Experimental Study on Superfine Grind Process for the Preparation of Calcium Carbonate Particles via Vibrated Mill

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Abstract

To obtain the minimum particle size calcium carbonate, the vibrated mill was used to grind analytically pure calcium carbonate. This experimental method was introduced to research what effect grinding time, grinding media size and filling rate have on grinding in order to select the optimal operation condition. The results showed that the vibrated mill could grind analytically pure calcium carbonate with size of about 1.5μm, and with the grinding time increased, the size of the particles decreased. However, its size remained even reversed when decreased to a certain degree. The optimum technological condition is a parameter combination including 10mm diameter grinding ball, 65% filling rate and 500g powder quality.

Keyword: Calcium carbonate; superfine grind; vibrated mill

1. Introduction

The special quantum size effect, small size effect and surface effect of super-fine calcium carbonate make it have distinct advantage over conventional powder material on corroborative mess, transparency, dispensability, levelling property and so on[1-2]. China began to pay attention to the study of super-fine calcium carbonate since 1980s, although several different types of super-fine calcium carbonate product have been developing and producing,
Problems that exist in our calcium carbonate product, such as less varieties, low yield, backward manufacturing technique and equipment, obliging us to import high grade product. Therefore, how to take full advantage of our abundant limestone mine resource and develop the super-fine calcium carbonate is of great significance for domestic papermaking, plastic, rubber industry and so on.\(^3\)\(^4\).

With the development of material industry, superfine grinding has quickly became a new technology recently, which can keep ordinary material ultrafine without changing its chemical constitution but surface and interfacial properties to achieve the super normal result. Vibrated mill is a kind of mechanical powder equipment used to produce material fines and ultra fines, whose outstanding merits such as simple structure, small size, light weight, low energy consumption, high production efficiency, small plate medium erosion, absence of disperse and so forth give it a significant advantage in the field of superfine grinding, moreover, it is widely applied in the fields of non-metallic ore grinding, beneficiation, metallurgy, Chemicals, medicine, building materials, food, etc.

This article used experimental vibrated mill to do experimental study on ultrafine grinding of analytically pure (AR) calcium carbonate powder, and will compare the test results between different size grinding media and filling rate for acquiring better technological conditions.

2. Testing apparatus

This experiment used experimental vibrated mill to ultrafine grind calcium carbonate particles, and had got good results\(^5\). The experimental vibrated mill is shown in Fig.1

![Fig.1 Structure chart of experimental vibrated mill](image)


The operating principle of the vibrated mill is first to put material and grinding media into grinding barrel supported by spring, then electric motor actuates centrifugal exciter by flexible coupling to generate exciting force which drives grinding barrel to produce high frequency vibration, making material and grinding media in the barrel produce cast, impact, shear, friction, rotary motion, thereby the material can get grinded. The grinding media built-in the grinding barrel can be of rod or ball with different sizes. The grinding media in the grinding barrel could be round or oval with different size. Centrifugal exciter was installed on the main shaft while working amplitude of the vibrated mill was adjusted by exciter.

3. Kinetic equation for vibration grinding system

In order to facilitate analysis, vibrated mill system was simpliied into vibrating system with two degrees of freedom variable mass, as shown in Fig.2.
Main system $m_1$ connected spring with stiffness $k_1$ and damper with damping coefficient $c_1$, it moved when exerted by vertical sine exciting force $F_0 \sin(\omega t)$, grinding media $m_2$ was included in and impacted with $m_1$. Supposed that the collision damping between $m_1$ and $m_2$ is $F_c$, $m_1$ was exerted by sine exciting force $F_0 \sin(\omega t + \phi)$. Kinetic equation for system is:

$$\begin{align*}
\dot{x}_1 + (c_1 + c_2) \dot{x}_1 - c_2 \dot{x}_2 + k_1 x_1 &= F_0 \sin(\omega t) \\
\dot{x}_2 - c_2 \dot{x}_1 + c_2 \dot{x}_2 &= F_0 \sin(\omega t + \phi)
\end{align*}$$

The equation was simplified to:

$$\begin{align*}
\dot{x}_1 + 2(\zeta_1 + \zeta_2) \omega_1 \dot{x}_1 - 2\zeta_2 \omega_1^2 \dot{x}_2 + \omega_1^2 x_1 &= f_1 \sin(\omega t) \\
\dot{x}_2 - \zeta_3 \dot{x}_1 + \zeta_3 \dot{x}_2 &= f_2 \sin(\omega t + \phi)
\end{align*}$$

There into: $w_0 = \sqrt{\frac{k_1}{m_1}}$; $\zeta_1 = \frac{c_1}{2\sqrt{k_1 m_1}}$; $\zeta_2 = \frac{c_2}{2\sqrt{k_2 m_2}}$; $\zeta_3 = \frac{c_2}{m_2}$; $f_1 = \frac{F_0}{m_1}$; $f_2 = \frac{F_0}{m_2}$.

### 4. Test method

The experiment adopted analytically pure (AR) calcium carbonate powder produced by Sinopharm Chemical Reagent Co. Ltd., with calcium carbonate content greater than 99.0%, molecular weight of 100.09, water content of 4.17%. Zirconia ceramic ball with diameter of 10mm and 20mm produced by Shanghai Xinmao Precise Ceramic Technology Co. Ltd. was chosen to be grinding media. Experimental facilities are as follows: experimental vibrated mill, with power rating of 0.4kw, rated frequency of 50Hz, and was set to be 35Hz in the experiment; Winner2005 laser particle size analyzer was adopted to analyze particle size.

In the experiment, analytically pure calcium carbonate powder was put in high frequency vibrated mill and ultrafine grinded by function of compounding force field. Then added a little calcium carbonate powder into deionised water and ultrasonic dispersion for 5mins to get suspension. Last, absorbed a little suspension into laser particle size analyzer injector.

### 5. Grinding results under different technological conditions

Grinding time, the size and filling rate of media, the filling ratio of material all affect grinding results a lot. In Zirconia ceramic ball with diameter of 10mm and 20mm were chosen to compare in the experiment; the filling rate of media refers to volumetric coefficient that incompact media group account for grinding barrel, the filling ratio of material refers to the volume ratio of powder to the interspace among grinding media. According to reference[8], the filling rate of media normally ranges from 65% to 85%, and the optimal range of the filling ratio of material is between 90% and 103%. Therefore, this experiment chose material with 100% filling ratio. Meanwhile, filling rates of media 65% and 80% were experimented and their results were compared with, whose mass of powder are 500g and 600g accordingly.
5.1. Grinding media with diameter of 10mm

(1) The filling rate of media is 65%

When the filling rate of media is 65%, particle size varied with grinding time as shown in Fig.3 and Fig.4.

Fig.3 The relationship between $d_{50}$ and grinding time     Fig.4 The relationship between $d_{90}$ and grinding time

Fig.3 and Fig.4 show that, as time increased, the fineness of calcium carbonate became higher and higher. Particularly, in the prime of grinding, that is in the first 60 minutes, both the median diameter $d_{50}$ that splits the distribution with half above and half below this diameter and $d_{90}$ which shows how biggish size particles distribute all descended quickly. However, particle size changed little when it had descended to about 1.5μm. The reason is that the grinding media had wrapped in material, the motion of grinding media and material in the grinding barrel were hindered, which leads to the weakening of impact and grinding, as a result, the grinding effect decreased.

Fig.5(a) The distribution of particle size in 65% filling rate after grinding for 10 mins

Fig.5(b) The distribution of particle size in 65% filling rate after grinding for 40 mins
Three typical times of particle size distribution were picked out to show that: as grinding time increased, the difference of particle size became bigger and bigger. The peak moved to the left, which shows again that the fineness of calcium carbonate became higher and higher as time increased. The range of particle size distribution became increasingly narrow, which shows grinding accuracy rose significantly as grinding time increased.

It is showed in Fig.6 that the percentage of small size particles rocketed in the first 60 minutes, after that, all the particle size had declined below 5 μm. 7 hours later, there are about 22% particles whose size was less than 1 μm and changes tended to be stable.

(2) The filling rate of media is 80%
When the filling rate of media is 80%, particle size varied with grinding time as shown in Fig.7 and Fig.8.

![Fig.6 The relationship between particle proportion(percentage of less than 1μm and 5μm) and grinding time in 65% filling rate](image)

![Fig.7 The relationship between d50 and grinding time](image)

![Fig.8 The relationship between d90 and grinding time](image)
Fig. 7 and Fig. 8 show that, just like the results of 65% filling rate, as time increased, the fineness of calcium carbonate became higher and higher, in the first 60 minutes, both the median diameter $d_{10}$ and $d_{90}$ descended quickly. Particle size changed little when it had descended to about 1.5μm.

In addition, by comparing with 65% filling rate, it is concluded that in the prime of grinding that is the first 30 minutes, grinding effect in 65% is much better, while the effect reversed after that.
It is showed in Fig. 10 that the percentage of small size particles rocketed in the first 60 minutes, after that, all the particle size had declined below 5\(\mu\)m. 9.5 hours later, there are about 25% particles whose size was less than 1\(\mu\)m and changes tended to be stable.

By comparing with 65% filling rate, it is concluded that in the first 30 minutes, the percentage of small size particles raised slowly, while it is on the contrary after that.

5.2. Grinding media with diameter of 20mm

(1) The filling rate of media is 65%

When the filling rate of media is 65%, particle size varied with grinding time as shown in Fig. 11 and Fig. 12.

Fig. 11 and Fig. 12 show that, as time increased, the fineness of calcium carbonate became higher and higher. In the first 30 minutes, both the median diameter \(d_{50}\) and \(d_{90}\) all descended quickly. The decrease of particle size became slow in 30 mins to 60mins. After that, both \(d_{50}\) and \(d_{90}\) show opposite change tendencies, i.e., the particle size increased over time, which called inverse grinding. The reason is that material particle condensed when particle size had descended to a certain degree. Particle size descended to critical size quickly by grinding, and when the grinding continued, materials tended to condense, for intermolecular attraction was greater than crushing force.
It is clear to see the inflection point in the three typical times of particle size distribution. As grinding time increased, getting 60 mins as a inflection point, the difference of particle size became bigger at the first and then reduced, likewise, the peak moved to the left at the first and then reversed.
It is showed in Fig.14 that the percentage of small size particles rocketed in the first 60 minutes, then, all the particle size had declined below 5μm. After that, opposite tendencies turned up, the percentage of small size particles decreased irregularly as time increased.

(2) The filling rate of media is 80%

When the filling rate of media is 80%, particle size varied with grinding time as shown in Fig.15 and Fig.16.

Fig.15 The relationship between $d_{50}$ and grinding time  
Fig.16 The relationship between $d_{10}$ and grinding time

Fig.15 and Fig.16 show that, just like the case of 65% filling rate, in the first 30 minutes, both the median diameter $d_{50}$ and $d_{10}$ all descended quickly. The decrease of particle size became slow in 30 mins to 50mins. After that, inverse grinding appeared.

By comparing with 65% filling rate, it is concluded that its inflection point appeared much earlier and much higher, while its particle size rebounded less. In the first 50 minutes, grinding effect in 80% is much better, while reversed after that.
Fig. 17(b) The distribution of particle size in 80% filling rate after grinding for 50 mins

Fig. 17(c) The distribution of particle size in 80% filling rate after grinding for 9.5 hrs

Similarly, three typical times of particle size distribution were picked out, which shows that as grinding time increased, getting 60 mins as an inflection point, the difference of particle size became bigger at the first and then reduced, likewise, the peak moved to the left at the first and then reversed.

Fig. 18 The relationship between particle proportion (percentage of less than 1 μm and 5 μm) and grinding time in 80% filling rate

It is showed in Fig. 18 that the percentage of small size particles rocketed to about 97% in the first 50 minutes. After that, opposite tendencies turned up, the percentage of small size particles decreased irregularly as time increased.

By comparing with 65% filling rate, it is concluded that the percentage of small size particles raised quickly, while it is on the contrary after the inflection point.
5.3. Results comparison of mill balls with 2 kinds of diameter

(1) Opposite tendencies turned up in the two group filling rates when the media is 20mm diameter mill ball. However, it didn’t happen when 10mm diameter mill ball acted as the media; (2) Both the smallest particle size it can achieve and the decrease velocity of the particle size all show that the grinding effect of 10mm diameter mill ball is better; (3) From the perspective of the minimum particle size can be, the grinding effect of 65% filling rate is always better, no matter the diameter of media is 10mm or 20mm.

6. Conclusion

Get the conclusion through researching of experiments on superfine grind process of calcium carbonate: (1) the vibrated mill was used to grind analytically pure calcium carbonate, in the first 60min, the particle size of material decrease to about 2 μm quickly, then slow down even reversed in 60 min to 7hrs; (2) Different degrees of inverse grinding appeared when the media is 20mm diameter mill ball, so the grinding should be cease when the particle size reach critical value in superfine grind, in order to save energy consumption while get the smaller particle size; (3) Grinding time, grinding media size and filling rate affect the grinding effect. The best process condition is the parameter combination that 10mm diameter grinding ball, 65% filling rate and 500g powder quality.

Acknowledgements

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References