IJISET - International Journal of Innovative Science, Engineering & Technology, Vol. 4 Issue 5, May 2017
ISSN (Online) 2348 – 7968 | Impact Factor (2016) – 5.264
www.ijiset.com

Preparation of Stable Suspensions for Production of Submicron Particles in Stirred Media Mill

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Abstract

Due to the possibility to achieve higher product homogeneity and thus higher product quality by the use of submicron particles in a diverse range of applications such as pigments, minerals ceramics, medicines, electronic materials, inks etc. is continuously increasing. One key criterion which is important across these range applications is suspension stability. Amongst different available methods, production of submicron particles using the top down approach by a wet grinding process is a very promising technique. Stirred mills are widely used for the said purposes due to their energy efficiency for desired product fineness compared with the conventional mill systems. In the present work, suspension stability of calcite ($CaCO_3$, d50=5.4 µm) samples was studied by measuring pH as a function of grinding time in a wet milling process. The experiments were conducted at different grinding times and the behaviour of suspension stability in wet submicron grinding with variation of pH was investigated.

Keywords: *Calcite, stirred media mill, zeta potential, suspension stability*

1. Introduction

In these days, the industrial demand for submicron particles increased a lot due to the specific properties of nanoparticles, particularly in the chemical and pharmaceutical industries where products with high homogeneity or solubility are often required. Among product properties, particle fineness, expressed by the median size or average particle size is of prime importance [1]. One way to produce submicron particles is wet grinding in stirred media mills. Submicron particles production using stirred media mill is very efficient technique for the large scale production of submicron particles. In general, there are two methods for production of submicron particles. (i) Bottom-up that the material is synthesized by means of chemical reactions (ii) Top-down that coarse particle sizes are ground to produce fine particle sizes.

In the past times, many researchers have studied various aspects of wet grinding process. Nowadays, it is known to a substantial extent how different operating parameters such as size, shape, media loading, the speed of mill and feed rate may effect size reduction process in stirred mills under certain conditions. Much of the published work reported on the effect of operating conditions in an stirred media mill [2-11]. Sakthivel et al. [12] mentioned that it is difficult to grind for a longer time due to the formation of paste even ultimately of cake.

Suspension stability of inorganic particles is directly dependent upon the pH, and thus submicron particles can be stabilized by adjusting the pH in order that particles have equal

electrical charges. If particles are equal charges, interactions between them are repulsive and can be measured by means of zeta potential, , *ζ-pot*, which is defined as surface potential at an electric double layer consisting of a compact layer and a diffuse layer. The higher the zeta potential is, the higher is the electrostatic repulsion between the particles [13, 14]. At a zero zeta potential, i.e. at the iso-electric point *IEP*, the particles tend to flocculate. It has been found in many studies that viscosity is highest at the iso-electric point and is lower for values far away from this point [2, 15-17]. When stabilizing $CaCO_3$ particles it should be remember that this material is sensitive to pH changes: calcite begins to dissolve below pH=7, leading to a decrease in the concentration of the solid phase, whereas it is positively charged in the pH range 7–10 and its surface becomes negatively charged when the pH is above 10 [18]. Production of submicron particles reported by Mende et al. [19] and Stenger et al. [20] in stirred media mill showed that electrostatic stabilization appears to be the key factor to producing stable submicron suspensions in stirred ball mill.

The aim of the present work is to investigate the behavior of suspension stability in wet grinding of calcite with variation of pH.

2. Experimental

2.1. Materials

Calcite ($CaCO_3$, d50=5.4 µm) powders that obtained from Mikron's (Nigde, Turkey) was used for experiments. Chemical composition and physical characteristics of the calcite samples are shown in Table 1 and Table 2, respectively. The SEM image of feed calcite is represented in Fig. 1. All the suspensions were prepared in the pure water. High density (6000 kg/m^2) yttria stabilized zirconia (ZrO_2) grinding media (chemical composition: 93% ZrO_2, 5% Y_2O_3 and 2% others) purchased from Cenotec Co., Ltd, Korea, were used for the submicron grinding experiments.

Table 1: Chemical composition of the calcite used in experiments (wt %)

$CaCO_3$	$MgCO_3$	SiO_2	Fe_2O_3	Al_2O_3	LOI
99.5	0.2	0.01	0.01	0.02	0.26

Table 2: Physical characteristics of the calcite samples

Real density (kg/m^2)	Mohs hardness	Refractive index	d10 (µm)	Average particle size d50 (µm)	Specific surface area (m^2/g)
2700	3.0	1.59	0.986	5.4	2.26

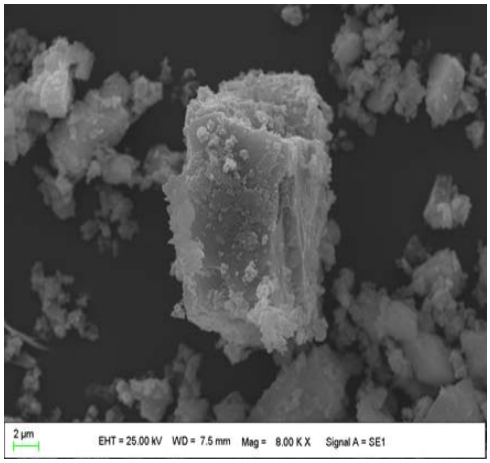

Fig. 1 SEM image of feed calcite.

2.2. Methods

Grinding tests were carried out in a vertical type stirred media mill Standard-01 Model manufactured by Union Process (U.S.A.) (Fig. 2). The net volume of the milling chamber is 0.75 Lt. In order to reduce the amount of wear from materials of the mill, the grinding chamber is made of ceramic (Al_2O_3). For cooling purposes, the grinding chamber is also equipped with a water jacket for cooling. The heat generated during wet grinding process must be dissipated by circulating cooling water through the grinding container jacket. In this work, solid mass fraction (cm) = 0.25, stirrer-tip speed (vt) = 600 rpm, grinding media size=1 mm and grinding media loading (J) = 70%, grinding time 60, 90, 120, 180 and 300 min. The initial pH of the sample was taken down to be 9.83. All these parameters were selected based on our preliminary experiments and capabilities of mill system.

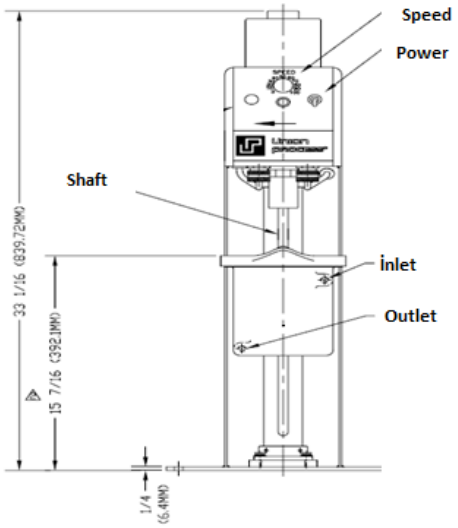

Fig.2 The schematic diagram of stirred mill.

2.3. Characterization

The particle size measurements of the ground sample and feed were carried out by Mastersizer 2000 (Malvern Ltd., UK). Mastersizer 2000 (manufactured by Malvern Instruments Ltd.) was used as a laser diffraction apparatus in this study. The equipment can measure the particle size of suspensions and dry powders. Before determining particle size, samples of the suspensions to be diluted. Malvern declares that the equipment can measure the particle size between 20 nm to 2000 μm under certain conditions. For zeta- potential measurement, using Zetasizer (Malvern Ltd., UK), calcite samples were prepared at different pH values by drop wise addition of 1M NaOH and 1M HNO_3. The pH of the suspension was measured by a table type digital pH meter.

3. Results and discussion

3.1. Effects of grinding time on submicron grinding

Particle size distributions of the product were measured at grinding time of 60, 90, 120, 180 and 300 min. Other operating conditions were kept constant and the results of experiments carried out to compare the wet grinding performances of different grinding times are given. Grinding results were represented in Fig. 3. It can be clearly seen that average particle size decreases with time up to a grinding time of 120 min but after 120 min of grinding, the average particle size (d50) has increased from 0.2670 μm to 1.088 μm. The similar situation also occurred between d10 and grinding time.

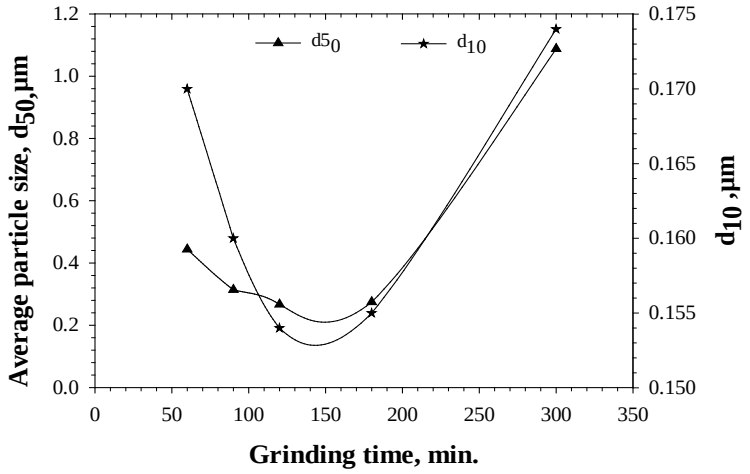

Fig. 3 Effect of grinding time on average particle size.

Fig. 4 shows that there is reversal of the positioning of the size distribution curves shifts to coarse particle size after 120 min of grinding time. This indicates that particles start to agglomerate with excessive grinding.

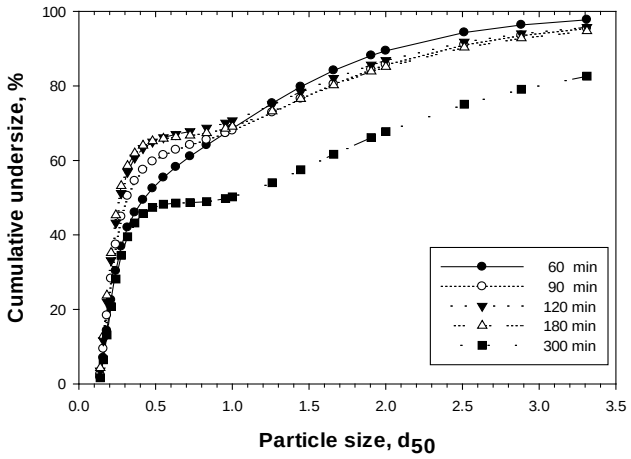

Fig. 4 Effects of grinding time on the cumulative undersize.

Stenger and Peukert [21] explained that behaviour of suspensions of submicron particles as mainly influenced by particle-particle interactions. With decreasing average particle size the inter particle attractive forces become increasingly primary, leading to agglomeration upon collision, which can importantly influence the grinding behaviour to extend a grinding limit. Agglomeration can make agglomerates bigger than the initial unbroken particles, which may be powerful enough to withstand further grinding process. This event, known as re-agglomeration, tends to neutralize the grinding process. To overwhelm this difficulty, the suspension in the mill has to be stabilized by creating repulsive forces between particles.

3.2. Effects of grinding time on pH of the suspension

To make out why particles do not get smaller mean particle size with grinding time, the samples of suspension were taken from the mill at grinding time of 60, 90, 120, 180 and 300 min and the pH values were measured table type digital pH meter. The pH meter was calibrated against certified buffer solutions supplied by Mettler Toledo. Fig. 5 shows the outcomes of pH measurements and temperature at different grinding times. Other operating conditions were kept constant.

It is evident from Fig. 5, the increase in grinding time from 60 to 300 temperatures from 25 to 29.1 C° and the reduction of pH value from 8.28 to 8.14 µm. The pH value decreased with grinding time from initial value of 9.83.

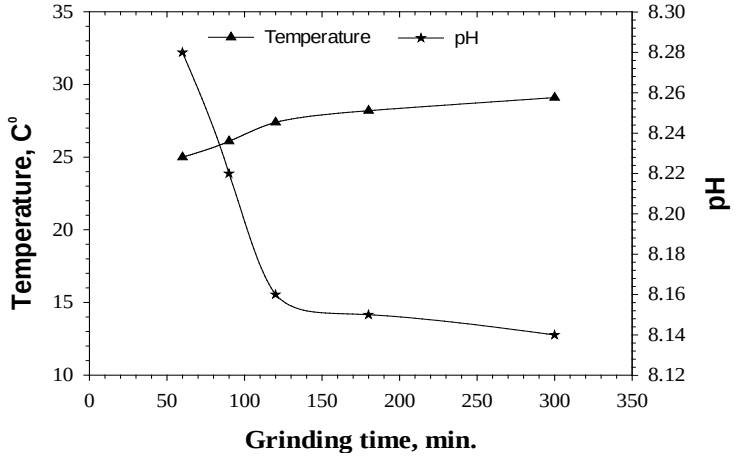

Fig. 5 Effects of grinding time on pH and temperature.

3.3. Zeta potential (ζ-Pot.)

Electrostatic repulsion can be measured by means of the zeta potential, *ζ-pot.*, which is one of the main parameters known to affect suspension stability. The higher zeta potential is, the higher is the electrostatic repulsion between the particles. The pH of a suspension decreases with grinding time may be related to suspension stability therefore *ζ- pot*. needs to be measured. The results of the measurement are shown in Figure 6. It shows that as pH increases from 2 to 11 *ζ- pot*. value also changes from +9,15; -17 mV. Vallar et al. [14] indicated that higher zeta potential values were get at higher pH values. The *ζ- pot*. value -17 mV suggests a strong inter-particle repulsive force that presents good stability and maximum electrostatic repulsion occurs at pH value 11. The iso-electric point (IEP) was get at pH around 3.3. As IEP approaches, the particles are easily aggregated and result into increase in particle size.

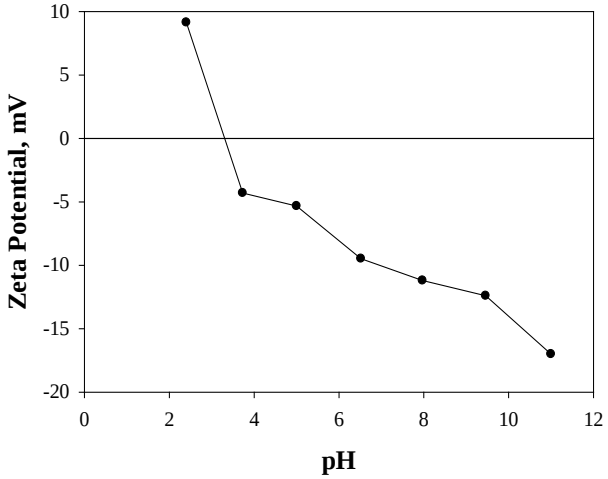

Fig. 6 ζ- Potential as function of pH for calcite.

4. Conclusions

In this study, the grinding behaviour of submicron particles and suspension stability with grinding time were investigated in stirred mill. The followings were found out:

- Experimental results show that particles start to agglomerate after 120 min.
- It is evident that pH of the suspension changes with grinding time and influences the suspension stability as a result of that affects size reduction.
- The higher the zeta potential with the same polarity, higher will be the electrostatic repulsion between particles.
- Stable suspension stability conditions are crucial to produce submicron particles in wet grinding.

Acknowledgments

The authors would like to thank the Ömer Halisdemir University Scientific Research Projects Directorate (Project No. FEB 2015/18) for funding of this research work. And they acknowledge Mikron's Company for providing of sample of this study.

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