Purification of Food-grade Magnesium Chloride

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Abstract: The application of the varying weights of bischofite dissolved in the distilled water was investigated. The effects of the temperature on the rate of evaporation and the thermal precipitation time on the purity of the crystal products were fully investigated. Two validation tests including magnifying tests and recycling residue were also studied. Our results demonstrate that the contents of NaCl、KCl and $CaSO_4$ in the filtrate reached a minimum value after the pretreatment of 350 g bischofite dissolved in 100 ml distilled water. In the crystal products from the second evaporating stage of the validation tests, the contents of $MgCl_2 \cdot 6H_2O$, SO_4 and NaCl+KCl are 99%, ≤0.1±0.01% and ≤0.8±0.04%, respectively. The content of magnesium chloride in the solution was increased to a greater extent, and the impurities reduced correspondingly through the dissolution pretreatments of bischofite. This could decrease energy consumption for the impurity removing stage, evaporation and crystallization process, and thus reduce costs for the industrial production of food-grade magnesium chloride

1 Introduction

The positive correlation between diet and health has led health agencies around the world to control the intake of certain food components that are thought to promote some disorders [1].According to the national standards for food safety (GB2760－1996－2005), the additives used in food production must be food grade additives. Edible magnesium chloride ($MgCl_2 \cdot 6H_2O$) as additive has more widely application in food, salt, mineral water, medicine and other industries [1-4].

The Qinghai salt lakes in the qaidam basin are well known for their huge reserves of potassium chloride (KCl) and magnesium chloride ($MgCl_2$) in China [5]. In recent years, about 4.5 $Mt \cdot a^{-1}$ potassium fertilizer has been produced with 24-30 $Mt \cdot a^{-1}$ magnesium chloride as by-product, and a large amount of magnesium chloride has been left as the by-product or even waste in salt lakes of Qinghai [6,7]. This has caused not only the waste of magnesium resources, but also the environmental pollution [8]. The production of food grade magnesium chloride used bischofite as raw material is another effective utilization way of magnesium resources of salt lake, in which it is playing an active role.

This study investigated the performance of the varying weights of bischofite dissolved in the distilled water, determined the optimal ratio relationship between bischofite and distilled water under the condition of the least amount of impurity in the filtrate, and confirmed the reliability and repeatability of the optimal dissolution ratio.

2 Experimental

2.1 Reagents and instrumentation

The raw ore used in this study included bischofite (Golmud zhenghai magnesium science and technology development Co., Ltd.)

The instruments used for the analyses included stirrer (IKA EUROSTAR 60; Shanghai Chuangyi Science and education equipment Co., Ltd.), oil bath pan (DF-101S; Gongyi Yuhua Instrument Co., Ltd.), an inductively coupled plasma–atomic emission spectrometer (ICAP6500 DUO; America Thermo Scientific, USA).

2.2 Experiments

2.2.1 Solution analysis

The solution with a certain amount of bischofite dissolved in the distilled water was mechanically stirred at a frequency of 300 rpm for 30 min at room temperature (20 ± 2 °C). Subsequently, the residue and filtrate were separated and weighed. The filtrate was analyzed using EDTA volumetric analysis to determine the Mg^{2+}, Cl^- concentrations, and inductively coupled plasma–atomic emission spectrometry (ICP) to determine the Na^+, K^+, Ca^{2+}, As, Pb, SO_4^{2-} and B_2O_3.

2.2.2 Evaporative crystallization

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(1) First evaporating stage

The filtrate was heated up to110±5 °C for some water loss, and then thermally precipitated for 1h, finally, conducted with thermal filtration.

(2) Second evaporating stage

In order to obtain crystals $MgCl_2 \cdot 6H_2O$, this filtrate from the first evaporating stage was heated up to140 °C again for some water loss, and then the thermal refrigerated to 40 °C for filtration. Finally, the product of crystals $MgCl_2 \cdot 6H_2O$ was obtained and analyzed using EDTA volumetric analysis to determine the Mg^{2+} concentrations, and ICP to determine the Na^+, K^+, Ca^{2+} and SO_4^{2-}concentrations.

The process flowsheet for purification of food-grade magnesium chloride was shown in Figure 1.

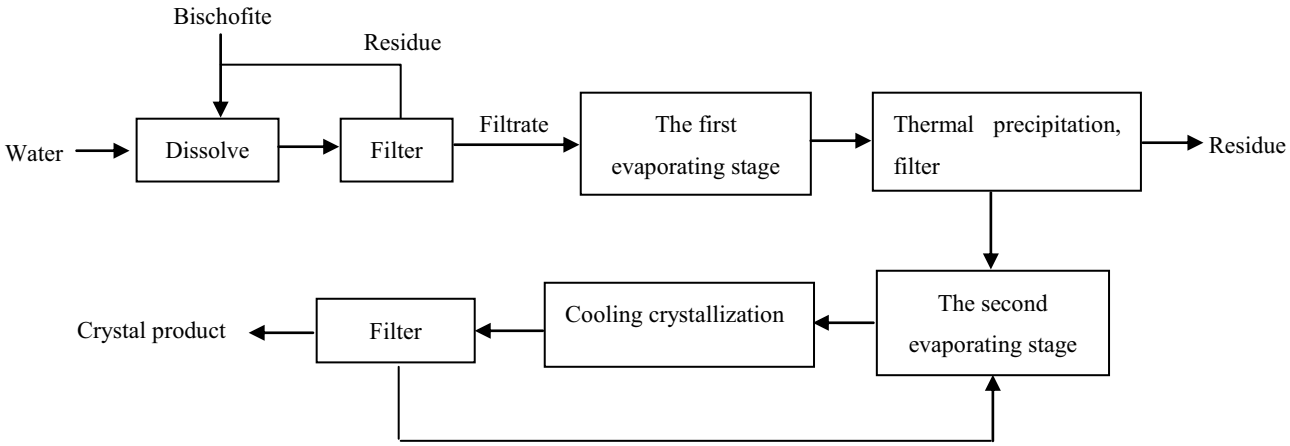

Figure 1. Process flowsheet for purification of food-grade magnesium chloride

3 Results and Discussion

3.1 Materials analysis

In order to obtain the composition of the bischofite, the solution with 50.0390 g bischofite dissolved in the distilled water was transferred into a 500 ml volumetric flask, and then analyzed using EDTA volumetric analysis and ICP. The result of such analysis is presented in table 1. The original magnesium chloride content (wt. %) is 44.77 %. The contents of impurities As, B_2O_3 and Pb in bischofite are unavailable due to extremely low values. The total contents of insoluble matter and soluble impurities (NaCl+KCl+$CaSO_4$) (wt. %) are $<$ 0.10 % and 4.6 %, respectively.

Table 1. Result of materials analysis

Constitutes	Content (wt. %)
As	0.00006595
B_2O_3	0.0003732
Ca^{2+}	0.2314
K^+	0.8693
Na^+	0.8469
Pb	0.00002598
SO_4^{2-}	0.5372
$MgCl_2$	44.77
NaCl	2.15
KCl	1.66
$CaSO_4$	0.79
Insoluble matter	0.095

3.2 Varying solubility experiment

The experiments were conducted to investigate the effect of the solubility of bischofite on the contents of soluble impurities in the filtrate. The bischofites with weights varying from 100 g to 500 g were dissolved in the distilled water of 100 ml. After filtering, the density of filtrate, the concentrations of $MgCl_2$ and the components of soluble impurities were analyzed respectively.

As is shown in Figure 2, the contents of residue gradually increased with increasing the weights of bischofite. The contents increased rapidly with bischofite weights higher than 350 g. Notably, a large amounts of mineral $MgCl_2 \cdot 6H_2O$ dissolved and remained in the residue. As observed in the Figures 2 and 3, the weight contents of $MgCl_2$ steadily increased with increasing bischofite weight. However, the contents of NaCl and KCl initially increased and then rapidly decreased with increasing bischofite weights. While the $CaSO_4$ contents declined straightly. When the bischofite weight was higher than 350 g, all the NaCl, KCl and $CaSO_4$ contents reached minimum levels. Therefore, the relationship of optimal ratio between bischofite and distilled water was determined as 350 g/100ml.

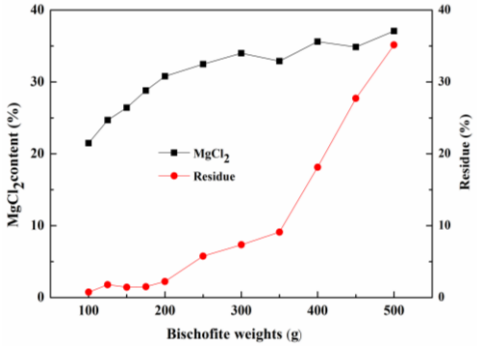

Figure 2. Relationship between $MgCl_2$ and residue with bischofite dissolved in the distilled water of 100 ml

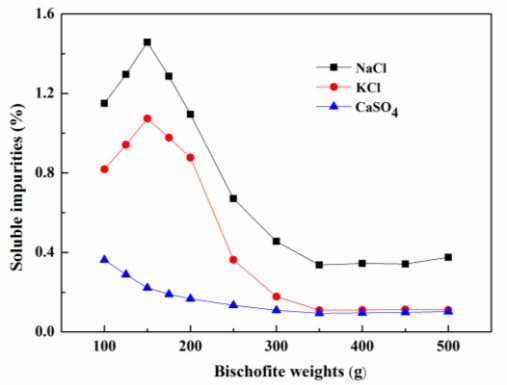

Figure 3. Relationship between soluble impurities with bischofite dissolved in the distilled water of 100 ml

3.3 Effect of temperature

To confirm the temperature for the second evaporating stage, the studies were carried out through varying temperature from 140 to 170 °C for 240 min. The results are shown in Figure 4 a and b. The evaporative loss of water initially decreased sharply and then gently declined with lengthening time.

The average speeds of evaporation during the time of 0 ~ 75 min were 0.46, 0.49, 0.53 and 0.55 g/min, respectively. While the average speeds during the time of 75 ~ 240 min were 0.051, 0.054, 0.063 and 0.053 g/min respectively. As observed, all the evaporation rates became slow after 75 min, and had nothing to do with the temperature. Therefore, the optimal evaporation temperature was 140 °C for the purpose of reducing energy consumption.

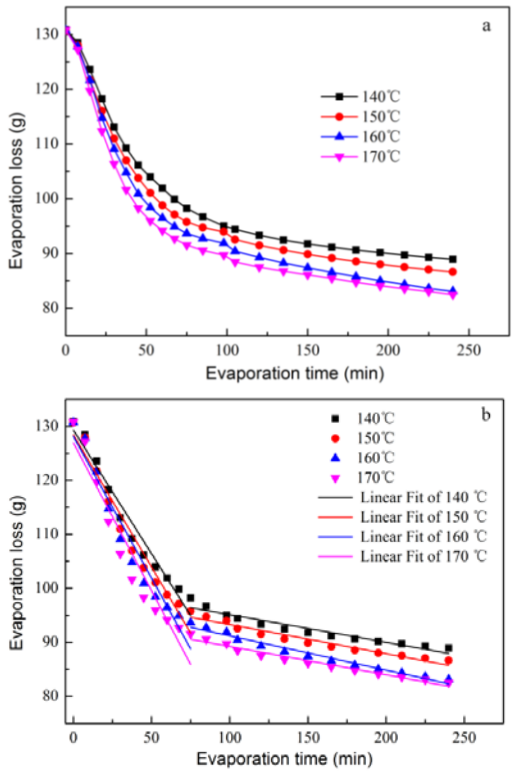

Figure 4. Effect of the temperature on the evaporation rate (a and b)

3.4 Effect of the thermal precipitation time

According to the optimal ratio of 350 g bischofite to 100 ml distilled water, the filtrate was obtained and heated up to 110±5 °C for some water loss, and then thermally precipitated for 1 ~ 5 h. Finally, it was conducted with filtration. The result for the effect of the thermal precipitation time on the purity of crystal product is listed in the Table 2. Table 2 shows that the purities of crystal product reached maximum levels when the thermal precipitation time was 1-3h. However, the purity value reduced as the thermal precipitation time was 5 h. Based on the energy consumption consideration, the optimum time is 1 h.

Table 2. Effect of the thermal precipitation time

Precipitation time (h)	**$MgCl_2$ (wt. %)**
1	46.30
2	46.18
3	46.39
5	45.37
Precipitation time (h)	**$MgCl_2$ $6H_2O$ (wt. %)**
1	98.86
2	98.61
3	99.06
5	96.88

3.5 Validation

3.5.1 Magnifying tests

The solutions were obtained with 1750 g bischofite dissolved in 500 ml distilled water, 5 times the original weights based on the optimal ratio in the section 3.2, and conducted to the first and second evaporating stages after filtration. The analyzed results of the products are shown in the tables 3 and 4. In those two products, the varying evaporation losses (17.32 g and 16.25 g) for the first stage gave rise to the different weight levels of crystals (12.68 g and 3.63 g, respectively) (Table 3). However, the total contents of $MgCl_2 \cdot 6H_2O$, SO_4 and NaCl+KCl （wt. %） were ＞ 99%, ＜ 0.1% and ＜ 0.6%, respectively (Table 4). This reveals that the varying evaporation losses for the first stage have no influence on the contents of the crystal products for the second stage.

Table 3. Weights of evaporation loss and crystal

Test 1 stages	**g**
Evaporation loss for the first stage	17.32
Crystal for the first stage	12.68
Evaporation loss for the second stage	45.65
Crystal for the second stage	194.79
Test 2 stages	**g**
Evaporation loss for the first stage	16.25
Crystal for the first stage	3.63
Evaporation loss for the second stage	45.34
Crystal for the second stage	203.84

Table 4. Contents of crystal products for the second stage

Product 1	**wt. %**
$MgCl_2$	46.41
$MgCl_2·6H_2O$	99.10
NaCl	0.47
KCl	0.12
$CaSO_4$	0.022
SO_4	0.015
Product 2	**wt. %**
$MgCl_2$	46.47
$MgCl_2·6H_2O$	99.23
NaCl	0.46
KCl	0.12
$CaSO_4$	0.031
SO_4	0.022

3.5.2 Recycling residue

(1) The solution with 350 g bischofite dissolved in the distilled water was mechanically stirred for 30 min, and then filtered.

(2) The residue from the section (1) was weighted and mixed with bischofite into mixture of total 350 g. Then, repeat the operation (1).

(3) Repeat the above (1) and (2) for 2 times. Finally, the obtained filtrate was conducted to the first and second evaporating stages after filtration. The analyzed results of the products are shown in the tables 5 and 6. In the two products, the varying evaporation losses (22.87 g and 29.62 g) for the first stage resulted in the crystals (27.78 g and 41.92 g, respectively) (Table 5). However, the total contents of $MgCl_2·6H_2O$, SO_4 and NaCl+KCl (wt. %) are 99% approximately, ≤ 0.1±0.01% and ≤ 0.8±0.04%, respectively (Table 6). This also indicates that the varying evaporation losses for the first stage have no influence on the contents of the crystal products for the second stage.

Table 5. Weights of evaporation loss and crystal

Test 1 stages	**g**
Evaporation loss for the first stage	22.87
Crystal for the first stage	27.78
Evaporation loss for the second stage	33.16
Crystal for the second stage	261.34
Test 2 stages	**g**
Evaporation loss for the first stage	29.62
Crystal for the first stage	41.92
Evaporation loss for the second stage	30.15
Crystal for the second stage	240.57

As shown in the validation results for magnifying tests and recycling residue, the products obtained meet the product qualification (GB 25584-2010), according to the optimal ratio relationship between bischofite and distilled water (350 g: 100 ml).

Table 6. Contents of crystal products for the second stage

Product 1	wt. %
$MgCl_2$	46.20
$MgCl_2·6H_2O$	98.65
NaCl	0.61
KCl	0.17
$CaSO_4$	0.14
SO_4	0.099
Product 2	wt. %
$MgCl_2$	46.36
$MgCl_2·6H_2O$	98.99
NaCl	0.64
KCl	0.20
$CaSO_4$	0.16
SO_4	0.11

4 Conclusions

(1) The optimal ratio relationship between bischofite and distilled water was 350 g : 100 ml.

(2) As shown in the validation results for magnifying tests and recycling residue, the products obtained according to the optimal ratio meet the product qualification. In the products, the total contents of $MgCl_2·6H_2O$, SO_4 and NaCl+KCl (wt. %) are 99% approximately, ≤ 0.1±0.01% and ≤ 0.8±0.04%, respectively.

Acknowledgments

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