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Preparation of $Mg_3(OH)_5Cl{\cdot}4H_2O$ Whisker with Brine

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In this study, took brine as raw materials, researched the influence factor of water bath method preparing basic magnesium chloride whisker, concentration of magnesium chloride solution, the molar ratio of magnesium chloride and ammonia, the effect of ammonia feeding speed of and water bath temperature on the reaction. Analyzed the feature of basic magnesium chloride whisker through scanning electron microscope and analyzed and discussed the whisker growth mechanism and put forward the optimum technological conditions of preparing basic magnesium chloride whisker.

Key Words: Brine, Magnesium chloride, Whisker.

INTRODUCTION

Brine is a by-product in sea salt industry, which contains a high concentration of valuable mineral, such as potassium, magnesium, bromine and sulphate, *etc*. The sea salt production in China has reached more than 22 million t/a, the corresponding by-product brine reached 18 million m^3, the large quantity of by-product not only pollutes the environment, but also wastes resources. This waste material can be transfer into whisker. Whisker has many excellent physical and chemical properties[1], such as high intensity, high modulus, high toughness, high insulation, resistant to abrasion, high temperature, acid, alkali and corrosion, good infrared reflection, easy to do surface treatment, easy to compound with polymer and non-toxic and so on, while there are rare report about research of basic magnesium chloride whisker.

The aim of this study is to purify magnesium ions in brine through the precipitation method, then get the magnesium chloride solution of higher content and prepare basic magnesium chloride whisker. Basic magnesium chloride whisker can dissolve fast in acid solution; has the strong scattering ability of light and good heat-resisting performance, it will decompose when heated in 405 ºC. So it is a kind of reinforcing and toughening materials[2-4] which can be applied to plastic, rubber, ceramic and many other domains, magnesium chloride whisker can be used as fire retardant[5,6], basic magnesium chloride whisker can be used as hot melt adhesive compound packing[7,8] when mixed with light calcium carbonate.

EXPERIMENTAL

Methods

Preparation of magnesium chloride solution by brine: Charged the refined brine into reactor, stirred, joined the precipitation agent, made the reaction liquid curing for 50 min after reacted exactly, conduct negative-pressure filtration to the lower sediment, used deionized water to wash filtering cake, in order to ensure the quality of product[9]. Stovinged the product which had been washed to constant weight. The obtained product was alkali type magnesium carbonate crystals. Measured certain concentration of ammonium chloride solution into tapered bottle, displayed in digital display auto tester, took certain quality of magnesium carbonate crystal, added into tapered bottle and stirred; placed for several hours after completely reacted then obtained the magnesium chloride solution of certain concentration.

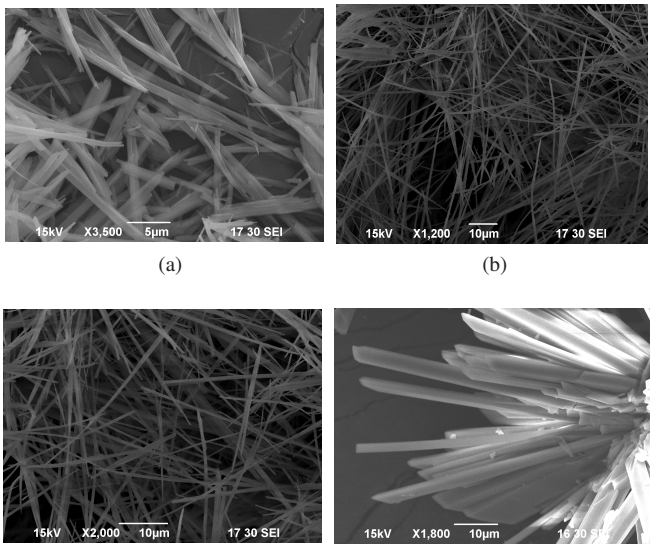
Preparation of basic magnesium chloride whisker[10]: Measured certain concentration of magnesium chloride solution into a beaker, played into water bath kettle, dropped the 25 % aqueous ammonia to the beaker at certain proportion, stirred for 1-2 h, the reaction temperature was 40 ºC. Matured and crystallized the saturated mother liquor at 30-70 ºC after reaction, the maturing time was 24-72 h. Washed the reacted products with distilled water and filtered with suction filter, then washed with absolute ethyl alcohol and dried at 55 ºC. The collected product was basic magnesium chloride whisker.

RESULTS AND DISCUSSION

We investigated the following four factors that affect the whisker formation *i.e.*, concentration of magnesium chloride solution, molar ratio of magnesium chloride and aqueous ammonia, feeding speed of aqueous ammonia and reacted temperature, determined the optimum technological conditions of basic magnesium chloride whisker preparation.

Effect of magnesium chloride concentration on whisker growth: The results are shown in Table-1.

The scanning electron microscope (SEM) images of part of the product were shown in Fig. 1(a-d), respectively on behalf of the obtained material crystal form when magnesium chloride concentration was 2, 3, 4 and 5 mol/L.



(a) (b)

(c) (d)

Fig. 1. Scanning electron microscope (SEM) images of different magnesium chloride concentration

According to above results, it was known that the magnesium chloride concentration had significant influence on the formation and shape of whisker. The variation curve of whisker biggest draw ratio and the concentration as shown in Fig. 2.

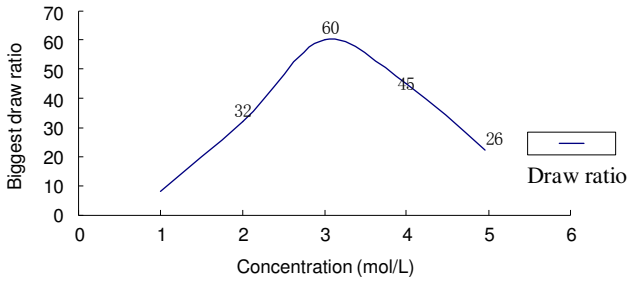


Fig. 2. Variation curve of whisker biggest draw ratio and the concentration

From Fig. 2, we could know that the draw ratio of basic magnesium chloride whisker changed with the magnesium chloride solution concentration and firstly increased then decreased. This is because with the relative saturated concentration of solution increased, maintain speed of crystal nucleus first fast and then slow and the rate of crystal shape formation was small first after large. When exceeded a specified concentration, the whisker draw ratio decreased for lacking of enough growth space. In low concentrations, for the system was in stable region, it couldn't conduct spontaneous crystallization and hard to get the products; while in high concentrations, the system was in not stable state, easy to quickly form nuclear, generated irregular crystal and difficult to get needle crystal. Predictably, the optimal concentration of magnesium chloride solution for preparing basic magnesium chloride whisker was 3 mol/L.

Influence of molar ratio of magnesium chloride and aqueous ammonia on growth of basic magnesium chloride whisker: The results are shown in Table-2.

The scanning electron microscope (SEM) images of the product were shown in Fig. 3(a-e), respectively on behalf of the obtained material crystal form when the molar ratio of NH_3 and $MgCl_2$ was 3, 4, 5, 6, 7.

According to Table-2, it was known that the mole ratio change of $MgCl_2$ and NH_3 had a great influence on whisker form, whisker biggest draw ratio, the variation curve of whisker biggest draw ratio and the molar ratio NH_3 and $MgCl_2$ as shown in Fig. 4.

As could be seen from Fig. 4, draw ratio of whisker changed with the mole ratio of $MgCl_2$ and NH_3 and first

TABLE-1
EFFECT OF MAGNESIUM CHLORIDE CONCENTRATION ON WHISKER GROWTH

No.	Magnesium chloride concentration (mol/L)	Molar ratio of magnesium chloride and aqueous ammonia	Feeding speed (mL/min)	Reacted temp. (ºC)	Crystal morphology
1	1	5	20	40	No product
2	2	5	20	40	Acicular, large grain size
3	3	5	20	40	Acicular, small grain size
4	4	5	20	40	Acicular, Particle size moderate
5	5	5	20	40	Acicular, mixed with uncertain form

TABLE-2
INFLUENCE OF MAGNESIUM MOLE RATIO ON WHISKER SYNTHESIS

No.	Magnesium chloride concentration (mol/L)	Molar ratio of magnesium chloride and aqueous ammonia	Feeding speed (mL/min)	Reacted temp. (ºC)	Crystal form
1	3	3	20	40	Acicular, mixed with impurities
2	3	4	20	40	Acicular, gathered, small granularity
3	3	5	20	40	Homogeneous acicular, small granularity
4	3	6	20	40	Homogeneous acicular, middle granularity
5	3	7	20	40	Acicular, scattered, small granularity

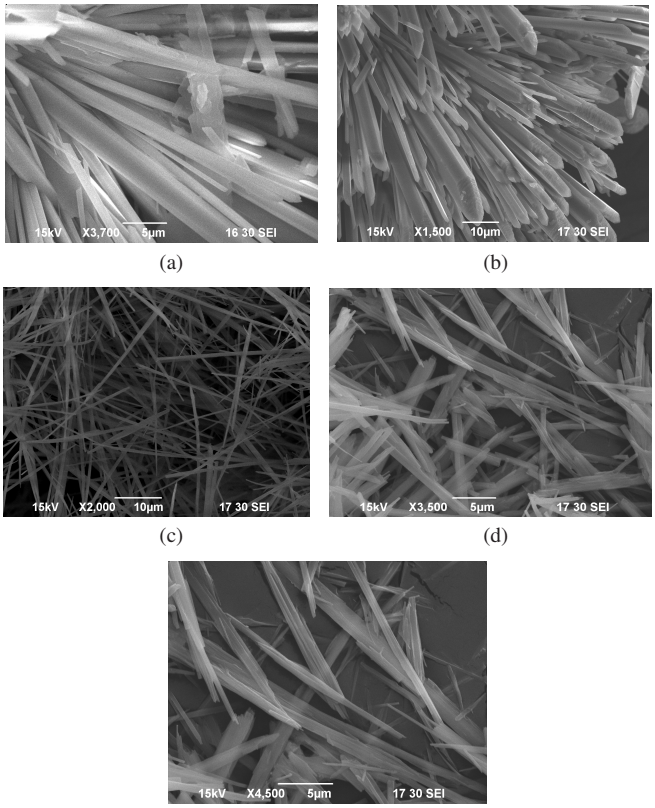


Fig. 3. Scanning electron microscope (SEM) images of different molar ratio of magnesium and ammonia

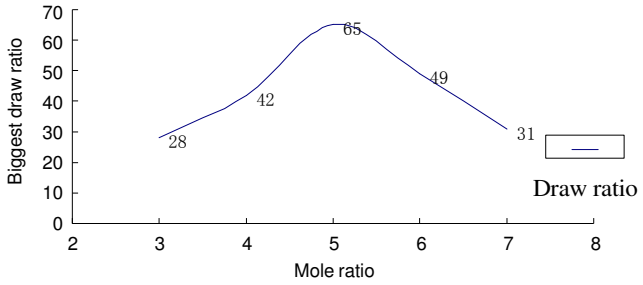


Fig. 4. Variation curve of whisker biggest draw ratio and the molar ratio of NH_3 and $MgCl_2$

increased then decreased, this is due to the addition of ammonia directly influenced the supersaturation of solution, caused change of crystals formed into nuclear and growth rate, generated crystals of different shapes and purity. Therefore, in magnesium chloride solution of appropriate concentration controlled the mole ratio of joined $MgCl_2$ and NH_3 in 5:1. Under this condition, the nuclear formation and growth of crystals were rapid, the obtained product presented needle crystal, big particle size and blance, easy to disperse and of high purity.

Influence of ammonia feeding speed on growth of basic magnesium chloride whisker: The results are shown in Table-3.

The scanning electron microscope (SEM) images of the product were shown in Fig. 5(a-d), respectively on behalf of the obtained material crystal form when the feeding speed was 10, 20, 30 and 40 mL/min.

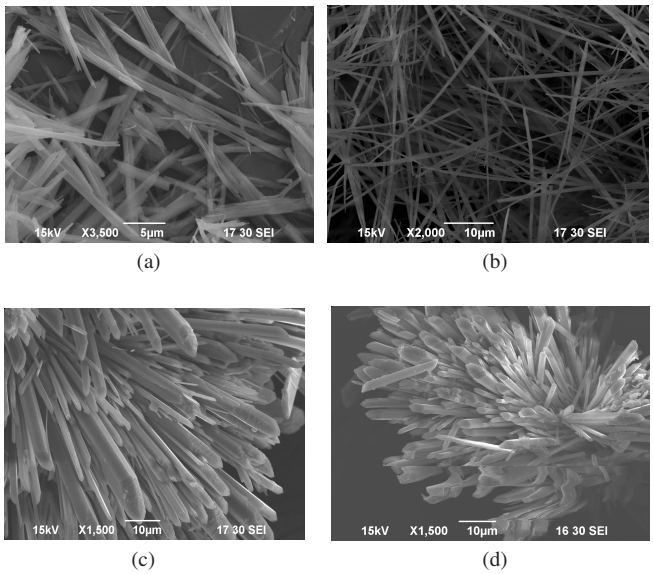


Fig. 5. Scanning electron microscope (SEM) images of different feeding speed

It can be seen from Table-3 that feeding speed of ammonia had major effect on crystals form, the variation curve of whisker biggest draw ratio and ammonia feeding speed as shown in Fig. 6.

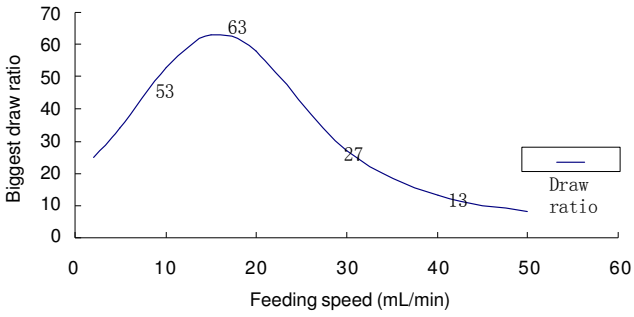


Fig. 6. Whisker draw ratio under different feeding speed of ammonia

As can be seen from Fig. 6, the whisker draw ratio also changed with the feeding speed of ammonia and first increased then decreased. When the feeding speed of ammonia was too low, the joined time of ammonia became longer, then it reacted with magnesium chloride fully. As a result, the obtained

TABLE-3
INFLUENCE OF AMMONIA FEEDING SPEED ON WHISKER SYNTHESIS

No.	Concentration of magnesium chloride (mol/L)	Mole ratio of $MgCl_2$ and NH_3	Feeding speed (mL/min)	Reacted temperature (ºC)	Crystal form
1	3	5	10	40	Acicular, middle granularity
2	3	5	20	40	Homogeneous acicular, middle granularity
3	3	5	30	40	Acicular, big granularity, gathered
4	3	5	40	40	Uncertain form

whisker was short and the production rate was low; but if the feeding speed of ammonia was too high, ammonia could not be scattered in solution system in time, easy to cause partial ammonia excessive in solution, then nonuniform nuclear hap-pened quickly, formed the amorphous crystallization. Therefore, the optimal ammonia feeding speed was 20 mL/min.

Conclusion

Through analysis of samples SEM, compared the biggest draw ratio of basic magnesium chloride whisker under various conditions and considered the utilization rate of raw materials, energy consumption and production problems at the same time, then determined the optimum technological conditions of preparing basic magnesium chloride whisker in brine-ammonia method were: concentration of magnesium chloride solution was 3 mol/L, mole ratio of magnesium chloride and ammonia was 5:1, feeding speed of ammonia was 20 mL/min, reacted temperature was 40 ºC.

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