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Preparation of Magnesium Hydroxide from Ammonium Chloride by Circulation Method

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In this paper, the technological conditions for preparation of magnesium hydroxide from ammonium chloride by circulation method are presented. The ammonia gas was prepared *via* treating carbide residue with ammonium chloride and subsequently passed into the magnesium chloride solution to form the magnesium hydroxide and ammonium chloride. The ammonium chloride was recycled consequently with precipitation separation of the magnesium hydroxide. Key facts on the productivity of magnesium hydroxide were investigated. The best condition is as follows: the molar ratio of ammonium chloride to magnesium chloride is 4.5, the magnesium is 1.5 mol/L, the reaction time is 1 h, the reaction temperature is 25 ºC and the aging time is 2 h. The productivity of magnesium hydroxide can obtain 89.10 % with a purity of above 99.12 % and the cycling rate of ammonium chloride is 69.47 % on this condition. The XRD and SEM were used to characterize the powder products. The results indicate the sheet-shaped magnesium hydroxides with 1 μm diameter were obtained.

Key Words: Carbide residue, Lake magnesium chloride, Magnesium hydroxide, Calcium chloride.

INTRODUCTION

Magnesium hydroxide has been widely used in fuel gas desulfurization process, waste water treatment process and food industry as an important inorganic material[1,2]. It is also a necessary starting material of magnesium chloride as well as many other industrial magnesium compounds. Compare with $Al(OH)_3$, $Mg(OH)_2$ has the merit of higher decomposition temperature, better thermostability and better flame retardancy. Besides, the small size of $Mg(OH)_2$ favours its application as a new type of green environmental-friendly flame retardants in the polymer industry around the world recently.

Carbide residue is the main production waste of acetylene, which prepared through calcium carbide method and is mostly composed of calcium hydroxide, as nearly above 85 wt %. It has been pointed out that 1 ton calcium carbide will yield 1.2-1.5 tons of carbide residue[3,4]. Generally the large amount of carbide residue has a rather poor reputation as its soil exhausting and low recycling ratio. A little carbide residue has been used in construction materials. However no one reports its application in $Mg(OH)_2$ production.

As is well known, the lake/sea magnesium resources in China are abundant[5]. But the magnesium salts have always been treated as the by-product of other salts. It is urgent to find a new way for large-scale application of magnesium resources for its low utilization ratio. One solution is producing $Mg(OH)_2$ to meet the increasing requirements as the clean green flame retardants, which can prevent it from being exported as the raw material. Consequently, we propose to produce $Mg(OH)_2$ *via* carbide residue reacts with $MgCl_2$ of the lake. On the one hand, this technique can diminish the excess of these two substances. On the other hand, such method is feasible and can produce satisfactory social benefits, economic benefits and an obvious environmental protection benefits.

EXPERIMENTAL

Experiment principle: This study shows the preparation of $Mg(OH)_2$ from ammonium chloride by circulation method. The ammonia gas was generated *via* carbide residue reaction with NH_4Cl and subsequently it was passed into the $MgCl_2$ solution and formed the $Mg(OH)_2$ and NH_4Cl. The NH_4Cl can be recycled with precipitation separation of the $Mg(OH)_2$. Moreover, the filtrate has the applicability in preparation of technical grade $CaCl_2$.

$$Ca(OH)_2 + 2NH_4Cl \xrightarrow{\Delta} CaCl_2 + 2NH_3\uparrow + 2H_2O$$

$$MgCl_2 + 2NH_3 + 2H_2O \longrightarrow Mg(OH)_2\downarrow + 2NH_4Cl$$

Carbide residue is the industry waste by Xinjiang Tianye Group which manufactures the acetylene gas. The raw material was preheated at 100 ºC for 2 h. This procedure can remove the H_2S gas, H_3P gas and residual acetylene gas from the raw material, keeping the purity of the NH_3 gas. $MgCl_2$ comes from the byproduct of potash produced by Golmud salina in

Qinghai. The raw material was dissolved and recrystallized for 2-3 times.

Experiment details: The excessive carbide residue was reactive with NH_4Cl at 85-95 ºC and the generated NH_3 gas was passed into $MgCl_2$ solution with stirring. The white deposited material was $Mg(OH)_2$. After centrifuging and washing the Cl^- ion was eliminated (confirmed by $AgNO_3$ solution). Then the $Mg(OH)_2$ is dried at 90 ºC and grounded. The key facts such as the molar ratio of NH_4Cl to $MgCl_2$, the solution concentration of $MgCl_2$, the reaction time, the reaction temperature and the aging time on the productivity of $Mg(OH)_2$ were investigated.

RESULTS AND DISCUSSION

Molar ratio of NH_4Cl to $MgCl_2$: In this section, the carbide residue is excessive, the $MgCl_2$ is 2.0 mol L^{-1}, the reaction time is 1 h, the reaction temperature is room temperature and the aging time is 2.5 h. The $Mg(OH)_2$ is prepared *via* different molar ratio of $NHCl_4$ to $MgCl_2$. Fig. 1 shows the productivity of $Mg(OH)_2$ under these conditions. It is found the productivity of $Mg(OH)_2$ increased with increasing the molar ratio of NH_4Cl to $MgCl_2$. Because the NH_3 gas will more produced and prompt the reaction to the positive orientation. However the productivity of $Mg(OH)_2$ does not change much when the molar ratio of $NHCl_4$ to $MgCl_2$ is above 4.5. This is because most of the NH_3 gas cannot take the next reaction and form the NH_3 -NH_4Cl buffer system in the solution at higher NH_4Cl to $MgCl_2$ ratio. Besides, the NH_3 -NH_4Cl buffer is favour of dissolving for $Mg(OH)_2$. When the dissolution reaches to balance, the productivity of $Mg(OH)_2$ keeps unchanged. So the molar ration of NH_4Cl to $MgCl_2$ is chosen of 4.5.

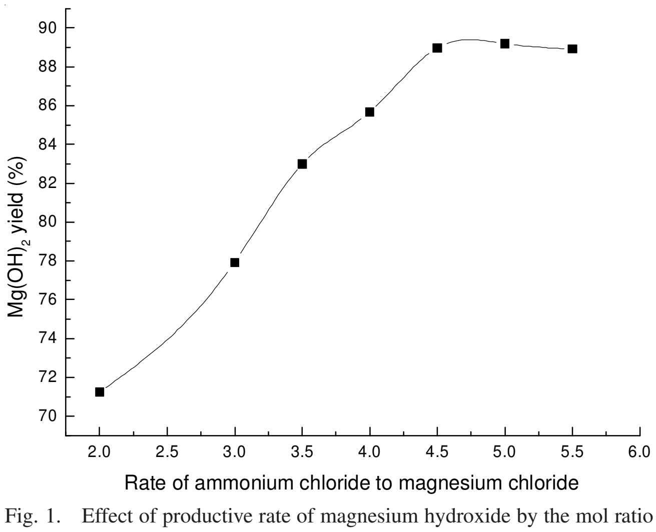

Fig. 1. Effect of productive rate of magnesium hydroxide by the mol ratio of ammonium chloride and magnesium chloride

Concentration of $MgCl_2$ solution: In this case, the carbide residue is excessive, the molar ration of NH_4Cl to $MgCl_2$ is chosen of 4.5, the reaction time is 1 h, the reaction temperature is room temperature and the aging time is 2.5 h. The $Mg(OH)_2$ is prepared by different concentration of $MgCl_2$ solution reaction with NH_3 gas. Fig. 2 shows the productivity of $Mg(OH)_2$ under these conditions. It is confirmed that the productivity of $Mg(OH)_2$ is increased with increasing the concentration of $MgCl_2$ solution, but the phenomena are not obvious. The minimum productivity of $Mg(OH)_2$ is higher than 74 % and still has little change. Because the NH_3 gas will more produced and prompt the reaction to the positive orientation. However the productivity of $Mg(OH)_2$ does not change much when the molar ratio of NH_4Cl to $MgCl_2$ is above 4.5. This is because most of the NH_3 gas cannot take the next reaction and form the NH_3 -$NHCl_4$ buffer system in the solution at higher NH_4Cl to $MgCl_2$ ratio. Besides, the NH_3 -NH_4Cl buffer is favour of dissolving for $Mg(OH)_2$. When the dissolution reaches to balance, the productivity of $Mg(OH)_2$ keeps unchanged at a concentration of 1.5 mol L^{-1} of $MgCl_2$ solution. Then the concentration of $MgCl_2$ solution is chosen as 1.5 mol L^{-1} in the next step.

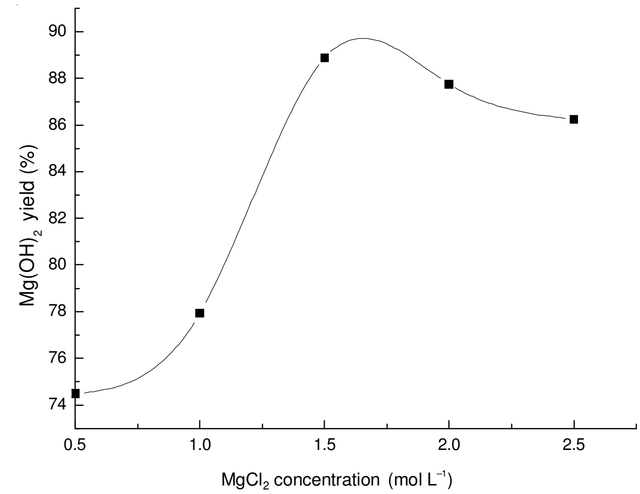

Fig. 2. Effect of productive rate of magnesium hydroxide by the concentration of magnesium chloride

Reaction time: In this experiment, the carbide residue is excessive, the molar ration of NH_4Cl to $MgCl_2$ is chosen of 4.5, the $MgCl_2$ is 1.5 mol L^{-1}, the reaction temperature is room temperature and the aging time is 2.5 h. The productivity of $Mg(OH)_2$ is evaluated by different reaction time. Fig. 3 shows that the reaction is more adequate and the productivity of $Mg(OH)_2$ is increased by elongation the reaction time. The maximum of $Mg(OH)_2$ is produced at the reaction time of 1 h.

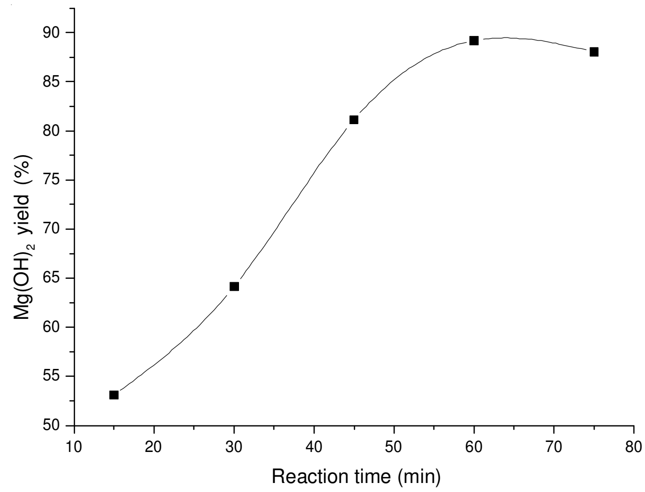

Fig. 3. Effect of productive rate of magnesium hydroxide by the reaction time

Reaction temperature: In this study, the carbide residue is excessive, the $MgCl_2$ is 1.5 mol L^{-1}, the reaction time is 1 h, the molar ration of NH_4Cl to $MgCl_2$ is chosen of 4.5 and the aging time is 2.5 h. The $Mg(OH)_2$ is prepared at different reaction temperature. Fig 4 presents the productivity of $Mg(OH)_2$ is favoured by raise the reaction temperature. However, too high temperature is not expected. For the NH_3 gas inclines to be separated out of the reaction system to stop the production of $Mg(OH)_2$. So the optimal reaction temperature is room temperature.

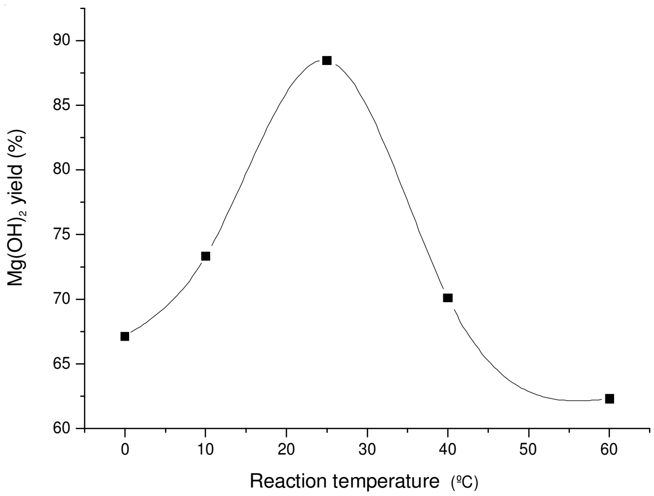

Fig. 4. Effect of productive rate of magnesium hydroxide by the reaction temperature

Aging time: The effect of aging time on the productivity is estimated at a excessive carbide residue, a molar ratio of NH_4Cl to $MgCl_2$ of 4.5, 1.5 mol L^{-1} of $MgCl_2$ solution and 1 h of reaction time. As Fig. 5 shows, an increased aging time is effective for the $Mg(OH)_2$ generation within 2 h and then it cannot have future effect. Then the aging time is set of 2 h.

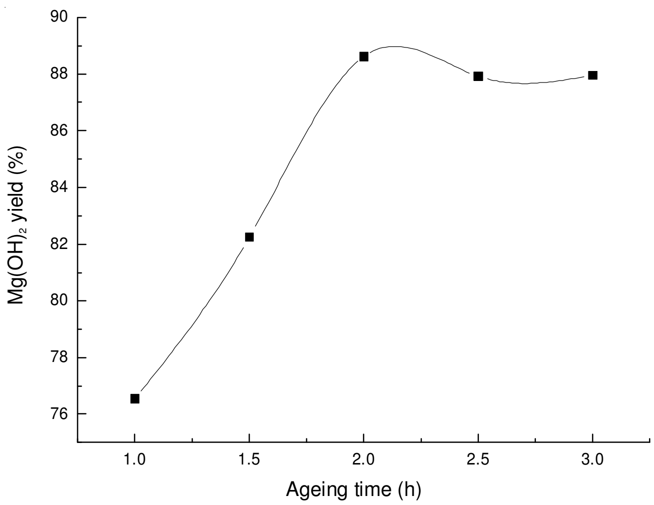

Fig. 5. Effect of productive rate of magnesium hydroxide by the aging time

In conclusion, the optimal technological conditions for preparation of magnesium hydroxide from ammonium chloride by circulation method are present, following a molar ration of NH_4Cl to $MgCl_2$ of 4.5, the $MgCl_2$ of 1.5 mol L^{-1}, the reaction time of 1 h and the aging time of 2 h. The $Mg(OH)_2$ is prepared at different reaction temperature. A replication experiment result is showed in Table-1.

TABLE-1
A REPLICATION EXPERIMENT RESULT

Experiment No.	Productivity of $Mg(OH)_2$ (%)	Purity of $Mg(OH)_2$ (%)	CaO (%)	Fe (%)	Insoluble matter
Exp.1	89.42	99.14	0.02	Not detected	No
Exp.2	88.36	98.91	0.04	Not detected	No
Exp.3	88.98	99.43	0.05	Not detected	No
Exp.4	89.62	99.01	0.04	Not detected	No
Average	89.10	99.12	0.04	-	-
Standard	-	97.50	0.10	0.005	0.10

Cycling of NH_4Cl: The circulation capability of NH_4Cl is examined. The filtrate of the reaction system and Mg-removal filtrate are heated to get the free ammonia and subsequently passed into water to produce the aqueous ammonia. The NH_4^+ content of the two kind of solutions is determined by formal titration. The ratio of NH_4^+ content to the added NH_4Cl is named the circulation rate. Table-2 shows a series of experiment results. The reaction is taken at the optimal condition with a NH_4Cl of 0.5 mol and 50 mL $MgCl_2$ solution (2 mol/L) and the NH_3 is homemade. The results show that a cycle use of NH_4Cl is achieved at a circulation rate of 69.47 %. It is not amazing to found a higher circulation rate of NH_4Cl, if the reaction has taken place at a closed system.

TABLE-2
CIRCULATION CAPABILITY OF NH_4Cl

	NH_4Cl from Mg-removal filtrate (g)	NH_4Cl from reaction filtrate (g)	Total recycled NH_4Cl (g)	Cycling rate of NH_4Cl (%)
Exp. 1	4.74	14.53	19.27	72.04
Exp.2	4.56	13.28	17.84	66.69
Exp.3	4.59	13.89	18.48	69.08
Exp.4	4.72	14.02	18.74	70.06
Average	4.65	13.93	18.58	69.47

Purity of $Mg(OH)_2$: The purity of $Mg(OH)_2$ is determined by EDTA complexometric titration method basing on National Standard HG/T3607-2007[6]. $Mg(OH)_2$ is made of solution and the Ca^{2+} and Mg^{2+} are tested by EDTA. The $Mg(OH)_2$ samples of experiment 1-experiment 4 are taken to get the purities. As Table-1 shows, the purity of $Mg(OH)_2$ is 99.12 % and reaches to the National Standard HG/T3607-2007.

XRD and SEM results: The XRD diagram in Fig. 6 indicated the produced $Mg(OH)_2$ has all of the diffraction peaks indexing as brucite structure (JCPDS7-239). The SEM picture in Fig. 7 shows the sheet-shaped magnesium hydroxides with an average diameter of 800 nm are obtained.

Conclusion

$Mg(OH)_2$ can be prepared by carbide residue and $MgCl_2$. The raw materials of this reaction are cheap and available. On the one hand, this technique can diminish the excess of these two substances. On the other hand, such method is feasible and can produce satisfactory social benefits, economic benefits and an obvious environmental protection benefits.

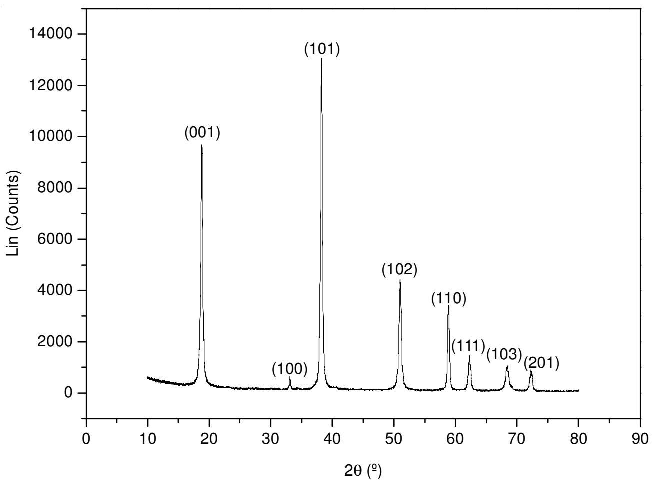

Fig. 6. XRD image of $Mg(OH)_2$

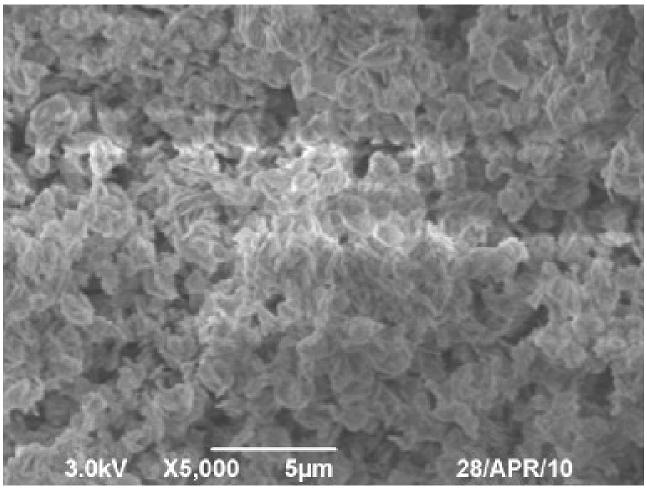

Fig. 7. SEM image of $Mg(OH)_2$

This technique realized a cyclic use of NH_4Cl and the circulation rate is 69.47 %. So the cost of production is reduced and the pollution of NH_3 gas is eliminated.

The optimal reaction condition is as follows:the molar ratio of ammonium chloride to magnesium chloride is 4.5, the magnesium is 1.5 mol/L, the reaction time is 1 h, the reaction temperature is 25 ºC and the aging time is 2 h. The productivity of magnesium hydroxide can obtain 89.30 % with a purity of above 99.12 % on this condition. The powder products have an average diameter of 800 nm.

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