One-step preparing magnesium hydroxide particles from mother liquor of salt production

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Abstract. In this study, MH particles were prepared from mother liquor of salt production in one-step through employing ammonia gas as precipitant and stearic acid as dispersant respectively. Since adopting microporous plate to bubble ammonia gas, the percent conversion of magnesium was boosted obviously. The influence of operating condition of reacting temperature, stirring rate, ammonia flowrate and pore size of plate to magnesium percent conversion were investigated, the maximum is 88.1 % at optimum condition according to experimental results. The MH particle preparing from mother liquor in optimum condition was characterized by XRD, the result indicated the volume of brucite was reach to 99.7% within the composition of the product. In addition, the size distribution and crystal morphology was also detected, the median particle diameter d50 is 883 nm and possessing good dispersibility. From the thermogravimetric analysis of MH particles, the thermostability of product is suitable as flame-retardant composite materials.

1. Introduction
Magnesium hydroxide (MH) particles is wildly used in flame-retardant composite materials due to its ability to endothermically decompose with water release at high temperatures without production of toxic or corrosive substances\textsuperscript{[1, 2]}. Normally, MH particles is produced by hydrothermal synthesis from magnesium chloride with alkaline solution as precipitant\textsuperscript{[3, 4]}. On account of magnesium metal ion ranks only second to sodium among cations in mother liquor of salt production and occupies approximately 43 % of the total amount of cations\textsuperscript{[5]}, hence there are a number of processes through using limewater or ammonia hydroxide for precipitation of MH particles from mother liquor of salt production\textsuperscript{[6-8]}.

However, the agglomeration and uniformity of MH particles is difficult to control in conventional precipitation process\textsuperscript{[9]}. Adjusting zeta-potential of the particles, adding dispersant in the reaction system and mixing water-soluble solvent in mother liquor was generally employed to solve above problem\textsuperscript{[10]}. In addition, employing liquid precipitant has greatly increased the amount of magnesium hydroxide slurry and aggravated the disposing burden of solid-liquid separation process, washing and a filtration step to concentrate the slurry\textsuperscript{[11]}. Yi used magnesium chloride and ammonia water to produce MH particles with employing reverse-titration precipitation method and the size of product has an excellent conformity\textsuperscript{[12]}. Hu et al. selected sodium dodecyl benzene sulfonate (SDBS) and octaphenyl polyoxyethyliene (OP-10) as composite dispersant to produce MH particles in one-step
and obtained the product with commendable dispersibility [13]. Zhai et al. dissolved magnesium chloride in ethanol-water mixed liquor with sodium hydroxide as precipitant to MH particles with the purpose of enhancing the separability of MH precipitate [14]. He et al. also proved the additional ethanol not only enhanced the dispersibility, but also improved the filtrability of the MH particles [15]. Tai et al. utilized spinning disk reactor strengthened the mass transfer to produce MH particles [16].

In this research, a novel method has been proposed regarding of preparing magnesium from mother liquor of salt production in one-step. Microporous plate for bubbling ammonia gas was assembled in reaction tank and employed to precipitation process, the gaseous ammonia and stearic acid was used as precipitant and dispersant respectively. The magnesium percent conversion, uniformity of particle size, shape, agglomeration and thermostability of product are well under controlled due to bubbling and dispersant addition. With this method, the conventional magnesium preparing steps from mother liquor of salt production which including chemical precipitation, hydrothermal treatment and surface modification were developed and simplified to one-step.

2. Experimental

2.1. Materials preparation
The mother liquor of salt production was collected from the saltwork which located in Laizhou bay and filtered with 0.45 μm microfiltration membrane before conducting experiment. The concentration of magnesium ion in mother liquor which has been measured is 43.5 g·L⁻¹ approximately. The Ammonia gas as precipitant was purchased from Hebei Yongchang Chemical Engineering Co. Ltd., Hebei. Stearic acid as dispersant was purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd., Shanghai. The reaction vessel is a self-made 4-necks stainless-steel tank which is used for preparing magnesium from mother liquor. The microporous plate is also self-made with drilling various pore diameters and being assembled in the reaction vessel. The tail-gas of ammonia was absorbed by diluted hydrochloric acid for security.

2.2. Experimental method
The flow chart of experimental apparatus was shown in figure 1. 100 mL mother liquor and 5 g stearic acid were added in 4-necks stainless-steel tank which was placed in a thermostatic water bath whose temperature was controlled at 40, 50, 60, 70 and 80 ºC respectively, then ammonia gas was inlet in mother liquor via microporous plate which has been assembled in the tank and replaced with pore diameters of 0.5, 1.0, 1.5, 2.0, and 2.5 mm. The flowrate of ammonia gas was adjusted to 600, 800, 1000, 1200 and 1400 mL·min⁻¹ respectively which was measured by flowmeter. During the whole process, the reaction solution was constantly being stirred with the speed of 100, 200, 300, 400 and 500 r·min⁻¹. At last, the MH particles were separated and washed by deionized water, dried under vacuum at 45 ºC. The magnesium concentration of percolate was measured under different molar ratio between ammonia and magnesium (NH₃/Mg²⁺ molar ratio).

2.3. Calculation of magnesium percent conversion
The percent conversion of magnesium under different molar ratio between ammonia and magnesium with the change of ammonia flow, reacting temperature, stirring rate, pore size of the microporous plate was measured. The percent conversion of magnesium [η(%) (mass)] and NH₃/Mg²⁺ molar ratio (α) is defined by equation (1) and (2) respectively as follows.

\[
\eta = 1 - \frac{c_p}{c_0} 
\]

where \(c_0\) (mg·L⁻¹) represents the magnesium concentration of mother liquor, however \(c_p\) (mg·L⁻¹) is the magnesium concentration of percolate after solid-liquid separation.
\[ \alpha = \frac{n_{NH_3}}{n_{Mg^{2+}}} \]  

where \( n_{NH_3} \) represents the molar mass of ammonia gas which was inlet in mother liquor, and \( n_{Mg^{2+}} \) is the molar mass of mother liquor which was added in tank.

### 2.4. Characterization

The laser particle analyzer (Mastersizer 2000, Malvern, UK) was used to analyze the volume percent and cumulative frequency distribution of the particles. The X-ray diffractometer (XRD, D/max-rB, Rigaku, Japan) equipped with monochromator giving Cu-\(\kappa\alpha \)=1.5406 Å radiation was used to quantify the phase composition of MH particles. The crystal morphology of MH particles also has been observed by scanning electron microscope (SEM, S4800, Hitachi, Japan). Moreover, the thermostability of MH particles prepared from mother liquor was tested by thermogravimetric analyzer (TGA, Q5000IR, TA Instruments, US).

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**Figure 1.** Flow chart of experimental apparatus. 1. Ammonia bottle, 2. Buffer flask, 3. Gas flowmeter, 4. 4-necks stainless-steel tank, 5. Microporous plate, 6. Mechanical stirrer, 7. Tail-gas absorption bottle, 8. Thermometer, 9. Thermostatic water bath.

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### 3. Results and discussion

#### 3.1. pH value change with \( NH_3/Mg^{2+} \) molar ratio

The percent conversion of magnesium is closed related with the concentration of \( OH^- \) ion, the pH value of mother liquor change with \( NH_3/Mg^{2+} \) molar ratio was measured and shown in figure 2. It indicates that the pH value was increasing with \( NH_3/Mg^{2+} \) molar ratio, the mother liquor changed from neutral to alkalinity. As well as the pH value was increasing quickly at beginning of insetting gas, then it was turn to change slowly when the \( NH_3/Mg^{2+} \) molar ratio was greater than 1.8. The maximum of pH value is 9.78 (<9.8) when \( NH_3/Mg^{2+} \) molar ratio is 2.6.

#### 3.2. Solubility of ammonia gas dissolved in water

As above, the concentration of \( OH^- \) ion is depended on the \( NH_3/Mg^{2+} \) molar ratio. However, the temperature of reaction system is also important, it influenced the solubility of ammonia gas due to the dissolving is an exothermic process from chemical equation (3).

\[ NH_3 + H_2O \rightarrow NH_4OH \]  

\( \Delta H = -34.5kJ \cdot mol^{-1} \)

Theoretically, the solubility of ammonia can be calculated by the following formula (4).

\[ S = Aexp \left( \frac{-\Delta H_A}{RT} \right) \]  

where \( A(\text{mol} \cdot \text{kg}^{-1} \cdot \text{Pa}^{-1}) \) is pre-exponential factor, \( \Delta H_A(\text{J} \cdot \text{mol}^{-1}) \) represents the enthalpy of solution, \( R(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \) is the universal gas constant.

The solubility of ammonia dissolved in water can be calculated by the following formula (5) which was corrected from formula (4).
\[ S = 0.574 \exp \left[ \frac{1452}{T} - 28.14 \right] \]  

(5)

where \( S[\% \text{mass}] \) is the solubility of ammonia at usual atmospheric pressure, \( T(K) \) represents the environment temperature.

At usual atmospheric pressure, the solubility of ammonia dissolved in water was shown in figure 3. As shown in this figure, the solubility of ammonia is influenced by the temperature to a great extent. With temperature increasing, the solubility of ammonia is decreasing quickly. When the temperature is higher than 80, the solubility of ammonia is only 7.0 \(<10.0 \%) \) in mass.

3.3. Percent conversion of magnesium change with operating conditions

3.3.1. Reacting temperature

The effect of percent conversion of magnesium change with \( \text{NH}_3/\text{Mg}^{2+} \) molar ratio at temperature of 40, 50, 60, 70 and 80 °C was shown in figure 4. From this figure, we can see that the optimum value of percent conversion of magnesium is 88.1 \((<90 \%) \) at temperature of 60 °C. In addition, the percent conversion of magnesium is approached in higher \( \text{NH}_3/\text{Mg}^{2+} \) molar ratio at temperature of 40, 50 and 60 °C, it was because that the solubility of ammonia dissolved in water was influenced by temperature seriously. With the reacting temperature increasing, the solubility of ammonia is decreasing and resulting in the shortage of \( \text{OH}^- \) ion in the reaction system, hence the percent conversion of magnesium is lower at temperature of 70 and 80 °C. Furthermore, the viscosity of water is decreasing with temperature increasing, and lower viscosity is beneficial to the formation and growth crystal nucleus, therefore the percent conversion of magnesium at temperature of 40 (85.3 \%) and 50 °C (87.0 \%) is slightly lower than temperature of 60 °C (88.1 \%).

3.3.2. Stirring rate

The effect of percent conversion of magnesium change with \( \text{NH}_3/\text{Mg}^{2+} \) molar ratio at stirring rate of 100, 200, 300, 400 and 500 r·min⁻¹ was shown in figure 5. As shown in this figure, the optimum value of percent conversion of magnesium appeared at stirring rate of 500 r·min⁻¹, and it was increasing with the stirring rate accelerating. In addition, the percent conversion of magnesium influenced by the stirring rate was even more obviously along with the increasing of \( \text{NH}_3/\text{Mg}^{2+} \) molar ratio. The percent conversion of magnesium is only 60.4 \% at stirring rate of 100 r·min⁻¹ when the \( \text{NH}_3/\text{Mg}^{2+} \) molar ratio is 2.6, however it was reach up to 88.1 \% at stirring rate of 500 r·min⁻¹. This was probably because the rapidly stirring could promote the dissolving of ammonia gas. In the condition of higher \( \text{NH}_3/\text{Mg}^{2+} \) molar ratio, the ammonia gas more possibly escaped from the reaction system due to there is not enough time to dissolve.

\[ \text{Figure 2. The pH value of mother liquor change with NH}_3/\text{Mg}^{2+} \text{ molar ratio.} \]

\[ \text{Figure 3. Solubility of ammonia dissolved in water at usual atmospheric pressure.} \]
3.3.3. Ammonia flowrate
The flowrate of ammonia gas as a significant operating parameter was also investigated in this experiment. The effect of percent conversion of magnesium change with NH$_3$/Mg$^{2+}$ molar ratio at ammonia flowrate of 600, 800, 1000, 1200 and 1400 mL·min$^{-1}$ was shown in figure 6. In this figure, the percent conversion of magnesium is superior with the ammonia flowrate of 600 mL·min$^{-1}$ towards to all levels of NH$_3$/Mg$^{2+}$ molar ratio. The percent conversion of magnesium is decreasing gradually along with ammonia flowrate increasing. At NH$_3$/Mg$^{2+}$ molar ratio of 2.4, the percent conversion of magnesium is 88.1 % and 76.4 % respectively when the ammonia flowrate is 600 and 1400 mL·min$^{-1}$, that demonstrated the percent conversion of magnesium was influenced by ammonia flowrate evidently. The course of ammonia dissolved in water is a dynamically equilibrium process, hence the faster flowrate will shorten the retention time due to the certain solubility in a constant reacting temperature, it will lead the ammonia gas escaped from the reaction system in the same way.

3.3.4. Pore size of plate
In this experiment, the microporous plate was integrated in the reaction system, the percent conversion of magnesium change with NH$_3$/Mg$^{2+}$ molar ratio at plate pore size of 0.5, 1.0, 1.5, 2.0 and 2.5 mm was displayed in figure 7. As shown in this figure, the percent conversion of magnesium greatly influenced by pore size of plate. At NH$_3$/Mg$^{2+}$ molar ratio of 2.4, the percent conversion of magnesium is 88.1 % when the pore size of plate is 0.5 mm, however the percent conversion of magnesium is only 49.7 %. In addition, the NH$_3$/Mg$^{2+}$ molar ratio which effect on percent conversion of magnesium is more distinct with using larger pore size than smaller pore size. This result was because that the smaller pore size will cut the bubbles more subtly, thus ammonia bubbles were capable of distributing more evenly and dissolved in water quickly. The point of higher or lower ammonia concentration is non-existent in this reaction system, therefore the process of ammonia dissolution is rapidly and evenly.

Figure 4. Percent conversion of magnesium in different reacting temperature condition.

Figure 5. Percent conversion of magnesium with different stirring rate.

Figure 6. Percent conversion of magnesium with different ammonia flowrate.

Figure 7. Percent conversion of magnesium with different pore size of plate.
3.4. Characterization of MH particles

3.4.1. Size distribution

The volume percent and cumulative frequency distribution of MH particles which prepared at NH₃/Mg²⁺ molar ratio of 2.0 (reacting temperature 60 °C, stirring rate 500 r·min⁻¹, ammonia flowrate 600 mL·min⁻¹ and pore size of plate 0.5 mm) was analyzed, the size distribution was shown as figure 8. The diameter of d₁₀, d₅₀ and d₉₀ is 430, 883 and 1749 nm respectively, from that we can calculated the unevenness of this sample is 1.49. On the whole, the distribution of particle size is from 224 to 3557 nm, and the maximum of volume percent is among at 893 and 1002 nm, approximately 8.2% of total. From this result, we can see that the particle size and dispersibility of MH particle is excellently used as flame-retardant.

3.4.2. XRD characterizing

The MH particles was characterized by XRD and the diffraction pattern was shown in figure 9. By comparing with standard pattern, the volume of brucite is reach to 99.7 %. This result demonstrated the type of the product is high-purity magnesium hydroxide. In addition, the crystal growing at crystal face 001 whose polarity is weak is more obviously than crystal face 101 whose polarity is strong. That indicates the polarity of crystal surface is relatively weak, hence the attractive force of the crystal particle to each other is lower, and the structure of particle is stabilized with better dispersibility.

![Figure 8](image8.png)  
**Figure 8.** Volume percent and cumulative frequency distribution of MH particles.

![Figure 9](image9.png)  
**Figure 9.** Diffraction pattern of MH particles.

3.4.3. Crystal morphology

The crystal morphology of MH particles also has been observed by SEM and the images were shown as figure 10. From figure 10(a), we can see that the morphology of MH crystal displayed irregularly lamellar and the size of particles is also evenly, and this result is consistent with the analysis of size distribution in section 2.4.1. At high magnification, figure 10 (b) showed that the crystal particles were well independent with each other and the MH particles were dispersing excellently. It indicated that using microporous plate to bubble ammonia gas continually, the concentration of OH⁻ ion will not appears a larger fluctuation, hence the distributional difference of OH⁻ ion concentration all round crystal nucleus is smaller, that is to say there is no high energy growing points of crystal nucleus and the degree of crystal anisotropy is relatively weak.
Figure 10. SEM images of MH particles.

4. Conclusion
The present work shows that the maximum of percent conversion of magnesium is 88.1 % at operating condition of reacting temperature 60 °C, stirring rate 500 r·min⁻¹, ammonia flowrate 600 mL·min⁻¹ and pore size of plate 0.5 mm. The size distribution and crystal morphology of MH particle preparing from mother liquor in optimum condition was detected, and the results showed the d50 diameter of particles is 883 nm and possessing good dispersibility. The XRD diffraction pattern indicated the volume of brucite is reach to 99.7 % within the composition of the product. In addition, from the thermogravimetric analysis of MH particles, the thermostability of product is suitable as flame-retardant composite materials.

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