Preparation of Plate-shape Nano-Magnesium Hydroxide from Asbestos Tailings

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Abstract. To prepare magnesium hydroxide is one of the effective methods to the comprehensive utilization of asbestos tailings. Nano-scale magnesium hydroxide was prepared and mechanisms of in-situ surface modification were characterized in the paper. Process conditions of preparation of magnesium hydroxide from purified hydrochloric acid leachate of asbestos tailings were optimized and in-situ surface modification of the product was carried out. Results showed that optimum process conditions for preparing nano-scale magnesium hydroxide were as follows: initial concentration of Mg$^{2+}$ in the leachate was 22.75g/L, precipitant was NaOH solution (mass concentration 20%), reaction temperature was 50$^\circ$C, and reaction time was 5min. The diameter and thickness of the plate nano-scale magnesium hydroxide powder prepared under optimal conditions were about 100 nm and 10 nm, respectively. However, particle agglomeration was obvious, the particle size increased to micron-grade. Dispersity of the magnesium hydroxide powder could be elevated by in-situ modification by silane FR-693, titanate YB-502 and polyethylene glycol and optimum dosages were 1.5%, 1.5% and 0.75% of the mass of magnesium hydroxide, respectively. All of the modifiers adsorbed chemically on surfaces of magnesium hydroxide particles, among which Si-O-Mg bonds formed among silane FR-693 and the particle surfaces and Ti-O-Mg among titanate YB-502 and the surfaces.

Keywords. asbestos tailings; magnesium hydroxide; in-situ surface modification

Introduction

Asbestos tailings are hazardous solid wastes mainly consists of serpentine. Accumulation of asbestos tailings threatens healthiness of animals and human around mining area severely [1] because of large amount of serpentine fiber it contains. So, safe disposal of asbestos tailings is of great significance to improve the ecological environment of the mining area.

Presently researches on recycling asbestos tailings mainly focus on: (1) preparing building materials such as non-burnt brick, steam brick, ceramic and glass-ceramic [2,3,4]; (2) extracting chemicals of magnesium and silicon including magnesium hydroxide, light magnesium oxide, precipitated silica and sodium silicate [5]. The main chemical components of asbestos tailings are SiO$_2$ and MgO$_2$ comprising 80% of the total weight. Producing magnesium hydroxide is an effective way to recycle asbestos tailings as a kind of resource [6]. Extraction of chemicals of magnesium and silicon mainly focus on preparing magnesium oxide and metal magnesium. Preparation of magnesium hydroxide has not yet been reported.

Magnesium hydroxide is an important chemical, which has a wide application in areas such as flame retardant for polymers, electric and electronic products, lithium battery, neutralization of acidic wastewater and preparation of metal magnesium and magnesium oxide [7]. Preparation, dispersion and modification of nano-scale magnesium hydroxide have been popular in recent years because of its
high flame retardance efficiency.

Taking purified hydrochloric acid leachate of asbestos tailings as raw material, by controlling reaction process conditions and in-situ surface modifications, flake nano-scale magnesium hydroxide was prepared in the paper.

1. Raw materials, reagents, instruments and methods

1.1. Experimental raw materials

The sketch map for preparing nano-magnesium hydroxide was as below:

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  asbestos + hydrochloric acid + leachate
  react  remove impurities such as Fe, Al, Ca
  purified leachate
  raw materials for preparing Mg(OH)2
  prepare Mg(OH)2
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Concentrations of ions in purified acid leachate for preparing magnesium hydroxide were (g/L): Mg$^{2+}$, 45.50; Na$^+$, 20.54; Fe$^{3+}$, 0.06; Al$^{3+}$, 0.10; Ca$^{2+}$, 0.25.

1.2. Experimental reagents

NaOH (A.R.) from Beijing Chemical Plant; titanate coupling agent YB-502 produced by Changzhou Yabanyayu Promoter Co., Ltd; silane coupling agent FR-693 provided by America Compton Company; polyethylene glycol (A.R., n=8.2) from Beijing Chemical Plant; Di-n-butyl phthalate (A.R., C$_{16}$H$_{22}$O$_4$) from Beijing Yili Fine Chemicals Co., Ltd.

1.3. Experimental instruments

BT-1500 Particle Size Distribution Analysis produced by DanDong Better Instruments Co., Ltd.; ST-2000 BET Determinator manufactured by Beijing Beifen Instruments Company; D/MAX 2500-PC X-Ray Diffractometer from Japan Rigaku Company; WQF-410 Flourier Infrared Spectrometer produced by Beijing Second Optical Instrument Company; S-3500N Scanning Electron Microscope from Japan Hitachi Company.

1.4. Experimental methods

Purified acid leachate was taken to study the effect of process conditions on apparent particle size of nano-Mg(OH)$_2$ powder. Influences of dosages of different modifiers on apparent particle size were analyzed. The properties of nano-Mg(OH)$_2$ powder were characterized by SEM, XRD and other approaches.

2. Results and Discussions

2.1. Preparation and characterization of nano- Mg(OH)$_2$ powder

NaOH was considered as precipitant because particle size of prepared Mg(OH)$_2$ powder using NaOH as precipitant was smaller [8]. There was NaCl in the solution already, so NaOH is adopted as precipitator.

2.1.1. Influence of initial concentration of Mg$^{2+}$ on apparent particle size

Experiment conditions: first measured 120mL Mg$^{2+}$ solution, regulated the concentration of Mg$^{2+}$ as 45.50g/L, 34.1 g/L, 27.30 g/L and 22.75 g/L, respectively, then put them into 500mL beakers, then titrated to pH=13 with 20% NaOH under 50°C, reacted for 8min and aged for 35min. Then filtrated, washed until no Cl$^-$ was detected in the leachate. Then sampled from filter cakes and measured the particle sizes and distributions. Results were shown in figure.1.

As was shown in figure.1, the apparent particle size of Mg(OH)$_2$ powder decreased with decreasing concentration of Mg$^{2+}$ solution. The Mg(OH)$_2$ powder prepared from lower initial concentration of Mg$^{2+}$ had better dispersity. This was because much higher crystal nucleus formation rate than crystal nucleus growth rate was required in order to prepare superfine powder and the
concentration of Mg\(^{2+}\) had a direct effect on supersaturation of Mg(OH)\(_2\) powder during reaction. But the lower the initial concentration of Mg\(^{2+}\) was, the more amount of water was needed. So the optimum concentration of Mg\(^{2+}\) was 22.75g/L.

2.1.2. Influence of reaction temperature on apparent particle size

Test conditions: the reaction temperatures were 30\(^\circ\)C, 50\(^\circ\)C, 70\(^\circ\)C and 90\(^\circ\)C, respectively, initial concentration of Mg\(^{2+}\) was 22.75g/L, other conditions were the same as that of section 2.1.1. Results were shown in figure.2.

As shown in figure.2, the prepared Mg(OH)\(_2\) powder has minimum apparent particle size and distribution at temperature 50\(^\circ\)C. So reaction temperature should be 50\(^\circ\)C in order to prepare superfine Mg(OH)\(_2\) powder with good dispersity.

2.1.3. Influence of reaction time on apparent particle size

Test conditions: initial concentration of Mg\(^{2+}\) was 22.75g/L, reaction temperature was 50\(^\circ\)C, and reaction times were 2min, 5min, 8min and 11min, respectively. Other conditions were the same as that of section 2.1.1. Results were shown in figure.3.
Supersaturation of Mg(OH)$_2$ powder in the reaction system was directly affected by reaction time, as a result crystal nucleus formation and growth rate of Mg(OH)$_2$ powder were affected consequently and properties of Mg(OH)$_2$ were affected as well. As was shown in figure.3, minimum apparent particle size of Mg(OH)$_2$ powder is prepared when the reaction time is 5 min.

2.1.4. Characterization of Mg(OH)$_2$ powder

Mg(OH)$_2$ powder was prepared under the conditions of initial concentration of Mg$^{2+}$ as 22.75g/L, reaction temperature as 50°C and reaction time as 5min. The apparent particle size are: $d_{50}$=1.60μm, $d_{97}$=7.23μm. The properties were characterized by SEM and XRD approaches.

Results of chemical analysis of the prepared Mg(OH)$_2$ were (%): MgO, 66.59; SiO$_2$, 0.07; Fe$_2$O$_3$, 0.09; CaO, 0.18; Na$_2$O, 0.04; K$_2$O, 0.01; LOI, 31.62. It is calculated accordingly that Mg(OH)$_2$ has a relatively high purity of as high as 96.6%. The SEM photo was shown in figure.4 and the XRD pattern was shown in figure.5.

Figure.4 showed nano-scale flake particles with diameter of about 100nm and thickness of about 10nm and the phenomenon of particle agglomeration was obvious, the largest particle size was about 10μm. Figure.5 showed sharp narrow characteristic peaks of Mg(OH)$_2$ at $d=4.795$nm, $d=2.369$nm and $d=1.799$nm, indicating high crystallinity. The peak at $d=2.728$nm was characteristic peak of NaCl and $d=3.042$nm of CaCO$_3$, indicating trace NaCl and CaCO$_3$, which was consistent with chemical analysis.

2.2. In-situ surface modification of Mg(OH)$_2$ powder

In-situ surface modification was carried out to improve dispersity of the Mg(OH)$_2$ powder. Research showed that dispersity of the powder in polymer matrix under dry condition could be
improved by silane FR-693 and titanate TB-502 while dispersity in hydrophilic environment be
improved by polyethylene glycol [9].

2.2.1. Modification by coupling agent

Conditions: first measured 120mL Mg\textsuperscript{2+} solution, regulated the concentration of Mg\textsuperscript{2+} as 22.75 g/L, then put it into 500mL beaker and added into certain amount of coupling agent (FR-693 or YB-502), then titrated to pH=13 with 20% NaOH under 50℃, reacted for 8min and aged for 35min. Then filtrated, washed until no Cl\textsuperscript{-} were detected in the leachate. Then sampled from filter cakes and measured the particle sizes and distributions. Results were shown in figure.6.

Figure.6 showed dispersity of the Mg(OH)\textsubscript{2} powder during the chemical preparation process could be improved to some extent by in-situ modification using silane FR-693 and the optimum dosage was 1.5% of the mass of Mg(OH)\textsubscript{2}. YB-502 had similar function, the apparent particle size \(d_{50}=1.51\mu m\) and \(d_{97}=4.23\mu m\) when the dosage was 1.5% of the mass of Mg(OH)\textsubscript{2}. But when the dosage was added up to 2.0% the apparent particle size of the powder increased slightly. So the optimum dosage of YB-502 was 1.5% of the mass of Mg(OH)\textsubscript{2}.

2.2.2. Modification by polyethylene glycol

Experimental conditions were the same as that of section 2.2.1 with polyethylene glycol as modifier. Results were shown in figure.7.

A-surface modification by FR-693, 
B-surface modification by YB-502.

Figure.6 Effect of coupling agent treatment on the size distribution of Mg(OH)\textsubscript{2} powder

Figure.7 Effect of surface modification by polyglycol on particle size of Mg(OH)\textsubscript{2} powder

Figure.7 indicated that dispersity of the powder can be improved by in-situ modification using polyethylene glycol. When the dosage of modifier was 0.75% of the mass of Mg(OH)\textsubscript{2} powder the particle size \(d_{50}=1.46\mu m\), \(d_{97}=5.02\mu m\), but the apparent particle size of the powder increased when the dosage of modifier was added up to 1.0%. So optimum dosage of polyethylene glycol was 0.75% of the mass of Mg(OH)\textsubscript{2}.

The SEM photos of the modified Mg(OH)\textsubscript{2} were shown in figure.8.

Comparison between figure.8 and figure.4 indicated that the dispersity of Mg(OH)\textsubscript{2} powder modified by silane was improved to some extent, and diameter-thickness ratio was smaller than that of non-modified powder, the modified powder had relatively good dispersive property. Dispersity of Mg(OH)\textsubscript{2} powder modified by titanate was improved significantly, flake micro-morphology of the particle was observed. Diameter-thickness ratio was a little bigger and the modified powder had relatively good dispersive property. Dispersity of the Mg(OH)\textsubscript{2} powder could be improved and agglomeration phenomenon was weakened by modification using polyglycol, the primary particle size of the Mg(OH)\textsubscript{2} powder was larger than non-modified powder and the dispersity was better. Of the
three coupling agents dispersity of titanate and polyglycol modified powders were improved by a larger extent.

(a) surface modified by FR-693  
(b) surface modified by YB-502  
(c) surface modified by polyglycol

Figure 8 SEM photos of surface modified Mg(OH)₂ powder

2.2.4. Mechanism of in-situ modification of Mg(OH)₂

The FTIR pattern of non-modified Mg(OH)₂ powder was shown in figure 9. Differential patterns of modified and non-modified powders were shown in figure 10.

Figure 9 FTIR pattern of Mg(OH)₂ powder  
Figure 10 FTIR differential patterns of Mg(OH)₂ powders between non-modified and modified
As was seen in figure 9, wave numbers at 693.96 cm\(^{-1}\), 3432.32 cm\(^{-1}\) and 1442.23 cm\(^{-1}\) were absorption peaks of OH\(^-\). Wave numbers at 440.31 cm\(^{-1}\) and 572.10 cm\(^{-1}\) were absorption peaks of Mg-O bond. Wave number at 1631 cm\(^{-1}\) was absorption peak of H\(_2\)O and 1442.23 cm\(^{-1}\) of CO\(_3\)^{2-}. Above peaks indicated that some of the prepared Mg(OH)\(_2\) transformed into magnesium carbonate hydroxide or magnesium carbonate in air [10].

Differential peak at 3696 cm\(^{-1}\) in figure 10 indicated absorption peak of H\(_2\)O migration induced by adsorption of modifier on the powder surface. In curve 1 the vibration adsorption peak of \(^{-}\)OH at 2921.67 cm\(^{-1}\), characteristic peak of -CH\(_2\) at 2852.95 cm\(^{-1}\), C-H bond in silane plane at 1398.03 cm\(^{-1}\) and C-H bond at 1488.34 cm\(^{-1}\) indicated adsorption peak migration induced by chemical adsorption of silane on powder surface. It was seen that Si-O-Mg bond was formed between Mg(OH)\(_2\) and silane on the powder surface. In curve 2 the vibration adsorption peak of \(^{-}\)OH at 2921.10 cm\(^{-1}\), \(^{-}\)C=O of titanate at 1743.36 cm\(^{-1}\), C-N bond of amine at 1079.88 cm\(^{-1}\) and characteristic peak of C-H bond at 1494.05 cm\(^{-1}\) indicated adsorption peak migration induced by titanate coating on surface of Mg(OH)\(_2\) powder and adsorbed chemically. That was Ti-O-Mg bond was formed between Mg(OH)\(_2\) and titanate on the powder surface. In curve 3 absorption peak migration induced by organic adsorption on powder surface at 3697.47 cm\(^{-1}\) and 3442.75 cm\(^{-1}\), characteristic peak of C-O at 1743.13 cm\(^{-1}\) and characteristic peak of C-H bond at 1509.70 cm\(^{-1}\) indicated coating on Mg(OH)\(_2\) surface by polyglycol and induced absorption peak migration.

3. Conclusions

(1) Optimum process conditions for preparing nano-scale magnesium hydroxide using Mg\(^{2+}\) solution from purified acid leachate of asbestos tailings were: initial concentration of Mg\(^{2+}\) solution 22.75 g/L, precipitant 20% NaOH solution, reaction temperature and reaction time 50°C and 5 min respectively. It was observed from SEM photos that diameter of the prepared flake nano-scale Mg(OH)\(_2\) powder was about 100 nm and thickness was about 10 nm. However, the phenomenon of agglomeration was obvious, the particle size increased to micron-grade.

(2) Dispersity of the Mg(OH)\(_2\) powder could be improved by in-situ modification using silane FR-693, titanate YB-5002 and polyglycol as modifier. Optimum dosage of the three kinds of modifiers were 1.5%, 1.5% and 0.75% of the mass of Mg(OH)\(_2\), respectively. All of the modifiers adsorbed chemically on Mg(OH)\(_2\) particle surface, among which Si-O-Mg chemical bonds were formed between silane FR-693 and particle surface, Ti-O-Mg bonds were formed between titanate YB-502 and particle surface.

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