Boric Acid Production From Sodium Metaborate With Sulfuric Acid

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Abstract
In this study, boric acid production with aqueous phase reaction of sodium metaborate with sulfuric acid is investigated. Sodium metaborate is the byproduct of catalytic hydrolysis of sodium borohydride reaction. It was reacted batchwise at 90°C for 30 minutes with 98% H_2SO_4 solution. After the boric acid production, purification was investigated using ethanol, acetone and saturated boric acid solution. 97.78%, 93.13% and 100% pure boric acid products were obtained, respectively. These results, supported by XRD analysis, indicate that the proposed method was successful and it is possible to produce boric acid by reacting sodium metaborate directly with sulfuric acid.

Keywords - sodium metaborate; boric acid; sodium borohydride

1 Introduction

Boric acid is white crystalline substance which is odorless, tasteless and stable in the air. Molecular weight is 61.83 g/mol, melting point is 169°C and boiling point is 300°C . Solubility in hot water is higher than cold water. It is soluble in alcohol and glycerin. It's percentage of B_2O_3 is minimum 56.25% [1]. When boric acid is heated up to 175°C, the crystalline water will evaporate forming meta boric acid (HBO_2).

Boric acid is a refined boron product used widely in chemical industry including textile, cosmetics, antiseptics, glass and nuclear applications as well as for the production of sodium borohydride. Extensive studies continue at the present time with the aim of providing means to increase production capacity and expanding boron products market. Moreover, these studies aim also to achieve the production in a cost effective way at the desired quality and property. There are various raw materials for boric acid production such as ulexite and HCl, tincal and H_2SO_4, colemanite and H_2SO_4, tincal and HNO_3.

During the 1st World War, boric acid production from ulexite mineral was employed using HCl. But after this period, sulfuric acid was preferred due to the fact that it costs half of hydrochloric acid.

There are patents about boric acid production from tincal and kernite in the U.S.A. But crystallization and purification are rather costly. In the Borax Consolidated Ltd. patents it was prescribed that first salt side-product must be separated at high temperatures (around 100°C), then H_3BO_3 is obtained by cooling the solution.

In literature there are many methods proposed for boric acid production. One of them is producing by using tincal and sufuric acid. Boric acid solubility increases with temperature (up to 100°C) whilst solubility of sodium sulfate increases approximately up to 33°C and after this temperature, it decreases slightly [2, 3 ,4]. Using the difference between the solubilities of sodium sulfate and boric acid, it is possible to separate sodium sulfate from boric acid by crystallization at low temperature [5].

In another study, boric acid production from tincal with sulfuric acid, 95% purity boric acid could be achieved. Purity could be increased to 99.95% with raffination [6]. The boric acid production from colemanite with H_2SO_4 was firstly used in industry by ETI Mine General Directorate in Turkey. This process is, however, more expensive and the energy requirement is also higher.

On the other hand, clean energy is very important in our modern world and there are lots of researches about renewable energy sources, improving energy efficiency and sustainability of the clean future. Hydrogen is one of the promising carrier of energy obtained from renewable energy sources. It is anticipated that hydrogen era will start in the very near future. There are different methods for hydrogen storage. Sodium borohydride ($NaBH_4$) is one of the best alternatives with its high storage capacity and, easiness and convenience in producing hydrogen on demand. Hydrogen can be generated by catalytic hydrolysis of sodium borohydride as seen in Equation 1. $NaBH_4$ fuel cell production and integration projects were also carried out. [7] . Improvement and development studies are still continuing.

$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2 \qquad (1)$$

Sodium metaborate is the byproduct of this reaction. It is important to recycle sodium metaborate to the process of sodium borohydride production. This seems to be a requirement for the widespread use of sodium borohydride. Direct recycling of sodium metaborate to sodium borohydride- is very difficult [8,9]. However, when sodium metaborate is converted to boric acid, it can be used as the raw material in the Schlesinger method [10], where boric acid ($B(OH)_3$ or H_3BO_3) is first converted to trimethyl borate ($B(OCH_3)_3$), which then reacts with sodium hydride to yield sodium borohydride ($NaBH_4$). Thus, in this research, boric acid production with aqueous phase reaction of sodium metaborate with sulfuric acid is investigated.

2 Experimental

Sodium metaborate was supplied from ETI Mine General Directorate. Its analysis is given in Table 1.

TABLE 1. ANALYSIS OF SODIUM METABORATE

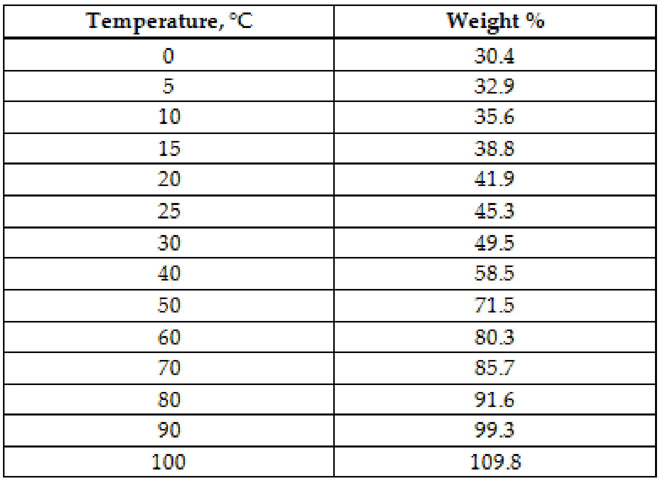
Table 1. Analysis of sodium metaborate

Na_2O %	B_2O_3 %	H2O%
22,78	25,60	51,80

2.1 Solution preparation and addition of H_2SO_4

Solubility of sodium metaborate in water is given in the following table.

Table 2. Solubility of sodium metaborate in water [11]



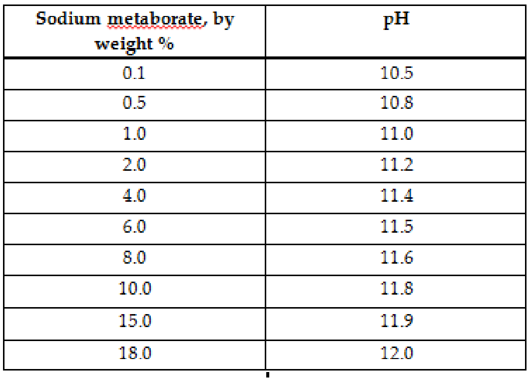
Temperature, °C	Weight %
0	30.4
5	32.9
10	35.6
15	38.8
20	41.9
25	45.3
30	49.5
40	58.5
50	71.5
60	80.3
70	85.7
80	91.6
90	99.3
100	109.8

The reaction between sodium metaborate and sulfuric acid in aqueous solution is as shown below.

$$2NaBO_2 + 2H_2O + H_2SO_4 \rightarrow 2H_3BO_3 + Na_2SO_4 \qquad (2)$$

Regarding the solubility of sodium metaborate given in Table 2 and stoichiometric ratios given above, reactant amounts were determined as 100 gr sodium metaborate, 200 ml water and 40 ml H_2SO_4 . Sodium metaborate was first mixed with water at 30°C and the pH of the solution was measured as 12 - when the solution reaches up a high concentration, the pH value doesn't change - (Table 3).. The temperatue was gradually increased to 90°C. After all of the sodium metaborate was dissolved in water, H_2SO_4 with a purity of 98% was added gradually. The solution was stirred for 15 minutes using a mechanical stirrer. At the end of the process, a foamy white product was observed at the top of the clear solution. The pH of the solution was measured as 2.3. Foamy white product was filtrated hot with vacuum pump.

Table 3. pH variation with sodium metaborate concentrations at 20°C [12]



Sodium metaborate, by weight %	pH
0.1	10.5
0.5	10.8
1.0	11.0
2.0	11.2
4.0	11.4
6.0	11.5
8.0	11.6
10.0	11.8
15.0	11.9
18.0	12.0

2.2 Crystallization and filtration of boric acid

After the reaction, due to the difference between the solubilities of boric acid and sodium sulfate salts (Fig.1), most of the Na_2SO_4 remained in the solution.

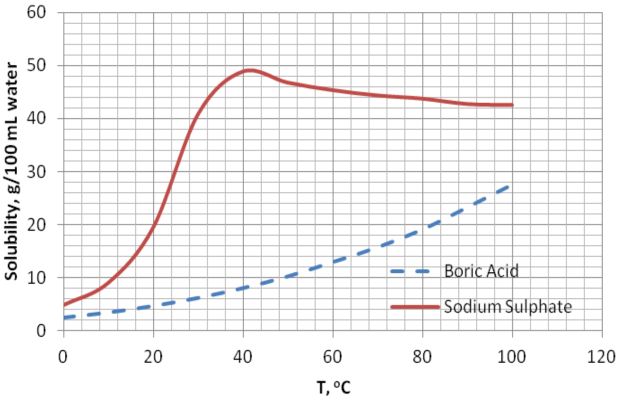


Figure .1 Solubilities of boric acid and sodium sulphate

For the crystallization of boric acid, an ice bath was prepared in a metal tray and the temperature of the solution was decreased to 10°C. Boric acid crystallization was observed at the surface layer. For filtration, vacuum pump and blue filter paper were used. After 15 minutes of filtration, all of the crystals were separated from the solution and the crystals and filtrate were weighed. The crystal product was kept in oven at 50°C for 6 hours in order to evaporate the remaining liquid. After the drying process, various analyses were made such as B_2O_3, and sulfate. Thereotically, we must have achieved 93.92 gr boric acid. But our product was 92 gr. Hence the yield was determined as 98% .

2.3 Purification of Boric Acid

Purification was also investigated using ethanol, acetone and saturated boric acid solution itself.

2.3.1 Purification with ethanol/acetone

The solubility values of boric acid in ethanol and acetone are given below in Table 4. On the other hand, sodium sulphate is not soluble in alcohol [13].

Table 4. Boric acid solubility in ethanol and acetone

Compound	Solvent	Temperature, °C	By weight %
Boric Acid	Ethanol, 95%	25	11,20
	Acetone 99%	25	0,6

Weighed solid boric acid product obtained in part II.B was firstly dissolved in ethanol at temperatures close to boiling conditions. The solution was filtered hot to remove any impurities as well as sodium sulphate which is known to be insoluble in ethanol. The filtrate was then cooled to 10°C with the ice bath in order to recrystallize the boric acid in the ethanol solution. The solution was then filtered again to obtain pure boric acid. Boric acid was then dried at about 50°C for 4 hours. Secondly, solid boric acid product obtained in part II.b was washed with acetone to remove any impurities and dried again as above.

2.3.2 Washing with saturated boric acid solution

Saturated solution prepared with ultra pure boric acid (56.36% B_2O_3, 17 ppm SO_4 and 2 ppm Cl) was used as the washing solution. This solution was prepared with 5 gr boric acid and 100 ml water as 5% wt . Boric acid product obtained in part II.B was washed with this saturated boric acid solution. Then it was filtered and dried as explained above. The difference between the solubilities of boric acid and sodium sulfate was utilized for this purification (Figure 1).

3 Results and Conclusion

Boric acid and sodium sulfate contents of both the solid product and filtrate are shown in Table 5. Solid boric acid without purification includes 54.15% B_2O_3. It corresponds to 96.15% purity of boric acid. These results indicate that, as it is also seen in Figure 2, the proposed method was successful and it was possible to produce boric acid by reacting sodium metaborate directly with sulfuric acid.

In order to increase the purity of the solid product, the difference in solubilities of boric acid and sodium sulfate in various potential solvents were examined, and ethanol and acetone were chosen as the wash liquid after this screening. As can be seen in Table 4, ethanol gave better result than acetone, with approximately 98% purity. While it is relatively easy to handle such a highly volatile solvent in the laboratory, it may cause problems in large scale plants. Therefore, washing the solid $B(OH)_3$ crystals with its own saturated solution was used to remove the impurities and the result was very successful, giving 100% purity after drying of washed crystals. It was concluded that this last purification method is very favorable, eco-friendly, economical and can easily be adapted in full scale plants.

Table 5. Purity of boric acid before and after washing

	After reaction and filtration		After washing with ethanol		After washing with acetone		After washing with saturated boric acid solution	
	$B(OH)_3$%	Na_2SO_4%	$B(OH)_3$%	Na_2SO_4%	$B(OH)_3$%	Na_2SO_4%	$B(OH)_3$ %	Na_2SO_4%
Solid	96.15	2.99	97.78	1.14	93.13	2.04	100	-
Liqui	3.22	19.24	-	-	-	-	-	-

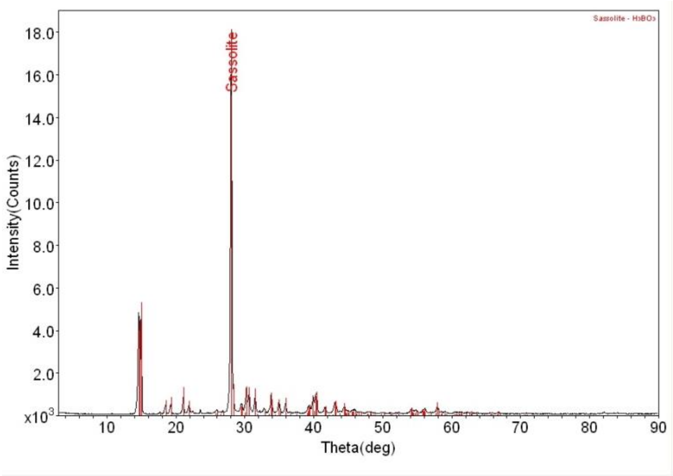


Figure 2. XRD analysis of boric acid that after reaction and filtration

4 Acknowledgment

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