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수산화칼슘 포화용액을 이용한 고순도 칼슘 보레이트의 합성

Synthesis of high purity calcium borate using saturated calcium hydroxide solution

지도교수 김 명 진

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한국해양대학교 해양과학기술전문대학원

해양과학기술융합학과
서 효 진

본 논문을 서효진의 이학석사 학위논문으로 인준함.

위원장 김 형 석 (인)

위 원 김 명 진 (인)

위 원 이 희 준 (인)

2016년 1월

한국해양대학교 해양과학기술전문대학원

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수산화칼슘 포화용액을 이용한 고순도 칼슘 보레이트의 합성

Hyo-jin Seo

Department of Convergence Study on the Ocean Science and Technology
Ocean Science and Technology School

Abstract

붕소화합물은 산업에서 광범위하게 쓰여지고 있다. 하지만 붕소의 육상 매장은 매우 국소적이며, 육상에 매장되어 있는 붕소화합물 중에서도 일부만이 산업적으로 이용가치가 있다. 이러한 이유로, 붕소를 해수로부터 석출하고자 하는 연구가 진행되고 있다. 이전 연구에서는 해수에서 석출하기에 앞서, 고농도의 붕소를 함유하고 있는 인공 폐수 혹은 염수(간수)로부터 붕소화합물을 석출하는 연구를 하였다. 본 연구에서는 이전 연구에서 해왔던 붕소 석출 과정에서 생긴 문제점들을 보완하였으며, 본 연구에서 개발한 수산화칼슘 포화용액을 이용하여 붕소화합물의 한 종류인 calcium borate를 합성하고자 하였다.

첫 번째 연구에서는 붕소 인공 폐수(500 mg-B/L)에 수산화칼슘을 첨가하여 붕소를 calcium borate의 형태로 합성하는 과정에서 최적 조건을 찾고자 하였다. 본 연구에서는 이전 연구에서 사용한 고체 수산화칼슘을 대신하여 수산화칼슘 포화용액을 이용하여 각각의 경우에 나온 calcium borate의 회수율 및

순도를 비교하였다. 가열온도, 수산화칼슘의 양, 반응온도는 포화용액을 이용하여 붕소를 회수하는 데에 고려되어지는 최적의 조건이었다. XRD 분석결과, $Ca_2B_2O_5 \cdot H_2O$ 형태의 calcium borate가 생성되었음을 확인하였다. 수산화칼슘 포화용액을 이용하여 생성된 calcium borate의 회수율과 순도는 각각 80 %, 71% 이었으며, 고체 수산화칼슘을 이용하였을 때는 회수율과 순도가 각각 93 %, 42 %이었다. 실험결과, 최적의 조건은 가열온도 100 ℃, 수산화칼슘의 양 1.71 g, 반응시간 60 분이었다. 본 연구의 최적조건은 이전 연구와 비교하였을 때 짧은 시간에서, 낮은 온도에서 높은 회수율을 가진 고순도의 calcium borate를 얻을 수 있음을 말한다. 이러한 점은 폐수로부터 회수한 붕소화합물을 산업에 재사용할 가능성이 더 높아졌음을 의미한다.

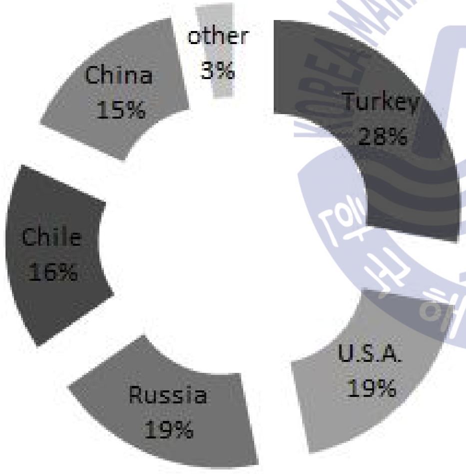
두 번째 연구에서는 붕소함유 인공염수(간수)를 수산화칼슘으로 포화시켜 calcium borate를 합성하는 반응에서, 첨가하는 황산이 미치는 영향을 알아보았다. 다양한 조건(반응온도, 반응시간, 가열반응 후 방랭온도)에서 calcium borate 합성을 시도하였고, 각 조건에서 황산 첨가유무에 따른 calcium borate의 회수율과 순도 변화를 알아보았다. XRD 분석을 통해 황산의 첨가유무에 상관없이 calcium borate($Ca_2B_2O_5 \cdot H_2O$)가 생성되었음을 확인하였고, 황산을 첨가하면 부산물로 황산칼슘($CaSO_4 \cdot 0.5H_2O$)이 생성되었다. 황산을 첨가하지 않았을 때, 실험한 모든 반응온도와 반응시간 조건에서 calcium borate의 회수율과 순도가 황산을 첨가했을 때보다 더 높았다. 황산을 첨가하면 수산화칼슘의 용해도는 높아지지만, 부산물로 생성되는 황산칼슘이 calcium borate의 생성을 방해하여 그 회수율과 순도가 낮아진다고 판단된다. 본 연구에서는 붕소함유(500 mg-B/L) 인공염수(간수)에 황산을 첨가하지 않고 수산화칼슘으로 포화시켜서 80-105 ℃에서 10분 이내로 가열하여 calcium borate를 합성하였고, 그 회수율과 순도는 각각 최대 80 %, 96 %로 매우 높았다.

KEY WORDS: Calcium borate 칼슘 보레이트; Calcium hydroxide 수산화칼슘; Purity 순도; Saturated solution 포화 용액; Sulfuric acid 황산

Chapter 1. General Introduction

1. Background

Boron occurs widely in various forms in nature. Boron is extracted for commercial applications from surface deposits. The reserves of boron occur in very few locations (FIg. 1); these are in the desert regions of the world, with the predominant supplies coming in Turkey, U.S.A., Russia, Chile, and China (Harben & Bates, 1990).



Country	Reserves (unit: one thousand tons)
Turkey	60,000
U.S.A.	40,000
Russia	40,000
Chile	35,000
China	32,000
other	7,000
total	214,000

Fig. 1 Boron reserves (Data source : USGS, Mineral Commodity Summaries, 2012)

Boron has many uses worldwide. The principal industrial uses of boron compounds (borates) are in the production of fiberglass insulation, borosilicate glass, and detergents. Other uses include fertilizers, metallurgy, and nuclear shielding (Power & Woods, 1997). Also, boron has been used in many industrial products, such as semiconductor (as an electronic receptor), ceramic (as a product enhancer) (Parks & Edwards, 2005). As shown in Fig. 2, It summarized the portion of borate that was globally consumed according to the usage in 1997.

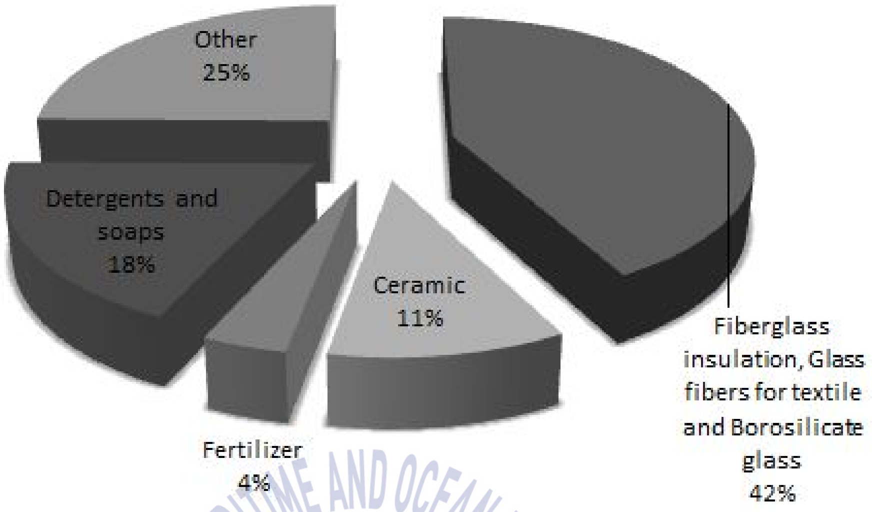


Fig. 2 The portion of world consumption by use borates (Date source: Roskill, The Economics of Boron, 1999)

Table 1 Major boron compounds having a commercial value (Data source: Roskill, The Economics of Boron 1999)

Boron compounds	Chemical formula	B_2O_3 content(%)
Natural borax	$Na_2B_4O_7 \cdot 10H_2O$	36.5
Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$	50.8
Ulexite	$NaCaB_5O_9 \cdot 8H_2O$	43
Borax pentahydrate	$Na_2B_4O_7 \cdot 10H_2O$	47.8
Borax decahydrate	$Na_2B_4O_7 \cdot 5H_2O$	36.5
Anhydrous borax	$Na_2B_4O_7$	69.2
Boric acid	H_3BO_3	56.3
Anhydrous boric acid	B_2O_3	100

Thus, the borates have been used extensively in industry. However, parts of the borates, which deposit in the land, have been used in industry. According to Table 1, there are major boron compounds having a commercial value;

such as, natural borax, colemanite, ulexite, borax pentahydrate, borax decahydrate, anhydrous borax, boric acid, and anhydrous boric acid. Therefore, before boron buried in the land run out, we have to extract boron elsewhere. Researchers are paying attention to seawater to extract boron.

Boron is the 10th most abundant element in oceanic salts, varying in concentration in seawater from 0.52 mg/L in the Baltic Sea to as much as 9.57 mg/L in the Mediterranean Sea. The global average, however, is approx 4.6 mg/L (Mellor, 1980). There are between $1.31*10^{21}$ and $1.4*10^{21}$ L of water in the world’s oceans (Ferguson, 1982; Shaw, 1994; Barry, 1971). If boron is present at 4.6 mg/L, then the world’s ocean hold between $6.026*10^{15}$ kg and $6.44*10^{15}$ kg of boron, or over 6 million tons (Argust, 1998).

In previous studies, it was to recover or remove boron using solid calcium hydroxide [$Ca(OH)_2$] in wastewater or the artificial solution containing high concentration of boron prior to extract of boron from seawater. For example, Tsai et al. (2011) said that oyster shell pretreated were used to recover boron from wastewater containing 500 mg/L boron (30 mL). The boron recovery efficiency reached around 95 % within 10 min of reaction time by adding 0.3 g at 130 ℃. And calcium borate [$Ca_2B_2O_5 \cdot H_2O$] is obtained as the final product. In another study, it was put into the solid calcium hydroxide to the wastewater and heated at 60 ℃ for 8 hours. It was scored relatively low recovery rate of 87% boron, and calcium borate ($Ca_2B_2O_5 \cdot H_2O$) was produced (Irawan et al., 2011). Itakura et al. (2005) said that it was found that the hydrothermal treatment using $Ca(OH)_2$ as a mineralizer converted boron in the aqueous media effectively into calcium borate, $Ca_2B_2O_5 \cdot H_2O$. In the optimal hydrothermal condition, more than 99 % of boron was collected from the synthetic wastewater of 500 ppm. Another researcher suggested that $Ca(OH)_2$ alone and $Ca(OH)_2$ with phosphoric acid [H_3PO_4] addition (P-addition) were used to recover boron from concentrated wastewater containing 500 mg/L boron (30 mL) using a microwave hydrothermal method. The experimental results showed that boron recovery efficiency reached 99 % within 10 min, and crystals of $Ca_2B_2O_5 \cdot H_2O$ were found in the precipitates as indicated by the XRD analysis (Tsai & Lo, 2011). In the last study, the initial pH was changed by adding sulfuric acid into the artificial boron wastewater to find the effect of the initial pH for the recovery of calcium borate. The initial pH was adjusted to 1.0 using sulfuric acid and the solution was heated at 80 ℃ after adding solid calcium hydroxide, the recovery of resulting calcium borate [inyoite, $CaB_3O_3(OH)_5 \cdot 4H_2O$] was about 96% (Yilmaz et al., 2012). The optimum conditions of the experiment in the previous study were placed and summarized in the following Table 2.

2. Objective

In this study, we suggested an effective method for synthesis of calcium borate from artificial boron solution. In chapter 2, we used saturated solution of calcium hydroxide instead of the solid calcium hydroxide to find a way to increase the purity and optimal conditions while maintaining a high recovery of calcium borate. And in chapter 3, the following saturated artificial boron bittern (brine) with calcium hydroxide was heated to proceed the reaction for synthesizing a calcium borate. At this time, we investigated the effect of the recovery and purity of the resulting calcium borate whether the addition of sulfuric acid.

Table 2. The optimum conditions to synthesize of calcium borate in previous study.

solution	pH	reaction temperature	reaction time	doses of $Ca(OH)_2$	boron recovery efficiency (%)	final product	references
wastewater (500mg B/L)	-	130 ℃	30 min	0.3 g/30 mL	95% (within 10 min)	$Ca_2B_2O_5 \cdot H_2O$	Tsai et al. (2011)
synthetic wastewater (750mg B/L)	pH 12.4±0.1	60 ℃	8 h	0.3 g/30 mL	87%	$Ca_2B_2O_5 \cdot H_2O$	Irawan et al. (2011)
500ppm-B	-	130 ℃	14 h	3.0 g/30 mL	99%	$Ca_2B_2O_5 \cdot H_2O$	Itakura et al. (2005)
wastewater (500mg B/L)	pH 13	130 ℃	30 min	0.3 g/30 mL	90% (within 10 min)	$Ca_2B_2O_5 \cdot H_2O$	Tsai & Lo (2011)
1000mg-B/L	pH 13	95 ℃	1 h	10 g/L	77.2-76.3%	$Ca_2B_2O_5 \cdot H_2O$	Tsai & Lo (2013)
wastewater samples synthetically using 1000ppm-B	initial pH 1	80℃	2 h	10 g/L	97%	calcium borate ores	Yilmaz et al. (2012)

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Chapter 2. Optimum conditions for the calcium borate formation reaction of recovering boron from wastewater

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1. Introduction

Boron is present as boric acid, borate, borosilicate minerals in nature (Holleman & Wiberg, 2001). Boric acid [$B(OH)_3$] acts as a weak acid in aqueous solution (Power & Woods, 1997), the following reaction takes place in water (Dean, 1987).

$$B(OH)_3 + H_2O \rightarrow B(OH)_4^- + H^+ \ (K_a = 5.8 \times 10^{-10},\ pK_a = 9.24\ at\ 25℃) \qquad (1)$$

The dissociation of boric acid is influenced by the pH. The main species is $B(OH)_4^-$ in the above pH 9.24, the main species is $B(OH)_3$ in less (Fig. 1).

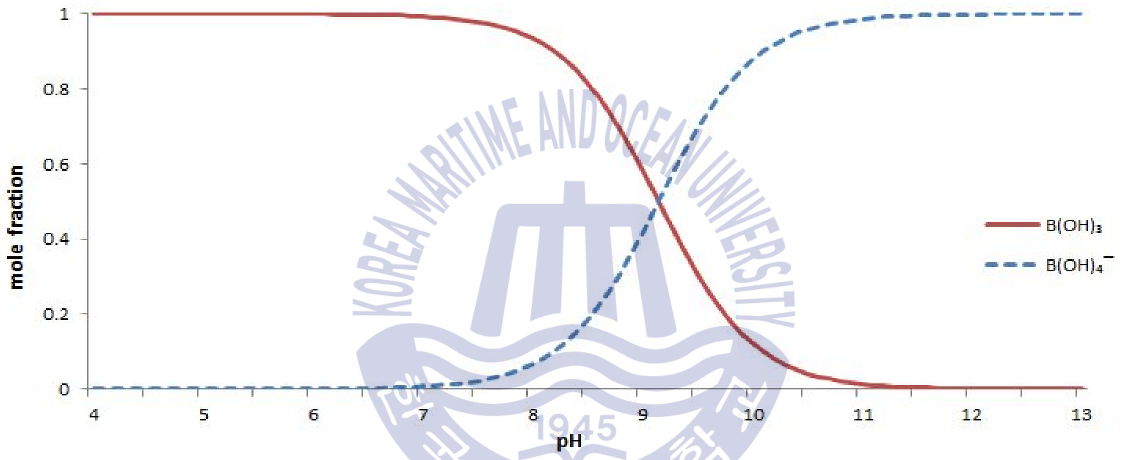

Fig. 1 Mole fraction of boric acid ($B(OH)_3$) and borate ion ($B(OH)_4^-$) according to pH.

The solubilities of most of the borate minerals are very low in water. Some solubilities of calcium borate minerals are organized in Table 1 (Mattigod, 1983). The solubilities of the calcium borate minerals are very low as shown in the table, this means that calcium borate is water-insoluble in water.

Table 1. Solubility product constants for calcium borate minerals

Mineral	K_{sp}	Solubility reaction
Colemanite	2.9×10^{-18}	$Ca[B_3O_4(OH)_3] \cdot H_2O + 4H_2O = Ca^{2+} + 3B(OH)_4^- + H^+$
Inyoite	2.9×10^{-18}	$Ca[B_3O_3(OH)_5] \cdot 4H_2O = Ca^{2+} + 3B(OH)_4^- + H^+$
Nobleite	1.7×10^{-48}	$Ca[B_6O_9(OH)_2] \cdot 3H_2O + 10H_2O = Ca^{2+} + 6B(OH)_4^- + 2H^+$

Most of the previous studies were carried out in a direction to remove the precipitated borate in the waste water with boron because boron has been considered as a target for removal, not recovery and reuse. Studies that the solid calcium hydroxide is added to wastewater containing boron by precipitation as calcium borate have been published several times in the country. Itakura et al. (2005) said that the solid calcium hydroxide and phosphoric acid were added in an artificial wastewater and then were heated at 130 ℃ for 14 hours. As a result, boron was recovered about 99% and was precipitated by calcium borate ($Ca_2B_2O_5 \cdot H_2O$). And Tsai et al. (2011) explained that oyster shells crushed was added in the wastewater instead of solid calcium hydroxide by heating the reaction at 130 ℃ for 10 minutes. The recovery of boron was about 95% and calcium borate ($Ca_2B_2O_5 \cdot H_2O$) was confirmed. In another study, it was put into the solid calcium hydroxide to the wastewater and heated at 60 ℃ for 8 hours. It was scored relatively low recovery rate of 87% boron, and calcium borate ($Ca_2B_2O_5 \cdot H_2O$) was produced (Irawan et al., 2011). Tsai and Lo(2015) said that the boron was removed by precipitation of boron in wastewater using the sub-micron calcium hydroxide synthesized with calcium chloride and calcium nitrate. The boron of 76.3~77.2% was precipitated as calcium borate ($Ca_2B_2O_5 \cdot H_2O$) at 95 ℃ by heating for one hour. The boron content in the precipitated solid was 7.0-7.1%, it was lower than that in Borax (11.3%). The recovery of boron was 67.2% using the commercially available calcium hydroxide in this study, this value was lower than using the sub-micron calcium hydroxide. That is, the recovery of calcium borate was higher when calcium hydroxide particle size was small (Tsai & Lo, 2015).

In previous studies, it was considered the recovery of calcium borate, not the purity of calcium borate, because the solid calcium hydroxide was always added to wastewater to remove boron and they obtained the insoluble solid, calcium borate. In other words, the recovery of calcium borate reached up to

99 % from wastewater, but the purity of the calcium borate was dropped significantly due to the residual solid calcium hydroxide, which was excessively added to increase the recovery of calcium borate.

In this study, we used a saturated solution of calcium hydroxide instead of the solid calcium hydroxide to find a way to increase the purity of calcium borate and optimal conditions while maintaining a high recovery of calcium borate.

2. Materials and Methods

Boric acid, calcium hydroxide, sulfuric acid and nitric acid used in the experiment was purchased from Junsei(Japan), all solutions were prepared with ultrapure water. We used the Azomethine-H method to measure the boron concentration of every solution, and the wavelength of the spectrophotometer (UV mini-1240, SHIMADZU) was fixed at 420 nm and was measured. X-ray diffractometer for the component analysis of the resulting solid (XRD, Bruker D2 Phaser, CuKα radiation of radiation of λ=1.5405 Å) was used. All experiments were performed two times in the same manner and conditions.

2.1 Effect of the state (saturated solution, solid) of the calcium hydroxide to produce calcium borate

The calcium hydroxide was prepared as two states of saturated solution and solid to produce calcium borate. They were compared to the recovery and purity of the product after reacting with boric acid, respectively.

2.1.1 Using a saturated solution of calcium hydroxide

The boron artificial wastewater (500 mg-B/L) was prepared by dissolving 0.71 g of boric acid in pure water (250 mL). And then, 0.695 mL of sulfuric acid (~18 M) was added to increase the dissolution of solid calcium hydroxide.

The 2.57g of solid calcium hydroxide was put into the boron artificial wastewater containing sulfuric acid. The solution was stirred at 250 rpm for 6 hours to dissolving a lot of calcium hydroxide, as much as possible. The solid calcium hydroxide undissolved was filtered through a 0.45 ㎛ filter paper. While the filtrate was heated at 100 ℃ for 80 minutes (150 rpm), white solids were formed during the reaction. After completion of the reaction, the solution was cooled until temperature of the solution in the reaction vessel was 70 ℃, and the solid was filtrated through a 0.45 ㎛ filter paper. The solid was dried using a dryer heating at 105.5 ℃ for 12 hours after washing with ultrapure water. The boron concentration was measured by dissolving 0.1 g of the dried solid by 50 mL of 1 M nitric acid to calculate the purity of calcium borate. The recovery of calcium borate was calculated as follows by measuring the residual boron concentration of the filtrate (2).

$$\text{Calcium borate recovery(\%)} = [C_0 - C_e] / C_0 \times 100 \qquad (2)$$

C_0: initial boron concentration (mg/L)

C_e: final boron concentration (mg/L)

2.1.2 Using solid calcium hydroxide

In this experiment, the solid calcium hydroxide was used instead of the saturated solution of calcium hydroxide. The artificial boron wastewater was prepared with sulfuric acid as “2.1.1. using the saturated solution of calcium hydroxide” . And then, 2.57 g of solid calcium hydroxide was put into the solution and stirred for 6 hours (250 rpm). The boron artificial wastewater with undissolved solid calcium borate was heated at 100 ℃ for 80 minutes (150 rpm). Other detailed experimental methods and conditions were same as it described in “2.1.1. Using the saturated solution of calcium hydroxide” .

2.2 The optimum conditions for generating the calcium borate with a saturated solution of calcium hydroxide

The following experiment was divided into five to derive the optimal conditions for generating calcium borate. Other detailed experimental procedures and conditions were same as it described in “2.1.1. Using the saturated solution of calcium hydroxide” .

2.2.1 Reaction temperature

The reaction temperature was changed to 70, 80, 85, 90, 95, 100, 105 ℃ when the reaction proceeded to produce calcium borate.

2.2.2 The amount of solid calcium hydroxide

The amount of solid calcium hydroxide added to the boron artificial wastewater with sulfuric acid was changed to 0.86, 1.71, 2.57, 4.28, and 8.57 g respectively. After stirring every suspension, the undissolved solid calcium hydroxide was removed by using a 0.45 ㎛ filter paper.

2.2.3 Reaction Time

The reaction time was changed to 10, 20, 30, 45, 50, 55, 60, 80 100, and 120 minutes by heating the filtrate at 100 ℃.

2.2.4 Stirring speed

While heating the filtrate at 100 ℃ for 80 minutes, the stirring rate was changed to 0, 150, 250, and 400 rpm.

2.2.5 Cooling temperature after the reaction

After the reaction was completed for generating calcium borate, the cooling temperature was changed to 30, 50, 60, 70, 80, 90, and 100 ℃.

3. Results and Discussion

The same experiment was conducted twice and error of results was small in ± 0.25~3.98 %, this means a very high reproducibility of the experiments. Exceptionally, the error was only large as 21.5% when the amount of solid was 0.86 g in the experiment ‘3.2.2. The amount of solid calcium hydroxide’.

3.1 Effect of the state (saturated solution, solid) of the calcium hydroxide to produce calcium borate

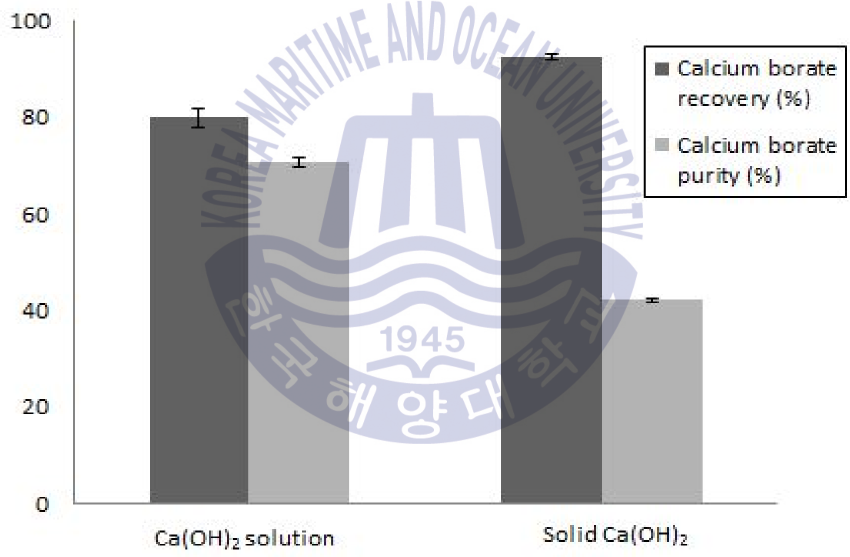

Fig. 2. Recovery and purity of calcium borates produced using both a saturated solution of calcium hydroxide and solid calcium hydroxide (B: 500 ppm, reaction temperature: 100℃, dose of solid calcium hydroxide: 2.57 g, reaction time: 80 min, stirring speed: 150 rpm, and cooling temperature: 70 ℃).

In both cases with a saturated solution of calcium hydroxide and solid calcium hydroxide, the white solid was produced during the reaction which was heated at 100 ℃. The resulting solid was confirmed by XRD analysis, calcium borate ($Ca_2B_2O_5 \cdot H_2O$) was produced. When using a saturated solution of calcium hydroxide, only two kinds of peaks, which were the calcium borate and the calcium sulfate, were detected. But it was added to the peak in the case of using solid calcium hydroxide. Calcium sulfate was produced by the reaction of calcium hydroxide and sulfuric acid added to increase the dissolution of calcium hydroxide. It has been reported that calcium sulfate was produced by the addition of sulfuric acid to produce a calcium borate in the experiment of the previous study (Yilmaz et al., 2012).

In Fig. 2, It was compared with the recovery and purity of calcium borate produced by each reaction with a saturated solution of calcium hydroxide and solid calcium borate. The recovery and purity of calcium hydroxide were respectively 80% and 71% when using the saturated solution. When using the solid, the recovery and purity were 93% and 42%. That is, when using the saturated solution, 13 % of the recovery was lower, but 29 % of the purity was higher than using the solid calcium hydroxide. The result, which the higher the purity calcium borate was produced using a saturated solution of calcium hydroxide, referred to the possibility to recover boron from the wastewater and then reuse in industry.

3.2 The optimum conditions for generating the calcium borate with a saturated solution of calcium hydroxide

3.2.1 Reaction temperature

When varying the reaction temperature at 70, 80, 85 90, 95, 100, and 105 ℃ to generate calcium borate, the recovery of calcium borate was shown as 18, 26, 63, 71, 73, 76, and 79% (Fig. 3). That is, until the reaction temperature reached at 85 ℃, the recovery of calcium borate increased sharply, and after that, the recovery was gradually increased.

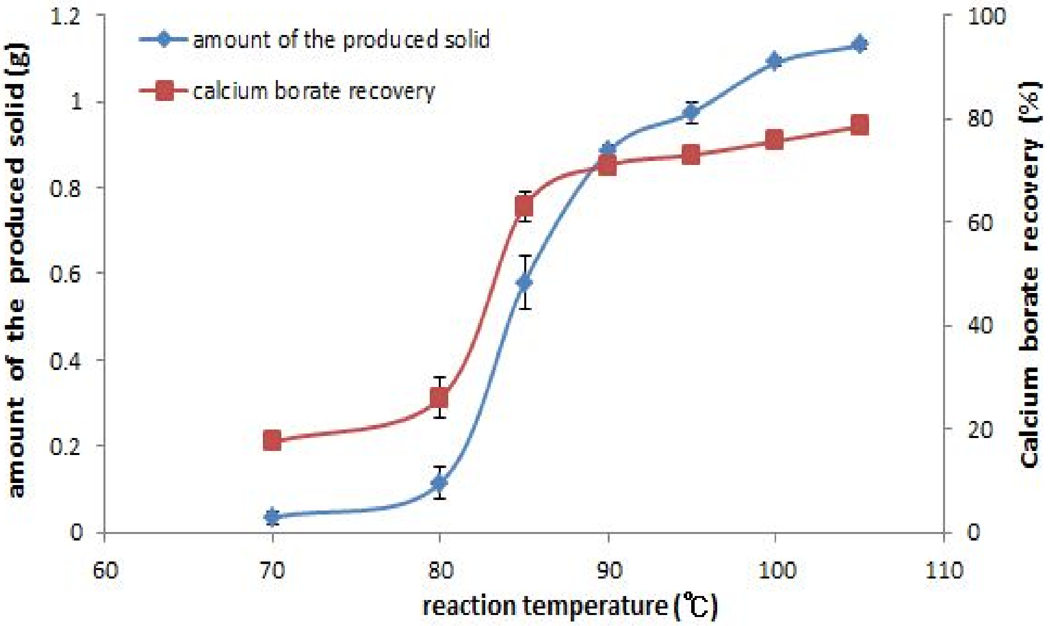

Fig. 3. Effect of reaction temperature on the calcium borate formation using a saturated solution of calcium hydroxide (B: 500 ppm, dose of solid calcium hydroxide: 2.57 g, reaction time: 80 min, stirring speed: 150 rpm and cooling temperature: 70 ℃).

When the reaction were conducted in the above 85 ℃, white solid was produced increasingly thought that calcium borate. As the higher heating temperature, the more amount of solid produced was precipitated. the same amount of solid was produced substantially up to 100 ℃. On the other hand, the white solid was hardly generated at temperatures below 85 ℃.

As the higher the heating temperature of the reaction, the final pH of the solution was low after the reaction had be completed. Before the calcium hydroxide was added, which fixing the pH range of the artificial boron wastewater with sulfuric acid to 1.3±0.07. And the pH of the filtrate with the addition of solid calcium hydroxide was made a constant at 13.45±0.12. But when the reaction temperature was 70, 80, 85 90, 95, 100, and 105 ℃, there were differences in 12.94, 12.86, 12.65, 12.15, 12.11, 12.04, and 12.01 of the final pH.

In the most of previous studies, the reaction temperature was an important factor influencing the formation of calcium borate, and the recovery was higher at higher temperatures (Tsai & Lo, 2011). Some researchers said that the recovery of calcium borate was high in 90–99 % at higher temperature such as 130 ℃ for a short time (10–30 mins) (Itakura et al., 2005; Tsai et al., 2011; Tsai & Lo, 2011), other investigators said that they obtained low recovery of calcium borate of 87 % at relatively low temperature (60 ℃) for a long time (8 hours) (Irawan et al., 2011).

The reaction temperature of optimum using a saturated solution of calcium hydroxide to precipitate calcium borate was determined to be 100 ℃ through the results from this study, since the experiments were fixed in the reaction temperature to 100 ℃.

3.2.2 The amount of solid calcium hydroxide

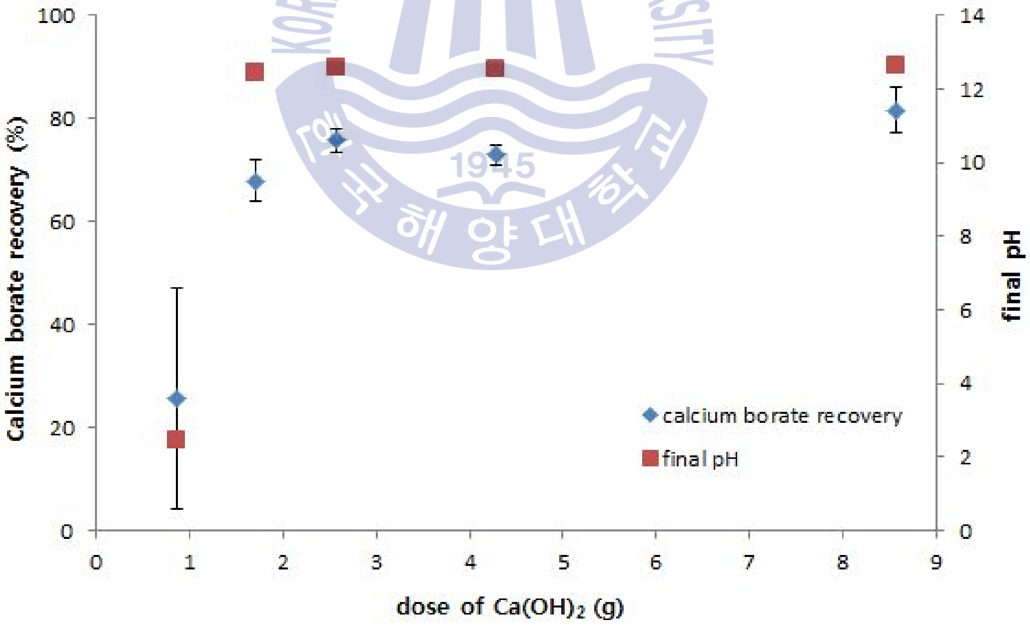

Fig. 4. Effect of the dose of solid calcium hydroxide on the calcium borate formation using a saturated solution of calcium hydroxide (B: 500 ppm, reaction temperature: 100 ℃, reaction time: 80 min, stirring speed: 150 rpm and cooling temperature: 70 ℃).

When varying the amount of solid calcium hydroxide with fixing the amount of boric acid to produce calcium borate, there were the pH change of the solution and the recovery of calcium borate in Fig. 4. Both of them showed the same trend as shown in the graph. That is, the greater the amount of solid calcium hydroxide, the recovery of calcium borate and pH were increased. While the recovery and pH were maintained constant over a certain amount of solid calcium hydroxide. The maximum recovery of calcium borate was 77 %, then the pH was 12.62.

According to experimental results, calcium borate was produced when a certain amount of solid calcium hydroxide was added and the pH of the reaction solution was more than pH 12. That is, the calcium borate have to be equipped with the high pH condition and the certain amount of calcium ions to be produced. The amount of solid calcium hydroxide was closely related to the pH of the solution and the amount of dissolved calcium ions. They have also a direct impact on the recovery of calcium borate (formula 3). When the amount was more than 1.71 g of solid calcium hydroxide, the pH was more than 13.2 prior to producing calcium borate. After the completion of producing calcium borate, the pH was maintained above 12.4. The recovery rate was 64 % or more in the conditions, even if the amount of solid calcium hydroxide increased, the recovery of calcium borate was maintained constant.

the reaction that calcium borate produced was assumed that the reaction was conducted as follows (Irawan et al., 2011; Tsai & Lo, 2011).

$$2B(OH)_4^- + 2Ca(OH)_2 \rightarrow Ca_2B_2O_5 \cdot H_2O + 5H_2O + 2OH^- \qquad (3)$$

As shown in Fig. 1, the dominant species is borate ion [$B(OH)_4^-$] at pH 12 or more. And when a large amount of calcium hydroxide was sufficiently dissolved, the concentration of calcium in the solution and the pH were high. In other words, In over pH 12, the recovery of calcium borate was high because borate ions and calcium ions existed enough to involve in the reaction.

Tsai and Lo (2011) explained that the pH is an important factor to produce calcium borate. For example, the recovery of calcium borate was more than 90 % at pH 13 and 10 % or less at pH 6-10 in the study of producing calcium borate to remove boron.

In this study, when the solid calcium hydroxide was put more than 1.71 g, the recovery of calcium borate was increased by up to 13 %. However, as the more the amount of solid calcium hydroxide, the amount of boric acid participating in the reaction was reduced, as a result, the amount of produced calcium borate was reduced. Because the amount of boric acid, which was adsorbed to the solid calcium hydroxide surfaces and removed, was increased before generating calcium borate. In addition, the large amount of calcium hydroxide did not participate in the reaction and was discarded. For this reason, the optimum amount of solid calcium hydroxide was 1.71 g.

3.2.3 Reaction time

It took about 20 min to increase the reaction temperature of the solution in the reaction vessel from room temperature to 100 ℃. In this study, the reaction starting was decided by the point of reaching at 100 ℃. As shown in Fig. 5, there was the changing recovery of calcium borate of the reaction time. Although, the recovery of calcium borate was lower in 38 % when the reaction time was 10 min. But when increasing slightly more than 20 min, the recovery reached 80% at 60 min, since that time was constant. The optimal reaction time of the this experimental conditions was determined by 60 min.

To produce calcium borate, it should be required the reaction temperature of at least 85 ℃ and over a period of time of the reaction time. When calcium borate was produced by heating the reaction in the previous study, as the reaction temperature was high, the reaction was completed in a short time and as the reaction temperature was low, the reaction was completed for a long time. For example, the recovery of calcium borate was over 90% at high temperature (130 ℃) in a relatively short reaction time of 10 min to 1 hour. However, when the reaction temperature was even as low as 45-80 ℃, the recovery was reached in 87%, it was required the reaction time was 4-18 hours, enough (Itakura et al., 2005; Tsai et al., 2011; Tsai & Lo, 2011).

In this study, the synthesis of calcium borate was conducted at the 100 ℃ of reaction temperature lower than previous studies and the recovery of calcium borate was reached in 70% within less than 30 min. It is considered that it is significantly advantageous economically.

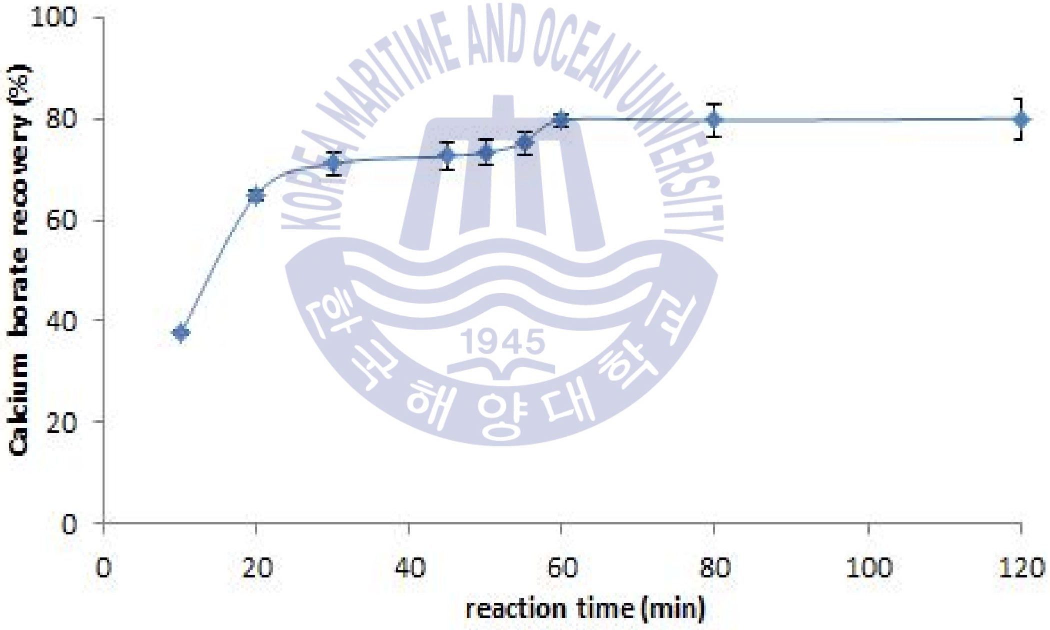

Fig. 5. Effect of reaction time on the calcium borate formation using a saturated solution of calcium hydroxide (B: 500 ppm, reaction temperature: 100 ℃, reaction time: 80 min, dose of solid calcium hydroxide: 2.57 g, stirring speed: 150 rpm and cooling temperature: 70 ℃).

3.2.4 Stirring speed

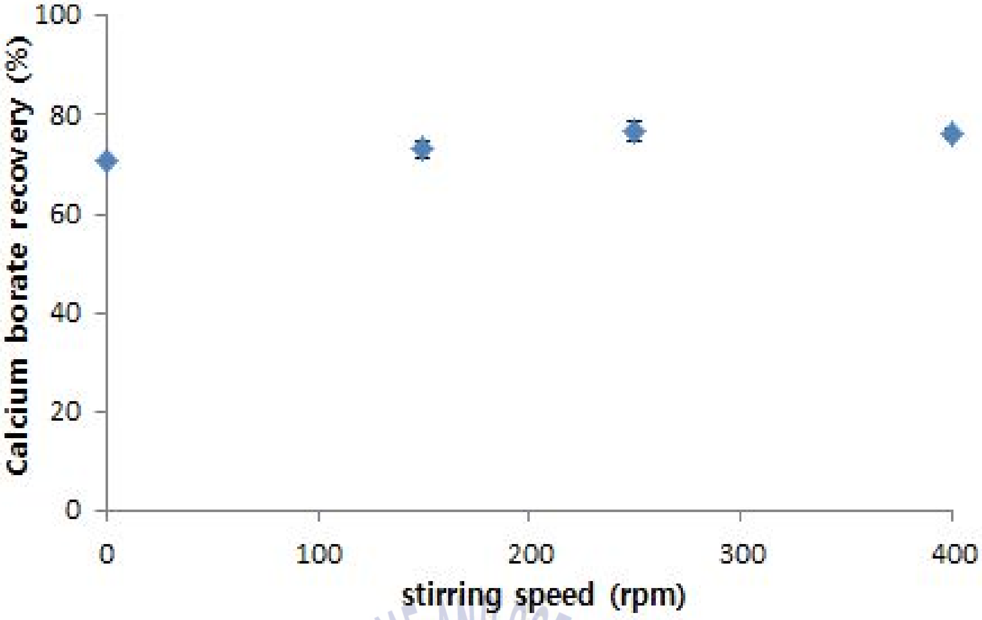

Fig. 6. Effect of stirring speed on the calcium borate formation using a saturated solution of calcium hydroxide (B: 500 ppm, reaction temperature: 100 ℃, reaction time: 80 min, dose of solid calcium hydroxide: 2.57 g and cooling temperature: 70 ℃).

There was the change of the recovery of the calcium borate according to the stirring rate in Fig. 6. The recovery of calcium borate was almost constant in 71-77 % despite varying the stirring speed to 0-400 rpm. Unlike this study, it announced that stirring speed affects the recovery of calcium borate in previous study (Yilmaz et al., 2012). In the study of Yilmaz et al. (2012), solid calcium hydroxide was used contrast to this study. They explained that the recovery of calcium borate was low due to the sink without mixing solid calcium hydroxide uniformly when the stirring speed was slow, opposite when the stirring speed was fast, the synthesis of calcium borate was interfered because the opportunity to contact between solid calcium hydroxide and boric acid. On the one hand, the stirring speed did not affect the recovery in this study using a saturated solution of the calcium hydroxide, because it did not exist at all in the solution until solid calcium borate was produced.

3.2.5 Cooling temperature after the reaction

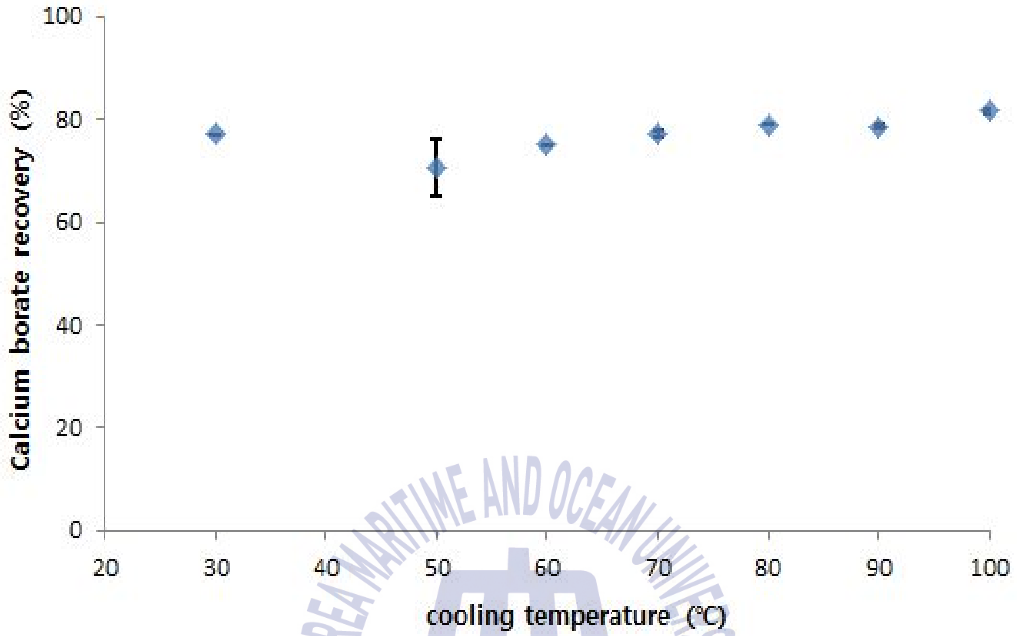

Fig. 7. Effect of cooling temperature on the calcium borate formation using a saturated solution of calcium hydroxide (B: 500 ppm, reaction temperature: 100 ℃, reaction time: 80 min, dose of solid calcium hydroxide: 2.57 g and stirring speed: 150 rpm).

As shown in Fig. 7, the recovery was not significantly different even if otherwise allowed to cool to the temperature after heating the reaction was completed in 100 ℃ to produce calcium borate. It was described that produced solid calcium borate was stable and not remelted allowed to cool in the process.

If the heat was blocked in the reaction process of calcium hydroxide and boric acid, the mineralization process produced calcium borate was interrupted. And it gave enough time for the reaction of remelting calcium borate to take place so that boron concentration of the solution was increased (Tsai & Lo, 2011). Itakura et al. (2005) explained that it is allowed to cool slowly for a long time with enough time to redissolve the solid and increase the concentration of boron. But it was allowed to cool rapidly by using the ice bath after producing calcium borate to prevent remelting of the product. They were added with phosphoric acid to prevent the redissolving the resulting calcium borate.

4. Conclusions

1) In this study, recovery and purity of calcium borate produced using a saturated solution of calcium hydroxide was 80 % and 71 %, respectively from artificial boron wastewater. This results was 13% lower, but the purity is 29% than with the solid calcium hydroxide. According to XRD analysis result, it was confirmed that the calcium borate ($Ca_2B_2O_5 \cdot H_2O$) was produced.

2) The factors affecting the reaction efficiency to produce the calcium borate using the saturated solution of calcium hydroxide was the reaction (heating) temperature, amount of solid calcium hydroxide (quantity of the dissolved calcium and pH), and the reaction time, stirring speed and cooling temperature has had little effect.

3) The optimum conditions using a saturated solution of calcium hydroxide in the experimental conditions of the this study to create calcium borate are as follows: 100 ℃ (reaction temperature), 1.71 g (amount of solid calcium hydroxide), and 60 min (reaction time).

4) In this study, while maintaining the recovery of calcium borate to some extent using the saturated solution of calcium hydroxide, at the same time the boron compound of higher purity was precipitated than previous studies. And the lower reaction temperature and shorter reaction time were required than previous studies to obtain the similar recovery of calcium borate. It means that the possibility of recycling the solids precipitated in the industry is more increased. Also, It has become more advantageous from the economic aspects.

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Chapter 3. Effects of sulfuric acid on the synthesis of highly pure calcium borate in the boron-containing brine and bittern

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1. Introduction

Boron, the 3A group in the periodic table, is semi-metal. Boron occurs in nature and mostly in the form of boric acid [$B(OH)_3$] and borates or boro-silicate. The boric acid is present in the form of boric acid [$B(OH)_3$] and borate ion [$B(OH)_4^-$] in the aqueous solution and the ratio of the two species depends on the pH (Tagliabue et al., 2014). Borate ion is the main chemical species at more than pH 9.24, boric acid is the main chemical species at less than pH 9.24.

Every concentration of boron is different in the seawater, brine and bittern. The concentration of boron is a very small amount (about 4.5-5.0 mg/L) in seawater(Güler et al., 2015). And boron concentration of bittern, remaining filtrate after manufacture of salt from seawater is about 15-120 mg/L (Ismail et al., 2014; Kim et al., 1992; Lozano et al., 1999). The boron concentration of the world's brine is 3-710 mg/L(An et al., 2012). The concentration of boron in the brine of Salar de Uyuni in Bolivia is highest with 710 mg/L.

The solubility of most of borate mineral is very low in water. There are representative borates such as colemanite ($CaB_3O_4(OH)_3 \cdot H_2O$, $K_{sp}=2.9\times10^{-18}$), inyoite ($CaB_3O_3(OH)_5 \cdot 4H_2O$, $K_{sp}=2.9\times10^{-18}$), nobleite ($CaB_6O_9(OH)_2 \cdot 3H_2O$, $K_{sp}=1.7\times10^{-48}$) and so on (Parks and Edwards, 2005). Using specificity of the insoluble in water, the precipitation reaction proceeded to remove boron in the form of calcium borate to remove the boron in the solution in previous study. For example, Itakura et al. (2005) said that the solid calcium hydroxide and phosphoric acid were added into the artificial boron wastewater, and then the solution was heated at 130 ℃ for 14 hours. At the result, the 99% of boron was precipitated as calcium borate [$Ca_2B_2O_5 \cdot H_2O$]. Other researchers demonstrated that sulfuric acid (50 g/L) and solid calcium hydroxide (50 g/L) were added in artificial boron solution (0.7 g/L), and it was heated at 90 ℃ for 2 hours. The boron concentration was lowered to less than 50 mg-B/L and calcium borate was precipitated (Remy et al., 2005). On the other hand, Yilmaz et al. (2012) said that the initial pH was changed by adding sulfuric acid into the artificial boron wastewater to find the effect of the initial pH for the recovery of calcium borate. The initial pH was adjusted to 1.0 using sulfuric acid and the solution was heated at 80 ℃ after adding solid calcium hydroxide, the recovery of resulting calcium borate [inyoite, $CaB_3O_3(OH)_5 \cdot 4H_2O$] was about 96%.

In most of previous studies, the sulfuric acid to lower the initial pH was added into the boron solution to synthesize calcium borate, and then it was heated after adding solid calcium hydroxide. In this case, the recovery of calcium borate was higher than 90%, however, the purity of calcium borate was very low due to the precipitation of calcium sulfate and calcium hydroxide as by-product. In this study, the saturated artificial boron bittern (brine) was saturated with calcium hydroxide, and the solution was heated to proceed the reaction for synthesizing calcium borate. At this time, we investigated the effect of the recovery and the purity of the resulting calcium borate according to the presence or absence of sulfuric acid.

2. Materials and Methods

Boric acid, calcium hydroxide, sulfuric acid, nitric acid used in the experiment were purchased from JUNSEI (Japan). All solutions were prepared using ultrapure water. We used a spectrophotometer (UV mini-1240, SHIMADZU) at a wavelength of 420 nm with the Azomethine-H method (Bingham, 1982) to measure the boron concentration of every solution. Calcium concentration of every solution was measured using an atomic absorption spectrometer (AAnalyst 200, PerkinElmer). And we used X-ray diffractometer (XRD, Bruker D2 Phaser, CuKα radiation of radiation of λ = 1.5405 Å) for the component analysis of the resulting solid.

Experiments were conducted at various conditions (reaction temperature, reaction time, heating the reaction and allowed to cool temperature) to know the effect on the synthesis according to the presence or absence of sulfuric acid. And then, it was divided into two individual tests: 1) the presence of sulfuric acid and 2) the absence of sulfuric acid. In both cases, the recovery and purity of calcium borate, and XRD analysis were compared. A saturated solution of calcium hydroxide was used as a non-solid state, all experiments were performed two times to confirm the reproducibility in the same manner and conditions.

2.1 Reaction temperature

2.1.1 The presence of sulfuric acid

A 500 mg-B / L artificial boron bittern (brine) was prepared by dissolving 0.72 g of boric acid with 0.05 M sulfuric acid (250 mL). The solution was stirred at 250 rpm for 1 hour after adding 2.50 g of solid calcium hydroxide, and the non-dissolved calcium hydroxide was removed using a 0.45 ㎛ filter paper. It was with 0.05 M sulfuric acid to lower the pH to enhance the solubility of solid calcium hydroxide. The filtrate, which was dissolved with boric acid and calcium hydroxide, was reacted at various temperatures (50-105 ℃) for 80 minutes and stirred at 150 rpm. White solid was formed during the reaction. After completion of the reaction, the solution was cooled until temperature of the solution in the reaction vessel was 70 ℃, and the solid was filtrated through a 0.45 ㎛ filter paper. The solid was dried using a dryer heating at 105.5 ℃ for 12 hours after washing with ultrapure water. The recovery of calcium borate was calculated as follows by measuring the residual boron concentration of the filtrate (1).

$$\text{Calcium borate recovery (\%)} = \frac{[Co - Ce]}{Co} \times 100 \qquad (1)$$

C_o : The initial boron concentration (mg/L)

C_e : The final boron concentration (mg/L)

The boron concentration was measured by dissolving 0.20 g of the dried solid in 50 mL of 1M nitric acid, the purity of calcium borate was calculated by using this.

2.1.2 The absence of sulfuric acid

The 500 mg-B/L artificial boron bittern (brine) 250 mL was prepared by dissolving boric acid with ultrapure water without the use of 0.05 M sulfuric acid. 2.50 g of solid calcium hydroxide was added into the solution was stirred at 250 rpm for 1 hour. And the non-dissolved calcium hydroxide was removed using a 0.45 ㎛ filter paper. Other details of methods and conditions were same as described in “2.1.1 the presence of sulfuric acid” .

2.2 Reaction time

The filtrate dissolved with boric acid and calcium hydroxide was changed to the reaction time (0-120 minutes) at 100 ℃. Other detailed conditions and methods were same as described in “2.1.1 The presence of sulfuric acid” and “2.1.2 The absence of sulfuric acid” .

2.3 Cooling temperature after the reaction

After completed the reaction for generating calcium borate, it was subjected to each experiment by varying the temperature allowed to cool (50-100 ℃). Other detailed conditions and methods were same as described in “2.1.1 The presence of sulfuric acid” and “2.1.2 The absence of sulfuric acid” .

3. Results and discussion

In this study, the same experiment was conducted two times and the error of the result was ± 0.22~7.39 %.

In heating the reaction for synthesizing calcium borate, It is shown about the concentration of boron and calcium present in the artificial boron bittern (brine) of the initial reaction, and a molar ratio of calcium and boron in Table 1.

Table 1 Boron and calcium concentrations, and mole ratios between B and Ca, in artificial boron-containing brine (bittern) saturated with calcium hydroxide, according to the presence or absence of sulfuric acid

	B concentration (mg-B/L)	Ca concentration (mg-Ca/L)	mole ratio (B : Ca)
without H_2SO_4	508±13	1837±41	1 : 1
with H_2SO_4	528±12	3513±57	1 : 1.8

The concentration of boron was constant at 508-528 mg/L, and the concentration of calcium with sulfuric acid (the presence of sulfuric acid) was higher as twice as that without sulfuric acid (the absence of sulfuric acid). The molar ratio of boron and calcium according to the presence or absence of sulfuric acid was 1:1, 1:1.8, respectively. In previous studies, the solid calcium hydroxide was added in excess to improve the recovery of calcium borate. And sulfuric acid was added to increase the solubility of calcium hydroxide (Yilmaz et al., 2012; Remy et al., 2004).

In heating the reaction for synthesizing calcium borate, the resulting white solid according to the presence or absence of sulfuric acid was measured by XRD analysis, the results are shown in Fig. 1. The peak of calcium borate [$Ca_2B_2O_5 \cdot H_2O$] was confirmed regardless of the presence or absence of sulfuric acid in all of the solid. In case of the absence of sulfuric acid, there was the only visible peak of calcium borate. While in case of the presence of sulfuric acid, the peak of calcium sulfate [$CaSO_4 \cdot 0.5H_2O$] was additionally appeared. Calcium sulfate has been generated by the reaction between calcium hydroxide and sulfuric acid added to increase the solubility of calcium hydroxide. The previous studies has been also reported the calcium sulphate with the calcium borate was generated when sulfuric acid had been added (Yilmaz et al., 2012; Remy et al., 2004).

$$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4(s), \qquad K_{sp} = 4.93 \times 10^{-5} \text{ at } 25\ ℃ \tag{2}$$

In this study, we used that a saturated solution of calcium hydroxide instead of solid calcium hydroxide, which was used mainly for synthesizing calcium borate in the previous study. Because of this, the peak of calcium borate was only detected without the peak of calcium hydroxide [$Ca(OH)_2$] or calcium sulfate in XRD analysis of this study. This means that the purity of the synthesized calcium borate was very high.

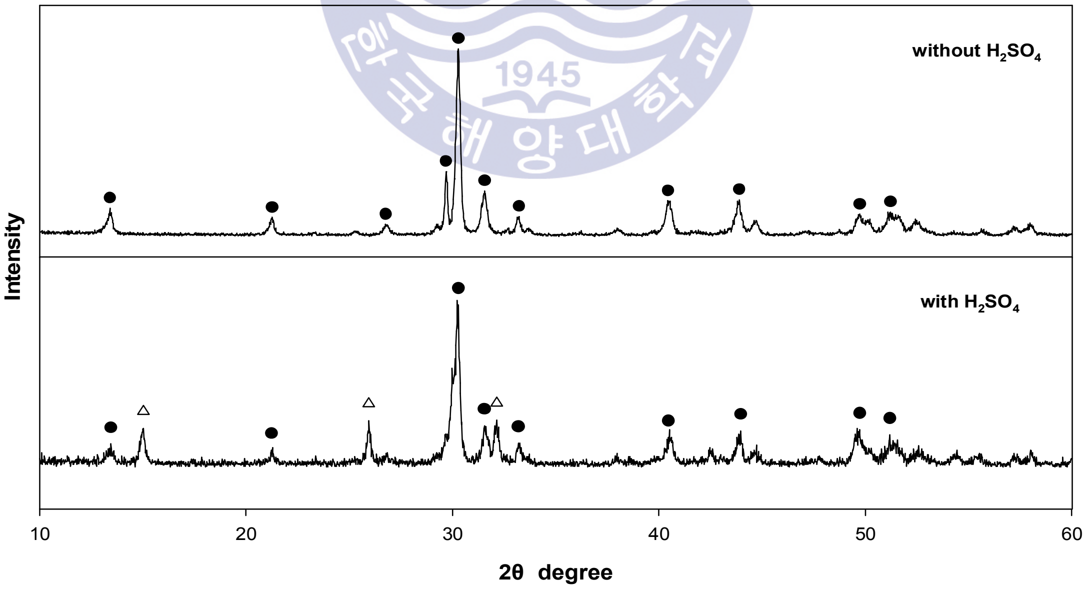

Fig. 1 XRD patterns of the produced solids in the presence or absence of sulfuric acid (reaction temperature: 100 ℃, reaction time: 80 min, stirring speed: 150 rpm and cooling temperature: 70 ℃) ● $Ca_2B_2O_5 \cdot H_2O$; △ $CaSO_4 \cdot 0.5H_2O$

3.1 Reaction temperature

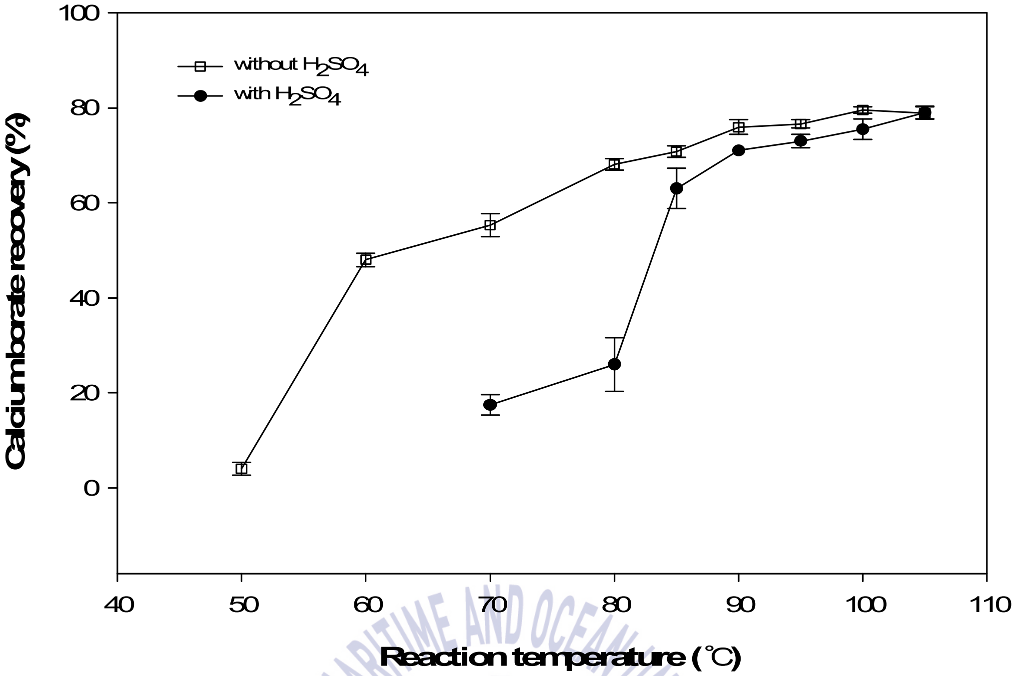

Fig. 2 Effect of sulfuric acid on the recovery of calcium borate according to reaction temperature

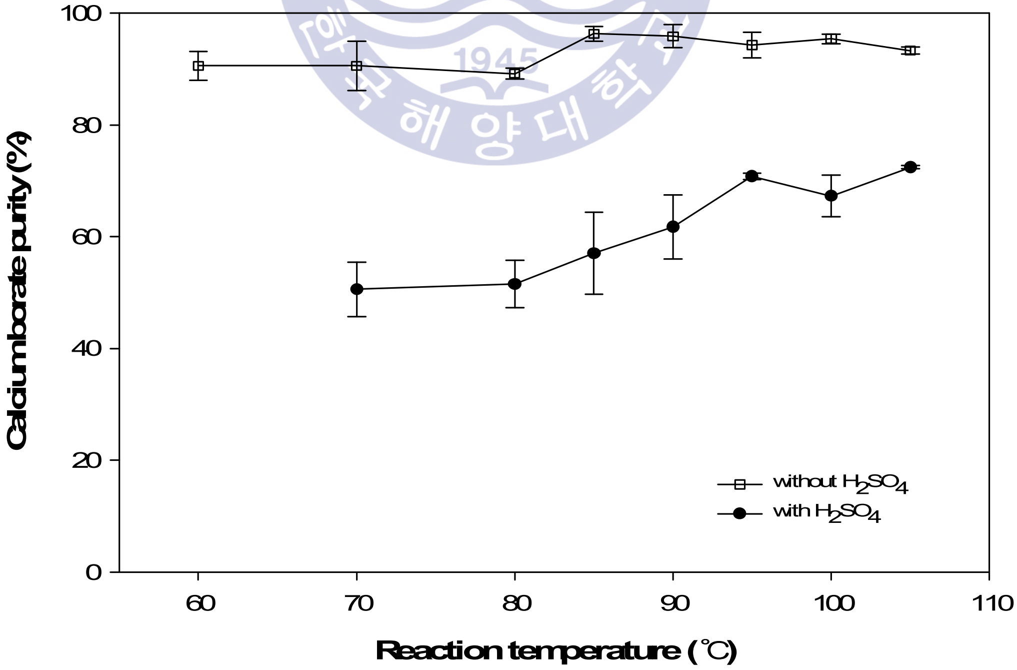

Fig. 3 Effect of sulfuric acid on the purity of calcium borate according to reaction temperature

When changing the reaction temperature to 50-105 ℃, the results of the recovery and purity of calcium borate was compared between the presence and the absence of sulfuric acid in Fig. 2 and Fig. 3, respectively. Regardless of the presence and absence of sulfuric acid, the higher the reaction temperature was greatly increased the recovery of calcium borate. compared to the recovery of calcium borate, the recovery of calcium borate without sulfuric acid was higher than that with sulfuric acid except for the 105 ℃ in all the tests, and the difference was great in the lower temperature. Especially, It appeared significantly different at temperature below 85 ℃. On the other hand, the purity of calcium borate was shown a significant difference in accordance with the presence or absence of sulfuric acid at each temperature. The purity of calcium borate without and with sulfuric acid were 89-96 % and 55-71 %, respectively. In the absence of sulfuric acid, the purity of calcium borate was almost constant regardless of the reaction temperature. However, in the presence of sulfuric acid, the higher the reaction temperature tended to increase the purity.

In the presence of sulfuric acid, the white solid started to be generated from 60 ℃ of the reaction temperature. As the temperature was increased, the mass of the resulting solid was also increased, but it did not show a significant difference in 0.68-0.85 g. As shown in Fig. 2, the recovery of calcium borate was sharply increased until the temperature reached at 60 ℃. After that, the recovery was gradually increased to 76 % at 90 ℃, and reached to 80 % at 100 ℃. When the addition of sulfuric acid, on the other hand, the white solid started to be generated from 80 ℃. As the temperature was increased, the mass of the resulting solid produced was increased about 1.13 g at 105 ℃. Until 80 ℃, the recovery of calcium borate reached at about 26%, but the recovery was suddenly increased by 63% at 85 ℃. At the further temperature, the recovery was gradually increased to reach 79% at 105 ℃.

In the reaction for synthesis of calcium borate to control the reaction temperature by 50-105 ℃, the addition of sulfuric acid did not help at all with the recovery of calcium borate by increasing the molar ratio of boron and calcium hydroxide. Rather, the synthesis of calcium borate got disturbed by calcium sulfate produced as a by-product. it was determined that the recovery and purity of calcium borate was significantly reduced due to calcium sulfate. In particular. Especially, It was significantly appeared the effect by the addition of sulfuric acid at a lower temperature than 85 ℃. Through this study, when the synthesis of calcium borate, using a saturated solution of calcium hydroxide without sulfuric acid was to how to increase the recovery and purity of calcium borate. when the reaction temperature was above 85 ℃, It can be obtained that the recovery of calcium borate was over 71 % and the purity was over 90%.

3.2 Reaction time

The temperature of the solution in the reaction vessel took about 18 minutes from room temperature to 100 ℃. In this study, a point in time at which the reaction temperature (100 ℃) reached was set at the start of the reaction time (0 min). While varying the reaction time, it showed results of examining the effect of the recovery and purity of calcium borate according to the presence of sulfuric acid in Fig. 4 and Fig. 5, respectively.

Looking at the recovery of calcium borate as the reaction time, the recovery of calcium borate was constant to about 73-80 % regardless of the reaction time when sulfuric acid had not been added (Fig. 4). The longer the reaction time and the little more the amount of the solid, but it was not a significant difference in 0.72-0.94 g. On the other hand, in the addition of sulfuric acid, although the recovery was lower in 38% at 10 min of the reaction time, the longer the reaction time, the recovery was increased gradually and reached 71% at 30 min (Fig. 4). As the reaction time, the mass of the solid was gradually increased. it was produced about 1.20 g of the solid in 60 min and a substantially constant amount was created, since that time.

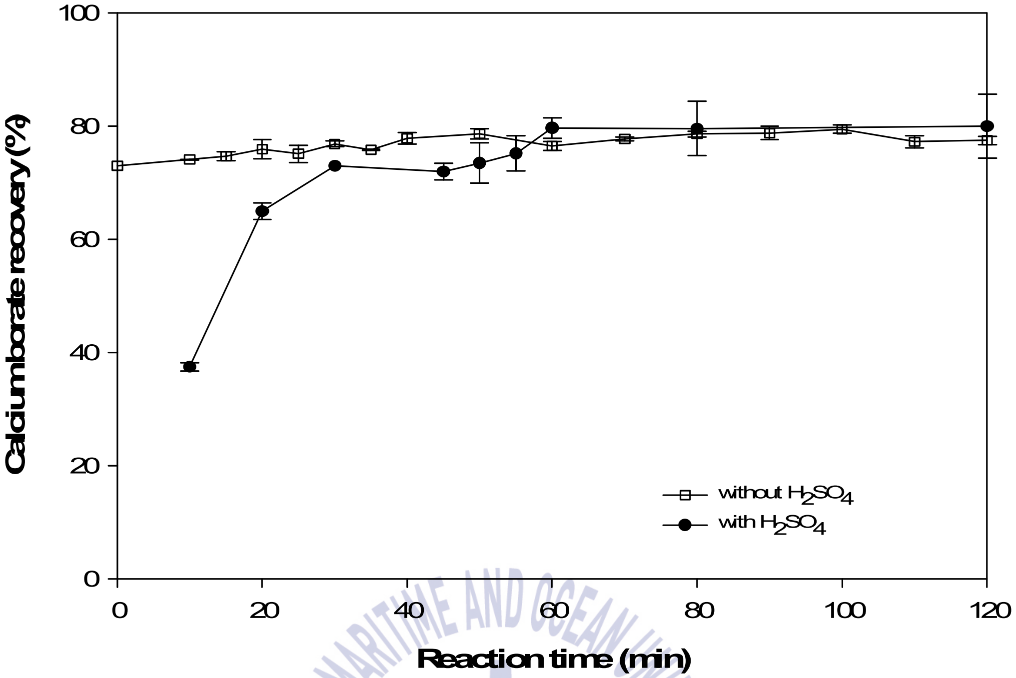

Fig. 4 Effect of sulfuric acid on the recovery of calcium borate according to reaction time

The purity of calcium borate in accordance with the reaction time showed different trends, each other. As shown in Fig. 5, When no addition of sulfuric acid, the purity of calcium borate was constant to 85-95 % regardless of the reaction time. While, when the addition of sulfuric acid, the purity of the calcium borate was very low at about 20% in 10 min, as the reaction time, the purity was gradually increased and reached about 70% in 60 min.

In this study, when the synthesis of calcium borate, it was not independent of the reaction time in the absence of sulfuric acid. But the reaction time have to be maintained for at least 60 minutes to increase the recovery and purity of calcium borate when the addition of sulfuric acid.

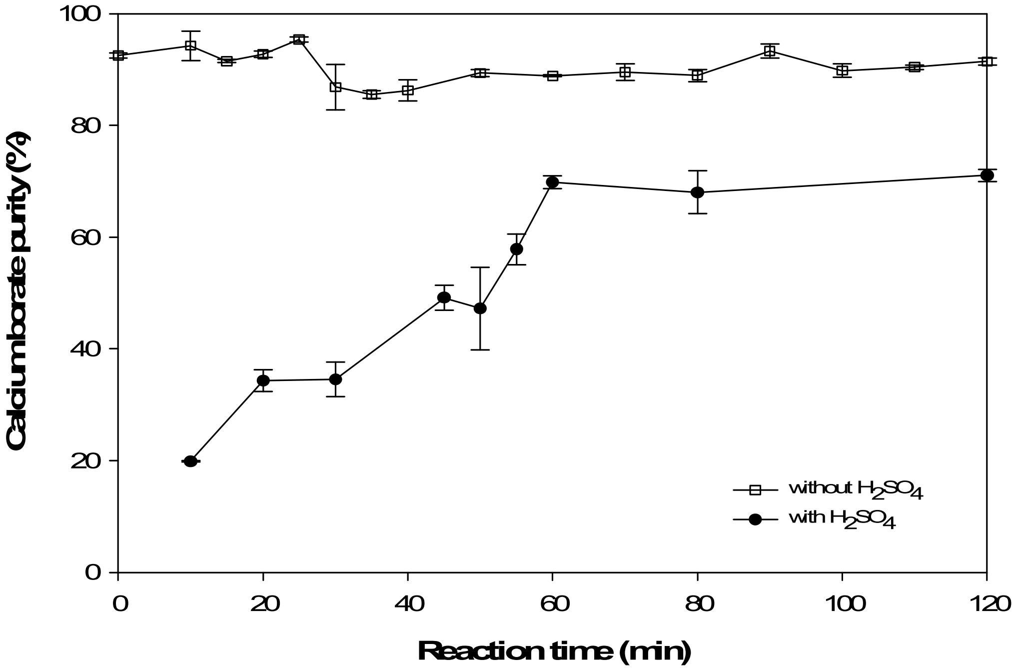

Fig. 5 Effect of sulfuric acid on the purity of calcium borate according to reaction time

3.3 Cooling temperature after the reaction

It was shown that the results of the recovery of calcium borate depending on allowed to cool while varying the temperature after calcium borate was created at 100 ℃ in Fig. 6. When sulfuric acid was not added, the recovery of calcium borate was substantially constant depending on the cooling temperature. It was also no significant change although the recovery of calcium borate with sulfuric acid was slightly higher Depending on the cooling temperature increased. The results were explained that solid calcium borate produced was very stable regardless of the presence of sulfuric acid, and it was not redissolved during cooling after the reaction.

In previous studies, the concentration of boron increased and the recovery of calcium borate decreased since calcium borate was redissolved during cooling after reaction of generating calcium borate was completed. (Tsai & Lo, 2011). Also, in another study, it was allowed to quickly cool to a lower temperature to prevent the re-dissolution of calcium borate (Itakura et al., 2005).

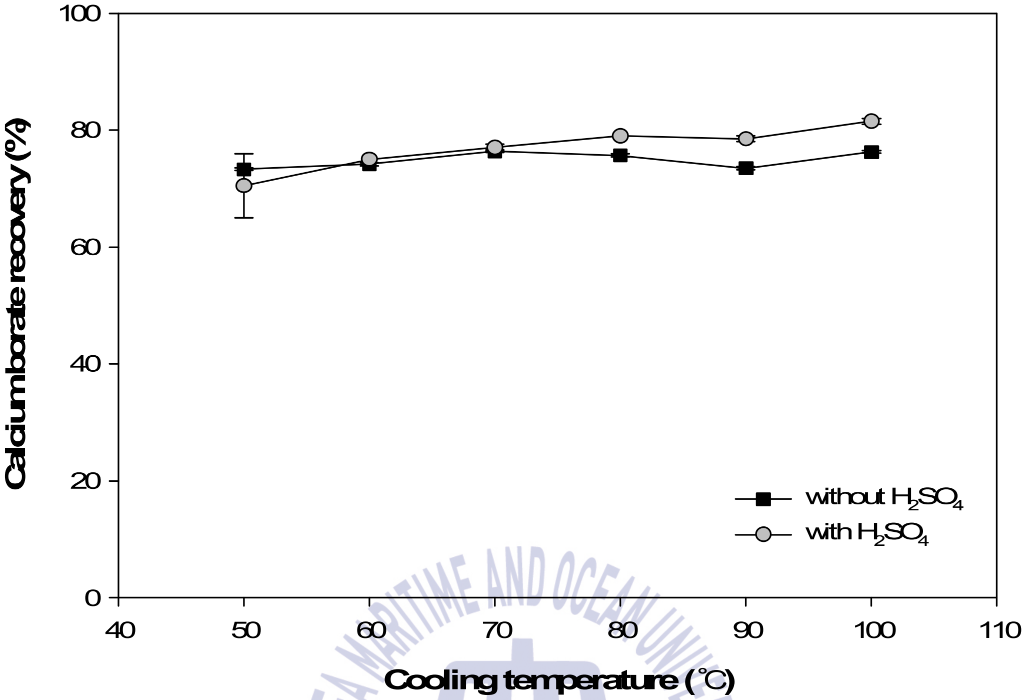

Fig. 6 Effect of sulfuric acid on the recovery of calcium borate according to cooling temperature after heating

3.4 Effect of sulfuric acid on the synthesis mechanism of calcium borate

In all the experiments of this study, the pH of saturated solution of calcium hydroxide was 12.98±0.17 before heating the reaction. At this pH, most of the boron is present as $B(OH)_4^-$, and reacts with calcium hydroxide to produce calcium borate, as follows (Tsai et al., 2011):

$$2B(OH)_4^- \ (aq) + 2Ca(OH)_2 \ (aq) \rightarrow Ca_2B_2O_5 \cdot H_2O \ (s) + 4H_2O \ (l) + 2OH^- \qquad (3)$$

On the other hand, the synthesis of calcium borate can be prevented due to the addition of sulfuric acid Because sulfuric acid reacts with calcium hydroxide and produces calcium sulfate. Although the calcium concentration in the saturated solution of calcium hydroxide with sulfuric acid was approximately as twice as high than without sulfuric acid, recovery of the calcium borate was rather low and purity was also low. And according to XRD results, when the addition of sulfuric acid, the resulting solid was the calcium sulfate and the calcium borate. In addition, the recovery of calcium borate when the addition of sulfuric acid was much lower, when heating the reaction temperature is low and the reaction time is short, than that of calcium borate when not adding the sulfuric acid. However, the recovery of calcium borate was same regardless of the presence the sulfuric acid if the reaction temperature was 90 ℃ or more and the reaction time is 60 minutes or more. Since it is required to synthesize calcium borate at high temperature or relatively low temperature for long time (Tsai & Lo, 2011; Tsai et al., 2011; Irawan et al, 2011). When the addition of sulfuric acid, the reaction is initially shown to produce predominantly calcium sulfate. But it is considered that calcium borate is synthesized and the recovery of calcium borate increases when the higher the reaction temperature, and the longer the reaction time.

Previous researchers reported that when sulfuric acid and solid calcium hydroxide were added to remove boron and heated, calcium borate was produced and calcium sulphate or calcium hydroxide was also generated as a by-product (Yilmaz et al., 2012; Remy et al., 2004; Tsai and Lo, 2011; Irawan et al., 2011; Itakura et al., 2005). Remy et al. (2004) suggested that the high concentration of sulfuric acid (50 g/L) and solid calcium hydroxide (45 g/L) was added and heated to remove boron (0.7 g/L), boron was removed after the boron compounds co-precipitated in the resulting calcium sulfate. They also said that borate ions may be substituted for sulfate ions of calcium sulfate crystal structure. And Bothe and Brown (1998) described that borate ion [$B(OH)_4^-$] and sulfate ion [SO_4^-] have similar structurally in that they have an oxygen tetrahedral structure which includes four oxygens. Reardon and Hobbs (1999) reported that the boron concentration in the solution decreases during the precipitation of calcium sulfate. As shown in the study of Remy et al. (2004), it can be explained that boron was co-precipitated in the calcium sulfate produced when excess sulfuric acid and calcium hydroxide are present in the solution, even if some calcium borate is generated. In this study, however, the concentration of boron (500 mg-B/L) was similar with in the study of Remy et al. (2004). But the amount of the resulting solid was very low and the possibility of co-precipitation was also very low since sulfuric acid (0.05 M, 4.9 g/L) and the concentration of calcium hydroxide (7 g/L).

4. Conclusions

In this study, when calcium borate was synthesized using the boron-containing artificial bittern (brine), It investigated whether the effect of the addition of sulfuric acid under various conditions (reaction temperature, reaction time, and cooling temperature after reaction). Results and their meanings are summarized as follows:

1) It was found that the way to improve the recovery and purity of calcium borate to use a saturated solution of calcium hydroxide prepared without addition of sulfuric acid than with addition of sulfuric acid. That is, addition of sulfuric acid was to increase the calcium concentration because calcium hydroxide was more soluble than without addition of that, but the recovery and purity of calcium borate were lower due to the influence of the calcium sulfate produced as a by-product.

2) In this study, calcium borate was synthesized by a saturation solution of calcium hydroxide without adding sulfuric acid to the boron-containing artificial bittren (brine) within 10 minutes by heating at a relatively low temperature (80-105 ℃). The recovery and purity of calcium borate was up to 80 % and 96 %, respectively. In this study, calcium borate of high purity was synthesized by an economical and effective way from brine (bittern). These results have great significance in that it suggests the possibility to reuse in the industry.

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