Preparation of submicron-sized $\text{Mg}(\text{OH})_2$ particles through precipitation

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Received 21 October 2004; received in revised form 18 April 2005; accepted 22 April 2005

Available online 13 June 2005

Abstract

Fiber and lamellar-like nanosized $\text{Mg}(\text{OH})_2$ particles were synthesized by precipitation of different magnesium salts with sodium hydroxide. An experimental design procedure was used to investigate the effects of salt concentration, base concentration, feed rate, and mixing rate on the mean particle size and the standard deviation of particle size distribution. The products prepared from MgSO_4 were found to be different from those from MgCl_2 and $\text{Mg}(\text{NO}_3)_2$. We concluded that the salt and the base concentrations were the key factors influencing the morphology of the final product, its particle size, however, was controlled mainly by the feed rate and the mixing rate.

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Keywords: Magnesium hydroxide; Nanoparticles; Experimental design

1. Introduction

Magnesium hydroxide, a very popular, environmental friendly and thermally stable flame-retardant filler in composite materials [1–4], is also used to neutralize acidic waste streams and gases rich in sulfuric oxides [5], as antacid excipient in pharmaceuticals [6], in pulp and paper industry, as fertilizer additive, and/or as the most important precursor for magnesium oxide. Magnesium hydroxide can be prepared by several methods, such as hydration of magnesium oxide [7], electrolysis of magnesium salt aqueous solutions, sol–gel techniques [8], and precipitation. Double hydroxides of magnesium and a different metal with layered structure similar to the brucite can also be obtained by coprecipitation [9]. Nanosized $\text{Mg}(\text{OH})_2$ was prepared by employing pulsed laser ablation technique. A Mg plate immersed in deionized water, with or without sodium dodecyl sulfate, was ablated; thus, obtaining brucite exhibiting different morphologies, such as wormhole-, tube-, rod-, and plate-like, depending upon the concentration of SDS [10]. Fiber-like $\text{Mg}(\text{OH})_2$ nanoparticles were synthesized by precipitation of magnesium nitrate with an alkaline solution, employing microwave irradiation as assistance [11]. The fiber and lamellar brucite

obtained by precipitation in the presence of poly(*N*-vinyl-2-pyrrolidone) after dispersion in ethylene-vinyl acetate were proven to have good flame-retardant properties [12]. Industrial production usually is based on precipitation of aqueous magnesium salt solutions with alkaline solutions. Magnesium hydroxide with plate-like crystalline structure, mean particle size around 1 μm , with 95% of the particle number smaller than 3.5 μm , and a small surface was prepared by flash precipitation, using MgF_2 , MgCl_2 , MgBr_2 , MgI_2 , MgBrO_3 , MgSO_4 , and MgClO_3 . Ultrasonic mixing was employed and the reaction was followed by a heat treatment [13]. After obtaining $\text{Mg}(\text{OH})_2$ from sea water or brine, followed by etching in a solution of organic or inorganic acid, magnesium hydroxide with a reduced average surface area was produced [14]. The refractory grains of $\text{Mg}(\text{OH})_2$ are highly dependent on the impurities in the material [15] and for good performances the mean surface area should be minimized. Magnesium hydroxide with BET lower than 10 m^2/g and average particle size between 0.5 and 10 μm was synthesized by precipitating a magnesium chloride aqueous solution with an excess of ammonia followed by hydrothermal recrystallization [16]. Rods and tubes of magnesium hydroxide were also synthesized by hydrothermal technique [17] and nanosized $\text{Mg}(\text{OH})_2$ with controlled size, shape, and structure was obtained through the same procedure. The magnesium hydroxide was subsequently

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Table 1
Typical 2^{4-1} factorial design for the present problem

Run	NaOH concentration (A)	Salt concentration (B)	Feed rate (C)	Mixing rate (D)	Treatment combination
1	–	–	–	–	(1)
2	+	–	–	+	AD
3	–	+	–	+	BD
4	–	+	–	+	AB
5	+	+	–	–	CD
6	+	–	+	–	AC
7	–	+	+	–	BC
8	+	+	+	+	ABCD
9	0	0	0	0	Central point
10	0	0	0	0	Central point

thermally decomposed leading to a high surface area MgO [18]. The influence of several factors, such as temperature, magnesium, and alkaline source, hydrothermal treatment on the morphology of nanosized $\text{Mg}(\text{OH})_2$ obtained by precipitation ion aqueous solutions was also discussed [19].

The present work focuses on obtaining magnesium hydroxide by means of precipitation from three magnesium salts, namely chloride, nitrate, and sulfate. One of our goals was to determine whether an experimental design technique could be used to investigate the influence of several parameters on synthesis of submicron magnesium hydroxide. To this end, the concentration of base, the concentration of salt, the feed rate, and the rate of mixing are chosen. For the synthesis of amorphous inorganic particles as silica and titania [20–23] and even crystalline as lead zirconate titanate [24], an experimental design approach was previously used successfully. In our study, we adopted a 2^{k-1} fractional factorial design, and Design-Expert 5, a statistical experimental optimization program was used.

2. Experimental

The samples were obtained by precipitation at 27 °C of a magnesium salt solution and an alkaline NaOH solution. The magnesium salts used (magnesium nitrate hexahydrate, minimum 98% purity; magnesium chloride hexahydrate, minimum 98% purity; magnesium sulfate anhydrous, 99.5% purity) were purchased from Sigma–Aldrich. The salt solution was fed into a glass reactor containing an alkaline solution, under permanent stirring by a mechanical stirrer using a peristaltic pump with a constant flow rate. The suspension was allowed to age for 1 day at room temperature and the precipitate was recovered by centrifugation at 5000 rpm, washed twice with water and ethanol, and dried at room temperature for powder characterization. The particle size was analyzed in the mother liquor using a Malvern particle sizer after preparation. The samples were previously sonicated for 2 min to ensure an appropriate dispersion. A transmission electron microscope JEOL JSM was used to obtain pictures of magnesium hydroxide in ethanol. The dried particles were visualized by a Hitachi H-2400 scanning electron microscope. Phase identification was done by X-ray diffraction

(Mac-Science/MXP) using Cu K α ($\lambda = 1.54056 \text{ \AA}$) radiation. IR spectra of the prepared powder were obtained on a KBr pellet using a Jasco Model FTIR 410 spectrophotometer. Thermogravimetric analysis (TGA) was performed under nitrogen flow using a DuPont Model 95, at a heating rate of 10 °C.

3. Experimental design

The key factors examined included the concentration of base *A*, the concentration of salt *B*, the feed rate *C*, and the rate of mixing *D*. To identify the significant factors and the interactions between them, a fractional factorial design was conducted and for each factor two values (low and high) were chosen and coded by (–) for the lower value and (+) for the high value. In the case of a two-level factorial design, a linear response is assumed. To protect against possible nonlinear effects, an appropriate method is to add a central point to the design and to have it replicated [25,26]. Table 1 summarized the coded levels of factors *A*, *B*, *C*, and *D* = *ABC* in a typical 2^{4-1} experimental design. The last two experimental runs correspond to the central points and may or may not be included in our experiments, as specified.

The main effects and the interactions between two main factors can be estimated by

$$l_A = A + BCD \quad (1)$$

$$l_B = B + ACD \quad (2)$$

$$l_C = C + ABD \quad (3)$$

$$l_D = D + ABC \quad (4)$$

$$l_{AB} = AB + CD \text{ (aliased with } CD) \quad (5)$$

$$l_{AC} = AC + BD \text{ (aliased with } BD) \quad (6)$$

$$l_{AD} = AD + BC \text{ (aliased with } BC) \quad (7)$$

4. Results and discussions

A typical XRD pattern is illustrated in Fig. 1, for samples prepared using MgCl_2 . The diffraction peaks correspond

Fig. 1. XRD powder diffraction pattern of $\text{Mg}(\text{OH})_2$ for the case when $C_{\text{NaOH}} = 0.2 \text{ M}$, $C_{\text{MgCl}_2} = 0.1 \text{ M}$, feed rate = 0.1 ml/l , and mixing rate = 500 rpm (a) and $C_{\text{NaOH}} = 0.02 \text{ M}$, $C_{\text{MgCl}_2} = 0.1 \text{ M}$, feed rate = 0.1 ml/l , and mixing rate = 2000 rpm (b).

to hexagonal structure magnesium hydroxide, according to JCPDS file no. 07-0239. The mean crystallite size can be estimated by applying Debye–Scherrer formula [27], based on full width at half-maximum. The pattern shown in Fig. 1 indicates a hexagonal, plate-like structure, with layers in $[001]$ direction. The different width of the peaks in the two spectra indicates a smaller crystalline size for sample (b), but also the restriction of the crystallite dimension along the crystallographic c -axis [28]. The TEM and SEM pictures shown in Figs. 2 and 3 also provide information about particle size and morphology. Although the crystallite size is below 100 nm , particles agglomerate and their redispersion is not possible even by sonication. Therefore, for the experimental design analysis, instead of crystallites size, the mean particle size of agglomerates is used. The FTIR spectrum, Fig. 4, is no different from that reported in literature for brucite, with a remarkable sharp $-\text{OH}$ stretching peak around 3700 cm^{-1} [29,30]. TGA was performed to investigate the decomposition process of the brucite obtained as shown in Fig. 5. As reported in the literature, a significant weight loss is observed in the temperature range of 280 – 450°C [7], corresponding to the decomposition of $\text{Mg}(\text{OH})_2$ to MgO . At 450°C , the weight loss reaches 29.9% , which is very close to the theoretical weight loss of 30.8% . A weight loss of around 32.7% is achieved at 700°C , due to the complete decomposition of the brucite and the desorption of the residual hydroxyl groups bonded to MgO lattice [31].

The operational parameters of our experimental design are summarized in Table 2. The central point conditions

Fig. 2. TEM images of $\text{Mg}(\text{OH})_2$ nanoparticles when $\text{Mg}(\text{NO}_3)_2$ was used as salt: (a) sample 8, (b) sample 2, and (c) sample 5.

were used only in the case of $\text{Mg}(\text{NO}_3)_2$, while for MgSO_4 and MgCl_2 , a simple 2^{k-1} fractional factorial design was employed. Tables 3 and 4 present the experimental conditions for each run and the results, including the crystalline form

Table 2
Operational parameters of the experimental design for the preparation of $\text{Mg}(\text{OH})_2$

Parameter	Low value	Central point	High value	Response
NaOH concentration (mol/l)	0.02	0.11	0.2	(1) Mean particle size, (2) standard deviation
Salt concentration (mol/l)	0.01	0.06	0.1	
Feed rate (cm^3/l)	0.1	0.4	0.7	
Mixing rate (rpm)	500	1250	2000

Fig. 3. SEM imagines of $\text{Mg}(\text{OH})_2$ nanoparticles: (a) $\text{Mg}(\text{NO}_3)_2$ sample 8, (b) $\text{Mg}(\text{NO}_3)_2$ sample 2, (c) $\text{Mg}(\text{NO}_3)_2$ sample 5, and (d) MgCl_2 .

Table 3

Statistical experiment parameters and results for the preparation of $\text{Mg}(\text{OH})_2$ for the case when MgSO_4 was used as salt

Run	NaOH concentration (mol/l)	MgSO_4 concentration (mol/l)	Feed rate (cm^3/min)	Mixing rate (rpm)	pH	Shape (TEM)	PS (μm)	S.D. (μm)
1	0.2	0.1	0.1	500	11.48	Fiber, lamellar	6.10	1.22
2	0.2	0.1	0.7	2000	11.52	Fiber, lamellar	4.40	3.36
3	0.02	0.1	0.1	2000	10.00	Fiber, few lamellar	1.96	1.31
4	0.02	0.1	0.7	500	10.00	Fiber, few lamellar	2.91	1.43
5	0.02	0.01	0.1	500	10.60	Fiber, lamellar, tube	2.19	1.70
6	0.02	0.01	0.7	2000	10.55	Fiber	1.89	0.34
7	0.2	0.01	0.1	2000	12.50	Fiber, lamellar	4.93	0.73
8	0.2	0.01	0.7	500	12.50	Fiber, lamellar, tube	4.47	2.87

Table 4

Statistical experiment parameters and results for the preparation of $\text{Mg}(\text{OH})_2$ for the case when $\text{Mg}(\text{NO}_3)_2$ was used as salt

Run	NaOH concentration (mol/l)	$\text{Mg}(\text{NO}_3)_2$ concentration (mol/l)	Feed rate (cm^3/l)	Mixing rate (rpm)	pH	Crystalline form (TEM)	PS (μm)	S.D. (μm)
1	0.02	0.01	0.1	500	10.5	Fiber	2.874	0.778
2	0.02	0.01	0.7	2000	10.4	Fiber	0.862	2.833
3	0.20	0.01	0.1	2000	12.4	Lamellar, fiber	1.602	0.582
4	0.02	0.1	0.1	2000	9.7	Lamellar	4.240	1.282
5	0.20	0.01	0.7	500	12.5	Lamellar, fiber	2.082	2.473
6	0.20	0.10	0.1	500	11.7	Lamellar	3.609	0.836
7	0.02	0.10	0.7	500	9.8	Lamellar	3.204	1.881
8	0.20	0.10	0.7	2000	11.7	Lamellar	0.764	0.592
9	0.11	0.06	0.4	1250	–	Lamellar	2.320	–
10	0.11	0.06	0.4	1250	–	Lamellar	2.322	–

Fig. 4. FTIR spectrum of $\text{Mg}(\text{OH})_2$ obtained in this study.

observed by TEM, mean particle size and standard deviation, when MgSO_4 and $\text{Mg}(\text{NO}_3)_2$ were used as salts. Magnesium chloride and nitrate yield very similar results, not only in morphology, but also in particle size distribution and mean particle size, as will be discussed later. The estimated effects

Fig. 5. Thermogravimetric analysis of $\text{Mg}(\text{OH})_2$ obtained in this study.

were calculated as discussed previously and the results in the case of magnesium sulfate are given in Table 5. The estimated values for the main factors hold a real meaning only if the interactions between two factors are insignificant; otherwise, further analysis is necessary. In Fig. 6(a–c), the effects of

Fig. 6. Effect of interaction AB (a), AC (b), and AD (c), on the mean particle size when MgSO_4 is used as salt.

Table 5

Estimated effects for particle size and standard deviation for the case when MgSO_4 is used as salt

Estimated effect	PS (μm)	S.D. (μm)
I_A	2.74	0.92
I_B	0.48	0.50
I_C	−0.38	0.84
I_D	−0.63	−0.30
I_{AB}	0.075	0.14
I_{AC}	−0.70	1.46
I_{AD}	6.5×10^{-3}	0.44

MgSO_4 concentration, feed rate, and mixing rate are plotted against the concentration of NaOH. The response surface plots indicate that a low concentration of both reactants and/or a high feed rate leads to a small mean particle size. Comparing to the effect of reactants concentrations, the feed rate has relatively little influence on the mean particle size. A similar effect is given by a high mixing rate. When the levels of B–D

factors are plotted against the levels of A, as in Fig. 7(a–c), the interactions between the factors can be detected. The curves in the Fig. 7(a and c) are almost parallel, meaning that there is no significant interaction between two factors. Fig. 7(b) indicates that the interaction between factors A and C is appreciable. At high concentrations of base the feed rate influences considerable the mean particle size, while at low concentration its influence becomes less pronounced. For a dilute solution of NaOH, the smaller the feed rate, the smaller the particle size is. On the other hand, if the concentration of NaOH is high, a high feed rate is necessary to achieve a smaller particle size. The effects of factors A–D on the standard deviation of particle size distribution are presented in Fig. 8. Fig. 8(a) indicates that a lower concentration of both NaOH and MgSO_4 leads to smaller standard deviation. The influences of the feed rate and the mixing rate are presented in Fig. 8(b and c). The latter suggests that a high mixing rate lowers the standard deviation; the interpretation of former, however, is not straightforward. Fig. 9 summarizes the

Fig. 7. Plot of AB interaction (a), AC interaction (b), and AD interaction (c), for the mean particle size when MgSO_4 was used as salt.

Fig. 8. Effect of NaOH concentration and MgSO_4 concentration (a), NaOH concentration and feed rate (b), NaOH concentration and mixing rate (c), on the standard deviation of particle size distribution when MgSO_4 is used as salt.

interactions *AB*, *AC*, and *AD* for the standard deviation of particle size distribution. Fig. 9(a) reveals no significant interaction between factors *A* and *B*. Fig. 9(b) shows that when the concentration of NaOH is low, a high feed rate leads to a smaller standard deviation, and for a high concentration of base, a narrower particle size distribution can be obtained by increasing the feed rate. As indicated in Fig. 9(c), any mixing rate between 500 and 2000 rpm results in similar standard deviation for high concentration of NaOH, but for low concentration of NaOH a higher mixing rate lowers the standard deviation.

The effects of salt concentration, base concentration, feed rate, and mixing rate on the mean particle size when MgCl_2 and $\text{Mg}(\text{NO}_3)_2$ are used as salts are presented in Fig. 10. Fig. 10(a and b) suggests that in both cases particle size decreases as the concentration of salt decreases and the base concentration increases. As in the case of MgSO_4 , a high feed

rate and a high mixing rate lead to a smaller mean particle size. As it can be seen in Fig. 11(a and b), for both salts, any base concentration between 0.02 and 0.2 mol/l leads to similar mean particle size. When the salt concentration is high, a higher concentration of base leads to a smaller mean particle size, and we can conclude that the *AB* interaction cannot be neglected. Also, both *AC* and *AD* interactions become weaker, but the plots show clearly that for the base concentration range examined, a higher feed rate and higher mixing rate are necessary to minimize the mean particle size. The mixing rate becomes important as the concentration of reactant NaOH is higher.

Regression models can be used to describe the dependence of the mean particle size (PS) and the standard deviation (S.D.) of particle size distribution on the key factors investigated. The estimated coefficients for the regression models for both the mean particle size and the

Fig. 9. Plot of AB interaction, (a) AC interaction (b), and AD interaction (c), for standard deviation of particle size distribution when MgSO_4 was used as salt.

Table 6

Estimated coefficients of the regression model for mean particle size (PS) and standard deviation (S.D.) for the case when MgSO_4 is used as salt

Salt	Response	R^2	Constant	A	B	C	$D \times 10^4$	AB	AC	$AD \times 10^3$
$\text{Mg}(\text{SO}_4)$	PS (μm)	1	1.91	19.81	4.27	0.78	-4.23	9.23	-12.92	0.0481
		0.9994	1.85	20.38	5.29	0.78	-4.176	-	-12.92	-
		0.9287	1.62	20.38		0.78			-12.92	
	S.D. (μm)	1	2.19	-9.33	3.74	-1.54	-5.45	8.36	25.51	2.717
		0.9987	2.14	-8.87	4.66	-1.54	-5.45		25.51	2.717
MgCl_2	PS (μm)	1	4.20	1.65	11.00	-3.54	-3.02	-58.44	11.47	-5.414
$\text{Mg}(\text{NO}_3)_2$	PS (μm)	1	2.99	4.96	22.44	-2.61	-2.37	-92.99	3.19	-4.361

standard deviation of particle size distribution calculated by

$$PS = \alpha_0 + \alpha_1 A + \alpha_2 B + \alpha_3 C + \alpha_4 D + \alpha_5 AB + \alpha_6 AC + \alpha_7 AD \quad (8)$$

$$S.D. = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 D + \beta_5 AB + \beta_6 AC + \beta_7 AD \quad (9)$$

are summarized in Table 6. For preparation of colloidal particles through precipitation, LaMer model is generally

Fig. 10. Effect of NaOH and $MgCl_2$ concentrations (a), NaOH and $Mg(NO_3)_2$ concentrations (b), NaOH concentration and feed rate of $MgCl_2$ (c), NaOH concentration and feed rate of $Mg(NO_3)_2$ (d), NaOH concentration and mixing rate of $MgCl_2$ (e), and NaOH concentration and mixing rate of $Mg(NO_3)_2$ (f), on the mean particle size.

accepted [32]. This model basically involves three stages: induction, self-nucleation and growth. In the induction step, the concentration of the product builds up until reaching a critical value, this state of supersaturation is followed by

the apparition of the nuclei. If the concentrations of the reactants are high, the rates of formation of products are fast, resulting in rapid nucleation and growth by diffusion. On the other hand, due to supersaturation, repetitive nucleation

Fig. 11. Plot of AB interactions (a and b), AC interactions (c and d), and AD interactions (e and f). MgCl_2 is used in (a), (c), and (e), $\text{Mg}(\text{NO}_3)_2$ is used in (b), (d), and (f).

occurs and the growth time, and subsequently, the size of a particle depends on the time at which the corresponding nucleus is formed. As a result, the particles are characterized by small size but a wide size distribution. Supersaturation can also be achieved by increasing the feed rate, lower feed rates resulting in a smaller number of nuclei that are enabled to grow uniformly. In our case, at least for MgSO_4 , concentrated solutions yield larger particles and smaller standard deviation. It was observed that for magnesium nitrate and chloride salts, a high concentration of base and a high feed rate lead to a smaller particle size and narrower particle size distribution. As suggested in the literature, the LaMer's model seems to be applicable only to certain systems, mostly to amorphous particles like silica or titania [33]. For crystalline, after the nucleation stage, primary particles agglomerate into final crystalline particles [34,35], though the exact mechanism is not clear. The crystalline magnesium hydroxide has a layered, CdI_2 -type structural arrangement in which Mg^{2+} ions arrange in hexagonal layers and the hydroxyl ions form similar layers below and above it [36,37]. Such an arrangement favors a lamellar crystallization product. Fiber and even rod and tube-like magnesium hydroxide were reported in literature when additives [12], organic base [18], and microwave radiation [11] were used. In our case, the fiber-like nanoparticles were obtained in all cases when the concentration of salt was 0.01 M. For the case of MgSO_4 , a mixture of fiber and platelet-like particles were obtained, and sporadic short tube-like particles appeared. On the other hand, if nitrate and chloride salts were used, it seems that the ratio (salt concentration/base concentration) is very important in determining the morphology of the product. The low concentration of base leads to the formation of fiber-like particles, while a high concentration of sodium hydroxide results in a mixture of fiber- and platelet-like particles. For the middle point of the present experimental design, the case of $\text{Mg}(\text{NO}_3)_2$ is characterized by a NaOH concentration of 0.11 M and $\text{Mg}(\text{NO}_3)_2$ concentration of 0.06 M. In this case, the nanoparticles obtained are of lamellar shape, which could strengthen the assertion that fiber-like particles can be obtained when the base concentration is below 0.1 M [11]. On the other hand, looking at the results we obtained for all the salts and judging the AB interaction in the case of magnesium chloride and nitrate, one can conclude that the concentration of salt is the decisive factor affecting the dimension of the final aggregate. The duplicated central point insures that there is indeed a linear response previously assumed and that disregarding the crystalline form of the magnesium hydroxide, an experimental design can be used at least as a qualitative tool to assess the effects of the reactant concentrations and other factors on the mean particles size of the final product. Also, it is worth noting that when MgCl_2 was used, particles were lamellar-like initially, and became globular after drying (Fig. 3(d)). This is consistent with the observations in the literature [19].

5. Conclusions

Submicron-sized $\text{Mg}(\text{OH})_2$ particles were prepared through precipitation, and the influences of the key factors on the nature of the final product were investigated based on a fractional factorial design approach. This approach has the merit of providing essential information on the conditions necessary to obtaining final product with desired characteristics by conducting a limited number of replications. The result of experimental study reveals that the morphology of the final product varied mainly as a function of both the type and the concentration of salt used and the concentration of base. Lamellar-, fiber-, and few tube-like particles were obtained by simple precipitation. LaMer model, which is commonly used to explain the formation of monodispersed particles, was found to have limited applicability in the production of crystalline particles as $\text{Mg}(\text{OH})_2$.

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