

Research Progress in Dehydration Technology of Bischofite for Preparing Anhydrous Magnesium Chloride

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Abstract: Abundant soluble magnesium salts with low impurity were produced as by-product in some industries of Qinghai. These soluble magnesium salts were exploited more easily than some solid minerals, such as magnesites, dolomite minerals, which could accord with the standards of electrolytic process for preparing magnesium materials under rough purification processing. Several different routes on dehydration technology of bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) for preparation of anhydrous magnesium chloride (MgCl_2) are reviewed in this article, including the partially hydrated magnesium chloride ($\text{MgCl}_2 \cdot n\text{H}_2\text{O}$, $n < 6$). In order to improve the quality of product (MgCl_2 or $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$), a few better proposals of improved dehydration technology are proposed. In dehydration process, many factors should be taken into consideration, such as economic benefits, production efficiency, environmental problems, purity.

Introduction

Magnesium is a significant nonferrous metal and could be applied to manufacture various kinds of magnesium materials, including binary and multicomponent alloys ordinarily [1,2], which have the characters of low density [3], high strength [4], specific plasticity [5], better damping capacity [6], fine electromagnetic interfere shielding [7], good mechanical properties [8] etc. However, a large amount of bischofite was produced as by-product or industrial trailings in numerous technology of exploiting abundant salt lake resources [9,10]. The discharge of bischofite without rational disposal could cause terrible environment pollution and even some bischofite was disposed in the way of piling up directly, which was also a tremendous waste of resources. The phenomenon is called “magnesium disaster” in salt lake chemical industry [11], so more measures of comprehensive exploitation technology on bischofite should be developed valuably. Most of bischofite utilization aim at achieving the goal that coordinated water molecules are dehydrated to obtain anhydrous magnesium chloride, then anhydrous magnesium chloride is distributed to produce other kinds of magnesium products. Many patents [12,13] have been applied in practical production. In this article the different dehydration technology of bischofite were reviewed, which focuses on how to improve the production efficiency.

Dehydration Data of Bischofite By TG-DSC

The structure of magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) is central symmetric octahedra. The crystal structure parameters of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is determined primitively in 1934 [14]. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ crystallizes in monoclinic space group $C2/m$, as illustrated in Fig.1, which showed that the crystal packing in a parallel projection approximately down the crystallographic c axis. The lattice parameters were listed in the corresponding reference [15], where the parameters and structures of $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ ($n=0,1,2,4,6$) were identified in detail.

With the thermogravimetry and differential scanning calorimetry analysis curve (TG-DTA) of bischofite [16,17], we could conclude that four main periods existed during dehydration of bischofite under the condition of continuous heating stage. We conducted an experiment TG-DSC of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. As shown in Fig.2, the mass change curve presented four gradients obviously. To a molecule of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, in the first step, from normal temperature to 125.9°C , the mass decreased

6.62%, and this dehydration stage corresponded to 0.75 molecule of H₂O equivalently. The second period was from 125.9°C to 173.8°C, during which mass decreased 23.79%, and the mass reduced the maximum among four dehydration stages. The corresponding molecule number of crystal H₂O was 3.43 in the first and second periods. Mass decreased 14.37% in the third stage, and the temperature ranged from 173.8°C to 205.9°C. The former three dehydration periods of bischofite reached 5.00 molecules of H₂O equivalently. In the last dehydration stage, the mass decreased 10.42% from 205.9°C to 261.4°C. In the four periods, the mass decreased 55.20% totally, which was equivalent to that 6.23 molecules of H₂O was dehydrated in the whole dehydration periods. Where the deviation mainly happened was in the third and fourth dehydration stages, because high temperature resulted in hydrolysis reactions of partially hydrated magnesium chloride (MgCl₂·nH₂O) and the main corresponding hydrolysis compounds were basic magnesium chloride [Mg(OH)Cl] and MgO and some other irregular impurities. These conclusions were confirmed finally by means of X-ray diffraction analysis. The results were close to the research data [18].

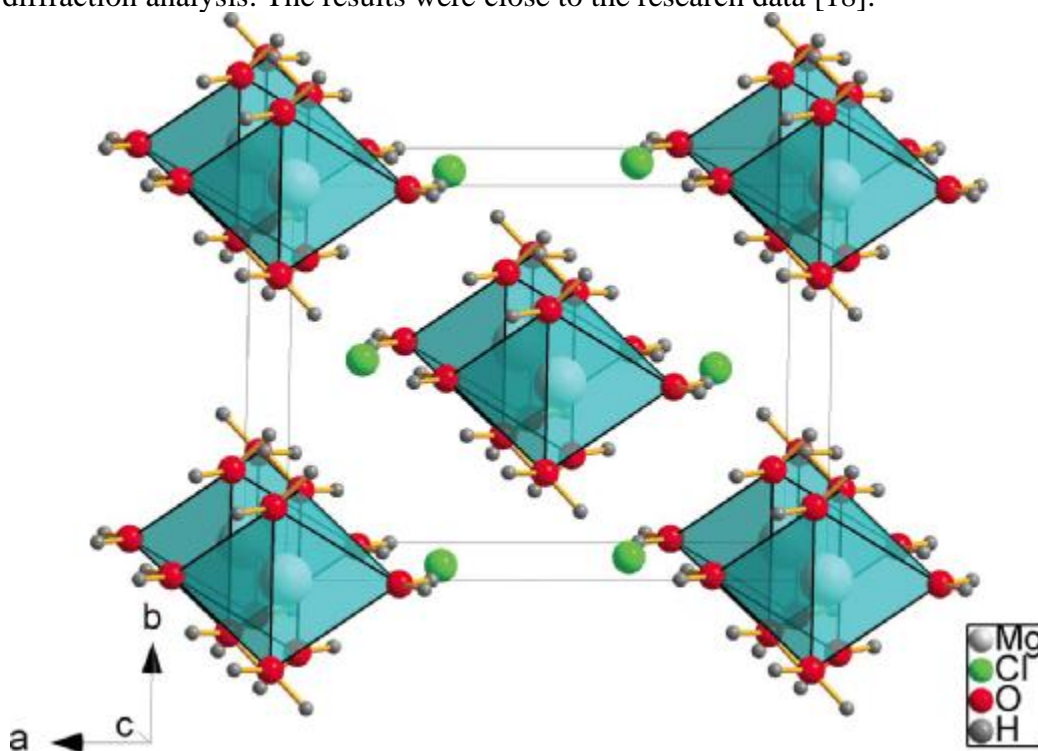


Fig.1 The crystal packing of MgCl₂·6H₂O in a parallel projection approximately down the crystallographic c axis.

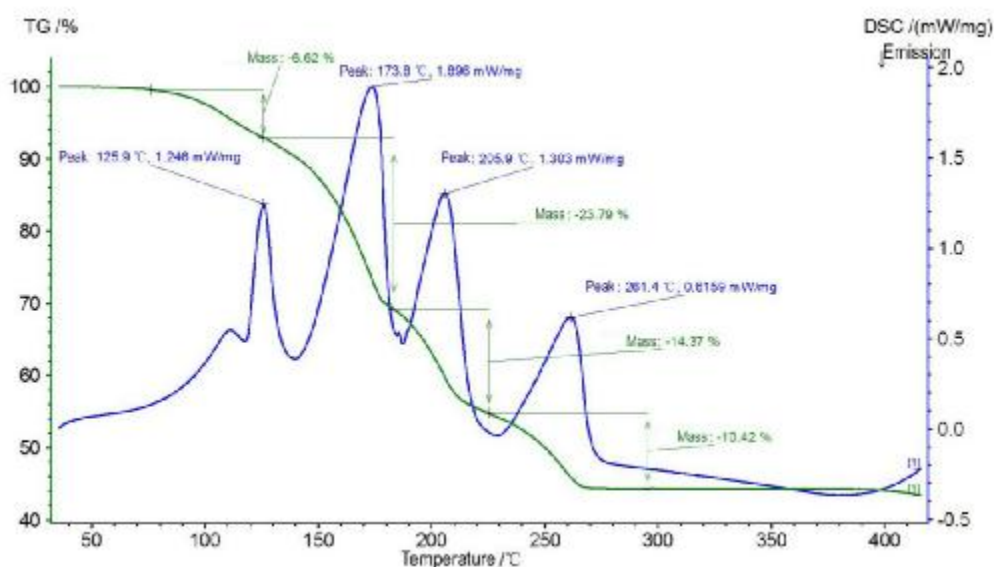


Fig.2 TG-DSC curves of bischofite

Dehydration of Bischofite

Dehydration by Shielding Gas

With the rise of dehydration temperature, MgO and Mg(OH)Cl were produced increasingly in the form of by-products. In order to inhibit these by-products formation and reduce energy consumption, some dehydration technology of bischofite produced MgCl₂ in the protection gas atmosphere of chlorine or hydrogen chloride gas [19]. The production conditions could contribute to restraining the proceeding of hydrolysis reactions, then the technology would produce high-purity MgCl₂ effectively and reduce the hydrolysis rate as much as possible through controlling proper concentration of shielding gas. One specific procedure [20] was as follows : (1) the magnesium chloride mother liquor was concentrated preliminarily; (2) concentrated liquor was produced in the form of MgCl₂·2H₂O under the heating air flow at 100°C~200°C; (3) then product MgCl₂·2H₂O was treated in the shielding gas atmosphere of Cl₂ or HCl gas at 620°C~650°C ,of which ultimate MgCl₂ content exceeded 95% and MgO content was lower than 0.5%.

The method of shielding gas dehydration should be manipulated in the appropriate concentration of Cl₂ or HCl, which benefited the process of non-equilibrium state and reaction kinetics conditions, such as reaction degree, energy consumption, hydrolysis rate, and reaction time. The technology had the advantages of great automation and could produce higher purity of MgCl₂, and suppressed the hydrolysis reaction effectively. The deficiencies of shielding gas dehydration were that the technology consumed lots of Cl₂ or HCl without good recycling, high energy consumption. What's more, the production equipment was subjected to serious corrosion, and parts of HCl may attach to the surface of MgCl₂.

In an American patent [21], shielding gas dehydration technology was different, which adopted two-stage dehydration. The first stage proceeded in spraying dryer to mix MgCl₂·nH₂O (n=0.5~1.5) with carbon to form much small caking, and the bulk density of small caking was between 0.6g/L and 1.3g/L and dimension distribution was between 1.5cm and 5cm. The second stage was carried out in the atmosphere of Cl₂ at 200°C~300°C for 2~4 hours. The end high-purity product MgCl₂ met the requirements of electrolytic conditions to prepare magnesium. If product MgCl₂ contained impurity beyond the standard, electrolysis process consumed more raw materials and Cl₂, and including a size of disadvantageous factors, such as low efficiency, poor quality, and more slag.

Dehydration by Complex Salt Methods

Dehydration by Potassium Carnallite Complex Salt Method

According to definite proportion with bischofite and potassium chloride as raw materials, these traditional technology synthesized potassium carnallite complex (KCl·MgCl₂·6H₂O) by reference of the ternary phase diagrams [22] to achieve the good effect of dehydration. In the circumstance, evaporation of salt lake brine was simulated [23], which was demonstrated that KCl·MgCl₂·6H₂O was synthesized easily with low concentration in ordinary conditions. The corresponding double-chamber boiling furnace was ever applied to produce KCl·MgCl₂ material [24]. The main operation steps were simple as follows: the base materials were added into the double-chamber boiling furnace, and heating carrier gas was injected to guarantee stable boiling stage in the first chamber under 150°C~160°C. Then carrier gas conditions were adjusted higher to keep in stable state of temperature of the second chamber reach 180°C~200°C for proper time. The entire reaction process was in the situation of continuous feeding and continuous discharging, which was a typically chemical technology. What should be focused on was that the feeding in the first chamber should be distributed uniformly, otherwise production caking phenomenon occurred in a high degree that might cause difficulty of operation. The final recovery ratio of MgCl₂ reached 91.5% and the content of MgCl₂ was between 51%~53%, of which the products in this technology met the requirements with the content of MgO below 0.5% .

This production method was a typical combination technology with reutilization of two salt lake resources simultaneously. There were large amounts of dust carried by heating carrier gas in

emissions, so the technology should be improved to increase the production efficiency and the yield of dust and recycle energy taken away.

Dehydration by Ammonium Carnallite Complex Salt Method

High-purity MgCl_2 could be prepared by the method of utilizing analytical-grade NH_4Cl [25,26] or ammonia gas and bischofite as raw materials, and analytical-grade alumina as covering agent [27]. The pretreatment of raw materials was that bischofite should be maintained at 120°C for 2~20 hours to guarantee the number of crystal water below 4, namely $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ ($n=0.1$ to 4). In the reaction design, the alumina could suppress decomposition of NH_4Cl efficiently and isolate MgCl_2 from ambient atmosphere. The $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ and solid NH_4Cl were mixed evenly by milling with a suitable proportion into a corundum crucible to synthesize ammonium carnallite complex ($\text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot n\text{H}_2\text{O}$). Then the mixtures with an appropriate thickness of alumina 1.3 cm above as covering agent were put in muffle furnace. Over a period of time the reaction temperature was set in an optimizing range. Subsequently, the mixtures were kept at 700°C for 1 hour to ensure the excessive NH_4Cl removed thoroughly. Through exploration of multiple orthogonal experiments, the reaction rules could be concluded as follows: $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ ($n=0.1$ to 4) reacted with NH_4Cl to form $\text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot n\text{H}_2\text{O}$, which could facilitate dehydration process. Gradually, the crystal water was dehydrated, and the part NH_4Cl of $\text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot n\text{H}_2\text{O}$ began decomposition and volatilization.

Although this method could produce the high-purity product MgCl_2 and the minimum value of MgO could achieve below 0.02%, the technology route was restricted in a small amount of production and batch production. The heating energy was released without reasonable recycling use. Inefficiency was the most evident defect, which has well room for improvement.

Dehydration by Aniline Hydrochloride Complex Salt Method

There were two routes of dehydration of aniline hydrochloride complex salt method through the same intermediate of $\text{MgCl}_2 \cdot \text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl} \cdot 6\text{H}_2\text{O}$, and the main distinction was the experimental equipment between the two routes mentioned above. One set of experimental equipment was simulating fixed bed, the other one was fluidized bed. Large amounts of thermodynamics research data indicated that there was no hydrolysis reaction during the heating decomposition of $\text{MgCl}_2 \cdot \text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl} \cdot 6\text{H}_2\text{O}$ [18].

In one experimental route the whole dehydration process of bischofite was tested in simulating fixed bed [28]. This experiment proceeded in a good condition of easy control. Firstly, hydrochloric acid and aniline were mixed uniformly with molar ratio of 1:1 in the simulating fixed bed for a while to form $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}$. In the following, the bischofite of proper ratio was added into the homogeneous phase solution above, while cooling water and nitrogen of equipment were turned on respectively. The power of heating apparatus was switched on at the heating rate of $5\sim 10^\circ\text{C}/\text{min}$. The most of free water and crystal water were dehydrated when the temperature reached 300°C . Finally, reactants were heated continuously until it rised to required temperature (below 400°C). Products were analysed by specific instruments. In the optimal experimental conditions, the final content of MgCl_2 was more than 98.6%, and the content of MgO was less than 0.38% , and the content of $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}$ was less than 0.12%, the content of H_2O was less than 0.68%. The advantages of this method were that the decomposed aniline hydrochloride could be condensed for recycling utilization, and that reduced emission pollution. The shortages mainly included that the device is corroded badly by hydrochloric acid, and the production output was limited.

In the fluidized bed the experiment was divided into the following steps [29]: synthesis of complex salt, granulation, and thermal decomposition in fluidization. Bischofite and $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}$ were added into reactor with correct proportion and formed fusion solution of complex salt by mixer at $180^\circ\text{C}\sim 190^\circ\text{C}$. The complex salt particles were produced by uniform droplets spray technology. The fusion droplets were sprayed from vibration granulation device in an appropriate vibration frequency. The fusion droplet was dripped into cooling petroleum ether to form uniform particles of complex salt. Then these complex salt particles were transferred into the fluidized bed to carry out dehydration. The carrier gas of nitrogen was adjusted in a moderate flow rate because

nitrogen with large-flow rate would take away excessive heat and nitrogen with small-flow rate couldn't play a role effectively to take away water and $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl}$ dehydrated. The optimal conditions of thermal decomposition were explored as follows: the time of dehydration was 0.5h at 300°C with the nitrogen in a rate of $1.6\text{m}^3/\text{h}\sim 1.8\text{m}^3/\text{h}$, and the time of removing $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl}$ was 1h at 350°C with the nitrogen in a rate of $1.0\text{m}^3/\text{h}\sim 1.2\text{m}^3/\text{h}$. Finally, the content of $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl}$ was less than 0.12%, and the content of H_2O was less than 0.68%. Obviously, the operation time was shortened greatly compared with the first method above, but recycling utilization of exhaust was not taken into consideration.

To the two dehydration of complex salt with $\text{MgCl}_2\cdot\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl}\cdot 6\text{H}_2\text{O}$ as intermediate, the dehydration process was similar, which both produced high-purity MgCl_2 ultimately. However, the processes were disparate. It's necessary to combine the two methods for more efficient technology, more environmental, more energy-saving, more time-saving, more abundant production etc.

Dehydration by Butanol Complexation

The foundation of dehydration was that Bischofite could react with butanol ($\text{C}_4\text{H}_9\text{OH}$) to form complexation, which was involved substitution reactions [30,31], namely the crystal water of bischofite was replaced partially by $\text{C}_4\text{H}_9\text{OH}$ in the heating state. The characteristics were gripped to be applied to dehydration technology of bischofite [32]. To a molecule of $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$, 4 molecules of inner crystal water were replaced first, and the other remaining 2 molecules were replaced next. The substitution reactions couldn't proceed completely in the synchronisation, so mixing complex compounds ($\text{MgCl}_2\cdot x\text{H}_2\text{O}\cdot y\text{C}_4\text{H}_9\text{OH}$) existed in solution. In the dehydration process, two steps were implemented necessarily. One step was that butanol should be added into reactor continuously to maintain the stable mole proportion of MgCl_2 to $\text{C}_4\text{H}_9\text{OH}$, because surrounding temperature exceeded the boiling point of $\text{C}_4\text{H}_9\text{OH}$ and $\text{C}_4\text{H}_9\text{OH}$ was volatile easily in the condition. The other one was that ultrasonic was introduced in the period of dehydration, of which strong vibration was useful to destroy the space structure of complex. The rate of dehydration rised when prolonging the time of ultrasonic pretreatment. The water and $\text{C}_4\text{H}_9\text{OH}$ that were distilled from reactor were separated by the means of fractionation, and $\text{C}_4\text{H}_9\text{OH}$ was recycled. The former 4 crystal water were dehydrated easily, but the latter 2 crystal water couldn't be removed absolutely, especially the last one. Under fine operation, the dehydration ratio could reach 90.25%. The analysis results showed that the dehydration efficiency factors of continuous distillation process were as the followings: ultrasonic time, temperature, the mole proportion of MgCl_2 to $\text{C}_4\text{H}_9\text{OH}$.

Improvement of Technology in Theory

According to our experiment with Figure 2, the thermal decomposition of $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ was shown in detail. Maybe, with the thermodynamics properties of $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ a series of more reasonable technology could be explored and applied to practical production. All data were demonstrated that $\text{MgCl}_2\cdot 4\text{H}_2\text{O}$ and $\text{MgCl}_2\cdot 2\text{H}_2\text{O}$ were obtained easily in the stage under direct heating from bischofite [33,34], and the purity of $\text{MgCl}_2\cdot 4\text{H}_2\text{O}$ and $\text{MgCl}_2\cdot 2\text{H}_2\text{O}$ were very high. In theoretical technology, $\text{MgCl}_2\cdot 4\text{H}_2\text{O}$ or $\text{MgCl}_2\cdot 2\text{H}_2\text{O}$ as intermediate is produced first in the appropriate conditions, then $\text{MgCl}_2\cdot 4\text{H}_2\text{O}$ or $\text{MgCl}_2\cdot 2\text{H}_2\text{O}$ production was devoted into the second processing to combine with varied techniques of dehydration, for instance, dehydration by shielding gas, by complex salt methods, by butanol complexation. What's the worthy of learning in preliminary processing are that preparation technology is simple, low energy consumption, moderate reaction, short production period, less impurities, no pollution, little wastes etc.

Exploiting Prospects

Based on the characters of well stability and strong mechanical properties, magnesium materials involve wide application domains, super-performance alloys [35], coating [36], biomedical materials [37], lightweight alloy etc. These lightweight alloy materials are necessary

structural materials in multitudinous fields, such as national defense [38], aviation industry [39], vehicle [40], architecture [41], which could form a layer of stable density oxidation film to prevent materials from corrosion [42]. In China soluble magnesium salt resources are widely distributed in giant reserves, especially the high level of bischofite produced in Qinghai salt lakes, which have well prospects as environmental protection materials. The developments technology of soluble magnesium salt save energy and cause environment pollution more slightly, which observes the principle of energy conservation and emission reduction and accords with our national conditions. Therefore, that the technology of the diversified research of high-purity MgCl_2 is produced with bischofite as raw materials has huge rising space, which is attracting more and more attentions of enterprises. Then, all kinds of magnesium materials are produced through MgCl_2 . The country would support and enlarge fund investment in the fields. We can solve the serious challenges of environment pollution, and we will create considerable economics benefits. Magnesium materials are one of the most influential composites as bright prospective materials of the 21th century, which will lead the wave of exploring relative new materials.

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