Boric Acid Waste (Boron-Gypsum) Evaluation at Different Mole Ratios for Magnesium Borate Synthesis

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Abstract:

As a result of crushing, washing, classification beneficiation operations which used in the production of concentrated boron, a large amount of waste is released. Since Boron content of waste is high enough to use in synthesis procedures, 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 strong thermal and mechanical properties. They can be synthesized at lower temperatures than 100^{o}C by hydrothermal methods. In this study, it is aimed to synthesize magnesium borates by the mixture of boron-gypsum and magnesium oxide at different mole ratios. At the end of the synthesis process, products are subjected to XRD to identify their crystal structure.

Key words: Boron-gypsum, magnesium borate, hydrothermal synthesis, XRD

1. Introduction

The material mainly consists of gypsum, B_2O_3 and some impurities and 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 pollution [1, 2]. Evaluation of wastes may be an alternative method instead of storage and disposal processes.

In nature, boron occurs with carbon and other elements as minerals and compounds. Boron minerals can be classified in five main groups; calcium borates, magnesium borates, sodium borates, sodium-calcium borates and other borate compounds. Analysis of the boron's geographical distribution shows that Turkey is the biggest boron manufacturer due to have 72% of boron reserves in world [3]. Boron products are one the strategic elements in the world due to its excellent features such as good thermal and chemical stability, neutron absorption, optical and electrical conductivity [4–7]. Boron minerals are the common additive materials at industry scale for years.

Magnesium borates which are a sub-group of boron minerals have important thermal and mechanical properties. Due to superior properties such as; high coefficient of elasticity, high heat resistance, corrosion resistance, the using areas of magnesium borates are ceramic industry,

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composition of detergent, production of superconducting materials, hydrocarbon catalysts, in the friction-reducing additives in oils and insulating coating composition. Also they can be used as the production of material against neutron and gamma radiation because of high boron oxide content [4].

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 such as $2MgO.3B_2O_3.17H_2O$, $MgO.3B_2O_3.3,5H_2O$, $2MgO.B_2O_3.H_2O$, $Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$ and $MgO.3B_2O_3.7H_2O$. The common points of these studies are the height of reaction temperature, which are higher than 100^oC [5–7]. In this study the hydrothermal production method of magnesium boron hydrates are studied with the mixture of boron-gypsum and magnesium oxide at low temperature than literature.

2. Materials and Method

2.1. Pre-treatments applied to raw materials

Waste of boric acid, which is called boron-gypsum, and magnesium oxide were determined as the raw materials of synthesis process. Magnesium oxide was supplied from Merck Chemicals and boron-gypsum was supplied Bandirma Boron Management Plant in Balikesir. Magnesium oxide used without pre-treatment.

2.2. Magnesium borate minerals synthesis

Hydrothermal synthesis method was studied in experiments. Mixtures of raw materials, which were prepared at different mole ratios, were reacted in 100 ml distilled water at 80^oC reaction temperature and reaction was continued for 1 hour. Mole ratios of MgO to boron-gypsum were determined as 1:14, 1:12, 1:10, 1:8 and 1:6. After synthesis, slurries were filtered with hot distilled water to separate impurities. After filtration, washed products were dried in oven at 40^oC.

Synthesized magnesium borate minerals were identified by the techniques of X-Ray Diffraction (XRD) analysis with Philips PANanalytical brand where in this equipment X-rays are produced from Cu-Kα tube at the parameters of 45kV and 40mA. Then characterization of products was studied with Fourier Transform Infrared Spectroscopy (FT-IR). In the FT-IR technique Universal ATR sampling accessory – Diamond / ZnSe is used and measurement range is selected as 1800–650 cm^{-1}, scan number is 4 and resolution set as 4 cm^{-1}.

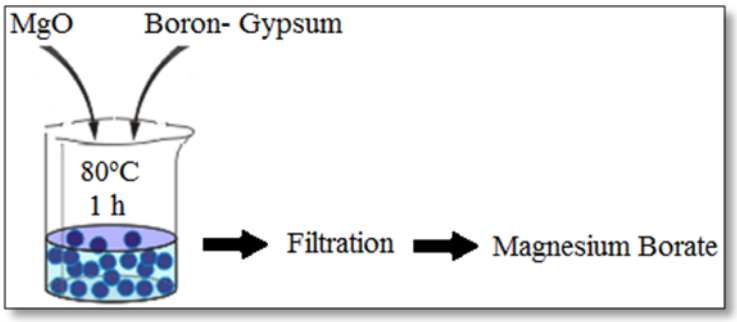

Figure 1. Hydrothermal synthesis scheme

3. Results

According to XRD results, synthesized magnesium borate minerals are Admontite ($MgO(B_2O_3)_3.7(H_2O)$) with powder diffraction file number of "01-076-0540", Mcallisterite ($Mg_2(B_6O_7(OH)_6)_2.9(H_2O)$) with powder diffraction file number of "01-070-1902" and Magnesium borate hydrate ($MgO(B_2O_3)_3.6(H_2O)$) with powder diffraction file number of "01-076-0539".

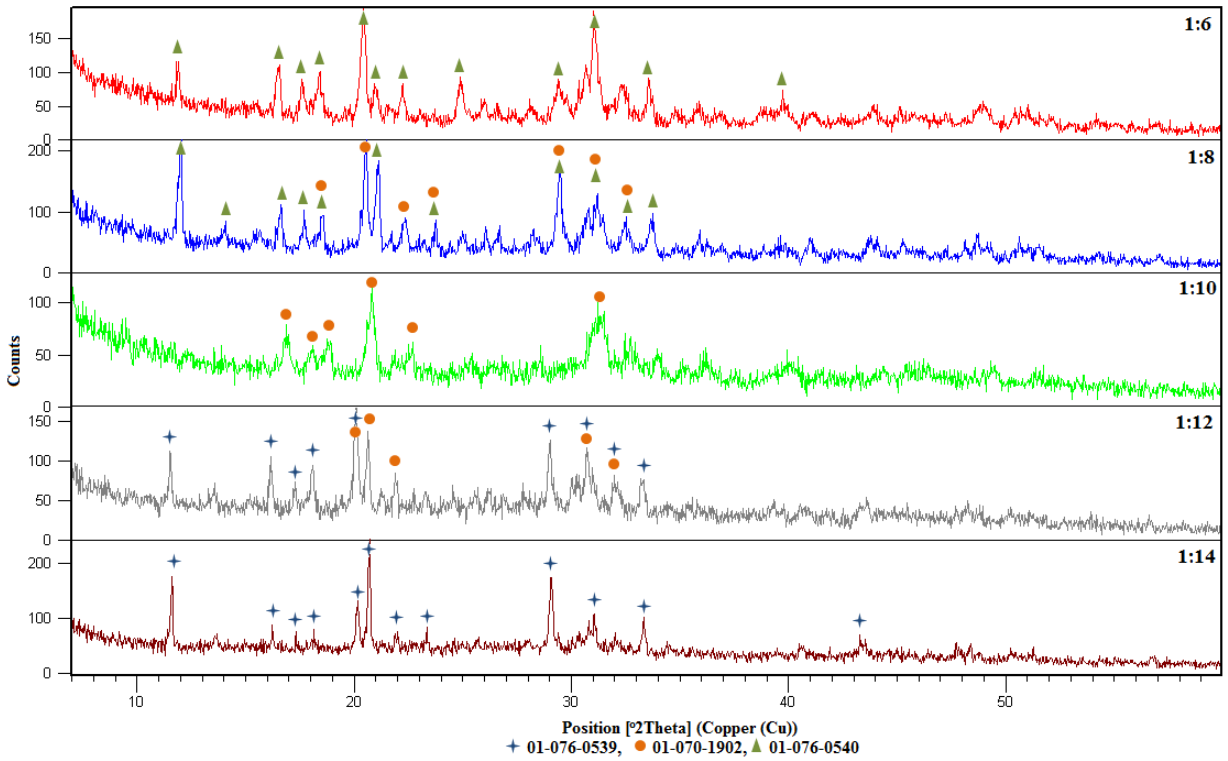

Figure 2. Identification of synthesized magnesium borates by XRD patterns

XRD patterns of synthesize magnesium borate mixtures are given in Figure 2. According to patterns, different kinds of magnesium borates are synthesized with the changing mole ratio of magnesium oxide to boron-gypsum. Admontite mineral is synthesized at the mole ratio of 1:6. Mixture of Admontite and Mcallisterite is seen in mole ratio of 1:8. In the ratio of 1:10,

Mcallisterite is produced. With increasing boron-gypsum in mixture of raw materials, mixture of Mcallisterite and Magnesium borate hydrate occurs at mole ratio of 1:12. Magnesium borate hydrate mineral is synthesized at the mole ratio of 1:14.

Characteristic peak values are seen in FT-IR spectrums, Figure 3. First peaks which have band values between 1653.88 and 1650.99 can be explain by crystal water in structure of magnesium borate mineral. The peaks might be the asymmetric stretching of three coordinate ($B_{(3)}$–O) boron with the bands between 1350.42 and 1339.58 cm^{-1}. Peaks in which band values change between 1079.33 and 959.57 cm^{-1}, show the asymmetric stretching of four coordinate ($B_{(4)}$–O) boron. Peaks between 899.69 and 857.49 cm^{-1} might be the symmetric stretching of three coordinate boron. Out-of-plane OH^{-1} bending band is formed between the band values of 810.12 and 808.72 cm^{-1}.

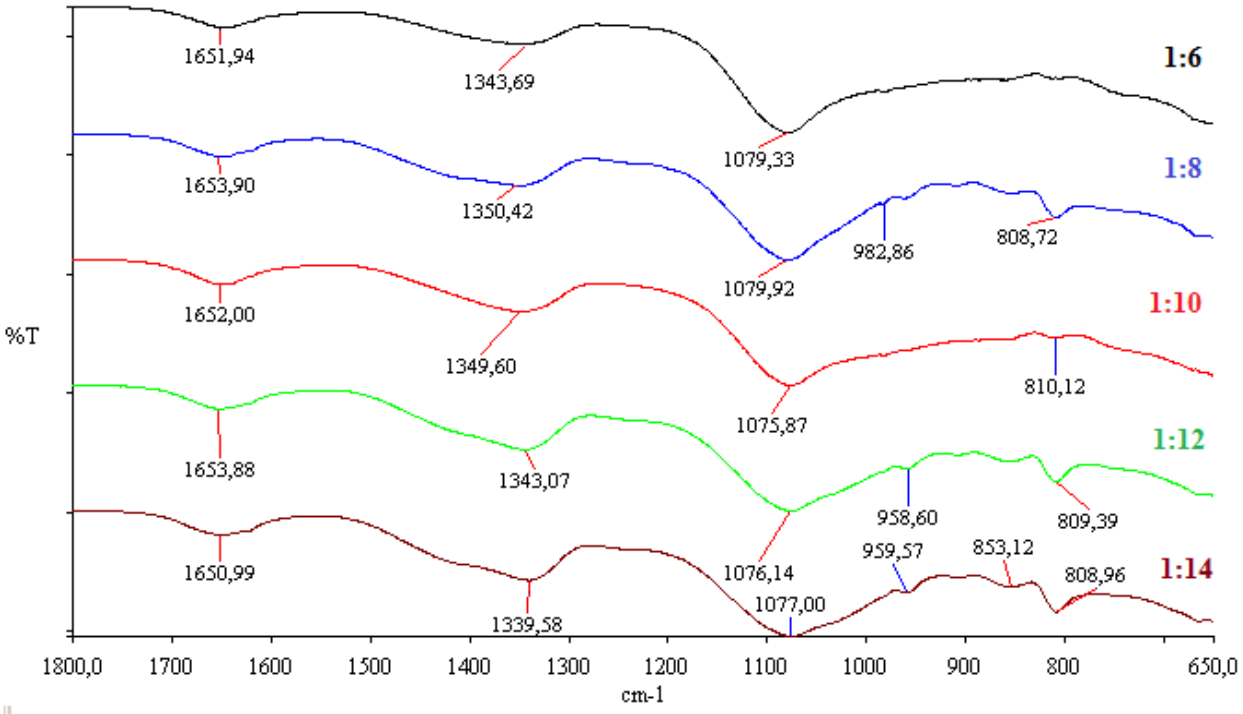

Figure 3. Characterization of synthesized magnesium borates by FT-IR spectrums

4. Discussion

Experiment results show that various kind of magnesium borate hydrate minerals can be synthesized purely, however, these products were at lower crystallinity features. Since boron-gypsum is not a homogeneous material; the amounts of boric acid in waste is not constant. So, in order to synthesize the magnesium borates at high crystal forms, purification process should be applied to boron-gypsum.

Conclusions

Magnesium borates production is an interesting topic for researcher approximately for a decade. During synthesis processes higher reaction temperatures than boiling point of mixtures, longer than reaction times and usually higher drying temperature than 60^{o}C [4–9]. Also Kipcak et al. studied the effect of drying temperature to product structure [10, 11]. Waste of boric acid may cause an environmental problem [1, 2]. This study showed that using wastes in production process as raw material might be an alternative evaluation method. In addition to this, synthesis of magnesium borate minerals is obtained at lower temperatures. Characterization stretching of minerals is compatible with the previous studies [10, 12]. According to results, to obtain products at higher crystallinity properties filtration operation can be added to process for the purification of boron-gypsum.

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