Effects of concentration of dispersions on particle sizing during production of fine particles in wet grinding process

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A B S T R A C T

Stirred media milling is a prospective technology for producing colloidal dispersions by means of wet grinding process. In the past, many researchers have studied the effects of different operating parameters such as size, shape, nature and quantity of grinding medium, the speed of agitator in grinding chamber, the feed rate of dispersions, etc. in stirred media mills. However, it is still less known how particle sizing which generates valuable information of particle size of the product to interpret, control and optimize the grinding process, is influenced by the concentration of the dispersion during stirred media milling where particles change their size from micron to colloidal range rapidly. One of the reasons of this lack had been our incapability in the past to study the particle size distribution of dispersions without dilution. The recent advent of acoustic attenuation spectroscopy is known to be capable of studying dispersions without dilution, under real process conditions and on line. The study employs acoustic attenuation spectroscopy to investigate the effects of concentration of dispersions of $CaCO_3$ on its particle sizing during size reduction process in a stirred media mill (LabStar manufactured by NETZSCH). The dispersions of $CaCO_3$ at 5%, 10%, 20% and 30% (m/m) were studied about six hours under a selected set of operating conditions. Contrary to the existing knowledge obtained through other techniques of particle sizing that are based on the principle of dilution, acoustic attenuation spectroscopy shows that, under certain grinding time at given operating conditions, increase in concentration of dispersion results in better grinding results yielding smaller particles. The causes behind the differences in results of acoustic attenuation spectroscopy and dynamic light scattering have been thoroughly investigated. We find certain limitations of acoustic attenuation spectroscopy in particle sizing. A typical phenomenon which causes misleading trends in particle sizing is multiple scattering in acoustic measurements. Multiple scattering, particularly, influences acoustic results when particles approach to fine size range during size reduction process.

1. Introduction

Many industries such as of paints, dyes, cosmetics, pharmaceuticals, ceramics, micro-electronics, etc. employ colloidal dispersions in fabrication of many products. The demand of such industries for stable colloidal dispersions is on increase because use of fine particles may improve homogeneity, solubility, strength, reactivity etc. In general, there are two approaches for production of fine particles: (i) Bottom-up (in which fine particles may be produced by a reaction, condensation or aggregation of molecules, etc.). (ii) Top-down (in which coarse particles are ground to produce fine particles). Wet grinding is often employed for production of fine and ultrafine particles suspended in a liquid. The stirred media milling is a prospective technology in domain of wet grinding because of many advantages such as relative low agglomeration tendency, low material losses, less possibility of oxidation, easy handling of toxic materials, elimination of need of employing a device for air cleaning, elimination of the problem of dust explosion, better heat transfer options, etc. In the past, many researchers have studied various aspects of wet grinding process. Today, it is known to a considerable extent how different operating parameters such as size, shape, nature and quantity of grinding medium, the speed of agitator in grinding chamber, and the feed rate of dispersions may affect size reduction process in stirred mills under certain conditions. However, it is still less known how particle sizing which generates valuable information of particle size of the product to interpret, control and optimize the grinding process, is influenced by the concentration of a dispersion during stirred media milling where particles enter from micron to colloidal size rapidly. One of the reasons of this lack had been our incapability in the past to study the particle size distribution of dispersions without dilution. The techniques of particle sizing based on principles of laser diffraction, dynamic light scattering, etc., may measure the particle size of dispersion but they require the sample to be diluted before measurement. The dilution step may result in

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destabilization of dispersion, formation or deformation of flocs and/or aggregates etc. All the techniques based on the dilution step have a risk of not showing the right information of particle size which is quite important in understanding, controlling, designing and optimizing the grinding processes.

Acoustic attenuation spectroscopy, which has appeared, relatively, in the recent past, is considered a solution for such problems. Different reviews on the technique explain that it has advantages over many existing techniques because of a wide range of particle sizing (10 nm to 1000 μm), because of being non-destructive, non-invasive and capable of measuring dispersions on line, at real process conditions and without dilution till a concentration of 50% (m/m) under certain conditions [1,2]. The technique has been employed in many studies for different applications. For example, Richter et al. [3] employ it for characterization of polydisperse particles in micrometer range, Stolojanu and Prakash [4] consider it for characterization of slurry systems, Tourbin and Frances [5] monitor aggregation process of dense colloidal silica suspensions with this technique. Takeda and Goetz [6] and other researchers like Hibberd et al. [7] use the technique for characterization of flocculation in different applications. The applications of the technique in domain of crystallization may be consulted in the work of Hipp et al. [8], Mougin et al. [9], Li et al. [10], etc. However, sufficient work has not been performed yet in application of the technique in fine wet grinding processes which are typical in the sense: (i) The change in average particle size of the product is rapid in the grinding mill due to breakage of particles. (ii) The degree of polydispersity changes with time in grinding process. (iii) The nature of interaction between particles is non-colloidal before grinding operation which changes to colloidal with increasing grinding time. This study is an attempt to explore such complexities. In particular, we investigate how different concentrations of a dispersion influence particle sizing during production of fine particles in wet grinding process carried out by means of a stirred media mill.

2. Fundamentals of the techniques of particle sizing

2.1. Acoustic attenuation spectroscopy

When a sound wave of certain frequency is passed through a particulate system, it interacts with the particles (transmission, reflection, absorption, scattering etc.) and as a result it undergoes attenuation (decrease in amplitude) that can be measured in terms of attenuation coefficient. It is defined as a decrease in the amplitude of the sound wave per unit distance travelled and may be expressed as [2]:

$$\alpha = -\frac{1}{x}\ln\frac{A_x}{A_0} \quad (1)$$

where A_0 is the initial amplitude of the sound wave ($x=0$) and A_x is the amplitude after it has travelled a distance x as illustrated in Fig. 1.

If a band of sound waves of different frequencies is passed through dispersion from a certain distance (x), the attenuations in each sound wave of certain frequency may be calculated using Eq. (1). An acoustic attenuation spectrum describes acoustic attenuation constants

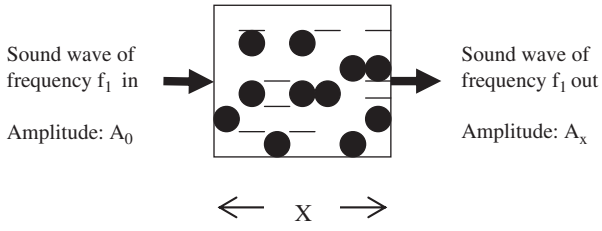

Fig. 1. Passage of a sound wave through dispersion.

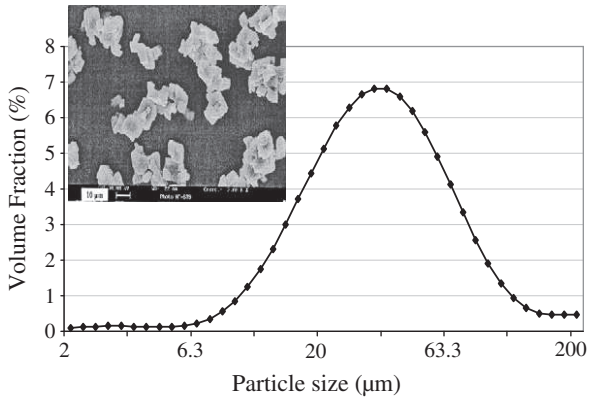

Fig. 2. Particle size distribution and shape of $CaCO_3$ used.

expressed as a function of frequencies of sound waves. There are two major steps in particle sizing by acoustic attenuation spectroscopy: (i) development of an acoustic attenuation spectrum. (ii) Interpretation of the resulting acoustic spectrum in terms of particle size distribution using an appropriate theory. A commercial acoustic attenuation spectrometer has appropriate arrangements for measurement of attenuation spectrum. Moreover, it has an appropriate software program to interpret acoustic attenuation spectrum in terms of particle size distribution based on some appropriate theory such as ECAH. This theory is based on differential wave equations that have been derived from fundamental laws of conservation of mass, energy, momentum, thermodynamic equations of state and stress–strain relations for isotropic elastic solids (or viscous fluids). The details of ECAH theory may be studied in papers of Epstein and Carhart [11] and Allegra and Hawley [12] who contributed to the development of this theory.

2.2. Dynamic light scattering

Dynamic light scattering is also known as photon correlation spectroscopy. The basic principle of this technique is when particles are illuminated with laser; the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles. Smaller particles are pushed further by the solvent molecules and move more quickly. Analysis of these intensity fluctuations gives the velocity of the Brownian motion and thus the particle size using the Stokes–Einstein relationship. Dynamic light scattering measures hydrodynamic diameter which refers how a particle diffuses within a fluid. Hydrodynamic diameter is the diameter of a sphere that has the same translational diffusion coefficient as the particle being measured.

3. Materials

The aqueous dispersions of calcium carbonate were used in grinding, in this study. Availability of good literature on dispersing behavior of $CaCO_3$, its non-corrosive nature, low hazards and

Table 1
Compositions of dispersions used.

	Disp. 1	Disp. 2	Disp. 3	Disp. 4
% Concentration (m/m)	5.000	10.000	20.000	30.000
% Concentration (v/v)	1.934	3.997	8.565	13.837
Water (g)	1700	1700	1700	1700
$CaCO_3$ (g)	89.47	188.89	425	728.57
Sodium polyacrylate (g) (8% of mass of $CaCO_3$)	7.158	15.111	34.000	58.286

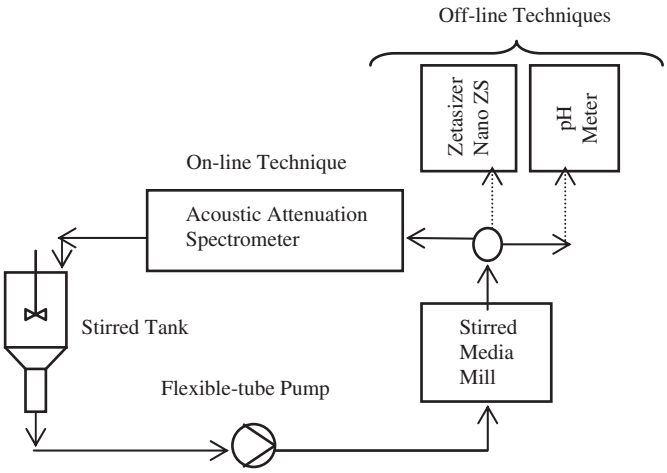

Fig. 3. Experimental setup.

reasonable price make it, relatively, a good choice as a material of grinding in our study.

3.1. $CaCO_3$

It was procured through Merck KGaA Germany. It had purity >99%, density = 2.656 g/cm^3 at 20 °C, thermal decomposition >825 °C, specific surface area (BET) = 0.5 m^2 g^{-1} and hardness in the Mohs scale = 3. Its mean particle size (in dry form) was found to be 30 μm using technique of laser diffraction (Malvern Mastersizer). Its particle size distribution, as shown in Fig. 1, explains that most of the particles had a size between a few microns and one hundred microns. To study the shape of $CaCO_3$, scanning electron microscopy (SEM) was employed. It was observed that the product is constituted by compact aggregates made of rhombohedral particles of about 30 μm in size, as shown in Fig. 2. A reasonable agreement was found in the results of both techniques.

3.2. Sodium polyacrylate

It was used as a dispersing agent. Foissy et al. have demonstrated its ability to disperse the particles of $CaCO_3$ in water [13]. It is based on anionic polyacrylate with a flexible chain able to form mono or bi coordinated complexes with the calcium ions of the solution. In ultrafine wet grinding for aqueous dispersions of $CaCO_3$, Garcia et al. have shown its suitability as a dispersing agent [14]. It was procured through Sigma-Aldrich Co. It had density of 0.55 g/cm^3 at 25 °C and average Mw ~ 5100 (determined by gel permeation chromatography (GPC)).

Table 2
Physical properties at 25 °C used in calculations for particle sizing.

$CaCO_3$	
Density (g cm^{-3})	2.6560
Sound speed (cm s^{-1})	5.5600×10^5
Thermal dilation (°C^{-1})	2.2130×10^{-6}
Thermal conductivity (erg cm^{-1} s^{-1} °C^{-1})	2.2594×10^5
Heat capacity (erg g^{-1} °C^{-1})	8.3680×10^6
Shear rigidity (dynes cm^{-2})	3.0800×10^{11}
Water	
Density (g cm^{-3})	9.9524×10^{-1}
Sound speed (cm s^{-1})	1.4970×10^5
Thermal dilation (°C^{-1})	2.5677×10^{-4}
Thermal conductivity (erg cm^{-1} s^{-1} °C^{-1})	5.9525×10^4
Heat capacity (erg g^{-1} °C^{-1})	4.1785×10^7
Viscosity (poise)	9.0300×10^{-3}

Table 3
Set of fixed operating parameters.

Grinding media	Zirconium oxide beads stabilized by yttrium
Size of grinding media	300–500 μm
Density of grinding media	3.7850 g/cm^3
Volume of grinding media	415 ± 2 cm^3
Volume of grinding chamber	670 cm^3
Flow rate of dispersion	4.82 ± 0.1 cm^3/s
Grinding system	Zeta
Speed of stirrer in grinding chamber	1500 rpm
Speed of agitator in stirred tank	600 rpm
Separating cartridge (filter)	100 μm
Temperature	25 °C

3.3. H_2O

Water served as dispersion medium in the dispersions employed in the study. Ultrapure water was produced by the equipment "Purelab Ultra" of VWS (UK) Ltd. Its density was found to be 0.9952 g/cm^3 at 25 °C where as its pH varied between 6.3–6.8 at 25 °C.

4. Experimental setup

Four dispersions, as mentioned in Table 1, were studied individually for about 6 h in wet grinding process carried out in a stirred media mill that is commercially known as LabStar and manufactured by NETZSCH.

In each of the four cases, the dispersions (suspensions) were prepared in conical flask. Sodium polyacrylate was first dissolved in water with the help of a magnetic stirrer followed by addition of $CaCO_3$. All dispersions were agitated at 1100 rpm. for about 20 min at 25 °C before transferring them to a stirrer tank for starting comminution. Fig. 3 shows the experimental setup that provides a circuit mode comminution of the product.

In general, in each of the four cases, the dispersion was pumped through the stirrer tank to the inlet of the grinding chamber of the stirred media mill (LabStar) with the help of flexible-tube pump. After experiencing a certain comminution in grinding chamber, the dispersion left through a steel (Cr–Ni–steel) separating cartridge (filter) that was installed at out let of the grinding chamber. The dispersion was recycled to the stirred tank after being passed through the acoustic attenuation spectrometer for online measurement of particle size in real environment (i.e. without need of dilution, on line and at process conditions). We had access to an acoustic attenuation spectrometer called Malvern Ultrasizer to measure the acoustic attenuation spectra of the dispersions and determining particle size distributions. The full details of the equipment are mentioned in US patent No. 5,121,629 3 [1]. Table 2 shows the set of physical properties (matrix) that was used in determination of particle size distributions using the software of the acoustic attenuation spectrometer. In

Table 4
Aqueous dispersions of $CaCO_3$ mixed with different proportion of coarse and relatively fine particles.

Dispersion no.	H_2O	$CaCO_3$ (30 μm)	$CaCO_3$ (1.6 μm)
	g	g	g
(1)	700	200	0
(2)	700	0	5
(3)	700	0	25
(4)	700	0	50
(5)	700	0	100
(6)	700	0	150
(7)	700	200	5
(8)	700	200	25
(9)	700	200	50
(10)	700	200	100
(11)	700	200	150

particle size determination by Malvern Ultrasizer, "spectral quality" and "residual" are two important quality parameters that must be ≤5 for acceptable results. All acoustic measurements in the study meet quality criteria.

From the outlet of the grinding mill after certain intervals of time, the samples of the product were taken manually to analyze with pH meter and Zetasizer Nano ZS. The latter is manufactured by Malvern Instruments, works on principle of dynamic light scattering and measures zeta potential and particle size distribution of dilute samples. A reasonable repeatability was found in all the measurements taken by Malvern Ultrasizer, Zetasizer Nano ZS and pH meter. In the grinding mill (LabStar), torque and number of revolutions were measured by a torque sensor that was installed at a stirrer shaft by the manufacturer of the mill. The problem of contamination of the product by the materials of the mill had been reduced in the grinding chamber by lining with Cr–Ni-stirred walls and equipping the agitator shaft with tungsten-carbide pegs. The core objective of the experiments was to study the influence of concentrations of dispersions (as mentioned in Table 1) on particle sizing of the product obtained after certain times under a set of fixed operating parameters as described in Table 3.

The residence times in case of 5%, 10%, 20% and 30% (m/m) aqueous dispersions of $CaCO_3$ were 52.3 min, 50.8 min, 47.6 min and 44.0 min respectively.

5. Results and discussion

5.1. General considerations in particle sizing

It has been discussed that particle sizing in fine wet grinding process is typical in the sense: (i) the change in average particle size of the product is rapid due to relatively fast breakage of particles. (ii) The degree of polydispersity in product changes with grinding time. (iii) The nature of interaction between particles is non-colloidal before grinding process; this interaction becomes colloidal after a certain grinding time. In our preliminary work (i.e. before experiments of stirred media milling), we have verified suitability of acoustic attenuation spectroscopy for measuring the changes discussed in (i) and (ii) by taking into consideration different dispersions prepared with different proportions of coarse $CaCO_3$ (30 μm) and relatively fine $CaCO_3$ (1.6 μm), as mentioned in Table 4.

Acoustic attenuation spectroscopy is capable of detecting the changes in dispersions due to increase in quantity of fine particles, and due to variation of proportion of relatively fine particles. Fig. 4(a) and (b) demonstrates this respectively.

The results have been further verified. We describe the method of verification with the help of an example that focuses on dispersion nos. (1), (6) and (11) referred in Table 4. For these dispersions, acoustic attenuation spectra were determined with the help of acoustic attenuation spectrometer. M. Tourbin and C. Frances [15] have given the expression for the attenuation spectrum of water as a function of frequency (f) as:

$$\alpha_w(f) = (0.0047f^2 - 0.0083f). \quad (2)$$

From the acoustic attenuation spectra of each dispersion, the acoustic contribution of water was subtracted in order to get the acoustic attenuation spectra merely due to particles present in the dispersions. Fig. 4(c) represents resulting acoustic attenuation spectra corresponding to (I) 200 g of $CaCO_3$ (30 μm), (II) 150 g of $CaCO_3$ (1.6 μm) and (III) a mixture of 200 g of $CaCO_3$ (30 μm) and 150 g of $CaCO_3$ (1.6 μm). If the sum of the acoustic attenuation spectra of (I) and (II) is equal to acoustic attenuation spectrum of (III), then it may be considered that the technique is able to detect the presence of both fine and coarse particles. Fig. 4(d) compares the sum of acoustic attenuation spectra of (I) and (II) with acoustic attenuation spectrum of (III). The reasonable agreement in the results confirms the

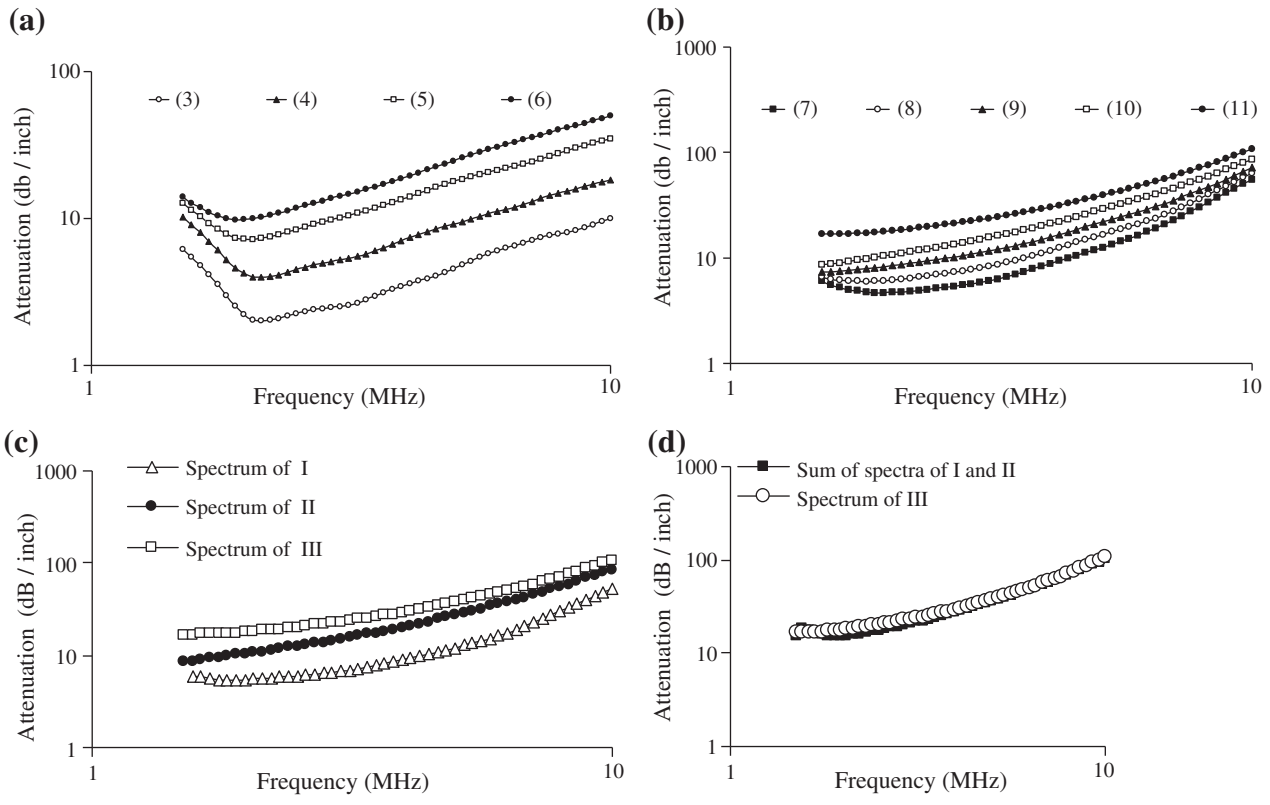

Fig. 4. (a): Changes in acoustic spectra due to increase in quantity of relatively fine particles. (b): Changes in acoustic spectra due to changes in proportion of relatively fine particles. (c): Acoustic spectra corresponding to different disperse media. (d): Comparison of acoustic attenuation spectra.

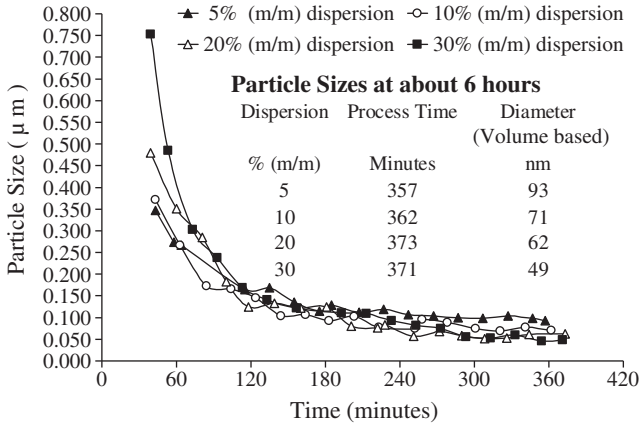

Fig. 5. Particle sizes measured by acoustic attenuation spectroscopy during size reduction process in stirred media mill.

suitability of acoustic attenuation spectroscopy for measuring the changes discussed in (i) and (ii).

5.2. Effects of concentration of dispersions on particle sizing during wet grinding

5.2.1. Particle sizing by acoustic attenuation spectroscopy

It has been mentioned that grinding experiments were planned to study the effects of concentration of aqueous dispersions of $CaCO_3$ at varying proportions (i.e. 5%, 10%, 20%, and 30% (m/m)). The particle sizing of aqueous dispersion of $CaCO_3$ was carried out online, at real process conditions and without diluting the sample by means of acoustic attenuation spectroscopy. The results of average particle size of the dispersions obtained at different grinding times have been mentioned in Fig. 5.

In the beginning of the grinding process (i.e. first hour), the comparative study reveals that the higher the dilution of a dispersion, the smaller its average particle size (i.e. use of dilute dispersion favors the process of size reduction). With time, when particles undergo further size reduction, a change in tendency is observed. From the second to sixth hour of grinding, it is evident that dispersion of 5% (m/m) has bigger average particle size in comparison with all other dispersions. From the second to third hour of grinding, the dispersion of 10% (m/m) mostly shows the least average particle size as compared to all other dispersions. The change in trend becomes more evident from the 3rd to 5th hour of grinding where dispersion of 20% (m/m) shows mostly least

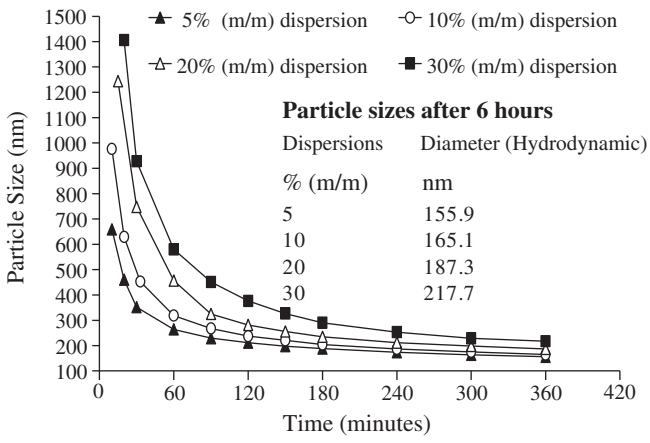

Fig. 6. Particle sizes measured by dynamic light scattering during size reduction process in stirred media mill.

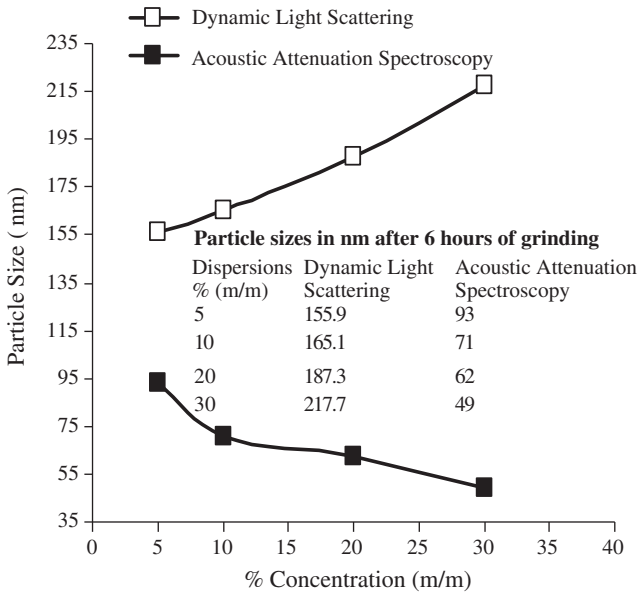

Fig. 7. Particle sizes of the dispersions measured by two different techniques after about 6 h of grinding.

average particle size in comparisons to other dispersions. The sixth hour of grinding shows a completely inverse trend as compared to the trend observed in beginning of the grinding process (i.e. the higher the concentration of a dispersion, the smaller its average particle size) or in other words, the use of concentrated dispersions favors the process of size reduction.

5.2.2. Particle sizing by dynamic light scattering

The technique of dynamic light scattering is different from acoustic attenuation spectroscopy in two major aspects: (i) it measures the particle size of dispersions in dilute state. (ii) The particle size measured by this technique is hydrodynamic and not volume-based as in acoustic attenuation spectroscopy. Fig. 6 demonstrates the results of average particle size of the dispersions obtained at different grinding times.

The results explain that size reduction process is favored by the use of dilute concentrations. The trend remains un-changed throughout the grinding process.

5.3. Causes of different trends

Techniques of acoustic attenuation spectroscopy and dynamic light scattering generate different results in terms of numerical values and trends as shown in Fig. 7.

In the absence of scientific explanation of such opposing trends, one may get misled during the process of controlling, designing and optimizing the wet grinding process for production of fine particles. It is, therefore, important to investigate the roots of the problem that may lie in the process of particle sizing. The following hypotheses were developed in order to investigate the problem. H1: Different

Table 5
Debye length and diameter of particle (D) at 25 °C in different dispersions.

Dispersion% (m/m)	Moles of electrolyte	Concentration (mol/L)	1/k (nm)	D_H (nm)	D (nm)
5	0.00140	0.000826	10.5800	155.9	134.7
10	0.00296	0.001743	7.2818	165.1	150.5
20	0.00667	0.003922	4.8545	187.3	177.6
30	0.01143	0.006723	3.7077	217.7	210.3

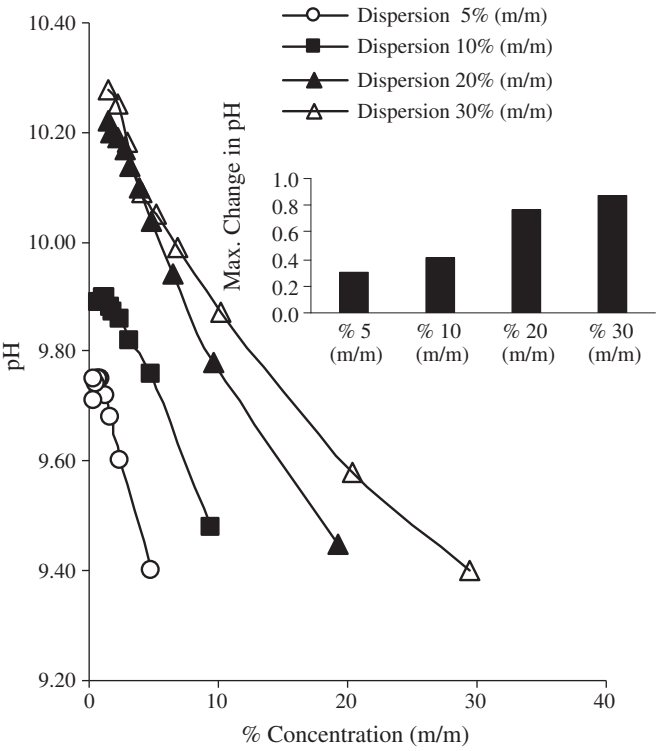

Fig. 8. Changes in pH during dilution of dispersion after grinding.

trends are due to different types of diameters of particles measured by two different techniques of particle sizing. H2: Different trends are due to dilution of samples, in case of particle sizing by dynamic light scattering, which changes the particle size generating misleading information. H3: The two different trends are due to multiple scattering in acoustic measurements that generates misleading information.

5.3.1. Effects of different diameters on measurements

The diameter of particles measured by dynamic light scattering is hydrodynamic diameter. Based upon the theory behind the technique (Section 2.2), hydrodynamic diameter may be regarded as the diameter of the particle plus the thickness of the layer of ions surrounding the particle, at both ends of the diameter [15]. Approximately, $D_H = D + 2/k$ (where D_H = hydrodynamic diameter, D = diameter of particle and 1/k = thickness of layers of ions around the particle, known as Debye length) [15]. The value of the thickness of the layer of ions (from both ends of diameters) may be subtracted from the hydrodynamic diameter in order to get diameter of the particle (D). The method proposed by Israelachivili for the calculation of Debye length was employed [16]. For the electrolytes at 25 °C

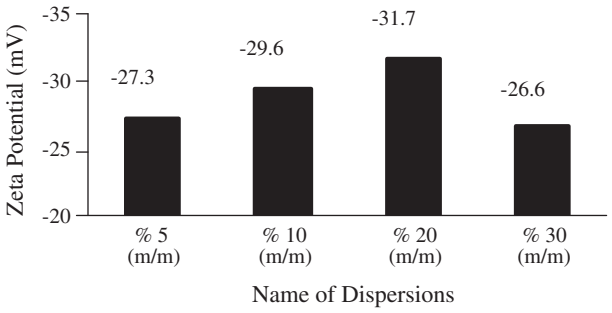

Fig. 9. Zeta potential for the dispersions measured after 6 h of grinding.

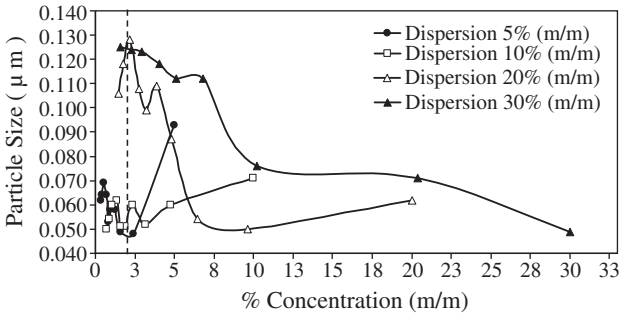

Fig. 10. Particle sizes studied by acoustic attenuation spectroscopy on diluting the dispersions after grinding experiments.

involving monovalent cations and anions (such as sodium polyacrylate), the following equation may be used for calculation of Debye length [16]:

$$\frac{1}{\kappa} = \frac{0.304}{\sqrt{[Electrolytes]}} \quad (3)$$

where 1/k = thickness in nanometers of layers of ions around particle known as Debye length, and [electrolytes] = concentration of the electrolyte in moles/litre. The magnitude of Debye length depends solely on the properties of the liquid and not on any property of the surface such as its potential or charge [16]. Table 5 shows the results for diameter of particles (D) at 25 °C when particles of $CaCO_3$ (insoluble) are surrounded by sodium polyacrylate (electrolyte).

The results demonstrate that the trend (i.e. use of dilute dispersions favors size reduction) as observed in Fig. 6 (in case of dynamic light scattering) remains the same even after subtracting the Debye lengths from the results of dynamic light scattering.

5.3.2. Effects of dilution

Acoustic attenuation spectroscopy and dynamic light scattering when employed for studying the effects of concentration on particle size in wet grinding, yielded two different trends disabling us to reach a conclusion. Particle sizing by dynamic light scattering requires the samples to be diluted before measuring the particle size. The step of dilution may change the particle size leading to different trends. In order to investigate, all the dispersions (5%, 10%, 20%, and 30% (m/m)) obtained after grinding experiments were diluted gradually. In principle, the zeta potential may show the stability of a dispersion indicating any change in particle size or otherwise; but the option could not be employed as measurement of zeta potential itself with Zetasizer Nano ZS require dilute of the sample. Therefore to study the change in particle size with dilution, pH values and acoustic spectra were measured at each step of dilution. The maximum changes in pH

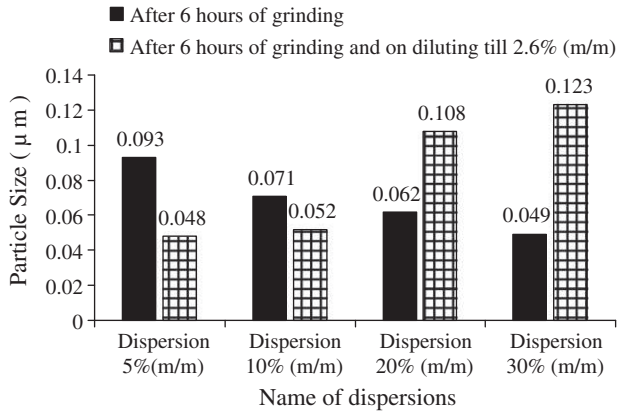

Fig. 11. Comparative study of particle sizes by acoustic attenuation spectroscopy.

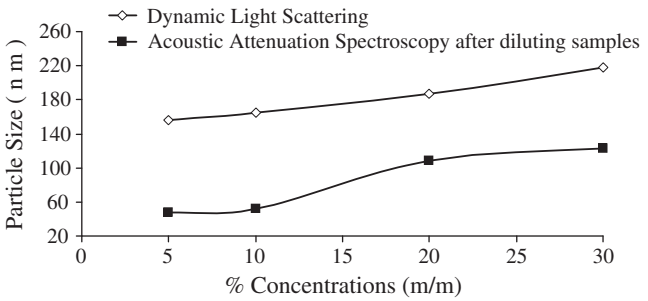

Fig.12. Comparative study of particle sizes by two different techniques after dilution.

values were found to be 0.31, 0.41, 0.77 and 0.88 respectively in the process of dilution of the dispersions of 5%, 10%, 20%, and 30% (m/m) as shown in Fig. 8.

The changes in values of pH are not considerably high. Zeta potential that can provide information about stability of dispersions was equally measured (by diluting the samples), in all dispersions after 6 h of grinding, as shown in Fig. 9.

All the dispersions were found to be having values less than −26.6 mV indicating reasonable repulsive forces between the particles in the dispersions. Change in Zeta potential depends upon change in pH, concentration or quantities of additives, etc. Based on the results as shown in Fig. 8 it can be considered that pH has not affected the zeta potential. It is difficult to study the effects of concentration change (dilution) on zeta potential using dynamic light scattering technique (Zetasizer Nano ZS). Acoustic attenuation spectroscopy, therefore, was employed at each step of dilution to understand how this technique explains the effects of dilution on stability and particle size. In general, we observed an ascending trend in particle size in dispersions of 20% (m/m) and 30% (m/m) whereas a descending trend in particle size in dispersions of 5% (m/m) and 10% (m/m) as shown in Fig. 10.

Acoustic attenuation spectroscopy is unsuitable for analyzing very dilute dispersions (suspensions) particularly below 1% (m/m) [2]. In our experiments, the limit of un-suitability seems to start from 2.6% (m/m) as shown by the dotted line in Fig. 10. A reason for ignoring the acoustic results during dilution process below the value of 2.6% (m/m) is our pH study of the dispersions that indicated that pH values remained almost constant below that concentration. Fig. 11 compares the results of particle sizes obtained after 6 h of grinding with the particle sizes of the same dispersions when each one was diluted to 2.6% (m/m).

It is observed that the trend is reversed. When this trend was compared with the trend in particle sizing by dynamic light scattering, both were found to be in accordance as shown in Fig. 12.

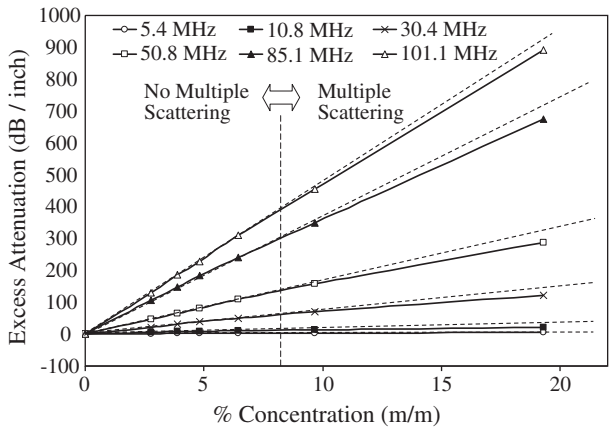

Fig. 13. Multiple scattering in 20% (m/m) dispersion.

5.3.3. Effects of multiple scattering

Multiple scattering is a phenomenon in which attenuated acoustic wave from one particle is scattered by other particles changing the acoustic signal and thus bringing to misleading results. Nonlinearity observed in acoustic curves (attenuation plotted as a function of concentration) may indicate the presence of multiple scattering [15,17]. The method adopted by M. Tourbin and C. Frances [15] was followed to confirm the existence of multiple scattering. The method takes into consideration the excess of attenuation which may be described as [15]:

$$\alpha_e(f) = \alpha_T - (1-\phi)(0.0047f^2 - 0.0083f) \quad (4)$$

Where $\alpha_e(f)$ = excess attenuation (db/in.) at a certain frequency f, α_T = total attenuation (db/in.) of the dispersion, ø = %volume concentration of the dispersion, and f = frequency (MHz) of acoustic wave. A new series of experiments was performed to obtain data required in Eq. (4). Each of the four dispersions (5%, 10%, 20%, and 30% (m/m)), after the grinding experiment was diluted to a certain volume concentration; ultrasound waves of different frequencies were passed through the dispersion to measure the excess and total attenuation in the sample. The same dispersion was diluted further to several levels of volume concentrations and at each level of dilution the excess and total attenuation were measured. The same procedure was adopted in all four cases of dispersions (5%, 10%, 20%, and 30% (m/m)).

Our investigation brings out that particles obtained after 6 hours of grinding process, in each case of the dispersions (5%, 10%, 20%, and 30% (m/m), show multiple scattering. Fig. 13 demonstrates the excess of attenuation measured against concentration for the 20% (m/m) dispersion as an example. Non-linearity at different frequencies indicates presence of multiple scattering.

6. Conclusions

The concentration of a dispersion plays an important role in particle sizing in size reduction process. This role emerges very distinctively when particles enter from micron to fine particle size range during stirred media milling. Acoustic attenuation spectroscopy, which is generally considered to be capable of measuring average particle size of the dispersions at different values of concentrations, shows certain limitations in stirred media milling. The technique explains that the use of relatively concentrated dispersions may be favorable in achievement of finer particles during stirred media milling carried out under a set of fixed operating parameters. However, dynamic light scattering demonstrates that the use of relatively dilute dispersions favors in achievement of finer particles during stirred media milling carried out under a set of fixed operating parameters. Our investigations bring out that particle sizing by acoustic attenuation spectroscopy cannot be considered valid at higher concentration of samples of dispersions during stirred media milling because of multiple scattering that influence the results. If concentration of the sample of dispersions is reduced considerably in particle sizing by means of acoustic attenuation spectroscopy in stirred media milling, then anomalies in the results may be avoided. In such cases both the techniques shows reasonable agreement that use of relatively dilute dispersions favors in achievement of finer particles during stirred media milling carried out under a set of fixed operating parameters.

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