World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:8, No:10, 2014

The Effect of Solution Density on the Synthesis of Magnesium Borate from Boron-Gypsum

N. Tugrul, E. Sariburun, F. T. Senberber, A. S. Kipcak, E. Moroydor Derun, S. Piskin

***Abstract*—**Boron-gypsum is a waste which occurs in the boric acid production process. In this study, the boron content of this waste is evaluated for the use in synthesis of magnesium borates and such evaluation of this kind of waste is useful more than storage or disposal. Magnesium borates, which are a sub-class of boron minerals, are useful additive materials for the industries due to their remarkable thermal and mechanical properties. Magnesium borates were obtained hydrothermally at different temperatures. Novelty of this study is the search of the solution density effects to magnesium borate synthesis process for the increasing the possibility of boron-gypsum usage as a raw material. After the synthesis process, products are subjected to XRD and FT-IR to identify and characterize their crystal structure, respectively.

***Keywords*—**Boron-gypsum, hydrothermal synthesis, magnesium borate, solution density.

I. Introduction

BORIC ACID is used as a raw material for the production of boron compounds. Also it is used in several industries as an additive. Turkey is the world's major source of high grade boron mineral such as; colemanite, ulexite and tincalconite [1], [2]. Colemanite ($2CaO{\cdot}3B_2O_3{\cdot}5H_2O$), which is one of the most important boron minerals in the world, is used as the raw material in the boric acid production [3]. Boric acid, is produced by dissolving colemanite in aqueous sulfuric acid where by gypsum ($CaSO_4{\cdot}2H_2O$) is formed as a byproduct and must be separated from the main product. This process consists of two steps as, dissolution of colemanite and formation of gypsum.

In the first reaction where boric acid is produced is a very fast reaction and given (1):

$$2CaO\cdot 3B_2O_3\cdot 5H_2O(s) + 2H_2SO_4(l) + 2H_2O(l) \rightarrow 2Ca^{2+} + 2SO_4^{2-} + 6H_3BO_3(aq) \quad (1)$$

In the second step, gypsum crystals are formed in the reaction mixture to up to a size large enough to be filtered out of the solution.

Gypsum crystallization reaction is given in (2):

$$Ca^{2+} + 2SO_4^{2-} + H_2O(l) \rightarrow CaSO_4\cdot 2H_2O(s) \quad (2)$$

Boron-Gypsum which is waste product of boric acid production process consist gypsum, B_2O_3 and some impurities that causes various environmental and storage problems. The content of B_2O_3 in boron-gypsum obtained during the boric acid production increases up to 7%. It is a valuable industrial raw material for its B_2O_3 content. In contrast, B_2O_3 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 pollutions [4], [5].

In literature, there are some studies about the reducing pollution and disposal of industrial wastes. Several works have been carried out for the utilization for borogypsum as calcium sulfate dihydrate (gypsum) in cement production. The addition calcinated borogypsum addition to Portland cement clinker increases the compressive strength. Therefore, the use of different forms of borogypsum in building industry as raw materials offers a potential alternative for utilization [6]. Also in another study it is concluded that hemihydrate borogypsum could be used as a retarder for Portland cement that would play an important role in preventing environmental pollution [5]. Hemihydrate borogypsum may also be useful for decreasing the radioactive permeability of concrete due to the boron content. As it is known, colemanite, borax and ulexite which have high boron content are used in nuclear reactors as shielding materials for radiation [5].

Magnesium borate minerals, as a source of magnesium and boron, can be used instead of other refined borates or metal borate [6]. Due to superior properties such as; high coefficient of elasticity, high heat resistance, corrosion resistance, the using areas of magnesium borates are ceramic industry, contact lens rinsing waters, corrosion inhibitor in paint, composition of detergent, production of superconducting materials, in the friction-reducing additives in oils and insulating coating compositions [7].

The production of high-purity boron is an expensive and difficult process in the industry [3]. Magnesium borates can be synthesized by hydrothermal procedures which involves the mixture of raw materials in a liquid phase. In literature, there are some examples of synthesized magnesium borate minerals by hydrothermal production procedure ($aMgO.bB_2O_3.cH_2O$) The common points of these studies are the high reaction

N. Tugrul is with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (phone: 0090-212-3834776; fax: 0090-212-3834725; e-mail: ntugrul@hotmail.com).

E. Sariburun, F. T. Senberber, E. Moroydor Derun and S. Piskin are with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (e-mail: edasariburun@gmail.com, tsenberber@gmail.com, moroydor@gmail.com, piskin@yildiz.edu.tr).

A. S. Kipcak is with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (phone: 0090-212-3834751; fax: 0090-212-3834725; e-mail: seyhunkipcak@gmail.com).

temperatures, which are higher than 100°C [8]-[11].

In this study, starting from a waste material of boron-gypsum, the symthesis of magnesium boron hydrates are aimed. Using the mixture of boron-gypsum and magnesium oxide Senberber et al. [12] studied 100 mL reaction medium, and found that the crystal formations were low. In order to achieve better crystal formations the reaction medium of this study is selected as 50 mL. So the effect of boron-gypsum content that dissolved in the water is experimented in the production of magnesium borates. After the synthesis the products were characterized by the techniques of X-Ray Diffraction (XRD) and Fourier Transform Infrared (FT-IR) Spectroscopy.

II. Materials and Methods

A. Materials

Boron gypsum was retrieved from Boron Management Plant in Bandirma, Turkey and grinded with ceramic mortar before usage (Fig. 1). MgO was supplied from Merck Chemicals and used without any pretreatment.

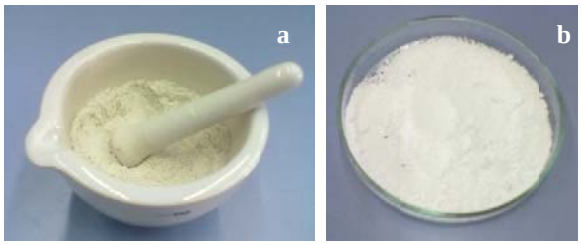

Fig. 1 (a) Boron gypsum grinding process, (b) ground boron gypsum

Then materials were subjected to XRD (Philips PANalytical XPert Pro used with Cu-Kα tube and the parameters of 45 kV and 40mA).

B. Methods

In the hydrothermal synthesis four different mole ratios of MgO and Boron gypsum is studied. These ratios were 1:4, 1:6, 1:8 and 1:10. Before the synthesis, boron gypsum is mixed with water at 80°C for 1h to dissolve the boric acid content inside the boron gypsum as Senberber et al. [12]. Then the solution is filtered and boric acid solution is used in the hydrothermal syntheses. Also in order to examine the solution phase, the solutions water phase is evaporated in an oven at 40°C.

The reaction temperature and reaction time were set to 80°C and 60 mins. Following to synthesis, the mixture is filtered through Whatman blue ribbon filter paper and unreacted MgO is removed. Then the solution part is put in an oven at 40°C to evaporate the excess water. After 48 hours, formed white crystals are washed with pure ethanol (96%) to remove the unreacted boric acid.

After obtaining the pure magnesium borate crystals, XRD (Fig. 2 (a)) technique is conducted with the parameter set explained in the Materials part. Also FT-IR (Perkin Elmer Spectrum One) (Fig. 2 (b)) analyses with Attenuation Total Reflection (ATR) apparatus was used for the determination of the characteristic bands of minerals. In FT-IR analyses scan number is set to 4, resolution is set to 4 $cm^{-1}$and scan range is set between 1800 – 650 cm^{-1}.

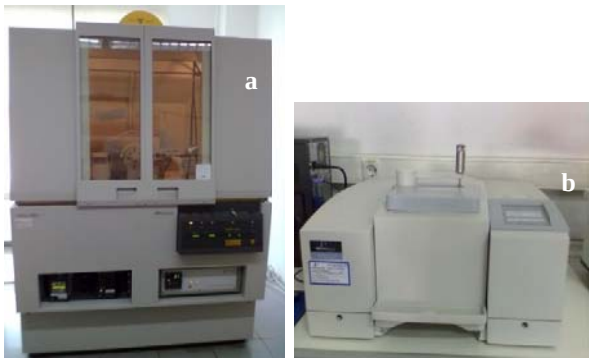

Fig. 2 (a) Philips PANalytical XPert Pro XRD, (b) Perkin Elmer Spectrum One FT-IR Spectroscopy

III. Experimental Results

A. Raw Materials Characterizations

From the XRD results of the raw materials, MgO was found from the previous study of [12] as similar to the powder diffraction file (pdf) number of "01-077-2179" that responds to phase "Priclase (MgO)", boron gypsum is similar to the pdf numbers of "00-06-0046" and "01-070-0983" that represents the two different phases of "Gypsum ($CaSO_4.2H_2O$)".

Before the synthesis gypsum was dissolved in the distilled water to extract the boric acid phase inside, as explained detailed in "Materials Part". The boric acid phase XRD result was mainly similar to pdf of "01-078-2158" that represents the "Boric acid (H_3BO_3)". The XRD patterns of the gypsum and boric acid is given at Fig. 3.

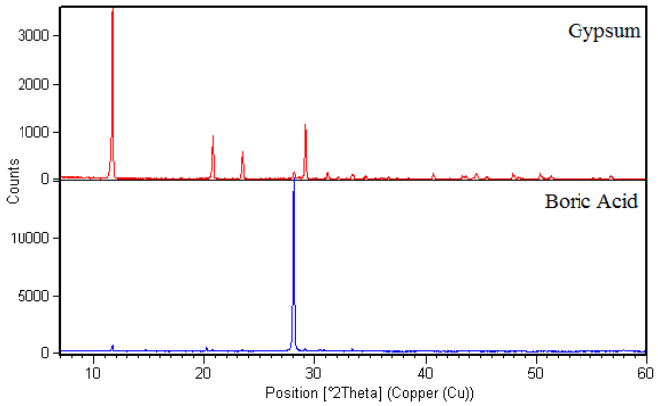

Fig. 3 XRD patterns of the gypsum and boric acid

B. Products Characterizations

XRD patterns and results are shown in Figs. 4, 5, Tables I and II, respectively.

The phases of; mcallisterite $Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$, admontite $MgO(B_2O_3)_3.7(H_2O)$, and magnesium borate hydrate $MgO(B_2O_3)_3.6(H_2O)$ were formed at the set of 50 ml reaction volume. From the XRD scores, where a perfect crystalline mineral have a score value of 100, the mcallisterite

phase was seen as the major phase. And the mole ratios of 1:4 and 1:8 had the best formations.

TABLE I
XRD RESULTS OF THE SYNTHESIZED MAGNESIUM BORATES IN 50 ML REACTION VOLUME

Mole Ratio	PDF No.	Mineral Name	Score
1:4	01-070-1902	Mcallisterite*	64
	01-076-0540	Admontite*	19
	01-076-0539	Magnesium borate hydrate*	24
1:6	01-070-1902	Mcallisterite	51
	01-076-0540	Admontite	18
	01-076-0539	Magnesium borate hydrate	16
1:8	01-070-1902	Mcallisterite	62
	01-076-0540	Admontite	17
	01-076-0539	Magnesium borate hydrate	19
1:10	01-070-1902	Mcallisterite	16
	01-076-0540	Admontite	18
	01-076-0539	Magnesium borate hydrate	22

* Mcallisterite $Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$,
* Admontite $MgO(B_2O_3)_3.7(H_2O)$,
* Magnesium borate hydrate $MgO(B_2O_3)_3.6(H_2O)$

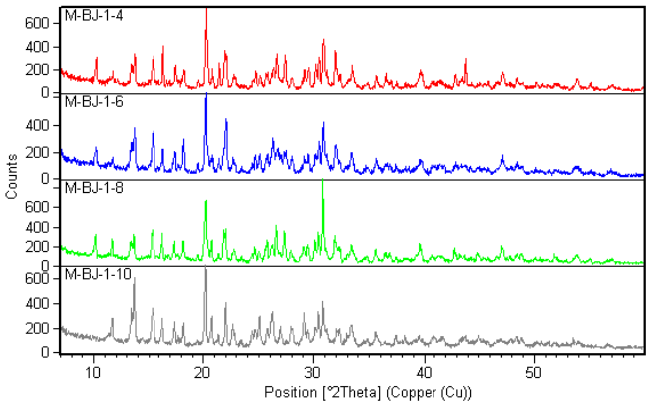

Fig. 4 XRD patterns of the synthesized magnesium borates in 50 mL reaction volume

TABLE II
XRD RESULTS OF THE SYNTHESIZED MAGNESIUM BORATES IN 100 ML REACTION VOLUME [12]

Mole Ratio	PDF No.	Mineral Name	Score
1:4	01-073-1254	Aksaite*	10
	01-070-1902	Mcallisterite	11
	01-076-0540	Admontite	6
1:6	01-070-1902	Mcallisterite	35
	01-076-0540	Admontite	6
1:8	01-070-1902	Mcallisterite	47
	01-076-0540	Admontite	14
	01-076-0539	Magnesium borate hydrate	12
1:10	01-070-1902	Mcallisterite	48
	01-076-0540	Admontite	11
	01-076-0539	Magnesium borate hydrate	9

* Aksaite $Mg(B_6O_7(OH)_6).2(H_2O)$

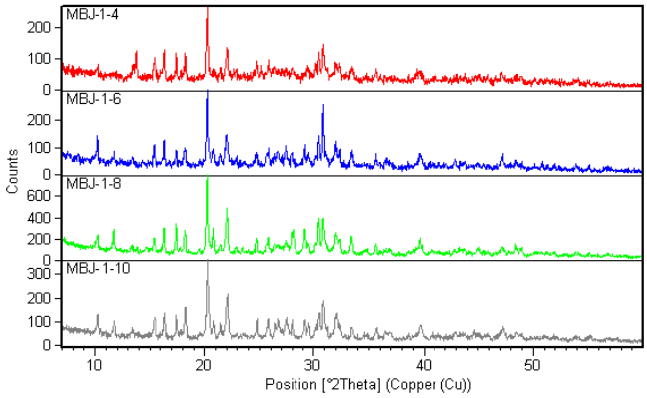

Fig. 5 XRD patterns of the synthesized magnesium borates in 100 mL reaction volume [12]

At the set of 100 ml reaction volume, the phases of mcallisterite, admontite and magnesium borate hydrate and Aksaite $Mg(B_6O_7(OH)_6).2(H_2O)$ were formed. The major phase was mcallisterite. The XRD scores were decreased compared to the results obtained at 50 ml reaction volume set. The best crystal formations were seen at the mole ratios of 1:8 and 1:10.

FT-IR spectra of the synthesized magnesium borates are shown in Figs. 6 and 7, respectively.

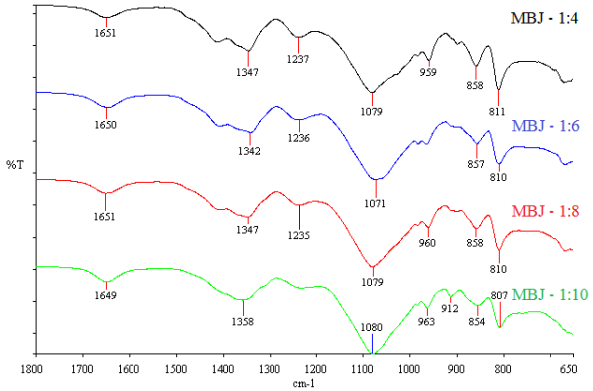

Fig. 6 FT-IR spectra of the synthesized magnesium borates in 50 mL reaction volume

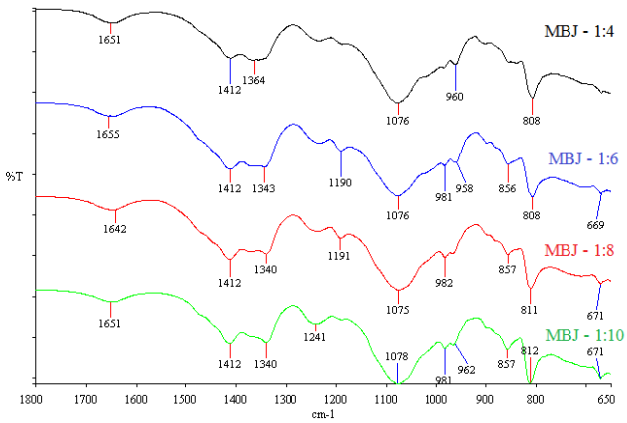

Fig. 7 FT-IR spectra of the synthesized magnesium borates in 100 mL reaction volume [12]

TABLE III
FT-IR PEAK INTERPRETATIONS

Peaks (cm^{-1})	Peak Explanation
1651-1642	δ(H-O-H)
1412-1340	$\nu_{as}(B_{(3)}\text{-O})$
1241-1235	δ(B-O-H)
1080-958	$\nu_{as}(B_{(4)}\text{-O})$
857-807	$\nu_{s}(B_{(4)}\text{-O})$
671-669	$\delta(B_{(3)}\text{-O})$

From the FT-IR results, the bending of H-O-H and asymmetrical stretching of three coordinate boron bands are seen at the peaks between 1651-1642 cm^{-1} and 1412-1340 cm^{-1}, respectively. At the peaks between 1241-1235 cm^{-1} and 1080-958 cm^{-1}, bending of B-O-H and asymmetrical stretching of four coordinate boron bands are observed, respectively. Last two bands are symmetrical stretching of four coordinate boron and bending of three coordinate boron are formed at the band values between 857-807 cm^{-1} and 671-669 cm^{-1}.

IV. DISCUSSION AND CONCLUSIONS

In this study the formation of magnesium borates was studied using the MgO and a waste material of boron gypsum. Several different mole ratios of the raw materials were experimented for the determination of the optimum crystal formation. From the experimental results it is seen that three different types of magnesium borate minerals namely; mcallisterite $Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$, admontite $MgO(B_2O_3)_3.7(H_2O)$, and magnesium borate hydrate $MgO(B_2O_3)_3.6(H_2O)$ were formed. The major phase is found as the mcallisterite phase. For the crystal formation the XRD scores of the minerals were compared. At the reaction volume of 50 ml, mcallisterite XRD score is 64 and 62 at the ratios of 1:4 and 1:8, respectively. At the previous study which the reaction volume of 100 ml [12], mcallisterite XRD score is 47 and 48 at the ratios of 1:8 and 1:10, respectively. Finally it can be said that the reaction volume decrease to 50 ml, yielded better crystal formation.

REFERENCES

[1] S. U. Bayca, "Recovery of boric acid from colemanite waste by sulfuric acid leaching and crystallization", in *2nd International Symposium on Sustainable Development*, Sarajevo, 2010, pp. 793-804.
[2] R. B. Kistler, and C. Helvacı, "Boron and borates", in *Industrial Minerals and Rocks*, 6 th Edition. Society of Mining, Metalurgy and Exploration, Inc., 1994, pp. 171-186.
[3] A. Erdogdu, "Dissolutıon of colemanite and crystallization of gypsum durıng boric acıd production in a batch reactor", A Thesıs Submıtted To The Graduate School Of Natural And Applıed Scıences Of Mıddle East Technıcal Unıversıty By In Partıal Fulfillment Of The Requirements For The Degree Of Master Of Scıence In Chemıcal Engıneerıng, June 2004.
[4] I. E. Elbeyli and S. Piskin, "Kinetic study of the thermal dehydration of borogypsum", *Journal of Hazardous Materials*, vol. B116, pp. 111–117, 2004.
[5] I. E. Elbeyli, E.M. Derun, J. Gulen and S. Piskin, "Thermal analysis of borogypsum and its effects on the physical properties of portland cement", *Cement and Concrete Research*, vol. 33 pp. 1729–1735, 2003.
[6] I. E. Elbeyli and S. Piskin, "Thermal dehydration kinetics of gypsum and borogypsum under non-isothermal conditions", *Chinese Journal of Chemical Engineering*, vol.12, pp.302-305, 2003.
[7] K. Othmer, "Boron Oxides, Boric Acid, and Borates", in Encyclopedia of Chemical Technology, 4th edition, vol. 4, pp. 365-413.
[8] A. Obut and Ismail Girgin, "Synthesis and characterization of magnesium borates", in. Proc. 2.Int. Boron Symposium, Eskisehir, 2004, pp. 133-138.
[9] F. T. Senberber, A. S. Kipak, E. M. Derun and S. Pişkin, "Boric Acid Waste (Boron-Gypsum) Evaluation at Different Mole Ratios for Magnesium Borate Synthesis" in *First International Symposium on Innovative Technologies for Engineering and Science*, Sakarya, 2013, pp. 58-62.
[10] W. Zhu, G. Li, Q. Zhang, L. Xiang and 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.
[11] L. Zhihong and H. Mancheng "Synthesis and thermochemistry of $MgO.3B_2O_3.3.5H_2O$" *Thermochimica Acta*, vol. 403 pp.181–184, 2003.
[12] F. T. Senberber, A. S. Kipcak, E. M. Derun and S. Piskin, "Magnesium Borate Synthesis from Boric Acid Sludges at Different Mole Ratios By Hydrothermal Method", Advanced Materials World Congress, Izmir, 2013, pp. 121.

Nurcan Tugrul was born in Gaziantep in 1973. Tugrul was graduated from B.Sc., M.Sc. and Ph.D. in Chemical Engineering Department at Yildiz Technical University, Istanbul. Her research interest is in the area of chemical technologies, evaluation of industrial wastes, food drying. She has many articles and studies in international and national conference proceedings and articles.

Eda Sariburun was graduated as B.Sc. from in Chemical Engineering Department at Yildiz Technical University in 2009. She is studied at her B.Sc. thesis on topic of evaluation of boric acid wastes in magnesium borates synthesis process.

Fatma Tugce Senberber was graduated from B.Sc. at Yildiz Technical University in 2010. After she completed her M.Sc. studies at Yildiz Technical University in 2012, she started to Ph.D. studies at the same year and same department of university. She is interested in boron technologies such as alternative synthesis methods of boron minerals and evaluation of industrial wastes in synthesis process. She also studied the characterization methods by instrumental analysis, kinetic studies of minerals and alternative application areas of synthesized minerals.

Azmi Seyhun Kipcak was graduated from Department of Chemical Engineering in Ege University in 2002. After completing the university studies he graduated from Bilgi University from the department of Master of Business Administration in 2004. He worked in Kultur University from 2003 to 2007 as a research assistant then he transferred to Yildiz Technical University at 2008, where he started his M.Sc. studies about Chemical Engineering in 2006. He completed his M.Sc. studies at Yildiz Technical University in 2009 and Ph.D. studies in 2013. Now he is studying on different types of borate synthesis from different raw materials and wastes.

Emek Moroydor Derun was born in Istanbul in 1976. Moroydor Derun graduated from B.Sc. in 1998, M.Sc. in 2000 and Ph. D. in 2005 from Chemical Engineering Department at Yildiz Technical University, Istanbul. Her research interest is in the area of waste management, lightweight concrete, semi conductive materials and boron technology. She has many articles and studies in international and national conference proceedings and articles.

Sabriye Piskin graduated from Istanbul Technical University on Chemical Engineering with M.Sc. degree in 1974. She completed a Ph.D. degree at the same department in 1983. Her research interests include boron minerals and compounds, hydrogen storage technologies, fuel cell applications, materials characterization, coal, waste management, corrosion, implants and synthetic materials production. She has more than sixty articles and hundred conference manuscripts pressed at the international area.