energy. The advantages of microwave energy usage can be listed as; reduced processing costs, better production quality, new materials and products, improved human health,

reduced hazards to humans and the environment and enhanced quality of life [7–9].

Microwave dehydration is the process of removal water content of structure via microwave energy. Ores from different regions show that minerals are responsive to microwave radiation, but optimal microwave exposures haven't any adverse effects on minerals [10]. In the experiments of Saito et al., dehydration behavior of goethite (FeO(OH) mineral was studied by microwave treatment [11]. The effects of microwave power levels and sample mass on drying characteristics of moisture content, drying rate, moisture ratio were studied for the ilmenite mineral. Experiment results showed that the moisture content and drying rates were found to be dramatically affected by microwave power density [12].

In this study, it is aimed to study the dehydration behavior of inderite mineral using the microwave energy. Also dehydration behavior of mineral experimented with thermal analysis method. Products were identified with X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) techniques; and characteristic features of products were compared.

2 Material and Methods

2.1Raw material preparation and characterization

Inderite mineral (Fig 1a) was used as raw materials in experiments. It was provided from Kırka Boron Management Plant (ETI Mine Kırka Works) in Eskisehir, Turkey. Mineral was grinded with Retsch agate mortar (Fig 1b) and sieved with Fritsch sieving equipment to the -90μm (Fig 1c).

For the identification, treated raw material (Fig 1d) was subjected to X-ray Diffraction (XRD) analysis with PANalytical Xpert Pro X-ray Diffraction Instrument was used. Raw materials was characterized by FT-IR analyses using a Perkin Elmer FT-IR with universal attenuation total reflectance (ATR) sampling accessory with a diamond/ZnSe crystal.

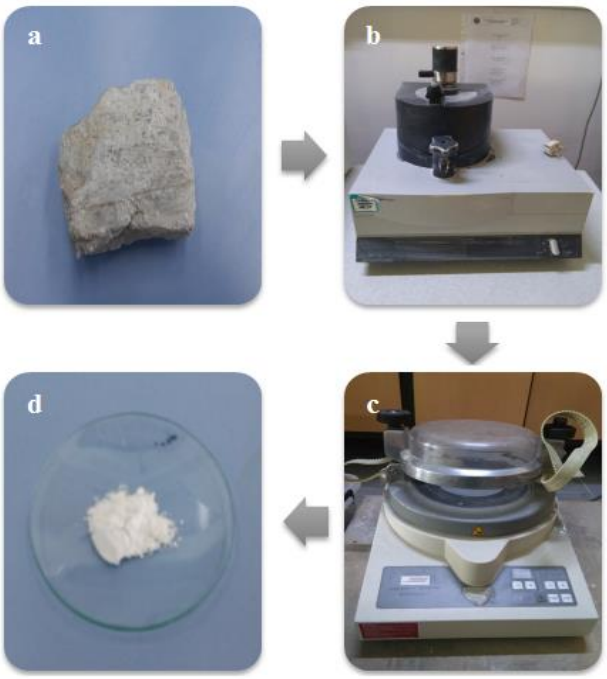

Figure 1. Preparation of Inderite a. Inderite (rock), b. Retsch agate mortar, c. Fritsch sieving equipment and d. Inderite (raw material)

2.2 Thermal dehydration of inderite

To compare with the microwave dehydration process conducted, Inderite mineral was studied with the TG/DTG analysis at Perkin Elmer Diamond DTA-TG Instrument. Thermal analysis experimented in the temperature range of 30–800°C, and heating rate was 10°C/min. Nitrogen atmosphere and platinum crucible were used during the experiments.

For the characterization of thermal dehydrated Inderite mineral, high temperature furnace of Protherm MOS180/4 was used. Mineral was calcined at 800°C in ceramic crucible with a heating rate of 10°C/min.

2.3 Microwave dehydration of inderite

A programmable domestic microwave oven (BOSCH-HMT72G 420, Turkey) with maximum output of 800 W and 2450 MHz was used for the drying experiments. The dimensions (H×W×D) of the microwave oven were 194×290×300mm.

In experiments, power level was selected as 600W for the dehydration. Dehydration procedure occured the cycles of 5 minutes microwave treatment and 5 minutes waiting time, respectively. Dehydration was ended after 40 mins. For each experiment, three parallels were done.

The crystal water and drying rate of synthesized Inderite mineral were calculated with using following equations (1) and (2):

$$m_c = (m_t/m) \times 100 \quad (1)$$

where m_c is the crystal water content of dried basis, %; m is the absolute amount of dried basis, g; m_t is the moisture amount at the time of t, g;

$$D = w/(A.t) \quad (2)$$

where D is the drying rate, g/s.cm^2; W is the amount of releasing water from structure, g; A is the area of drying surface of Inderite, cm^2; t is the drying time, min.

Dried samples were identified and characterized using XRD and FT-IR techniques.

3 Results and Discussion

3.1 Characterization

3.1.1 XRD results of samples

XRD pattern of raw mineral can be seen in Figure 2. According to XRD result raw mineral was identified as Inderite with the chemical formula of $Mg(B_3O_3(OH)_5).5H_2O$. XRD score of raw Inderite was 68. Crystal parameters of raw Inderite were given in Table I. In Table I, it is seen that raw Inderite mineral has the reference code of 01-070-0041 and the monoclinic crystal system.

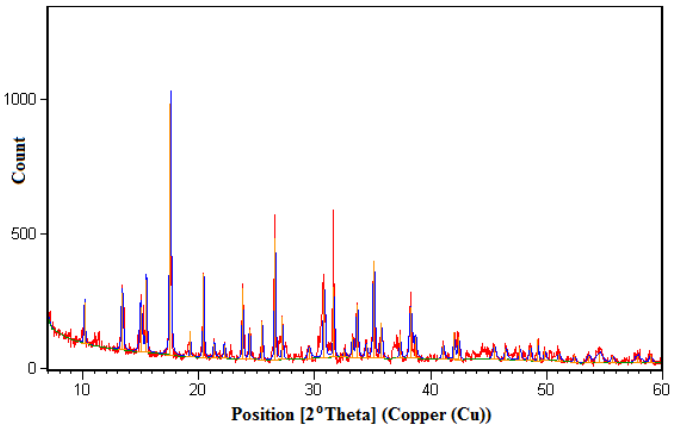

Figure 2. XRD pattern of raw Inderite

Table 1. XRD results of raw inderite

Crystal Parameters	
Mineral Name	Inderite
Reference Code	01-070-0041
Crystal System	Monoclinic
a (Å)	6.8221
b (Å)	13.1145
c (Å)	12.0350
Alpha (°)	90.0000
Beta (°)	14.5520
Gama (°)	90.0000

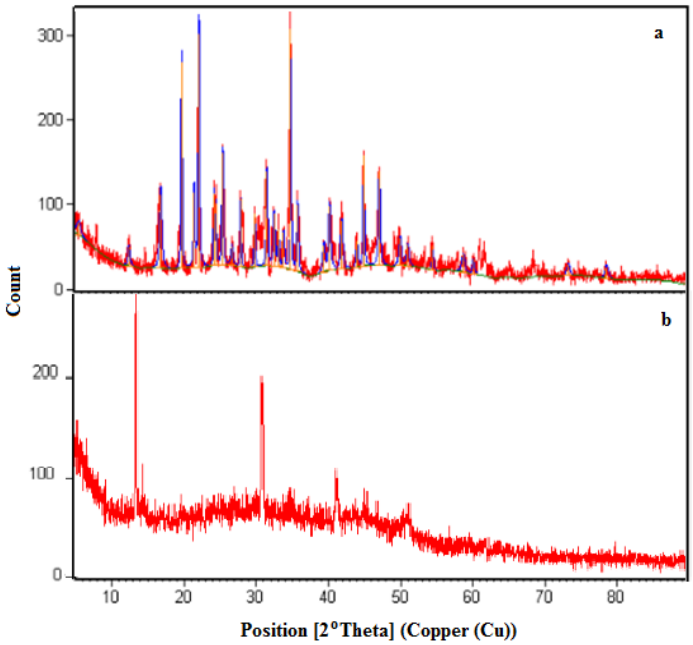

Figure 3. XRD patterns of dehydrated minerals a. Calcined mineral, b. Microwave dehydrated mineral

XRD patterns of dehydrated samples were presented in Figure 3. In Fig. 3a, calcined mineral was a mixture of two types of magnesium borates; MgB_4O_7 (XRD Score: 60) and $Mg_2B_2O_5$ (XRD Score: 20).

In Fig. 3b, microwave dehydrated sample can not be identified due to the amorphous phase formation. Microwave treatment affects the crystallinity of mineral adversely.

3.1.2 FT-IR results of samples

FT-IR spectrum of raw Inderite is presented Fig. 4. Interpretation characteristic strechings are given below;

- The band values of 3618, 3199 and 1684 cm^{-1} indicates stretching due the crystal water content of mineral.
- The peaks in the range of 1442, 1392 and 1346 cm^{-1} can be explain with the asymmetric stretching of three coordinate boron oxygen bending,
- In plane of OH^{-1} bending is seen at 1279, 1176 and 1132 cm^{-1},
- Asymmetric stretching of four coordinate boron oxygen bending is shown at the band values of 1040 and 982 cm^{-1},
- The band values of 859 and 798 cm^{-1} can be explain with the symmetric stretching of three coordinate boron oxygen bending,
- The last peak at 745 cm^{-1} indicates the plane of OH^{-1} bending.

Stretcthing between boron and oxygen atoms is compatible with literature [13].

FT-IR spectra of samples applied calcination and microwave dehydration process is shown in Fig. 5. It is seen that some peaks disappeared at the band values caused the water content in the method of traditional calcination of Inderite mineral (Fig. 5a). There are minor changes between the band values of boron oxygen strechings.

In Fig. 5b, the characteristic strechings caused crystal water gets lower. However, there are disappearing band values which indicate the strechings between boron and oxygen atoms in structure.

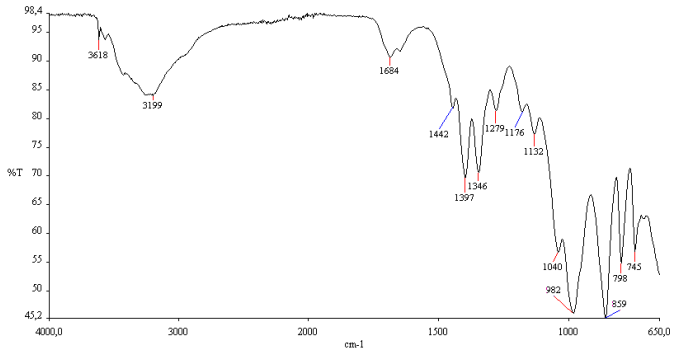

Figure 4. FT-IR spectrum of raw Inderite

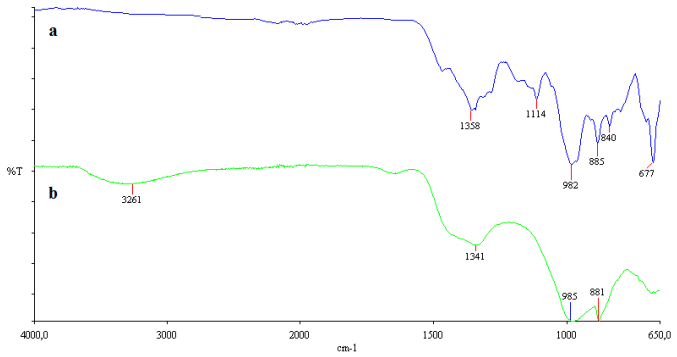

Figure 5. FT-IR spetra of dehydrated minerals a. Calcined mineral, b. Microwave dehydrated mineral

3.2 Dehydration behavior of inderite

3.2.1 Thermal analysis results

Thermal analysis result of Inderite mineral is shown in Fig. 6. According to thermogram of raw mineral, dehydration process occurs at one step. Water removal of Inderite mineral is seen between the temperatures of 30–662.6°C. DTA and DTG peak points are 138.1 and 133.6°C, respectively. Total mass loss (Δm) is 45.7% which is suitable with literature [1].

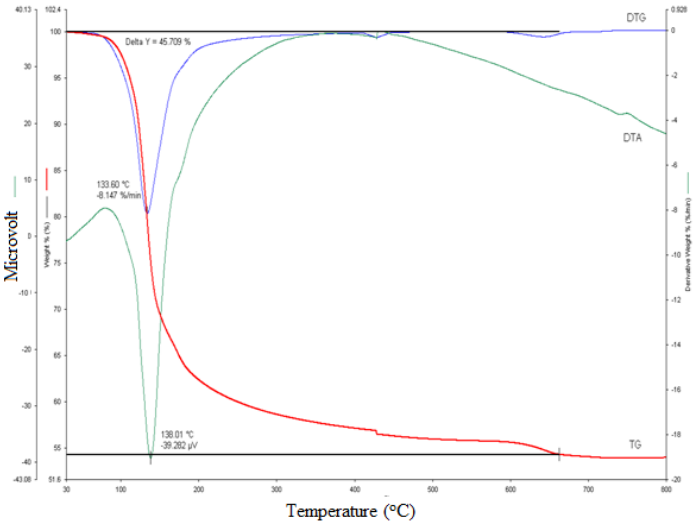

Figure 6. Thermogram of Inderite

3.2.1 Microwave treatment results

The relationship between mass change of hydrate structure and water content under microwave treatment is given in Fig. 7 and Table II. According to experiments and calculations, total mass loss (Δm) is 42.86% which is compatible with the result of thermal analysis result. At the end of 40 mins, crystal water content decreased to 2.84 %. This shows that major part water content is removed from the structure successfully.

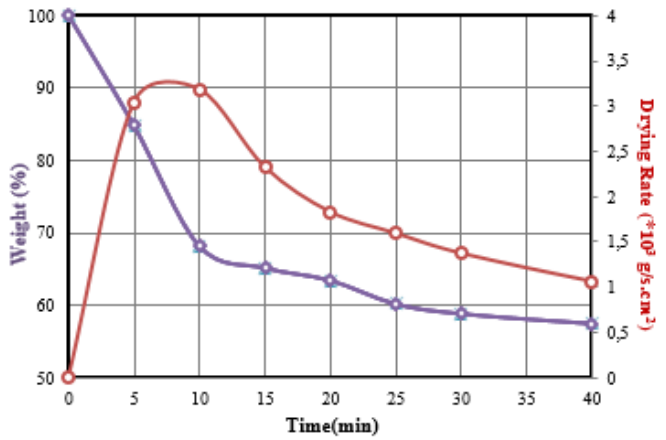

Figure 7. Microwave dehydration at 600W

Rate of removal water from the crystal structure, which could be described as drying rate, changed with crystal water content in structure. With the releasing of capillary and mineral bond water in Inderite, drying rate is higher in first minutes of dehydration. By the decreases of residual water content below 13.88%, drying rate approximately decreases in a linear way. The highest drying rate is seen at the dehydration time of 10 mins.

Table 2. Microwave dehydration at 600 W

Time (min)	Weight (%)	Water Content (%)	Water Content (Mole)	Drying Rate (*10³ g/s.cm²)
0	100.00	45.70	7.50	0.00
5	84.81	30.51	5.00	3.04
10	68.18	13.88	2.27	3.19
15	65.13	10.83	1.77	2.33
20	63.43	9.13	1.49	1.83
25	60.18	5.88	0.96	1.59
30	58.84	4.54	0.74	1.37
35	57.49	3.19	0.52	1.22
40	57.14	2.84	0.46	1.07

4 Conclusion

Determination of thermal behavior is essential for the use of mineral or materials in applications. Traditional determination method is calcination method which requires high temperatures.

In these experiments, it is seen that microwave treatment may be used in dehydration processes alternatively. Water content and drying rate values are determined with changing of dehydration time in microwave dehydration process. At end of the dehydration time of 40 mins, 7.04 moles water removed from the hydrated structure and the comparison of thermal dehydration to microwave dehydration is studied. There may be adverse effects in the crystallinity of dehydrated sample. However, these effects may be improved by the optimization of operation parameters.

In conclusion, boron minerals are suitable materials for the investigation of thermal dehydration kinetics using microwave energy. After optimum operating parameters determination, calculation of kinetic parameters can be experimented in future studies.

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