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Magnesium Waste Evaluation in Moderate Temperature (70^oC) Magnesium Borate Synthesis

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Abstract**—**Waste problem is becoming a future problem all over the world. Magnesium wastes which can be used in recycling processes are produced by many industrial activities. Magnesium borates which have useful properties such as; high heat resistance, corrosion resistance, supermechanical strength, superinsulation, light weight, high coefficient of elasticity and so on. Addition, magnesium borates have great potential in the development of ceramic and detergents industry, whisker-reinforced composites, antiwear, and reducing friction additives.

In this study, using the starting materials of waste magnesium and H_3BO_3 the hydrothermal method was applied at a moderate temperature of 70^oC with different reaction times. Several reaction times of waste magnesium to H_3BO_3 were selected as; 30, 60, 120, 240 minutes. After the synthesis, X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) techniques were applied to products. As a result, the forms of Admontite [$MgO(B_2O_3)_3.7(H_2O)$] and Mcallisterite [$Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$] were synthesized.

Keywords**—**Hydrothermal synthesis, magnesium borates, waste magnesium.

I. INTRODUCTION

THE increase in the rate of waste formation is likely to bring about a couple of issues for future of the world due to storage and disposal of wastes. Recently, studies about waste storage and evaluation are brought forth in order to overcome with these issues. Some sorts of wastes are hazardous for public and environment. One of the dangerous wastes is metal wastes and scraps. Distribution of waste per person in the United States and Turkey are 8.9% and 7% of metal waste, respectively [1].

Evaluation of wastes is getting more interesting for industrial activities more than storage because of the increasing cost of raw materials and energy. One of evaluation method is recycle process [2].

Magnesium is a chemical element with the symbol Mg, atomic number 12, and common oxidation number +2. Magnesium is the lightest of all design metals. It's light in weight just like a plastic material and also tough like a metal. It's high specific toughness and rigidity, good machinability, cast ability and weld ability with known methods makes it attractive for chemical industry. Also magnesium's scrap material can be used in recycling processes all over the world [3].

Boron, the fifth element in the periodic table, has widespread commercial uses. Boron (B) has an atomic weight of 10.81g/mol with two isotopes, ^{10}B and ^{11}B, neither of which is radioactive. Boron-containing minerals are almost all inorganic salts of boron and commercially important deposits are found in the United States, Turkey, South America, Russia, and China. Turkey has 72.2% of the boron minerals that are present in the world, which can sufficiently meet world's needs for many years. Approximately world's total reserves are reported to be 1.2 billion tons [4], [5]. In addition, boron as borates or boric acid is ubiquitously present in soil, water, and food where its presence is due to its being an essential element for plant growth [6].

Boric acid (H_3BO_3) is produced industrially from borate minerals and brines. Alkali and alkaline earth metal borates (such as borax, colemanite, ulexite or kernite) react with strong acids to form boric acid. In Turkey, boric acid which has the 65% of world reserves is obtained from colemanite ($2CaO.3B_2O_3.5H_2O$) [7].

Boric acid is an important industrial resource and it is widely used in many kinds of the manufacturing processes, such as glass, semiconductor, ceramics, electroplating industry and nuclear industry. Boric acid is also the most commonly used boron compound in the preparation of boron chemicals such as synthetic organic borate salts, borate esters, boron carbide, fluoroborates and boron trihalides. In recent years, boric acid has gained special attention as the catalyst in organic synthesis [8].

The synthesis of magnesium borates has attracted the attention of many researchers owing to their useful properties, such as high heat resistance, corrosion resistance, supermechanical strength, superinsulation, light weight, high coefficient of elasticity and so on [9]. Also magnesium borate has great potential in the development of thermoluminescence phosphor materials, whisker-reinforced composites, antiwear, and reducing friction additives [10].

Magnesium borates and minerals could be used as a sorce of magnesium element and boron supply. In general, magnesium borate compounds are mainly used for the following applications which are purifications of percides from the land, manufacturing of superconductor MgB_2, in order to attenuator of abrasion and friction as oil doping, coating materials for the insulated metal surfaces, for the production of the thermo-

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chromic ink materials, for the dyes as inhibitor in order to prevent corrosion, for the washing of detergents and similar materials and also as flame retardants [11].

Magnesium borates can be synthesized by liquid-state or solid-state methods. In literature, synthesized magnesium borate minerals with liquid-state method can be listed as; $MgBO_2$ (OH) [12], $MgO.3B_2O_3.17H_2O$ [13], $MgO.3B_2O_3.3{,}5H_2O$ [14], $2MgO.2B_2O_3.MgCl_2.14H_2O$ [15], $2MgO{\cdot}B_2O_3{\cdot}H_2O$ and $MgO{\cdot}3B_2O_3{\cdot}7H_2O$ [16]. Synthesized magnesium borate minerals with solid-state method can be listed $Mg_2B_2O_5$ [17]–[18], $Mg_3B_2O_6$ [19], [20]. The common feature of all studies done as a raw material MgO or $Mg(OH)_2$ is to use in synthesis.

In this study, magnesium wastes were used as magnesium source in magnesium borate production. It can be sample as a new perspective in evaluation of metal wastes.

II. Experimental

A. Raw Material Preparation and Characterization

Magnesium wastes (Fig. 1 (a)) were order from local gold factory in Turkey. These wastes were occured from the instance of plastic molding in the manufacturing processes where these wastes stored in the factory.

Boric acid (Fig. 1 (b)) is retrieved from the Boron Management Plant in Bandırma, Turkey. It was grinded with agate mortar (Fig. 1 (c)) and sieved (Fig. 1 (d)) to a particle size below 200 mesh.

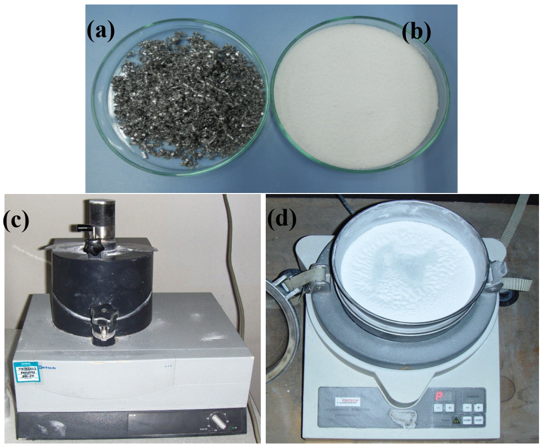

Fig. 1 (a) Waste Mg, (b) Boric acid, (c) Grinding process, (d) Sieving process

Magnesium wastes and boric acid were subjected to X-Ray Diffraction (XRD) analysis with Philips PANanalytical brand (Fig. 2 (a)) where in this equipment X-rays were produced from Cu-Kα tube at the parameters of 45kV and 40mA [4].

Magnesium wastes were subjected to X-Ray Fluorescence (Fig. 2 (b)) analysis by Philips PANanalytical brand Minipal Model 4 with silicon drift detector [10].

(a) (b)

Fig. 2 (a) Philips PANalytical XRD, (b) Philips PANanalytical XRF

Also magnesium wastes were analyzed with Scanning electron microscope with Energy Disperse Spectroscopy (SEM-EDX) by CamScan Apollo 300 field-emission SEM (Fig. 3) and EDS detector brand is Oxford.

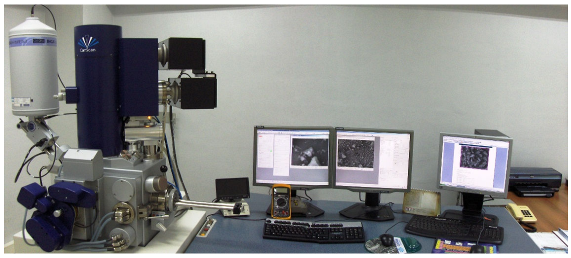

Fig. 3 CamScan Apollo 300 SEM

Boric acid was subjected to Perkin Elmer Spectrum One (Fig. 4) Fourier Transform Infrared Spectroscopy (FT-IR) and Perkin Elmer Brand, techniques. In the FT-IR technique Universal ATR sampling accessory – Diamond / ZnSe is used and measurement range is selected as 4000–650cm^{-1}, scan number is 4 and resolution set as 4cm^{-1}.

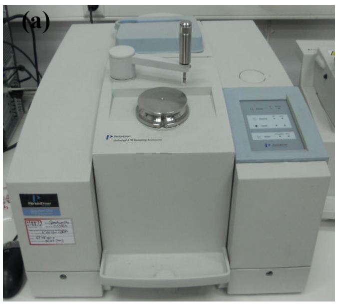

Fig. 4 (a) Perkin Elmer Spectrum One FT-IR

B. Hydrothermal Synthesis of Magnesium Borates

For the hydrothermal synthesis, starting molar ratio of waste magnesium to boric acid was selected as 1:6 [21]. The liquid phase was used as ultra-pure water (18.3 mΩ.cm) that was produced from the equipment of Human Power I+ Water Purification System.

Experiment temperature was selected as 70^{o}C, and four different reaction times (30, 60, 120, 240min) were conducted to investigate the phase transition between different types of magnesium borates according to the reaction time changes.

After the reaction, the first filtration process was used for the removal of excess magnesium and other trace amount of metals inside the waste magnesium. In this process, 70°C hot water was used for the washing and dispersing the synthesized magnesium borates below the filter paper. After that the slurry content was dried in Ecocell model oven at 40°C. The dried content was washed and filtered with pure alcohol (96°), supplied from Merck Chemicals, in order to remove excess boric acid content that was unreacted in the hydrothermal reaction. Then the filtered content was dried in Ecocell model oven again at 40°C.

C. Characterization of the Synthesized Magnesium Borates

At this step synthesized materials were subjected to XRD and FT-IR techniques with the parameter set explained at Part II *A:* "Raw Material Preparation and Characterization".

III. Results and Discussion

A. Raw Material Characterization Results

XRD patterns of the waste magnesium and boric acid were shown in Figs. 5 and 6, respectively.

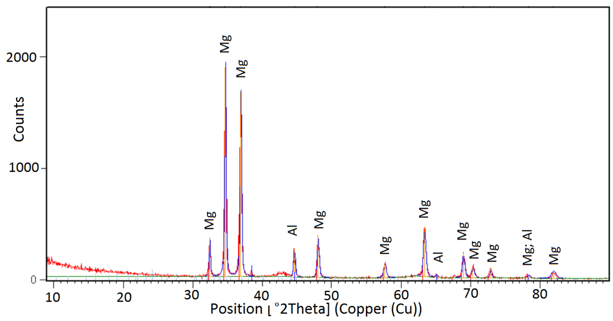

Fig. 5 XRD pattern of waste magnesium [22]

From the waste magnesium XRD pattern, the major peaks represents the 01-089-5003 numbered powder diffraction file (pdf) magnesium also some aluminum minor peaks are observed with pdf number of 01-089-2769 [22].

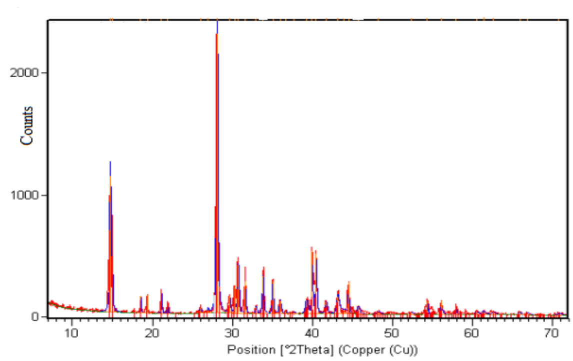

Fig. 6 XRD pattern of boric acid

From the boric acid XRD pattern, peaks represents the "H_3BO_3 (Sassolite)" formulated and pfd numbered "01-073-2158'' boric acid.

XRF and SEM-EDS results of the waste magnesium were shown in Table I.

TABLE I
XRF and SEM-EDS Results of the Waste Magnesium [22]

Elements	XRF Content (%)	SEM-EDS Content (%)
Mg	93.30	93.12
Al	3.67	3.54
Zn	0.88	1.72
Mn	0.90	1.02
S	0.08	0.21
Ca	0.11	0.14
Cr	0.03	-
Fe	0.93	-
Cu	0.14	0.25

Both XRF and SEM-EDS results showed that the major element in the waste magnesium is "magnesium" and the minor element is "aluminum". Other elements can be classified as trace elements. XRF and SEM-EDS analysis supports the XRD analysis.

FT-IR spectrum of the boric acid is shown in Fig. 7.

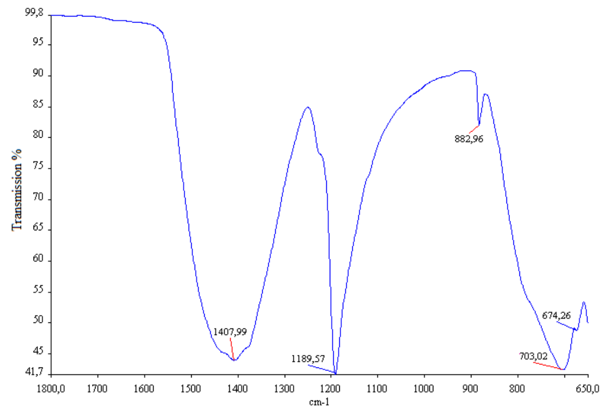

Fig. 7 FT-IR spectrum of the boric acid

According to the FT-IR analysis of the boric acid, the first peak at 1407.99cm^{-1} shows the asymmetric stretching of tri-coordinate boron ($B_{(3)}$–O). The peaks at 1189.57cm^{-1} represents four coordinate boron asymmetrical stretching. Symmetric stretching of $B_{(3)}$–O can be seen at 882.96cm^{-1}. The last peaks with 703.02 and 674.26cm^{-1} explains the out-of-plane OH^{-1} bending band and stretching of $B_{(3)}$–O in the structure.

B. Synthesized Magnesium Borate XRD Results

XRD patterns and results of the synthesized magnesium borates were shown in Fig. 8 and Table II, respectively.

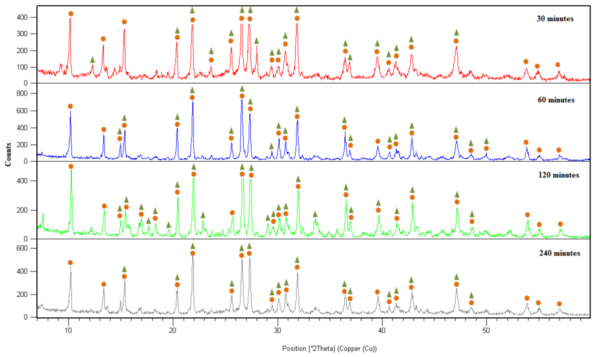

Fig. 8 XRD patterns of the synthesized magnesium borates; ● Mcallisterite, ▲ Admontite

TABLE II
XRD RESULTS OF THE SYNTHESIZED MAGNESIUM BORATES

Reac. Time	Pdf #	Mineral Name	Mineral Formula	Score
30	01-076-0540	Admontite	$MgO(B_2O_3)_3.7H_2O$	8
	01-070-1902	Mcallisterite	$Mg_2((B_6O_7)(OH)_6)_2.9H_2O$	93
60	01-076-0540	Admontite	$MgO(B_2O_3)_3.7H_2O$	20
	01-070-1902	Mcallisterite	$Mg_2((B_6O_7)(OH)_6)_2.9H_2O$	85
120	01-076-0540	Admontite	$MgO(B_2O_3)_3.7H_2O$	38
	01-070-1902	Mcallisterite	$Mg_2((B_6O_7)(OH)_6)_2.9H_2O$	76
240	01-076-0540	Admontite	$MgO(B_2O_3)_3.7H_2O$	14
	01-070-1902	Mcallisterite	$Mg_2((B_6O_7)(OH)_6)_2.9H_2O$	82

From the XRD results obtained it is seen that "01-076-0540" and "01-070-1902" pdf numbered "Admontite" and "Mcallisterite" minerals were found at all the reaction times. From the waste magnesium XRD pattern, the major peaks represent mcallisterite minerals and the minor peaks represent admontite minerals. The highest mcallisterite and admontite formations were seen on 30 and 120 minutes of reaction times, respectively.

C. Synthesized Magnesium Borate FT-IR Results

FT-IR spectrums of synthesized minerals were shown in Fig. 9.

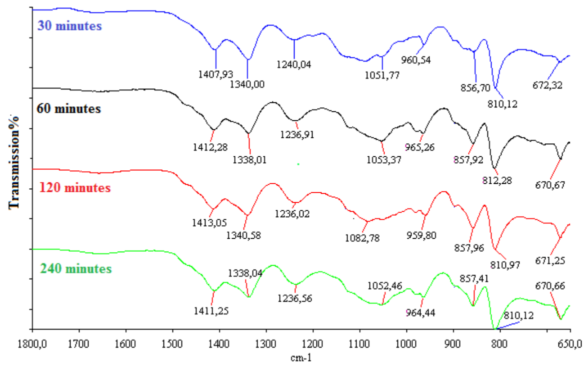

Fig. 9 FT-IR spectrums of synthesized minerals

In the FT-IR spectrums the peak values between 1407.93 and 1413.05cm^{-1} represents the three coordinate boron asymmetrical stretching. Other two peaks at around 1338.01 and 1240.04cm^{-1} was OH^{-1} in plane stretching due to the crystal waters inside the magnesium borates. The peaks with 1051.77 and 959.80cm^{-1} represents four coordinate boron asymmetrical stretching. Symmetric stretching of $B_{(3)}$–O can be seen between 857.96 and 856.70cm^{-1}. Also in magnesium borates OH^{-1} out of plane stretching was seen between 812.28 and 810.12cm^{-1}. The last peak represents the stretching of three coordinate boron with the peaks values are at around 670cm^{-1}.

TABLE III
FT-IR PEAK INTERPRETATIONS

Peaks (cm^{-1})	**Peak Interpretation**
1600-1400	B_3-O asymmetrical stretching
1400-1200	OH^{-1} in plane stretching
1200-950	B_4-O asymmetrical stretching
950-850	B_3-O symmetrical stretching
850-750	OH^{-1} out of plane stretching
750-650	B_3-O stretching

IV. CONCLUSIONS

Evaluation of waste is a serious problem due to increasing of the industrial activities all over the world. Also the storage of this waste is the other big problem. The use of wastes as a raw material provides the decreasing cost of raw materials and energy. Therefore in this study magnesium wastes were used as a raw material in the production of magnesium borate production. From the results of this study it is seen that magnesium wastes can be used in the hydrothermal synthesis of magnesium borates at such a moderate temperature of 70°C. The analysis results (XRD and FT-IR) showed that combined hydrothermal synthesis of magnesium borates in different times. From the experiment results obtained the overall yields of the productions were found between 60-85%.

REFERENCES

[1] T. R. Ministry of Education, "Environmental protection, solid waste collection", Ankara, 2009.

[2] A. S. Kipcak, F. T. Senberber, E. Moroydor Derun, S. Piskin, Hydrothermal Synthesis of Magnesium Borate Hydrates from MgO and H_3BO_3 at 80^{o}C, 2011 Research Bulletin of the Australian Institute of High Energetic Materials, Vol. 1, pp. 47-55, 2011.

[3] O. Atalay, Magnezyum ve alasımlarının konstrüksiyon malzemesi olarak otomotivde kullanımı. Istanbul Technical University, M.Sc. Thesis, Istanbul, 2006 [in Turkish].

[4] A. S. Kipcak, The investigation of the usability of boron minerals as a neutron shielding material. Yildiz Technical University, M.Sc. Thesis, Istanbul, 2009 [in Turkish].

[5] E. Moroydor Derun, A. S. Kipcak, "Characterization of some boron minerals against neutron shielding and 12 year performance of neutron permeability", J Radioanal Nucl Chem, to be published.

[6] A. R. Scialli, J. P. Bonde, I. Hohlfeld, B. D. Culver,Y. Li, F. M. Sullivan,'' An overview of male reproductive studies of boron with an emphasis on studies of highly exposed Chinese workers'', Reproductive Toxicology, vol. 29, pp. 10-24, 2010.

[7] A. Mergen, M. H. Demirhan, M. Bilen, '' Processing of boric acid from borax by a wet chemical method'' Advanced Powder Technology, Vol. 14, pp. 279– 293, 2003.

[8] L. Jie, F. Zhan-guo, L. Yan-li, L. Su-lan, J. Tao, X. Zheng-ping, '' Preparation of boric acid from low-grade ascharite and recovery of magnesium sulfate'', Transactions of Nonferrous Metals Society of China, vol. 20, pp. 1161-1165, 2010.

[9] L. Dou, J. Zhong, H. Wang, ''Preparation and characterization of magnesium borate for special glass'', Physıca Scrıpta, vol. 139, pp. 1-4, 2010.

[10] H. Guler, F. Kurtulus, E. Ay, G. Celik, I. Dogan, *"Solid-State and Microwave-Assisted synthesis and characterization of $Mg_2B_2O_5$ ve $Mg_3(BO_3)_2$"*, IV International Boron Symposium, October, 2009.

[11] X. Tao, X. Li, ''Catalyst-free synthesis, structural, and mechanical characterization of twinned $MG_2B_2O_5$ nanowires'', Nano Letters, vol. 8, pp. 505-510, 2008.

[12] W. Zhu, G. Li, Q. Zhang, L. Xiang, S. Zhu, "Hydrothermal mass production of $MgBO_2(OH)$ nanowhiskers and subsequent thermal conversion to $Mg_2B_2O_5$ nanorods for biaxially oriented polypropylene resins reinforcement", Powder Technology, vol. 203, pp. 265 – 271, 2010.

[13] L. Zhiyong, H. Mancheng, G. Shiyang, "Studies on synthesis, characterization and thermochemistry of $Mg_2[B_2O_4(OH)_2]$ H_2O", Journal of Thermal Analysis and Calorimetry, vol. 75, pp. 73 – 78, 2004.

[14] L. Zhihong, H. Mancheng, "Synthesis and thermochmistry of $MgO.3B_2O_3.3,5H_2O$", *Thermochim Acta*., vol. 403, pp. 181 – 184, 2003.

[15] L. Zhihong, H. Mancheng, "New synthetic method and thermochemistry of szaibelyite", *Thermochim Acta,* vol. 411, 27 – 29, 2004.

[16] L.Dou, J. Zhong, H. Wang, "Preparation and characterization of magnesium borate for special glass" *Physica Scripta*, vol. 30, pp. 413– 418, 2010.

[17] S. Li, X. Fang, J. Leng, H. Shen, Y. Fan, D. Xu, "A new route for the synthesis of $Mg_2B_2O_5$ nanorods by mechano – chemical and sintering process", *Mater. Lett.*, vol. 64, pp. 151 – 153, 2010.

[18] Y. Zeng, H. Yang, W. Fu, L. Qiao, L. Chang, J. Chen, H. Zhu, M. Li, G. Zou, "Synthesis of magnesium borate ($M_2B_2O_5$) nanowires, growth mechanism and their lubricating properties" Materials Research Bulletin, vol. 43, pp. 2239 – 2247 2008.

[19] U. Dosler, M. M. Krzmanc, D. J. Suvorov, "The synthesis and microwave dielectric properties of $Mg_3B_2O_6$ and $Mg_2B_2O_5$ ceramics", *Eur Ceram Soc.,*vol. 30, pp. 413– 418, 2010.

[20] A. S. Kipcak, F. T. Senberber, E. Moroydor Derun, S. Piskin, "Characterization of Magnesium Borate Hydrates Produced from MgO and H_3BO_3 at 80^{o}C, for two Different Drying Temperatures", *12th Mediterranean Congress of Chemical Engineering*, November, 2011.

[21] E. Moroydor Derun, A. S. Kipcak, A. Kaplan, S. Piskin, ''*The effect of waste magnesium to boric acid ratio in hydrothermal magnesium borate synthesis at 70^{o}C''*, International Conference on Materials and Materials Processing, Prague, July 08-09, 2013.

[22] A. S. Kipcak, Synthetic production of magnesium borates from different magnesium and boron sources by various methods and the investigation of their production parameters. Yildiz Technical University, Ph. D. Thesis, Istanbul, 2013 [in Turkish].

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