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REUSE OF MAGNESIUM WASTES IN HYDROTHERMAL SYNTHESIS OF A MAGNESIUM BORATE MINERAL: ADMONTITE

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Abstract

Magnesium wastes are among the gradually ascending and therefore challenging metal wastes, which are produced by many industrial activities. The purpose of this study is the usage of magnesium waste, a raw material in magnesium borate production by hydrothermal synthesis. Boron sources (boric acid (H_3BO_3) and boron oxide (B_2O_3)) react with magnesium wastes in order to synthesize the magnesium borate mineral of admontite ($MgO(B_2O_3)_3 \cdot 7(H_2O)$). In addition to the synthesis from waste magnesium, magnesium oxide (MgO) and B_2O_3 are also used to produce magnesium borates, in order to compare the results. Techniques of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and scanning electron microscopy with energy disperse (SEM-EDX) are used for further characterization analysis. The products' boron oxide contents and overall yields are also calculated. According to the results, synthesized minerals are identified as admontite ($MgO(B_2O_3)_3 \cdot 7(H_2O)$), mcallisterite ($Mg_2(B_6O_7(OH)_6)_2 \cdot 9(H_2O)$) and magnesium borate hydrate ($MgB_6O_7(OH)_6 \cdot 3(H_2O)$). It is seen that magnesium borates could be obtained as a mixture of different types of magnesium borate minerals or pure magnesium borate. A pure magnesium borate mineral of admontite is synthesized at the reaction temperature of $100^\circ C$ and the reaction time of 240 minutes using magnesium waste (W) and both H_3BO_3 (W) and B_2O_3 (B). B_2O_3 content and overall yields of pure admontite for the W-H were found as $51.15 \pm 0.52\%$ and $81.45 \pm 3.20\%$, respectively. Similarly, pure admontite synthesized from W-B have the $51.72 \pm 0.52\%$ of B_2O_3 content and $74.56 \pm 3.20\%$ overall reaction yield.

Key words: admontite, hydrothermal synthesis, magnesium borate, magnesium waste, overall yield

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1. Introduction

The increase in the rate of waste formation will be a problem for the future of the world challenges regarding the storage and disposal of wastes. Hence in recent years, studies concerning waste storage and evaluation are being carried out to solve this problem. Some kinds of wastes are hazardous for people and environment, one of which is metal wastes and scraps.

Metal wastes constitute 1% of solid wastes and 3% of the recovered wastes (TRMFWM, 2008). Metal waste formation per capita in the United States of America and Turkey are given as 8.9% and 7%, respectively (Derun et al., 2013). Among these wastes, Mg wastes, which are produced by many industrial

activities, are generally categorized into four groups. Type 1 is high-grade scrap, generally materials such as gates, runners and drippings from die-casting operations that is uncontaminated with oils. Type 2 is oil-contaminated scrap, type 3 is dross from magnesium-processing operations and type 4 is chips and fines (Kramer, 2004). Magnesium wastes used in this study, can be categorized as type 3 waste, obtained from a local gold factory, which were formed in the stage of plastic moulding.

Valorisation of wastes is getting more interesting for industrial activities more than storage because of the increasing cost of raw materials and energy. One of these evaluation methods is recycle process. Waste recycling process includes separate

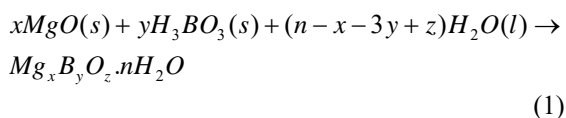
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collection, magnetic extraction, and smelting factory and recycled metal steps for the case of procuring new metal products (TR Ministry of Forest and Water Management, 2009).

Kipcak et al. (2012) showed that the use of magnesium wastes as a raw material in the production of the magnesium borate hydrates is possible. There has not been any other specific application of metallic magnesium wastes as a raw material, whereas some other metallic wastes studied. For example; Shih et al. (2005) studied the effects of heavy metal content in the cement raw mix on the crystalline formation in cement production by using heavy metal-containing sludge from surface finishing and electroplating industries. Jing et al. (2009) evolved synthesis process of forsterite refractory which involves the steps of production of magnesium iron solid (Mg_{1-x}Fe_xO) and magnesium metasilicate (MgSiO₃), formation of the fayalite, and creation the forsterite by iron ore tailings. Lee et al. (2003) used iron metal waste for the removal of Cr (VI) from water using a batch process.

Magnesium borates, which are a class of boron minerals, were diverse according to their structural waters. Inderite [MgB₃O₃(OH)₅·5(H₂O)], pinnoite [MgB₂O₄·3(H₂O)], admontite [MgB₆O₁₀·7(H₂O)] and mcallisterite [Mg₂B₁₂O₁₄(OH)₁₂·9(H₂O)] were the most known magnesium borate minerals that have special names. Also MgB₆O₁₀·6(H₂O) and MgB₆O₁₀·3(H₂O) type of magnesium borates were found in nature. Magnesium borates can be used as a both magnesium and a boron source. The percentage of B₂O₃ is an important index for boron minerals and products, as these borates have excellent mechanical and thermal properties, such as corrosion resistance, high coefficients of elasticity and high heat resistance, which increase by means of the increase in B₂O₃ content. The B₂O₃ content varies between 36.5% and 62.2% in magnesium borates. In admontite, the B₂O₃ content is 55.6%. Magnesium borates can be used in the ceramic industry, in detergent formulations, in the production of superconducting materials, and as catalysts for the conversion of hydrocarbons, due to the content of boron in the friction-reducing additives in oils and insulating coating compositions (Elssfah et al., 2007; Koruk and Girgin, 2009; Li et al., 2010; TRPMSPPO, 2006).

Magnesium borates can be synthesized by hydrothermal method, where raw materials usually react in an aqueous solution. In this method the hydrated magnesium borates can be produced, the reaction of which is given in the equation stated below (Eq. 1):



Zhihong and Mancheng (2003) produced MgO·3B₂O₃·3.5H₂O at the boiling point of the solution. Another study made by the same authors involves the production of Mg₂B₂O₅·H₂O from the

raw materials of 2MgO·2B₂O₃·MgCl₂·14H₂O and H₃BO₃. Their production parameters are 180°C reaction temperature and 30 minutes of reaction time (Zhihong and Mancheng, 2010). Zhu et al. (2009) synthesized nanowire type magnesium borates using the raw materials of H₃BO₃, MgCl₂ and NaOH at a reaction temperature of 240°C and a reaction time of 18 hours. Another study made by Zhu et al. (2010) is about the production of Mg₂B₂O₅ from monoclinical MgBO₂·(OH) at 700°C and 6 hours, where MgBO₂·(OH) is produced from MgCl₂·H₂O, H₃BO₃ and NaOH at 200°C reaction temperature and 12 hours of reaction time. Zhihong et al. (2004a) synthesized Mg₂[B₂O₄(OH)₂]·H₂O at a reaction temperature of 120°C and a reaction time of 3 days. The main advantage of the hydrothermal method in powder preparation is that it can be used to directly synthesize homogeneous, extremely fine and narrowly dispersed particles easily with good uniformity of composition. In the magnesium borate synthesis studies conducted by several authors, the temperatures higher than 100°C are used and long reaction times were preferred (Dou et al., 2010, Zhihong and Mancheng, 2003; Zhihong and Mancheng, 2010, Zhihong et al., 2004a).

The novelty of this study is to synthesize magnesium borate minerals using magnesium wastes along with the lower synthesis temperatures (≤ 100°C) and lower reaction times (≤ 4h) using the green chemistry approach. For this purpose magnesium wastes were used with both H₃BO₃ and B₂O₃ as reactants, and a batch-type reactor was employed at different reaction temperatures and reaction times. Also in order to compare the results that were synthesized with magnesium wastes, pure MgO was also used with B₂O₃ after waste synthesis. Another originality of the paper arises from the calculation of the overall reaction yield of the products.

The synthesized products of magnesium borate hydrates were investigated and characterized by the methods of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and scanning electron microscopy with energy disperse (SEM-EDX), and their B₂O₃ contents were determined experimentally.

2. Material and methods

2.1. Preparation of the reactants

The boron sources of H₃BO₃ (99.90%) and B₂O₃ (98%) were retrieved from Boron Management Plant of Kirka in Eskisehir-Turkey. Magnesium waste was obtained from a local gold factory's plastic molding wastes. MgO (99.30%) was obtained from Merck Chemicals. Before the reaction, the boron sources (H₃BO₃ and B₂O₃) were crushed, grounded and sieved to +200 mesh with an agate mortar. MgO was used without any pre-treatment.

The reactants were taken for identification analysis, which was performed with PANanalytical Xpert Pro XRD with a Cu-Kα tube inside working with the parameters of: 45 kV, 40 mA, step size of

0.03°, times for step is 0.5s, scan speed of 0.06°C/s and scan range of 7-90°.

In order to investigate the magnesium content of a waste, CamScan Apollo 300 Field Emission SEM-EDX was used both with area scan and map scan at 20kV voltage. To investigate the contents of magnesium wastes, PANanalytical Minipal 4, X-ray fluorescence (XRF) analyses were made with a silicon detector working at between 4kV and 30kV.

2.2 Hydrothermal synthesis of magnesium borate hydrates

Magnesium to boron molar ratio of 1:6 was determined after lots of pre-syntheses. Ultrapure water (18.3 mΩ.cm) used in the experiments was supplied from a Human Power I⁺ Water Purification System. The raw materials were reacted in a closed vessel with a temperature control unit. After the reaction, the solution filtered and residue was dried in an Ecocell oven at 40°C. The dried sample was washed and filtered with pure alcohol (96%), supplied from Merck Chemicals, to eliminate the excess H₃BO₃ content. Then, the filtered content was dried in an oven again at 40°C. This experimental procedure was performed at the reaction temperatures of 80, 90 and 100°C and for reaction times of 30, 60, 120 and 240 minutes. The scheme of the procedure is shown in Fig. 1.

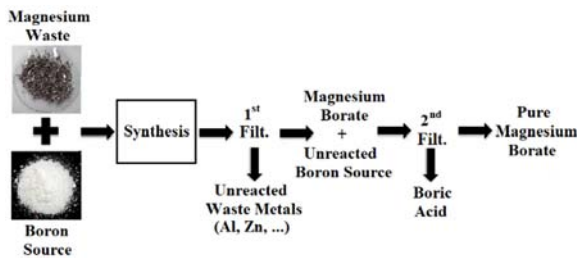


Fig. 1. The scheme of the synthesis procedure

2.3. Reaction yields

For the case of reaction yield based on molar flow rates, the overall yield, Y_D , is defined as the ratio of moles of product formed at the end of the reaction, N_D , to the number of moles of the key reactant, A, that have been consumed. N_{A0} and N_A are the initial and final moles of consumed reactant, respectively. For a batch system (Fogler, 1999) Eq. (2):

$$Y_D = \frac{N_D}{N_{A0} - N_A} \quad (2)$$

Using waste magnesium as the key reactant, five parallel experiments were conducted. Because pure admontite was synthesized at 100°C and a reaction time of 240 minutes, the reaction yields were calculated using Eq. (2).

2.4. Characterization of the synthesized products

The synthesized products were subjected to XRD analyses, with the parameters described in Section 2.1. Since the magnesium borates characteristic peaks observed below 60° (Derun et al., 2013, Derun and Senberber, 2014), scan range was selected between 7-60°. The products were also subjected to “Vibration Spectroscopy” techniques of both Infrared region and Visual region spectra. Infrared region spectra were recorded in the range 650-1800 cm⁻¹, with Perkin Elmer Spectrum One FT-IR with universal attenuated total reflectance (ATR) sampling accessory – Diamond/Zn and scan number was used as 4 and resolution set as 4 cm⁻¹. Visual region spectra were performed by Perkin Elmer Raman Station 400F Raman spectroscopy, with using the exposure time (s) and number of exposures as 4. A measurement range of 1400–250 cm⁻¹, and data interval set as 2 cm⁻¹ were chosen. Full (100%) laser power and the “auto baseline” option were also used.

The B₂O₃ contents of the boron minerals are very important properties for the determination of their qualities and commercial values. In the procedure B₂O₃ content determination, 1g of synthesized mineral was dissolved in 3 ml of 37% HCl and then diluted to 100 ml. As the reference material pure H₃BO₃ prepared was used in the same manner. Then, B₂O₃ amounts were determined through acid–base titration with a METTLER DL-25 titrator (Derun and Kipcak, 2012; Derun et al., 2013).

SEM analysis was conducted using a backscattering electron (BEI) detector with magnification of 1000 and 5000x to analyze the surface morphology and particle size distribution of the products.

3. Results and discussion

3.1. Identifications and characterizations of the reactants

The XRD patterns and results of the magnesium and boron sources are given in Table 1.

Table 1. XRD results of raw materials

Raw material	Pdf number	Mineral name	a (Å)	b (Å)	c (Å)	Crystal system
Magnesium waste	01-089-5003	Magnesium	4.2114	4.2114	4.2114	Hexagonal
	01-089-2769	Aluminum	4.0495	4.0495	4.0495	Cubic
Magnesium oxide	01-077-2179	Periclase	4.2114	4.2114	4.2114	Cubic
Boric acid	01-073-2158	Sassolite	7.0390	7.0530	6.5780	Anorthic
Boron oxide	00-006-0297	Boron oxide	10.0550	10.0550	10.0550	Cubic
	01-088-2485	Boron oxide	2.8790	2.8790	7.0520	Hexagonal

The XRD patterns and results of the magnesium and boron sources are given in Fig. 2, respectively.

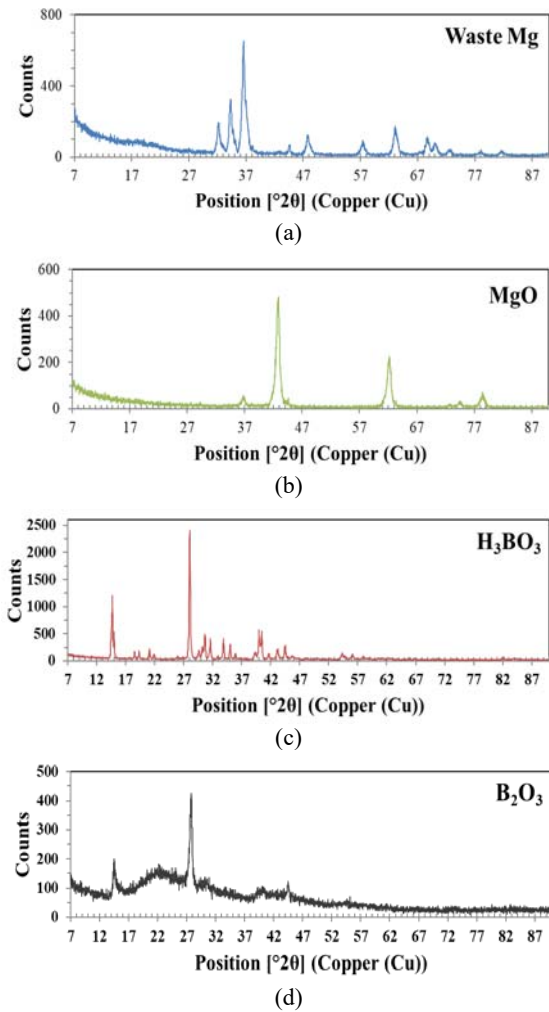


Fig. 2. XRD patterns of raw materials: (a) Waste Mg, (b) MgO, (c) H₃BO₃, (d) B₂O₃

According to the XRD results of magnesium source, magnesium oxide was found as “Periclase [MgO]” with powder diffraction file (pdf) number of “01-077-2179”, waste magnesium’s major and minor components were found as “Magnesium [Mg]” with pdf number of “01-089-5003” and “Aluminum [Al]” with pdf number of “01-089-2769”, respectively. The XRD results of the boron sources showed that boric acid was “Sassolite” [H₃BO₃] with “01-073-2158” pdf number, boron oxide’s major and minor

components were “Boron Oxide [B₂O₃]” with “00-006-0297” pdf number and “Boron Oxide [B₂O]” with “01-088-2485” pdf number, respectively.

Waste magnesium’s SEM-EDX and XRF results are given in Table 2. According to the results, the aforementioned major and minor components of magnesium and aluminium both front and back layers, which were detected in XRD analyses, were seen again. Also XRF analyses results were compatible with SEM-EDS results. In yield calculations, the magnesium ratio of waste was considered as 93.55%, which was average of front and back layers’ Mg element ratios. SEM mapping analysis of magnesium waste is shown in Fig. 3. According to the results, zinc and aluminum impurities in the wastes can be seen and the impurities were distributed uniformly. Element distributions can be seen by white points on the black background.

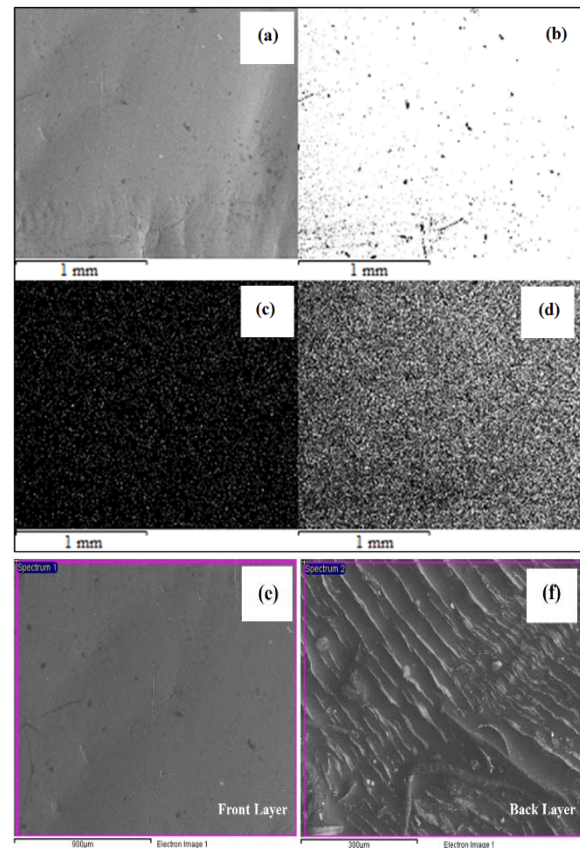


Fig. 3. SEM mapping of: (a) magnesium waste, (b) magnesium distribution, (c) zinc distribution, (d) aluminium distribution, (e) front layer of magnesium waste, (f) back layer of magnesium waste

Table 2. XRF and SEM-EDS results of magnesium waste

Analysis	Atomic Ratio of Elements (%)								
	Mg	Al	Zn	Mn	S	Ca	Cr	Fe	Cu
XRF	93.30	3.67	0.88	0.90	0.08	0.11	0.03	0.93	0.14
SEM-EDS (Front layer)	96.38	2.88	0.27	0.18	-	0.10	0.03	0.07	0.08
SEM-EDS (Back layer)	90.73	3.18	0.55	0.13	1.62	1.47	0.09	2.01	0.22

3.2. X-ray diffraction results of the products

XRD results and the crystallographic data of the synthesized products are shown in Table 3 and Table 4, respectively. Sets of synthesized products were coded according to initial letter of used raw materials (Waste of magnesium: W, MgO: M, B₂O₃: B, H₃BO₃: H). From the XRD results of the syntheses, three different types of magnesium borates, namely admontite with pdf number of "01-076-0540" and structural formula of MgO(B₂O₃)₃·7(H₂O), mcallisterite with pdf number of "01-070-1902" and structural formula of Mg₂(B₆O₇(OH)₆)₂·9(H₂O), and magnesium borate hydrate with pdf number of "01-073-0638," and structure formula of MgB₆O₇(OH)₆·3(H₂O) are formed. Typically dual or ternary formations were occurred and pure admontite minerals were synthesized only with magnesium wastes-boric acid (W-H) and magnesium wastes-boron oxide (W-B) at 100°C reaction temperature and 240 minutes of reaction time.

Also in the study of Derun et al. (2013), admontite mineral was synthesized from pure magnesium oxide and boric acid. In order to compare the synthesized admontite minerals both synthesized from W-H and W-B, admontite XRD patterns were given with the reference pattern of Derun et al. (2013) in Fig. 4.

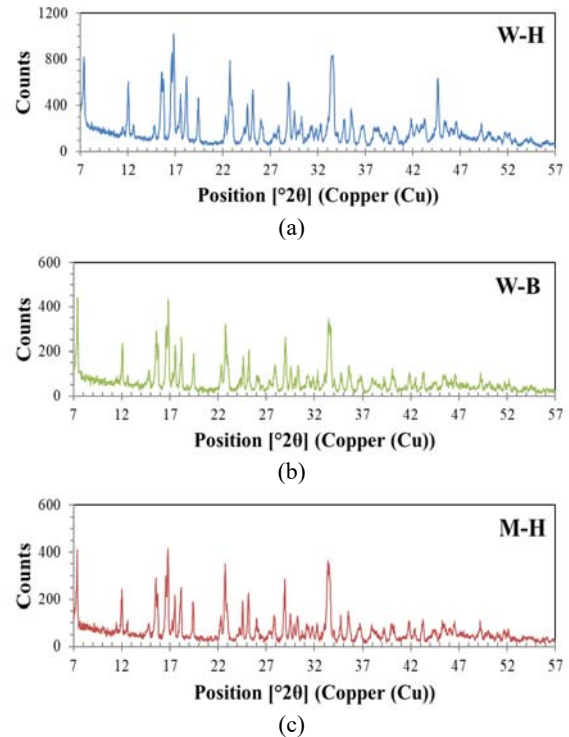


Fig. 4. XRD patterns of synthesized admontite from: (a) W-H, (b) W-B, (c) M-H

Table 3. XRD results of synthesized minerals with hydrothermal procedure

Temperature (°C)	Time (min)	XRD scores of								
		M-B			W-H			W-B		
		▲*	●*	■*	▲	●	■	▲	●	■
80	30	12	26	-	52	60	14	26	82	26
	60	38	-	12	30	85	29	73	38	-
	120	56	76	16	8	83	-	48	50	19
	240	71	50	15	58	82	-	45	35	13
90	30	39	77	18	46	80	20	2	68	-
	60	43	6	11	65	81	28	22	34	9
	120	38	15	9	59	80	-	21	64	15
	240	5	60	-	17	84	26	53	21	10
100	30	23	65	-	10	87	27	-	87	15
	60	57	-	11	60	79	22	40	74	27
	120	7	78	-	45	84	-	71	-	23
	240	17	-	7	78	-	-	54	-	-

Table 4. Crystallographic data of synthesized magnesium borate hydrates

Mineral name	Admontite	Mcallisterite	Magnesium borate hydrate
Pdf number	01-076-0540	01-070-1902	01-073-0638
Chemical formula	MgO(B ₂ O ₃) ₃ ·7(H ₂ O)	Mg ₂ (B ₆ O ₇ (OH) ₆) ₂ ·9(H ₂ O)	MgB ₆ O ₇ (OH) ₆ ·3(H ₂ O)
Molecular weight (g/mole)	375.27	768.56	357.26
Crystal system	Monoclinic	Rhombohedral	Monoclinic
Space group	P21/c (No. 14)	Pr3c (No. 167)	P21/c (No. 14)
Unit cell dimension (Å)	a= 12.6610	a= 11.5490	a= 11.3070
	b= 10.0910	b= 11.5490	b= 10.4440
	c= 11.3220	c= 35.5670	c= 10.8350
z	4	6	4
Density (calculated) (g/cm ³)	1.83	1.86	1.86

Generally Mcallisterite formation is seen as the major phase among the others where magnesium borate hydrate formation is the minor phase. Admontite formations were seen typically at 240 minutes of reaction times with some exceptions. The best formations according to the crystal scores (for a perfect crystal structure XRD score is equal to 100), were seen with the W-H precursor. In synthesis experiments, mixtures of two or three types of magnesium borates were synthesized. It is seen that reaction temperature and time was more effective in crystallinity features than structure of magnesium borate. Higher crystallinity products can be obtained at higher temperature and reaction times. Magnesium borate hydrate minerals might transform each other with the change of reaction parameters. According to XRD results, magnesium borates, which were synthesized with the reaction of magnesium waste, had higher XRD scores. In other words, these products showed higher crystallinity properties than other synthesized minerals.

A three-dimensional model graph of admontite formation was obtained from the XRD data and drawn using Statistica (Fig. 5). In this graph, the z, y and x axes represent the XRD score, the reaction time in minutes and the reaction temperature in °C, respectively. From the graph of W-H, it is seen that the admontite formation is higher at around 100°C and the highest at the 240 minutes of reaction time. At the W-B again the admontite formation is higher at around 100°C and this time the highest admontite formation occurred at the reaction time of 120 minutes. In FT-IR results; first two peaks with peak values of 1659.42 and 1418.17 cm^{-1} can be explained with the asymmetric and stretching of the three coordinate boron ($\text{B}_{(3)}\text{-O}$). The peaks between 1348.10 and 1231.96 cm^{-1} show the in-plane OH^{-1} bending. The peak values between 1087.23 – 955.21 cm^{-1} and 898.22 – 809.10 cm^{-1} can be the vibrations of asymmetric and symmetric stretching of four-coordinate boron ($\text{B}_{(4)}\text{-O}$), respectively. Bending of $\text{B}_{(3)}\text{-O}$ occurred at the peak values of 670.70 cm^{-1} .

According to Raman results, the peak values of 1381.21 and 1376.10 cm^{-1} may be explained with the asymmetric stretching of $\text{B}_{(4)}\text{-O}$. Symmetric stretching of $\text{B}_{(3)}\text{-O}$ is seen between the peaks at

963.66 and 962.29 cm^{-1} . Symmetric stretching of $\text{B}_{(4)}\text{-O}$ is only observed in the 240 minute synthesis of W-B, with the peak value of 881.20 cm^{-1} . The $\nu_p[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}/\nu_p[[\text{B}_3\text{O}_3(\text{OH})_4]$, which are characteristic peaks of magnesium borates, are seen between the peak values of 639.14 and 636.12 cm^{-1} . The peak values between 425.29 – 319.75 cm^{-1} can be explained with the bending of $\text{B}_{(3)}\text{-O}$ and $\text{B}_{(4)}\text{-O}$.

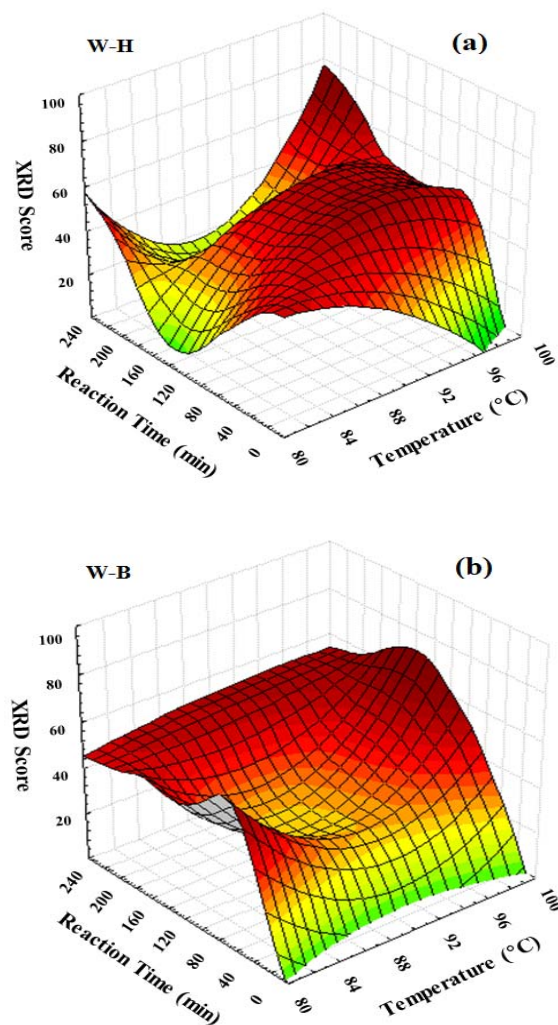


Fig. 5. Three-dimensional model graph of admontite formation: (a) W-H and (b) W-B

Table 5. B_2O_3 contents of synthesized minerals

Temperature (°C)	Time (min)	M-B (%)	W-H (%)	W-B (%)
80	30	50.26±1.05	50.26±2.09	41.33±0.52
	60	49.89±0.52	50.26±1.05	46.94±1.57
	120	50.63±1.57	48.41±0.52	45.39±2.09
	240	53.96±1.05	48.04±2.09	46.07±1.57
90	30	48.78±2.09	49.52±1.05	50.26±1.05
	60	48.04±1.05	49.15±0.52	48.78±1.05
	120	50.82±0.78	49.52±1.05	49.15±0.52
	240	51.00±1.05	41.02±0.52	48.41±0.52
100	30	48.23±0.78	48.41±0.52	49.52±3.14
	60	50.08±1.31	47.68±0.52	53.22±2.09
	120	47.31±1.05	48.41±0.61	48.41±0.52
	240	46.94±1.57	51.15±0.52	51.72±0.52

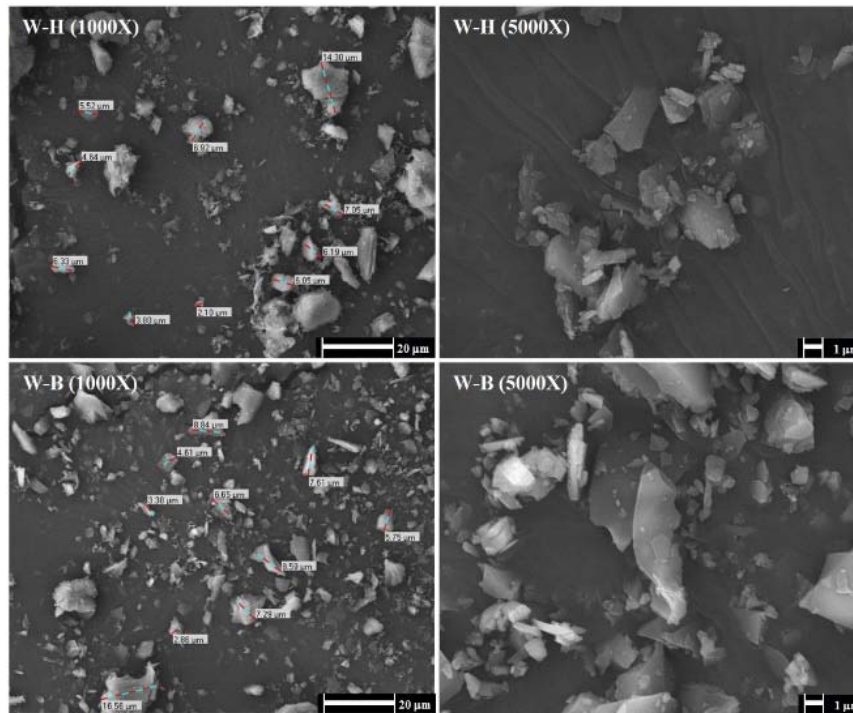


Fig. 6. SEM surface morphologies of admontite minerals synthesized with the reaction of W-H and W-B at 100°C and 240 min

From the results of both FT-IR and Raman spectra, identified peaks were found to be compatible with previous studies (Yongzhong et al., 2000; Zhihong et al., 2004b). This shows that syntheses with different reactants, the structure does not change the characteristic bond stresses. Content of B_2O_3 results and SEM morphology photos are also given in Table 5 and Fig. 6, respectively. B_2O_3 results show that all the synthesized products have similar B_2O_3 contents, which were between $45.39 \pm 2.09\%$ and $53.96 \pm 1.05\%$. B_2O_3 contents of pure admontites for the W-H and W-B reactions were found $51.15 \pm 0.52\%$ and $51.72 \pm 0.52\%$, respectively. In literature, the B_2O_3 content of admontite and mcallisterite minerals have been reported to be 55.66% and 54.35%, respectively (T.R. Prime Ministry SPO, 2006). It is seen that the synthesized admontite minerals theoretical and experimental B_2O_3 contents were close.

The SEM morphologies of the minerals produced from W-H and W-B are shown. Transparent, rectangular shaped admontite crystals are occurred from both W-H and W-B. Generally; from W-H and W-B, the particle size of the admontite minerals was formed at between 2.10 – 14.30 μm and 2.86 – 16.56 μm , respectively (Fig. 6). In accordance with the yield calculations of pure admontite, yield values were calculated and found as $81.45 \pm 3.20\%$ and $74.56 \pm 3.20\%$ at reactions of W-H and W-B, respectively. It is seen that admontite synthesized with the reaction of W-H has higher overall reaction yield.

4. Conclusions

In this study, magnesium wastes are evaluated as a raw material in the production of magnesium

borates. A Special type of magnesium borate mineral namely admontite is obtained at 100°C and 240 minutes from both sets of W-H and W-B. XRD crystal scores showed that H_3BO_3 is more suitable for the high crystalline admontite synthesis. B_2O_3 contents, FT-IR and Raman bands of the synthesized minerals are in good agreement with literature B_2O_3 value and characteristic peaks of magnesium borates, respectively. Also admontite minerals particle sizes are found between 2.10 – 14.30 μm and 2.86 – 16.56 μm at W-H and W-B.

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