

# STUDY ON THE NEW TECHNOLOGY OF BORACIC ACID EXTRACTION FROM LAKE BRINE

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**Abstract:** Based on the chemical properties of boracic acid and the chemical composition of the bittern discharge from Xi Tai Ji Nai Er Lake after lake brine concentration, the paper studied the new production process of extraction of boracic acid from the bittern, including crystallization of  $\text{CaSO}_4$  and boracic acid from the bittern step by step, and the refining of the crystallized raw boracic acid by vacuum evaporation method.

**Key words:** Boracic acid, lake brine, flashing cooling crystallization, crystallization of  $\text{CaSO}_4$  and boracic acid step by step

## INTRODUCTION

In recent years, many countries start to study the extraction process of boracic acid. It is researched and applied in industrial production widely in United States, Russia, and Chile. From 1950's, USA potash & chemical corporation started to extract borax from the lake brine through the method of brine concentration, borax crystallization step by step, then built a pilot plant to produce borax by extraction process. Also in Chile, boracic acid is produced by acidification & precipitation method.<sup>[1]</sup>

In 2007, Salt Research Institute is requested by Qinghai Zhongxin Guoan Technological Development Co. Ltd. to carry out the design of 30,000t/year boracic acid project of the comprehensive utilization of the lake brine from Xi Tai Ji Nai Er Lake. According to the chemical properties of the lake brine and boracic acid, the new production process is offered as follows: (1) The crystallization of  $\text{CaSO}_4$  & boracic acid step by step; (2) The dissolving of raw

boracic acid and the refining of the resulted boracic acid liquor; (3) The crystallization of boracic acid through two stage vacuum evaporation. This new production process has the advantages of high boracic acid yield, high production efficiency, continuity of the operation and low energy consumption and so on. It is accepted by Qinghai Zhongxin Guoan Technological Development Co. Ltd. with satisfaction and high praises.

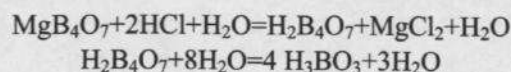
1. The process principle of the crystallization of raw boracic acid from bittern and the refining of crystallized boracic acid

### 1.1 The acidification of bittern and the crystallization of raw boracic acid

There will be bittern discharged from the lake after the concentration of lake brine and some salts crystallization, the chemical composition of the bittern includes  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{B}_4\text{O}_7^{2-}$ ,  $\text{SO}_4^{2-}$  and some others. When adding  $\text{HCl}$  into the bittern, the  $\text{HCl}$  will react with  $\text{B}_4\text{O}_7^{2-}$  and  $\text{H}_2\text{B}_4\text{O}_7$  is obtained,

then the obtained  $\text{H}_2\text{B}_4\text{O}_7$  will react with  $\text{H}_2\text{O}$  quickly and  $\text{H}_3\text{BO}_3$  is produced when add

more  $\text{HCl}$  into the bittren continuously<sup>[2]</sup>, the reaction formula are as follows:



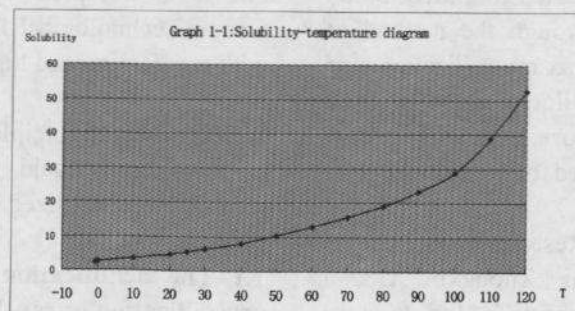
Because of the low solubility of boracic acid in bittren, with the concentration of the acid-treated bittren, large quantity of boracic acid crystallizes from the liquor according to the data of Mr. Yang Cundao, when adding  $\text{HCl}$  to the bittren with the content of  $\text{B}_2\text{O}_3$  is 2.5%, the pH value of the bittren will vary in three steps: the first step, with the adding of  $\text{HCl}$ , the pH value decreases from 4.55 to 2.64 smoothly, small quantity of boracic acid crystallizes from the liquor; the second step, when adding  $\text{HCl}$  to the liquor continuously, the pH value increases from 2.64 to 3.04 slowly, large quantity of boracic acid crystallizes from the liquor; the third step, add  $\text{HCl}$  to the liquor continuously, the pH value decrease quickly, and when the value reach 2.4, most of boracic acid crystallizes from the

liquor. In the first step, the crystallized solid is  $\text{H}_2\text{B}_4\text{O}_7$ , and in second and third steps the solid is  $\text{H}_3\text{BO}_3$ . because the high content of soluble and insoluble impurities in the bittren, and the crystallized boracic acid will carry some bittren when it crystallizes, so the crystallized boracic acid should be refined to remove the impurities mixed in it.

## 1.2 The refinement of the raw boracic acid

The following Figure 1-1 is the solubility-temperature diagram, when the temperature increases, the solubility of boracic acid will increase accordingly, and the detailed solubility data in different temperature are shown in the below table 1-1<sup>[4]</sup>:

Solub	Temp	Solub	Temp	Solub	Temp
2.46	-0.76	6.3	30	19.11	80
2.6	0	8.02	40	23.3	90
3.6	10	10.35	50	28.7	100
4.8	20	12.90	60	38.7	110
5.5	25	15.70	70	52.4	120



According to the solubility property of boracic acid, firstly adding steam, water and the mother liquor discharged after the cooling crystallization step to the crystallized boracic acid solid, after the removing of insoluble impurities by settlement and filtration, the purified boracic acid liquor then enter

cooling-crystallization step to re-crystallize boracic acid solid, then through steps of centrifugation, washing and drying, the final boracic acid is produced.



## 2. THE COMPARISON OF THE NEW PRODUCTION PROCESS WITH THE OLD ONE

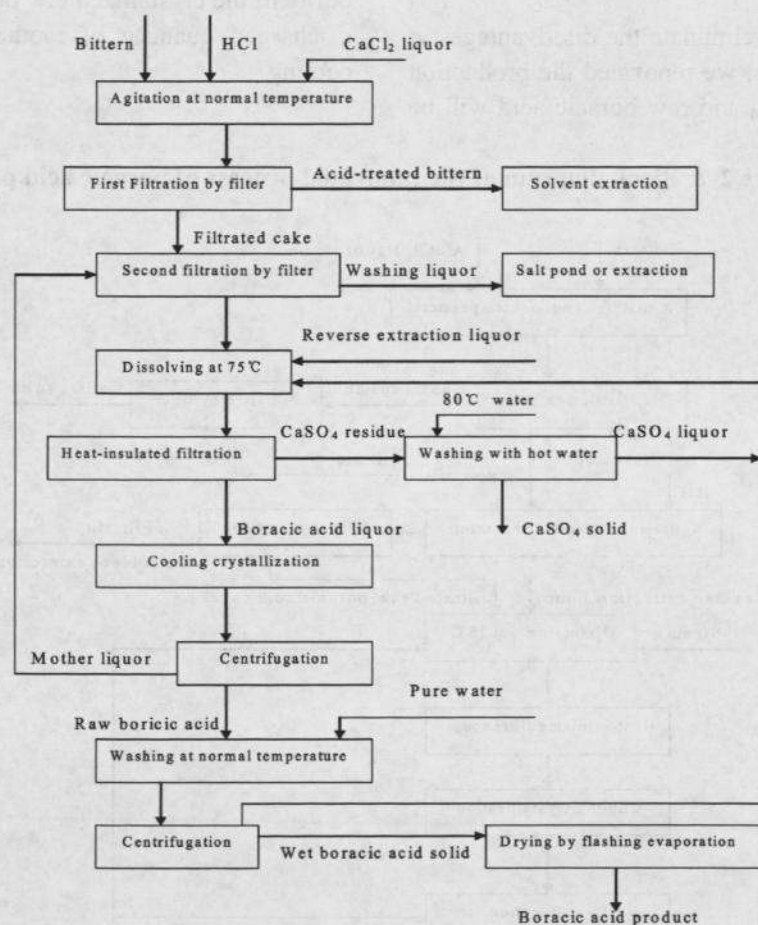
### 2.1 The old production process adopted by Qinghai Zhongxin Guoan Technological Development Co. Ltd. in the experiment in laboratory

#### 2.1.1 The process flow

In order to use the lake brine of Xi Tai Ji Nai Er Lake reasonably, firstly Qinghai

Zhongxin Guoan Technological Development Co. Ltd. made experiment in the laboratory and defined the production process of boracic acid, mainly including: joint crystallization of  $\text{H}_3\text{BO}_3$  &  $\text{CaSO}_4$ ; The dissolving of mixed solid and refining of resulted liquor; boracic acid re-crystallization from the liquor through cooling evaporation, the washing and drying of re-crystallized boracic acid. The schematic diagram is shown in Figure 2-1<sup>[5]</sup>.

Figure 2-1: Schematic diagram of the old process of boracic acid production



#### 2.1.2 The disadvantages of the old process flow

(1) In the old process, large quantity of  $\text{CaSO}_4$  crystallized simultaneously with the crystallization of boracic acid from the bittern, and the crystallized  $\text{CaSO}_4$  will circulate in the process, so the consumption figures of energy and washing water are high. From experiment data in laboratory it will consume

5.3.5 tons water of 80°C for 1 ton boracic acid product.

(2) Because of the joint crystallization of  $\text{CaSO}_4$  and raw boracic acid solid, 7.533m<sup>3</sup> of mother liquor will be discharged after the cooling crystallization step, so the production efficiency of boracic acid is low, it is about

58.27%-65% from the experiment data in laboratory.

(3) Because the particle size of the crystallized  $\text{CaSO}_4$  is fine, it needs many times of washing to guarantee the production efficiency of boracic acid. In the experiment in laboratory, the  $\text{CaSO}_4$  residue should be washed 4 times.

## 2.2 The new production process of boracic acid selected by Salt Research Institute in the designing of boracic acid production line with the production capacity of 30,000ton/year.

### 2.2.1 The renovated process.

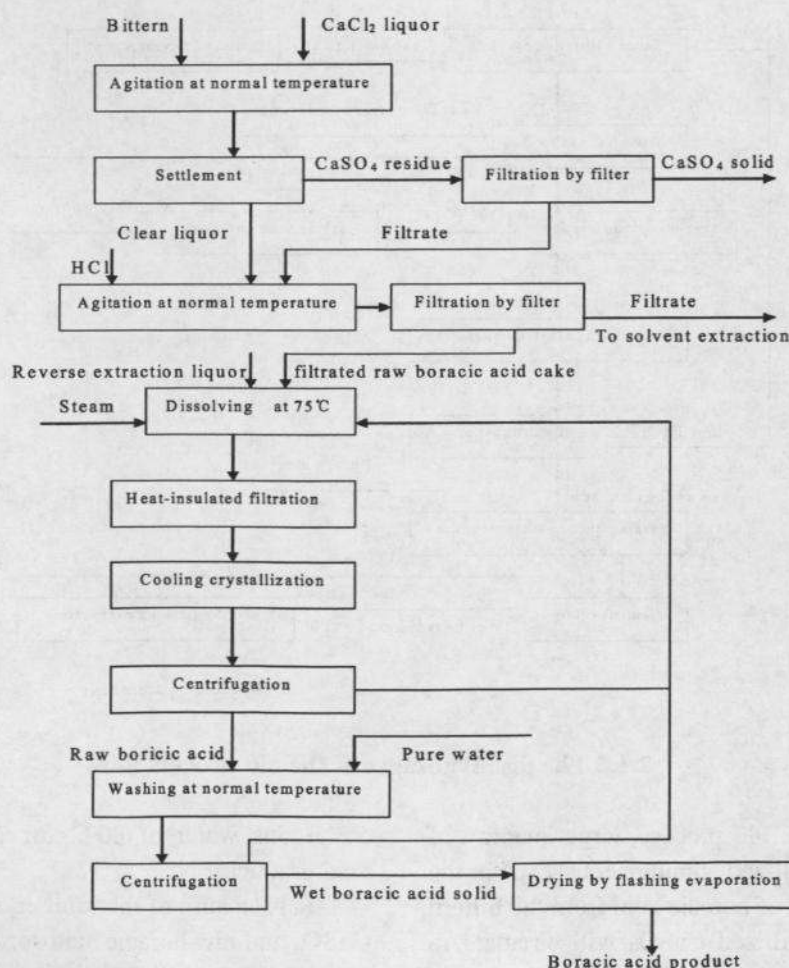
Aimed to eliminate the disadvantages in the old process, we renovated the production process,  $\text{CaSO}_4$  and raw boracic acid will be

crystallized from the bittren separately, and in the hot dissolving step, such measures should be taken as reverse extraction, cooling, proportionally mixing of boraci acid washing solution and raw boracic acid. The detailed process is shown in Fig 2-2.

### 2.2.2 The advantages of the new process.

(1) In the new process,  $\text{CaSO}_4$  and boracic acid crystallized from the bittren separately, the crystallized raw boracic acid solid is pure, so the following refinement steps are easy, and consumption figures of energy and washing water are low, the first figure can be decreased by 30%, the second be decreased by 80%. (2) Because of the high purity of the crystallized raw boracic acid, the discharged quantity of mother liquor after cooling

Figure 2-2: Block diagram of the renovated process of boracic acid production



crystallization is low, the yield of boracic acid can be more than 75%, increases by 10%

compared with the old process.

(3) In the new process,  $\text{CaSO}_4$



crystallize from the bittern firstly, the quantity of boracic acid crystallized in this step is low, so the washing of  $\text{CaSO}_4$  is easy, and the energy consumption is also low accordingly.

### **3 THE OPTIMIZATION DESIGN FOR COOLING CRYSTALLIZATION STEP IN THE NEW PROCESS**

#### **3.1 The selection for cooling crystallization step in the old process**

Cooling crystallization step is a main step in the production process of boracic acid. In the old production process, jacket cooling method is selected by Qinghai Zhongxin Guoan science and technology developing Co. Ltd for the cooling crystallization step, the disadvantages of which include low processing capacity, low heat transfer coefficient and heavy fouling on the heat-exchanging surface.

#### **3.2 The optimization design for cooling crystallization step in the new process**

At present, in many chemical industries, flashing cooling crystallization method is used widely in cooling crystallization step when the required cooling temperature is not very low. In boracic acid industry, flashing cooling crystallization method is also widely used. Such as in Turkey Eti Bor company with production capacity of 160,000ton/year of boracic acid, and USA Rio Tinto Borax company with production capacity of 220,000ton/year of boracic acid, both of them adopted two stage flashing cooling crystallization method in cooling crystallization step. In China, the production capacities of most of existing boracic acid production line are not more than 5,000ton/year, so jacket cooling method is selected by domestic companies.

Flashing cooling crystallization method is used in other industries. For example, in Germany K+S company, three stage flashing cooling crystallization method is used in KCl production line with sylvinites as the raw material. Some company in China also adopted two staged continuous flashing cooling crystallization technology in

10,000ton/year production of KCl. Another example is the application of flashing cooling crystallization method in sodium glutamate industry in China, our institute has rich experience in designing, building, managing flashing cooling crystallization equipment.

In overseas, Large scale of flashing cooling crystallization has been used in boracic acid production, other industries also see the successful implementation of flashing cooling crystallization technology. And our Salt Research Institute mastered the technology of flashing cooling crystallization and had the successful experience of using three stages flashing cooling crystallization method in designing a production line with capacity of 10,000ton/year of KCl product. So when we design the boracic acid production line for Qinghai Zhongxin Guoan Technological Development Co. Ltd., we renovate the old process, and adopt two stages flashing cooling crystallization method in cooling crystallization step.

### **4. CONCLUSION**

Based on the old production process of boracic acid extraction adopted by Qinghai Zhongxin Guoan Technological Development Co. Ltd. in laboratory, we study the new technology through the design of 30,000t/year boracic acid project of the comprehensive utilization of the lake brine from Xi Tai Ji Nai Er Lake. The new process includes: (1) The crystallization of  $\text{CaSO}_4$  & boracic acid step by step; (2) The dissolving of raw boracic acid and the refining of the resulted boracic acid liquor; (3) The crystallization of boracic acid through two stage vacuum evaporation. Compared with the old process, it has the advantages as follows:

#### **(1) The low consumption figures**

Through the new process, the consumption figures of energy and washing water are low, the first figure can be decreased by 30%, the second one can be decreased by 80%.

#### **(2) The high boracic acid production efficiency**

In the new process, the yield of boracic acid product will be more than 75%, increasing 10% compared with the old process.

(3) The simplified process and easy operation

In the new process,  $\text{CaSO}_4$  crystallized from the bittern firstly, the quantity of boracic acid crystallized in this step is low, so the washing of  $\text{CaSO}_4$  is easy, and the energy consumption is also low.

(4) The increased processing capacity in cooling crystallization step

Because of the application of two stage flashing cooling crystallization in cooling crystallization step, the new process increase the capacity of the whole production line, and overcomes the disadvantages of low processing capacity, low heat transfer coefficient and heavy fouling on the heat-exchanging surface in jacket cooling method.

(5) The new process has other advantages of continuously operation of the production line, and is easy to achieve auto-control.

So we conclude the new technology of boracic acid extraction be practicable in boracic acid industry.

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