Slurry Rheology of Industrial Minerals and Its Effects on Wet Ultra-fine Grinding

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DOCTORAL THESIS

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December, 2007
To my wife and families
for their love and support

献给我亲爱的妻子和家人
Preface

The experimental work in this thesis was carried out during September, 2002 - February, 2005 and June, 2005 - March, 2006 at the Division of Mineral Processing, Luleå University of Technology (LTU), Sweden. This thesis and parts of papers 4 and 5 were written from May, 2006 to June, 2007 in Adelaide, Australia. The financial support is acknowledged from the Swedish National Energy Administration and Hesselmanska Stiftelsen in Sweden (MinFo’s Process Technology Program) for my licentiate studies (September, 2002 - February, 2005) and from LKAB and Agricola Research Center (ARC), Luleå University of Technology, Sweden for my Ph.D studies (June, 2005 - March, 2006).

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I am deeply indebted to my parents and my two young sisters for their selfless love, unconditional support and everything else they have been bestowing upon me.
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何明照

Mingzhao He

June, 2007 in Adelaide, Australia
This thesis investigates slurry rheology of industrial minerals (limestone and quartzite) and its effects on wet ultra-fine grinding in order to reduce energy cost, increase the throughput as well as the product fineness.

The influences of solid concentration, molecular weight of a dispersant, and particle size and distribution on the rheological behaviour of original limestone slurries have been investigated. The results reveal that when the solid concentration of a limestone slurry (< 100 μm) is increased from 60 wt.% (35.71 vol.%) to 78.5 wt.% (57.49 vol.%), the rheological behaviour of the slurry is transformed from a weakly dilatant or Newtonian characteristic to a pseudoplastic one with a yield stress, which is in combination with a thixotropic property at a higher solid concentration (i.e., ≥ 75 wt.% or 52.63 vol.%). At a certain shear rate, the apparent viscosity and the relative viscosity of the slurry both increase exponentially with solid concentration. The extrapolated Casson yield stress increases in a power-law form with increasing solid concentration when the solid concentration is larger than 70 wt.% (i.e., 46.36 vol.%). The maximum attainable packing solid fraction ($\phi_m$) is predicted as 64.6 vol.% at the limestone-water suspension.

A polymeric dispersant named Dispersant S40 with a molecular weight of 5,500 Da appears most efficient for the reduction of the apparent viscosity of limestone slurry. The smaller the particle size and the narrower the size distribution, the more evident the pseudoplastic behaviour of limestone slurry is with a higher yield stress and a larger apparent viscosity at a given shear rate in the range 12 - 1200 s⁻¹. However, a sufficient addition dosage of Dispersant S40 significantly decreases or even eliminates the rheological differences of limestone slurries (apparent viscosity and extrapolated yield stress) resulting from differences in particle size and distribution.

Wet ultra-fine grinding of a limestone material (< 100 μm) has been investigated in a stirred media mill with respect to the effect of slurry rheology. The results obtained by varying operation parameters (i.e., molecular weight of a dispersant, solid concentration, addition dosage, addition method and bead load) are evaluated in terms of energy efficiency and the fineness. Dispersant S40 gives the superior results compared to the other dispersants (i.e., BCX-476 and BCX-552). For a certain level of bead load, an optimal solid concentration exists for more effective grinding. At 0.1
wt. % of addition dosage of Dispersant S40 or more (≤ 0.6 wt.%), a smaller addition amount of Dispersant S40 leads to a higher energy efficiency and a smaller median size at a lower level of specific energy input. However, the excessive amount of the dispersant causes the grinding less efficient. This can be avoided by either the multi-point addition of the dispersant or a higher bead load (≥ 83 vol. %).

The role of slurry rheology in stirred media milling of quartzite has also been performed by varying important grinding parameters such as media bead density, addition of chemicals, solid concentration, stirrer rotational speed as well as the combined effect of these factors. Media bead density has an evident but complex effect on stirred milling performance, depending on stirrer rotational speed and solid concentration. Addition of Dispersant S40 or a lower solid concentration results in better grinding performance (i.e., a higher energy efficiency and a smaller median size) due to maintenance of lower viscosities at shear rates investigated during grinding. Stirrer rotational speed interacts with solid concentration. For a given solid concentration, an optimal stirrer speed exists. The observed phenomena can be explained by the effect of slurry rheology on the stress intensity of individual grinding bead.

The flowability of ground limestone slurries during grinding has been monitored and characterized. The rheological behaviour of ground limestone slurries varies with grinding from a starting dilatant flowability to a resultant pseudoplastic one with an evident Casson yield stress in combination with a thixotropic character. The appearance of pseudoplastic flowability with a thixotropy is related to the fineness of a ground product and its specific surface area, which are both correlated to solid concentration and the addition amount of Dispersant S40. However, the rheological characterization of time-dependent fluids is dependent upon the instruments used and operating conditions.

In addition, an empirical particle size-energy model provides a good fit to the wet ultra-fine grinding results for both limestone and quartzite under the experimental conditions investigated.

**Keywords:** Slurry rheology; Non-Newtonian flowability; Limestone; Quartzite, Stirred media mill; Wet ultra-fine grinding; Ultra-fine particles; Solid concentration; Dispersant; Molecular weight; Particle size and distribution; Milling media bead.
List of publications

This thesis is based on the work contained in the following five articles:

1. **Slurry rheology in wet ultra-fine grinding of industrial minerals: A review**
   Mingzhao He, Yanmin Wang and Eric Forssberg

2. **Parameter studies on the rheology of limestone slurries**
   Mingzhao He, Yanmin Wang and Eric Forssberg

3. **Parameter effects on wet ultrafine grinding of limestone through slurry rheology in a stirred media mill**
   Mingzhao He, Yanmin Wang and Eric Forssberg

4. **Influence of slurry rheology on stirred media milling of quartzite**
   Mingzhao He and Eric Forssberg,

5. **Rheological behaviors in wet ultrafine grinding of limestone**
   M. He and E. Forssberg

(Contribution to the included paper 1-5: Most of the work was done by the author with supervision and comments by the co-authors of the papers.)

During my postgraduate studies, the following articles were authored or co-authored but not included in this thesis


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1 Introduction

1.1 Slurry rheology and its characterization

Rheology is a science of deformation and flow of materials (Tanner, 2000; Whorlow, 1992). The principal theoretical concepts are kinematics, dealing with geometrical aspects of deformation and flow; conservation laws, forces, stress and energy interchanges; constitutive relations special to classes of bodies. The constitutive relations, namely, the relationships between stress, strain and time for a given test sample, serve to link motion and forces to complete the description of the flow process, which may then be applied to solve engineering problems. There are the Newtonian and non-Newtonian fluids based on the constitutive relations. For the fluids, the apparent viscosity, $\eta$, is defined by (Whorlow, 1992)

$$\eta = \frac{\tau}{\gamma}$$

where $\tau$ is the shear stress and $\gamma$ is the shear rate. The apparent viscosity, $\eta$, is a useful parameter. In the case of Newtonian fluids, $\eta$ is constant. For non-Newtonian fluids, $\eta$ is variable, which means that the shear stress ($\tau$) varies with the shear rate ($\gamma$). As known, most semi-solids such as mineral slurries, which are either found in nature or synthesized in laboratory, exhibit non-Newtonian fluids (Klimpel, 1999; Somasundaran and Moudgil, 1988; He et al., 2004). The information for characterisation of the rheology of time-independent non-Newtonian mineral slurries is outlined in Figure 1.

However, the time-dependent non-Newtonian fluids are usually encountered in fine and concentrated solid suspensions (Papo et al., 2002; Lemke et al., 1999). The time-dependent non-
Newtonian fluids are characterized by a change in viscosity with time at a constant shear rate. There are two categories of this type of fluids: thixotropic and rheopectic. A thixotropic fluid undergoes a decrease in viscosity with time when it is subjected to constant shearing, whereas a rheopectic fluid essentially exhibits an opposite behaviour to thixotropy, thus the rheopectic fluid’s viscosity increases with time as it is sheared at a constant rate (Figure 2). When a time-dependent fluid is subjected to a varying shear rate which is increasingly increased to a certain value first and then decreased to the starting point, the “up” and “down” rheological curves do not coincide. This hysteresis loop is caused by a decrease or increase in the fluid’s viscosity with increasing shearing time, as shown in Figure 3. Such effects may or may not be reversible. Both thixotropy and rheopexy may occur in combination with time-independent flow behaviour, or only at a certain shear rate. The time element is extremely variable. Under conditions of constant shear rate, some fluids will reach their final viscosity values in a few seconds, while others may take up to several days.

1.2 Grinding mechanisms in stirred media mills

Most of the mills used in wet ultra-fine grinding are stirred media mills (Bernhardt et al., 1999; Zheng et al., 1997; Kapur et al., 1996; Blecher et al., 1996; Gao and Forssberg, 1993a) due to their high unit outputs and high-energy efficiencies. The stirred media mills are equipped with a stationary grinding chamber and a high-speed
stirrer (disks or pins) fixed on a drive shaft. The grinding chamber is filled with small grinding media (normally spherical annealed glass, steel, or ceramic beads) at a high bead load. An intensive grinding action of slurry-bead mixture in the chamber is generated at a high stirring speed. The respective kind of flow determines the spatial distribution of zones with a high grinding intensity as well as the predominant types of grinding mechanisms and their composition (Blecher et al, 1996; Kwade et al, 1996). Thus, the predominant grinding mechanisms in stirred media mills are dependent on compressional, shear and torsional stresses, which are invoked by stirring the slurry-bead mixture at a very high velocity (Kwade, 1999a and b; Theuerkauf and Schwedes, 1999; Blecher et al, 1996; Gao and Forssberg, 1995; Orumwense and Forssberg, 1992).

The grinding process in a stirred media mill is usually determined by (i) how often each feed particle or a fragment arising from the feed particles is stressed (i.e., the number of stress events) and (ii) how high the stress intensity at each stress event is. In a batch grinding process, the average number of stress events of each product particle, SN, is determined by the number of media contacts, Nc, and by the probability that a particle is caught and sufficiently stressed at a media contact, Pc, and by the number of product particles inside the mill, Np. Thus, the average number of stress events of each product particle, SN, can be written by (Kwade, 1999a and b)

$$SN = \frac{N_c \cdot P_c}{N_p}$$  \hspace{1cm} (2)

It can be assumed, that the number of media contacts is proportional to the number of revolutions of the stirrer and to the number of grinding media in the chamber, N_{GM}:

$$N_c \propto m N_{GM} \propto n t V_{GC} \phi_{GM} (1 - \varepsilon) \frac{\pi}{6} d_{GM}^3$$  \hspace{1cm} (3)

where n (s⁻¹) is the number of revolutions of the stirrer per unit time, t (s) is the comminution time, V_{GC} (m³) is the volume of the grinding chamber, \phi_{GM} is the filling rate of the grinding media, \varepsilon is the porosity of the bulk of grinding media and d_{GM} (m) is the diameter of the grinding media.

An important condition that particles are stressed between two grinding media is that the particles are captured by the grinding media and are not carried out with the
displaced fluid. In case of grinding of crystalline materials (e.g., minerals and ceramic materials), the number of captured particles depends on the solid concentration of a suspension and the particle size, and can be evaluated by the ratio between the diameter of the active volume between two grinding media, $d_{act}$, and the average distance between two particles in the suspension, $y$. The active volume between two grinding media is defined to be the volume, in which a particle with a size of $x$ is captured between two grinding media with a diameter $d_{GM}$. The diameter of the active volume, $d_{act}$, is the maximum distance between two captured particles at the minimum distance of the grinding media, $a$, as shown in Figure 4.

![Figure 4 Active volume (stressing zone) between two grinding media](image)

The average distance $y$ between the centres of two particles is a function of the solid volume concentration of the suspension, $c_v$, and the particle size, $x$. Based on this, the following equation can be given for the ratio $d_{act}/y$:

$$\frac{d_{act}}{y} = \sqrt{\frac{6c_v}{\pi}} \left[ 2 \left( 1 - \frac{a}{x} \right) \left( \frac{d_{GM}}{x} \right) + 1 - \left( \frac{a}{x} \right)^2 \right]$$  \(4\)

Thus, the probability, $P_s$, is proportional to the ratio, $d_{act}/y$,

$$P_s \propto \frac{d_{act}}{y}$$  \(5\)
The number of product particles is proportional to the overall volume of the product particles and can be given as follows:

\[ N_p \propto V_p = V_{GM} (1 - \varphi_{GM} (1 - \varepsilon))c_v \]  

(6)

Combination of Equations (2)-(6), the average number of stress events of each product particle for the grinding of crystalline materials is given by

\[ SN \propto \frac{\varphi_{GM} (1 - \varepsilon)}{(1 - \varphi_{GM} (1 - \varepsilon))c_v} \frac{mt}{d_{as}^3} \frac{d_{as}}{d_{GM} y} \]  

(7)

For the elasticity of a feed material, such as limestone, is much smaller than that of the grinding media, the stress intensity (SI) in stirred media mills is proportional to the third power of the media diameter, \( d_{GM} \), and the square of the circumferential velocity of the stirring discs, \( v_t \), and the media density, \( \rho_{GM} \). The detailed deduction has been discussed in the literature (Kwade, 1999 b). Therefore, the stress intensity, SI, is given by

\[ SI \propto d_{GM}^3 \rho_{GM} v_t^2 \]  

(8)

**1.3 Role of slurry rheology in wet ultra-fine grinding**

The effective motions of slurry-bead mixture are much related to its flow behaviour in the grinding chamber. The optimisation of the rheological behaviour of a ground slurry can enhance energy efficiency and throughput in wet ultra-fine grinding operation. From a diagnostic point of view, the rheological behaviour of a mineral slurry is indicative of the level of interparticle interaction or aggregation in the slurry (Muster and Prestidge, 1995). Therefore, slurry rheology is a useful variable to be controlled in industrial processes such as transportation of slurries, dewatering and wet grinding.

Since the product fineness significantly increases with grinding time in wet ultra-fine grinding operation characterized by a very fine product size and a high solid concentration, the surface properties tend to predominate in the system (Bernhardt et al., 1999; Zheng et al., 1997; Klimpel, 1999). Inter-particle forces, such as van der Waals forces (Greenwood et al., 2002; Reinisch et al., 2001a) and electrostatic forces
(Bernhardt et al., 1999; Muster and Prestidge, 1995), lead to the formation of agglomeration and aggregation. This results in changes in rheological property of the ground slurry in wet ultra-fine grinding. The role of slurry flowability in wet ultra-fine grinding becomes particularly important. The optimization of the rheological behaviour of a ground slurry can enhance the energy efficiency and throughput in wet ultra-fine grinding operations. For instance, addition of an optimum dispersant to a given feed slurry can result in a drastic reduction or even elimination of yield stress and permits a higher solid concentration of the ground slurry (He et al., 2006b; Klimpel, 1999; Greenwood et al., 2002; Reinisch et al., 2001b). In the absence of any dispersant, the typical maximum percentage solid in a slurry is approximately 27.4 vol. % for the feed of ultra-fine grinding in stirred media mills, whereas an upper limitation of solid concentration is up to 60.15 vol. % in the presence of an optimal dispersant (Greenwood et al., 2002). Therefore, the improvement of rheological behaviour of a feed slurry with addition of a suitable dispersant can enhance the productivity and throughput for wet ultra-fine grinding.

1.4 Aims and objectives

Although many studies related to the slurry rheology in conventional tumbling ball mills have been done, there is still little understanding on the role of slurry rheology in ultra-fine grinding process characterized by a very fine product size and a high slurry concentration due to complex slurry rheological behaviour in stirred media mills (Blecher and Schwedes, 1996; Gao and Forssberg, 1993 a). Besides, findings from tumbling ball mills involving the effect of slurry rheology on the grinding results can not completely apply for the stirred media milling case due to their different breakage mechanisms (Kwade, 1999 a, b; Gao and Weller, 1993; Austin et al, 1984). Therefore, it is necessary for wet ultra-fine grinding process to systematically investigate parameter effects on slurry rheology, which is how to influence the ultra-fine grinding performance, for scientific understanding and industrial application.

The major aim of this study is to investigate slurry rheology of industrial minerals (limestone and quartzite) and its effects on wet ultra-fine grinding performance. The rheological behaviour of the mineral slurries will be studied through parameter modifications (i.e., solid concentration, addition of dispersant, particle size and distribution) to improve the understanding of the overall view of the flowability of the
mineral slurries. The effect of slurry rheology on wet ultrafine grinding of limestone (<100 μm) will be performed through parameter variations (i.e., molecular weight of a dispersant, solid concentration, addition dosage, addition method, and bead load) in a stirred media mill. The role of slurry rheology in stirred media milling of quartzite will be investigated as well by varying important grinding parameters such as media bead density, addition of chemical, solid concentration, stirrer rotational speed as well as the combined effect of some factors. The grinding results are evaluated by energy efficiency and the median size of a ground product with respect to specific energy consumption. The objective is to enhance the grinding efficiency, the product fineness and the throughput. In addition, the rheological behaviour of a ground limestone slurry (<100 μm) will also be explored in a stirred media mill. The dependence of slurry rheology of the ground limestone slurry (<100 μm) on solid concentration, addition of a dispersant, particle size and specific surface area of a product is to be built up.

2. Materials

A limestone powder sample (93.7 wt.% CaCO₃, 2700 kg/m³, Mohs hardness: 3) provided by SMA Karbonater AB, Sweden and a quartzite material (94.52 wt.% SiO₂, 2710 kg/m³, Mohs hardness: 7) provided by LKAB, Sweden were used for experiments. Table 1 shows the chemical analysis of the limestone and quartzite samples. To study the effect of particle size and distribution on slurry rheology, another two finer limestone samples were prepared from the received limestone powder. One is a sieved sample with a size < 74 μm, as designated as limestone finer-1; the other has a size < 40 μm through a sieve, as designated as limestone finer-2. Figure 5 shows the particle size distributions of three limestone powders and quartzite sample, which were determined by an X-ray Sedimentometer Sedigraph 5100D (Micromeritics Co., Ltd., USA).
Three sodium polyacrylate dispersants with different molecular weights, i.e., BCX-476, Dispersant S40 and BCX-552 (provided by CDM AB, Sweden) were used as dispersants for limestone suspensions, whereas Dispersant S40 and Genamin CC 100 (Flotigam P) were chosen as grinding aids for quartzite. Table 2 gives the physical
and chemical properties of these chemicals. In this investigation, the addition amount of a dispersant is the percent of the pure dispersant (i.e., active content) by weight relative to the weight of solids in a slurry.

### Table 2 Physical and chemical properties of chemicals

<table>
<thead>
<tr>
<th>Physical and chemical properties</th>
<th>BCX-476</th>
<th>Dispersant S40</th>
<th>BCX-552</th>
<th>Genamin CC 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active content (wt. %)</td>
<td>40 % Sodium polyacrylate</td>
<td>40 % Sodium polyacrylate</td>
<td>26 % Sodium polyacrylate</td>
<td>100 % C8-C18 amine</td>
</tr>
<tr>
<td>pH</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>N/A</td>
</tr>
<tr>
<td>Density at 20 ºC (g/cm³)</td>
<td>1.30</td>
<td>1.30</td>
<td>1.315</td>
<td>0.78</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
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<td>5,500</td>
<td>85,000</td>
<td>198</td>
</tr>
<tr>
<td>Water content and other (wt. %)</td>
<td>55 %</td>
<td>55 %</td>
<td>70 %</td>
<td>N</td>
</tr>
<tr>
<td>Other content (wt. %)</td>
<td>5 %</td>
<td>5 %</td>
<td>4 %</td>
<td>N</td>
</tr>
<tr>
<td>Solubility (in water)</td>
<td>Very soluble</td>
<td>Very soluble</td>
<td>Very soluble</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

3 Experimental methods and data analysis

3.1 Experimental methods

3.1.1 Mixing

A limestone- or quartzite-water slurry was prepared for rheological measurements by addition of 40 to 50 kg of limestone or quartzite powder into a certain amount of water determined by a pre-determined solid concentration for each slurry sample. The slurry was stirred as the limestone or quartzite powder was added into water, and the stirring was continued for 15 min to make the slurry uniform after the completion of adding limestone or quartzite powder. If a given amount of a chemical was added, the slurry was stirred for 15 min again after addition of the chemical to disperse the chemical uniformly in the slurry. About 200 ml slurry was taken for each sample, and was used to analyse the particle size distribution and to measure the rheological behaviour of the slurry.
3.1.2 Grinding experiments in a stirred media mill

A stirred media mill utilized for grinding experiments is PMH 5 TEX Drais mill (Draiswerke GmbH, Mannheim, Germany). Figure 6 (a and b) schematically shows the mill set-up and the grinding chamber, respectively. It consists of a \(150\times420\) mm stainless steel cylinder chamber (5.6 L of net grinding chamber volume) and a stirrer with six \(120\times10\) mm perforated discs installed on a horizontal driven shaft. For cooling purpose, the grinding chamber is equipped with a water jacket. The flowrate of the feed slurry is controlled by a feeding pump. Discharge of the product is facilitated by means of two specially designed screen cartridges inserted at the end of the cylinder. The grinding operation in the PMH 5 TEX is the mode of circulation pass by pass, as shown in Figure 6.

A limestone- or quartzite-water slurry was prepared at a pre-determined solid concentration by mixing 40 to 50 kg of limestone or quartzite powder with a given amount of water to make up about 35 L of slurry. 15 L of 35 L of the slurry were fed through the mill first and then discarded in order to attain a steady milling state with regard to solid concentration. About 20 L of the remaining slurry were circulated through the mill pass by pass for several passes. This means that the entire 20 L of slurry was passed through the mill, collected at the discharge outlet and then passed through again. The grinding operation conditions for both limestone and quartzite are shown in Table 3. About 200 ml of slurry sample was taken after each pass. The samples were then analysed for particle size, rheological property and specific surface area, respectively.

3.1.3 Measurements

3.1.3.1 Particle size and specific surface area

An X-ray Sedimentometer Sedigraph 5100D (Micromeritics Co. Ltd., USA) was used to analyze the particle size and distribution of samples. Its measurement range of particle size ranges from 0.1 to 300 \(\mu\)m, which is suitable for the samples in this study. A representative amount of sample was directly dispersed in an aqueous solution with 0.1 wt. % of Calgon for the measurement.

The specific surface area of a sample was measured by Flow Sorb II 2300 (Micromeritics Co. Ltd., USA), which is an instrument designed to take the measurements on bone-dried powders by \(N_2\) gas adsorption and desorption at liquid nitrogen temperature and room temperature (BET), respectively. A representative
amount of sample was taken from each sample, and then was dried in an oven at 110°C for 24 hours in order to remove the residual moisture in the sample prior to measurements. The mean value of the adsorption and desorption specific surface areas of a sample was regarded as its real value.

Figure 6 Drais stirred media mill with a grinding chamber of 5.6 L net volume.

(a) Stirred media mill set-up

(b) Grinding chamber of 5.6 L net volume.
| Constants: | Stirrer speed (rpm): 1808 (11.36 m/sec), Feed flowrate (L / min): 1.5, ZrSiO₄ grinding beads: 1.6-2.0 mm, 3.7 g/ml, |
| Variables: | (1) Solid concentration (wt.%): 65, 70, 75 (2) Filling rate of grinding media (vol.%): 65 - 83 (3) Dispersants: BCX-476 (2000 Da) (wt.%): 0.2, Dispersant S40 (5500 Da) (wt.%): 0 - 0.6, BCX-552 (85000 Da) (wt.%): 0.2 |
| For Limestone | For Quartzite | Filling rate of grinding media (vol.%): 70, Feed flowrate (L / min): 1.5, (1) Solid concentration (wt.%): 65, 70 (2) Grinding media type, size and density: Al₂O₃ beads: 0.75-1.0 mm, 3.7 g/ml, Al₂O₃ beads: 1.0-1.5 mm, 3.7 g/ml, ZrSiO₄ beads: 1.6-2.0 mm, 3.7 g/ml, SiO₂ beads: 1.6-2.0 mm, 2.5 g/ml, ZrO₂ beads: 1.6-2.0 mm, 5.4 g/ml (3) Stirrer speed (rpm): 1204, 1808, 2255 (4) Chemicals: Dispersant S40: 0.04 wt.%, Flotigam P: 0.04 wt.% |

3.1.3.2 Rheological measurements

Slurry samples were aged for several hours and then shaken at an intensity of 225 min⁻¹ (TH-30 shaker from Edmund Bühler, Germany) for 1 hour to re-disperse the samples prior to rheological measurements.

A rotational viscometer called a Bohlin Visco 88 BV (Bohlin Reologi UK Ltd., UK) was utilized to determine the rheological property of slurries. It employs a concentric cylinder geometry with a rotating inner cylinder and a stationary outer cylinder. The concentric cylinder system can be configured in 8 different measurement systems (3 DIN, 2 ‘Wide Gap’, 3 ‘Infinite Sea’), corresponding to SYSTEM knob 1 to 8 on the instrument, and their design allows measurement of samples to be made in-situ (e.g. in a container) as well as on a laboratory bench. Any inner cylinder has 8 different rotation speeds to be chosen, which is from 20 to 1000 rpm corresponding to a shear-rate range of 4 to 1200 s⁻¹. The torque developed on the inner cylinder due to a sample is directly related to the sample viscosity and should be in the range of 0.5 to 9.5 mN·m for the accuracy. In this study, all samples were measured by the use of C30 system (C30 DIN), which has a gap width of 1.5 mm between the inner and outer cylinders and can provide a viscosity range of 0.007 to 6.18 Pa·s. A thermal jacket allows the use of an external fluid circulator to control or regulate the temperature of a sample measured.

The sedimentation of particles has always been a major problem in measuring the rheology of mineral slurries (Kawatra et al., 1996 and 1999), but unfortunately, no
modification for the viscometer was made to prevent particle settling in this study. The viscometer employs a so-called “viscosoft” computation program so the digital readings (measured parameters), such as shear rate, shear stress, viscosity, and torque, are directly displayed on the screen of the viscometer. Each slurry sample was first pre-sheared for 3 min at 1000 rpm (i.e., 1200 sec⁻¹) prior to the measurement; then the measurement started at such a high shear rate. The shear rate was stepped down one by one until the torque reading was less than 0.5 mN·m. The digital readings (viscosity, shear rate, shear stress, and torque) were recorded at each shear rate. About 25 ml of slurry sample was required for each measurement. Each sample was measured three times, and the mean values of shear stress, shear rate, and viscosity were used for analysis.

A controlled-stress rheometer called a TA Instruments CSL² 500 (TA Instruments, Leatherhead, UK) was used to characterize the time-dependent flowability of a ground slurry because it can give far more shear rate-viscosity points than Bohlin Visco 88 BV viscometer. According to measurement requirements, TA Instruments CSL² 500 can calibrate and optimize parameter options itself through an auxiliary computer software called TA Instruments Rheology Solutions. Also, the rheometer can accurately maintain a given temperature varying in the range of ± 0.1 °C using a heating-refrigerating bath and circulator system. Samples were measured in the shear-rate range of 20 to 600 sec⁻¹ using a cone-and-plate geometry with a 3° angle and 60 mm diameter cone. A sample was first pre-sheared at 800 sec⁻¹ for 5 sec rather than 3 min to avoid evaporation; then was subjected to a varying shear rate, which was first increasingly increased from 20 to 600 sec⁻¹ (“up”) in 2 min and then was decreased to 20 sec⁻¹ (“down”) in 2 min.

In addition, the rheological data were fitted using both Bingham plastic (Gao and Forssberg 1993a; Prestidge 1997; Muster and Prestidge 1995) and Casson (Yue and Klein, 2004; Yang et al., 2001) models (Eqs. (9) and (10)) as these two models are simple two-parameter equations.

\[
\begin{align*}
\tau &= \tau_0 + \eta_0 \gamma \\
\tau^\frac{1}{2} &= (\tau_c)^\frac{1}{2} + (\eta_c \gamma)^\frac{1}{2}
\end{align*}
\]

where \(\tau_0\) and \(\tau_c\) are the yield stress terms, and \(\eta_0\) and \(\eta_c\) are the viscosity terms.
Figures 7 (a) and (b) show the fits of rheological data at various solid concentration into Bingham and Casson equations, respectively. It is shown that Casson model (average correlation coefficient, $R^2 = 0.998$) fits the data a little bit better than Bingham model ($R^2 = 0.996$), as is in agreement with previous results for quartz suspensions (Yue and Klein, 2004). Therefore, the Casson model was utilised to fit the rheological data to obtain Casson yield stress.

![Figure 7 Fitting rheological data of original limestone slurries at various solid concentrations into Bingham (a) and Casson (b) models, dots: experimental; solids lines: modelling. (by Bohlin viscometer)](image)

3.2 Calculations of specific energy consumption and energy efficiency

3.2.1 Specific energy consumption

The energy consumed by the mill was measured by an electrical meter named Micro VIP (Elcontrol Co., Italy). In this study, only the active power (kW) was recorded and used by considering the power factor. The active power of the mill is sensitive to the current change at all levels up to the rated power of the motor. An active power reading was recorded every minute during each grinding pass, and about
10 readings were done for each pass. The mean active power of each pass was regarded as its real one. The mean active power, $P_{mn}$ (kW), of the $n^{th}$ pass for a grinding experiment was determined by

$$P_{mn} = \frac{\sum_{i=1}^{m} P_{ni}}{m} \quad (11)$$

where $P_{ni}$ is the $i^{th}$ discrete power reading of the $n^{th}$ pass, and $m$, the number of readings of the $n^{th}$ pass. The milling energy of the $n^{th}$ pass was calculated by taking away the idle power draw of the mill, $P_0$ (kW) (without grinding media or ground material) from the mean active power, $P_{mn}$ (kW) at a given rotation speed. And only the power adsorbed by the mill chamber was accounted in all the tests in this work. In order to evaluate the net energy consumption of the Drais mill, the mass specific energy consumption, $E_m$ (kW h/t), was determined by (Stehr and Weyand, 1990):

$$E_m = \frac{P_{mn} - P_0}{3.6M_pC} \quad (12)$$

where $M_p$ (kg/s) is the mass flowrate of a slurry suspension fed to the mill, and $C$ is the solid concentration by weight. Due to the volume flowrate of a feed slurry being controlled and measured in this study, the formula (12) is modified as

$$E_m = \frac{P_{mv} - P_0}{3.6M_vC_v\rho} \quad (13)$$

where $M_v$ (m$^3$/s) is the volume flowrate of a slurry suspension fed to the mill, and $C_v$, the volume concentration of the slurry, and $\rho$ (kg/m$^3$), the density of solid.

### 3.2.2 Energy efficiency

Energy efficiency or energy utilization, $E_f$ (m$^2$/Wh), which is defined as the increment of specific surface area per unit of specific energy consumption (Zheng et al., 1997; Gao and Forssberg, 1993 b), was calculated by

$$E_f = \frac{1000\Delta S}{E_m} \quad (14)$$
where $\Delta S = S - S_0$, $S$ and $S_0$ are the specific surface areas (m$^2$/g) of a ground product and its feed by BET, respectively.

3.3 Reproducibility of experimental data

3.3.1 Rheological measurements

The accuracy of Bohlin viscometer was examined by the reproducibility of the rheological measurements of a limestone slurry ($<100 \mu m$) over a wide range of shear rates. The results are shown in Table 4. It is evident that the viscometer exhibits good reproducibility with a rather small standard deviation for all the measured parameters. The sample standard deviation of viscosity is less than 0.0013 Pa·s when the torque is larger than 0.5 mN·m. Even though the measured torque is less than 0.5 mN·m, the sample standard deviation of viscosity is still less than 0.0018 Pas. Thus, the viscometer accurately gives a resolution of 0.001 Pa·s at a torque larger than 0.5 mN·m.

3.3.2 Grinding results

Table 5 shows the mean value and the sample standard deviation for the measured values from three grinding tests, which were performed under the same conditions. It is evident that the grinding results with the stirred media mill (PMH 5 TEX) exhibit good reproducibility with a rather small sample standard deviation for all the measured parameters, as was confirmed and emphasized by Reinisch et al. (2001a).
### Table 4 Reproducibility of the rheological data for 70 wt. % of solids concentration without dispersants

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Test</th>
<th>Measurement data</th>
</tr>
</thead>
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</tr>
<tr>
<td></td>
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</tr>
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<td></td>
<td>3</td>
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<td>Shear rate (1/s)</td>
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<tr>
<td></td>
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<td></td>
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<td>Shear stress (Pa)</td>
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<tr>
<td></td>
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<tr>
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<td>3</td>
<td>0.103</td>
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<tr>
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<td>0.27</td>
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<td>Sample standard deviation</td>
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### Table 5 Reproducibility of grinding results for 70 wt. % of solids concentration with 0.2 wt. % BCX-476 at 74 vol. % of beads load

<table>
<thead>
<tr>
<th>Test</th>
<th>E_m (kWh/t)</th>
<th>ΔS (m^2/g)</th>
<th>xo (μm)</th>
<th>xo (μm)</th>
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<td>5.269</td>
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<td>32.65</td>
<td>2.413</td>
<td>5.191</td>
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<td>32.86</td>
<td>2.33</td>
<td>5.293</td>
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<tr>
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<td>2.368</td>
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</tr>
<tr>
<td>Sample standard deviation</td>
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<td>0.479</td>
</tr>
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</tr>
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<td>111.4</td>
<td>6.363</td>
<td>1.891</td>
<td>5.92</td>
</tr>
<tr>
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<td>109.01</td>
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<tr>
<td>Mean value</td>
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<td>Sample standard deviation</td>
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<td>0.053</td>
<td>0.095</td>
</tr>
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</table>
4 Results and discussion

4.1 Slurry rheology (Paper 2)

4.1.1 Effect of solid concentration

The influence of solid concentration on the rheology of limestone slurry is significant since a range of solid concentrations can lead to different types of flows, as shown in Figure 8. The result shows the rheological properties of seven solid concentrations of original limestone slurries (< 100 μm) without dispersant at 25 ± 0.2°C. Clearly, the slurry appears to be a weakly dilatant flow at a solid concentration ≤ 65 wt.% (40.75 vol.%) if the effect of particle settling is neglected. This is because in a dilute slurry (i.e., ≤ 65 wt.% or 40.75 vol.%), the interparticle distance is so large that the limestone particles in the slurry are not subjected to the attractive forces between the particles.

At lower shear rates, the particles have enough opportunities to slip over each other and are free to move as individuals. Increasing shear rate increases the degree of shear-induced aggregation, leading to an increase in viscosity (Klein and Hallbom, 2002). Alternatively, the slurry at a solid concentration ≤ 65 wt.% may present Newtonian fluid if particle sedimentation is eliminated.

A decrease in apparent viscosity with reducing shear rate may arise from particle settling. Unfortunately, there was no effort to overcome the issue of particle settling in the study. At the solid concentration up to 67 wt.% (42.92 vol.%), the flowability of the slurry exhibits a pseudoplastic characteristic without a definite yield stress at shear rates less than 663 sec⁻¹ and a weakly dilatant or Newtonian flow at shear rates larger than 663 sec⁻¹. This indicates that at shear rates < 663 sec⁻¹, the interparticle attraction is predominant over the hydrodynamic force exerted by a flow field at 67 wt.% of solid concentration, as opposite at shear rates > 663 sec⁻¹.

With further increasing the solid concentration to 70 wt.% (46.36 vol.%) or more, the slurry rheology is changed into a pseudoplastic flow with an evident shear yield stress at low shear rates, followed by a transition to a Casson plastic flow (with a higher extrapolated Casson yield stress) at high shear rates. Furthermore, the degree of pseudoplasticity, the apparent viscosity at a given shear rate and the shear yield stress increase with increasing solid concentration when the solid concentration is larger than 70 wt.% (Figure 8).
Similar phenomena were observed for quartz (Yue and Klein, 2004), and titanium dioxide suspensions (Yang et al., 2001). The effect of solid concentration on the extrapolated Casson yield stress and the apparent viscosity at a given shear rate for the slurry is shown in Figures 9 and 10, respectively. The yield stress and the viscosity increase in power-law and exponential forms with increasing solid concentration when the solid concentration is larger than 70 wt. % (46.36 vol. %), respectively. The influence of solid concentration on the rheological behaviour (apparent viscosity and Casson yield stress) of quartzite slurry is quite similar to that of limestone slurry and is not described in detail here due to limited space.
This is similar to a previous conclusion (Tseng and Chen 2003). This indicates that at a high solid concentration (i.e., > 70 wt.% for limestone), there are strong interactions between the particles to hold the particles together in the slurry and form loosely packed flocs, immobilizing some water within them, which is indispensable to flow. This is because a smaller interparticle distance in a denser slurry produces an increased attractive potential and a larger possibility of collisions between the particles, resulting in more particles attracting each other. A shearing force over a certain shear yield stress has to be exerted on the slurry to overcome the internal friction among the particles constituting the flocs and to make it flow again. Once the
slurry flows, the flocs are broken down into smaller flow fragments with increasing flow intensity (i.e., shear rate for a given slurry system). The fragment size is mainly determined by the balance between the strength of the aggregation structure and the flow intensity (Higashitani et al., 2001). An increase in shear rate (flow intensity) gives smaller flow units and thus decreases the viscosity of the slurry.

The effect of solid concentration on the apparent viscosity of the limestone slurry at a certain shear rate (see Figure 10) is consistent with previous conclusions for dolomite (Velamakanni and Fuerstenau, 1993) and for quartz slurries (Tangsathitkulchaisri and Austin, 1988). By fitting the experimental data, we found that a relation between the apparent viscosity of limestone slurry at a given shear rate and solid concentration can be described by

\[ \eta_p = a(\gamma)e^{b(\gamma)\phi} \]  

where \( \eta_p \) is the apparent viscosity; \( \phi \) is the solid concentration by volume; \( a(\gamma) \) and \( b(\gamma) \) are the coefficients related to a used shear rate, and the higher the shear rate is, the larger \( a(\gamma) \), and the smaller \( b(\gamma) \).

This model gives good accuracy in the investigated range of solid concentration, as shown in Figure 10. The errors between the experimental and predicted viscosities at a certain solid concentration are less than 14.28 % at a shear rate of 1191 s\(^{-1}\), 26.08 % at 663 s\(^{-1}\), 19.39 % at 362 s\(^{-1}\), or 19.94 % at 194 s\(^{-1}\).

It is evident that in the case of solid concentration over 75 wt.% or 52.63 vol.%, the slurry viscosity increases rather sharply in the range of shear rate investigated, tending towards infinity at a limited solid concentration. Consistent phenomenon is observed when the apparent viscosity (\( \eta_p \)) of the slurry is substituted by the relative viscosity, \( \eta_r \) (the viscosity of the slurry with respect to the viscosity of the suspending fluid, \( \eta_0 \), at a given shear rate). Figure 11 shows a relation between the relative viscosity of the slurry and solid volume concentration at the shear rate of 663 s\(^{-1}\).
Besides, the relation between the relative viscosity ($\eta_r$) and the volume fraction of solid in the slurry ($\phi$) allows to calculate the theoretical, maximum solid volume fraction ($\phi_m$, at which the relative viscosity approaches toward infinity and the slurry ceases from flowing) attainable in the limestone-water slurry according to (Tseng and Chen, 2003):

$$1 - \eta_r^{-1/n} = a\phi + b$$  \hspace{1cm} (16)

where $a$ and $b$ are constants, which can be determined from the $(1 - \eta_r^{-1/n}) - \phi$ relationship, and $n$ is an integer in the range of 2 to 4 (Tseng and Chen, 2003). Table 6 lists the values of parameters obtained by fitting experimental data into Equation (16) with three different n-values, i.e., 2, 3 and 4. The experimentally determined $\eta_r$ derivative, i.e. $(1 - \eta_r^{-1/n})$ appears to be linearly proportional to $\phi$ with a reasonable correlation factor for all three n-values. The theoretical, maximum solid concentration can hence be obtained from the fitted equation by extrapolating the linear line to $1 - \eta_r^{-1/n} = 1$. The corresponding $\phi_m$ is given in Table 6.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$n$</th>
<th>$a$</th>
<th>$b$</th>
<th>$\phi_m$ (vol.%)</th>
<th>$R^2$ (correlation factor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.0195</td>
<td>-0.2597</td>
<td></td>
<td>64.6</td>
<td>0.9925</td>
</tr>
<tr>
<td>3</td>
<td>0.0191</td>
<td>-0.3771</td>
<td></td>
<td>72.1</td>
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<td>4</td>
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<td>-0.3909</td>
<td></td>
<td>79.94</td>
<td>0.9839</td>
</tr>
</tbody>
</table>

Figure 11 Effect of solid concentration on the relative viscosity at the shear rate of 663 s$^{-1}$ at 25 ± 0.2 °C: solid points, experimental; lines, modeling.
The calculated $\phi_m$ is compared with the $\tau_{c-\phi}$, $\eta_{r-\phi}$ and $\eta_{s-\phi}$ relations, which are shown in Figures 9, 10 and 11, respectively. The apparent viscosity, relative viscosity and extrapolated Casson yield stress approach infinity at the solid concentration of 65 vol. % or 83.37 wt. %. Thus, the exponent $n=2$ in equation (16) is applicable to the limestone slurry at a high shear rate of 663 s$^{-1}$, and gives a good correlation factor (Figure 12) and a reasonable maximum packing volume fraction of 0.646, which is close to the random close packing fraction ($\phi=0.64$) for spheres.

In addition, it is interesting to note that the 75 wt. % limestone slurry or more presents a thixotropic characteristic (Figure 13). For a given solid concentration, the apparent viscosity of the slurry decreases with time at a certain shear rate. The time to reach a stable apparent viscosity is about 3 min for 75 wt. % of solid concentration at 1191 s$^{-1}$ and 4 min for 77 wt. % at 663 s$^{-1}$. The shear-thinning behaviour with a definite yield stress associated with thixotropic characteristics is typical of agglomerated or flocculated slurries (Muster and Prestidge, 1995; Papo et al., 2002; Hackly, 1998). A similar conclusion was drawn for kaolin suspensions with sodium tripolyphosphate (Papo et al., 2002), for concentrated alumina suspensions (Lemke et al., 1999), for sphalerite slurries (Muster and Prestidge, 1995) and for galena slurries (Prestidge, 1997).
4.1.2 Effect of molecular weight of a dispersant

The effect of the concentration of sodium polyacrylate dispersants with various molecular weights on the rheological behaviour of 70 wt.% and 75 wt.% of original limestone slurries (< 100 μm) was investigated, respectively. Figure 14 shows the effect of the concentration of a sodium polyacrylate called Dispersant S40 (Mw: 5500 Da) on the flowability of original limestone slurry at 75 wt. % of solid concentration. The slurry with less than 0.01 wt.% of Dispersant S40 shows a pseudoplastic characteristic with a yield stress and possesses a higher apparent viscosity than that without the dispersant at a given shear rate. This reason is that an insufficient dispersant causes the flocculation of particles in the slurry by bridging attraction forces, leading to larger flow units (Johnson et al. 2000). At the addition amount of Dispersant S40 up to 0.015 wt. %, the apparent viscosity of the slurry is lower than that without the dispersant, and the slurry still exhibits a pseudoplastic flow with a smaller yield stress. When the addition dosage of Dispersant S40 is up to 0.03 wt. % or more, the slurry is transformed into a weakly dilatant flow if the effect of particle settling is neglected, and the apparent viscosity in the range of shear rates investigated slightly decreases with the further addition of Dispersant S40 and is down to a minimum at the addition level of 0.1 wt. %. In this case, it is supposed that the saturation adsorption of the dispersant on the particle surface has been attained, and electrostatic and steric stabilizations (i.e., electro-steric stabilizations) occur. By further adding the dispersant, the apparent viscosity at a given shear rate insignificantly reverts. The excessive dispersant can increase the ion strength of the
slurry, which reduces the zeta potential of the particles in magnitude and leads to a compression of the adsorbed dispersant layer onto the particle surface as well. This results in reduction of repulsive electro-steric forces between particles (Papo et al., 2002; Banash and Croll, 1999; Ewais et al., 2002). In addition, the excessive dispersant above the saturation adsorption exists in the slurry but not adsorb on the suspended particles, and can cause depletion flocculation (Hunter 1987; Milling and Biggs, 1995; Johnson et al. 2000).

In case of BCX-476 and BCX-552 dispersants, similar phenomena were noted with adding the dispersants. Figures 15 and 16 show the results. With increasing

Figure 14 Flowability of original limestone slurry at 75 wt. % solid concentration with various dosages of Dispersant S40 at 25 ±0.2°C, (by Bohlin viscometer)

In case of BCX-476 and BCX-552 dispersants, similar phenomena were noted with adding the dispersants. Figures 15 and 16 show the results. With increasing
Figure 15 Effect of dispersant concentration on the apparent viscosity at 194 s\(^{-1}\) and 663 s\(^{-1}\) for 75 wt.% of solid concentration at 25 ±0.2 °C. (by Bohlin viscometer)

Figure 16 Effect of dispersant concentration on the extrapolated Casson yield stress for 75 wt.% of solid concentration at 25 ±0.2 °C. (by Bohlin viscometer)
the addition dosage of dispersants, the apparent viscosity of the 75 wt.% limestone slurry at a given shear rate first increases and reaches a respective maximum at the addition amount of 0.004 wt.% for each dispersant and then decreases. It marginally reverts for BCX-476 and Dispersant S40, and distinctly does for BCX-552 after reaching a respective minimum (Figure 15), which is located at an addition level of 0.2 wt.% for BCX-476, 0.1 wt.% for Dispersant S40 and 0.04 wt.% for BCX-552. For dispersant BCX-552, it possesses a much larger molecular weight (i.e., 85,000) with a longer molecular chain than BCX-476 and Dispersant S40, so the depletion flocculation is more significant besides the reduction of electro-steric force (Banash and Croll, 1999; Kiratzis, 1999). Therefore, further addition of BCX-552 above the saturation adsorption significantly raises the apparent viscosity of the slurry at a given shear rate (Figure 15 (b)). The extrapolated Casson yield stress of the 75 wt.% limestone slurry first increases and then decreases with increasing the addition dosage of dispersants with different molecular weights. The extrapolated Casson yield stress reaches a respective maximum at 0.004 wt.% addition level and is eliminated when the addition amount exceeds 0.03 wt. % for each dispersant (Figure 16).

Similar phenomena were observed for kaolin suspensions with sodium tripolyphosphate and sodium polyphosphate (Papo et al., 2002), and zirconia slurries with tri-ammonium citrate (Ewais et al., 2002), and silica suspensions with polyethylene oxide (Zaman et al., 2000).

For 70 wt. % of the limestone slurry, similar rheological behaviour was also noted with addition of dispersants with various molecular weights (Papers 2 and 5). The apparent viscosity of 70 wt. % of the limestone slurry reaches a respective minimum at an addition level of 0.1 wt. % for BCX-476 or Dispersant S40 and 0.04 wt.% for BCX-552. Figures 17 and 18 show the accessible minimum viscosity for 70 wt. % and 75wt. % of the limestone slurry in the presence of a given addition amount for each dispersant, respectively. In the case of reduction of the apparent viscosity of the limestone slurry, Dispersant S40 and BCX-476 are better than BCX-552. Dispersant S40 and BCX-476 show quite similar effect for 70 wt. % of the limestone slurry, while the former is better than the latter for 75 wt. % of the slurry. The reason could be that Dispersant S40 gives a better steric stabilization than BCX-476 in a denser limestone slurry due to its relatively larger molecular weight with respect to BCX-476.
4.1.3 Effect of particle size and distribution

Tangsathitkulchai and Austin (1988) have indicated that the rheological theory of concentrated slurries is strongly related to the viscosity-dependence on the particle size. Furthermore, a prolonged grinding will give a higher fineness of a ground product. Investigation of the rheological behaviour of limestone slurries with respect to particle size and distribution is necessary. In this work, the limestone materials with three particle sizes and distributions (Figure 5) were used to study the effect of particle size and distribution on the slurry rheology in the absence of any dispersant. It was found that the particle size distributions of these materials could be fitted by the Rosin – Rammler equation over the size range:
\[ P(x) = 1 - \exp \left( -\left( \frac{x}{k} \right)^m \right) \]  

where \( P(x) \) is the cumulative fraction less than a sieve size \( x \), \( k \) is the fineness modulus (i.e., the 63.21%-passing size) and \( m \) is the distribution modulus. Table 7 lists the results obtained by fitting experimental size-distribution data into equation (17), which show a good correlation.

<table>
<thead>
<tr>
<th>Test samples</th>
<th>( m )</th>
<th>( k )</th>
<th>( R^2 ) (correlation factor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>0.9658</td>
<td>37.2</td>
<td>0.9955</td>
</tr>
<tr>
<td>Limestone finer-1</td>
<td>1.0967</td>
<td>22.14</td>
<td>0.9981</td>
</tr>
<tr>
<td>Limestone finer-2</td>
<td>1.3137</td>
<td>13.01</td>
<td>0.9951</td>
</tr>
</tbody>
</table>

Figures 19 and 20 show the rheological properties of the limestone slurries with three different particle size distributions for 70 wt. % of solid concentration at 25 ± 0.2 °C. The slurries exhibit a pseudoplastic flow with an evident shear yield stress in a lower range of shear rates, followed by a transition into an approximate Casson plastic flow (with a higher extrapolated Casson yield stress) in a higher range of shear rates. Furthermore, the degree of pseudoplasticity is more evident, the viscosity at a given shear rate and the yield stress of the slurries increase at a finer particle size with a narrower size distribution. The extrapolated Casson yield stress exponentially increases and decreases with increasing the distribution modulus (\( m \)) and the characteristic sizes (i.e., \( d_{50} \) and \( k \)), respectively (Figure 20). Some researchers have also drawn a similar conclusion for titanium dioxide (Yang et al., 2001), for coal (Tangsathitkulchaisai and Austin, 1988; Logos and Nguyen, 1996) and for quartz slurries (Tangsathitkulchaisai and Austin, 1988). This is because the interparticle attractions become stronger in a slurry with finer particles. Also, the packing efficiency reduces in a material with a narrower particle size distribution at a fixed solid concentration, and more water is required to fill the inter-particle voids.

In addition, when 0.04 wt.% of Dispersant S40 is added into these three slurries, the rheological behaviour of the slurries is transformed from pseudoplastic flows with a yield stress to dilatant ones (Figure 21 (a)). The difference in viscosity resulting from the particle size and distribution decreases with increasing the addition amount of the dispersant. At an addition dosage of the dispersant up to 0.1 wt. %, the difference
becomes smaller and the difference in viscosity between limestone and limestone finer-1 is insignificant (Figure 21 (b)). This can be attributed to the dispersion effect of Dispersant S40. This is consistent with a previous observation for dolomite slurries with Dispex N40 (Gao and Forssberg, 1993a).

Figure 19 Effect of particle size and distribution on the flowability of 70 wt.\% of solid concentration in the absence of dispersants at 25 ±0.2 °C. (by Bohlin viscometer)

Figure 20 Effect of particle size and distribution on the extrapolated Casson yield stress for 70 wt.\% of solid concentration in the absence of dispersants at 25 ±0.2 °C. (by Bohlin viscometer)
4.2 Effect of slurry rheology on wet ultra-fine grinding

4.2.1 Limestone (Paper 3)

4.2.1.1 Effect of molecular weight of a dispersant

The ultra-fine grinding process is characterized by a high solid concentration and the presence of excessive fines, which are two of the primary factors leading to the formation of agglomeration or flocculation and hence the development of a yield stress of a ground slurry. Polyacrylic acids or their salts as efficient dispersants for wet ultra-fine grinding have been identified (He et al., 2004). A polyacrylic acid or its salt with an optimal molecular weight used as a grinding aid can change the surface nature of particles in a ground slurry, resulting in inter-particle forces being entirely repulsive and improving the slurry flowability by decreasing the slurry viscosity and by reducing or eliminating the shear yield stress. This can enhance the product fineness, energy efficiency and throughput in wet ultra-fine grinding.
Figure 22 shows the effect of three sodium polyacrylates with different molecular weights on the grinding results at 75 wt.% of solid concentration at 0.2 wt.% addition. Clearly, Dispersant S40 with a molecular weight of 5,500 Da gives better grinding results (i.e., a higher energy efficiency and a smaller median size) in wet ultra-fine grinding of limestone when other operation conditions are kept constant. The reason is that Dispersant S40 maintains a lower apparent viscosity during the grinding (Figure 23). The feed of 75 wt. % of solid concentration with BCX-552 exhibits higher viscosities in the shear rate range studied (Figure 23 (a)). This leads to a lower energy efficiency and a larger median size during pass 1. The feeds of 75 wt. % of solid concentration with BCX-476 and Dispersant S40 display the similar rheological property in the shear rate range and thus produce an insignificant difference in grinding results during pass 1. After pass 1, Dispersant S40 gives better grinding results due to its maintenance of lower apparent viscosities in the shear rate range studied.

Figure 22 Effect of chemicals with various molecular weights at the addition level of 0.2 wt. % on the grinding results for 75 wt. % of solid concentration at 74 vol. % of bead load
However, whatever dispersant exists at 75 wt. % of solid concentration, the grinding operation is forced to automatically stop due to a high pressure inside the mill chamber by a safety control device when a ground slurry presents a pseudoplastic flow with a definite extrapolated Casson yield stress (Figures 23(d) and 24). The more viscous slurry with a yield stress could be the reason since the slurry is circulated through the mill by a pump, which has to use more power to make the slurry flow. This increases the pressure in the mill up to the limit. The slurry of 75 wt. % of solid concentration with 0.2 wt. % of BCX-552 can only be ground for one pass, but three passes for BCX-476 or Dispersant S40. Similar results were also obtained in the case of 70 wt. % of solid concentration with these dispersants.
4.2.1.2 Effect of solid concentration

Figure 25 shows the grinding results for limestone slurries with three different solid concentrations in the presence of 0.2 wt.% of Dispersant S40 at 74 vol.% of bead load. The cumulative energy efficiency first increases and then decreases with increasing solid concentration from 65 wt.% to 75 wt.% at a given specific energy input. The median size of the product varies with solid concentration in an opposite way to the cumulative energy efficiency. This is in agreement with a previous conclusion (Bernhardt et al., 1999). The best grinding results are obtained at 70 wt.% of solid concentration with 0.2 wt.% of the dispersant. The reason is that the slurry of 70 wt.% of solid concentration with 0.2 wt.% of the dispersant exhibits proper viscosities in a wide range of shear rates (Figure 26) and produces better stress conditions (i.e., a higher stress intensity and a larger average number of stress events for each particle). In the case of 65 wt.% of solid concentration with 0.2 wt.% of the dispersant, a lower viscosity and a larger average inter-particle distance make it difficult that particles are effectively captured by grinding beads. This increases the possibility of the direct collision between beads, resulting in more energy loss. A higher solid concentration (i.e. 75 wt.%) gives a smaller average inter-particle distance, which increases the average number of stress events of particles. However, at 75 wt.% of solid concentration, the larger viscosity damps the motion of grinding beads in the mill and significantly increases the
attenuation of the velocity and kinetic energy of the beads, which leads to lower stress intensities of collisions among beads/particles/chamber inner wall. The decrease in stress intensity is dominant, compared with the increase in the number of stress events. Therefore, the captured particles cannot effectively be ground, which causes an ineffective milling operation. However, the grinding operation at a solid concentration from 65 to 75 wt. % with 0.2 wt. % of Dispersant S40 automatically ceases when a ground slurry exhibits a pseudoplastic flow with an evident extrapolated Casson yield stress (Figures 26(d) and 27).

Figure 25 Effect of various solid concentrations with 0.2 wt. % of Dispersant S40 on the grinding results at 74 vol. % of bead load.
Figure 26 Change of rheological behaviours of three different solid concentrations with 0.2 wt. % of Dispersant S40 with increasing pass number (grinding time) at 74 vol. % of bead load; a: feed; b: after pass 1; c: after pass 3; d: in that case where grinding is force to stop. (by Bohlin viscometer)

Figure 27 Extrapolated Casson yield stress in that case where grinding process is forced to automatically stop for three solid concentrations with 0.2 wt.% of Dispersant S40 at 74 vol.% of bead load. (by Bohlin viscometer)
4.2.1.3 Effect of addition dosage of Dispersant S40

A small addition of a suitable dispersant can reduce energy consumption and increase throughput for wet ultra-fine grinding processes. An insufficient amount of the dispersant is a problem since some particles will be flocculated by bridging mechanisms, which increases the viscosity of a ground slurry. However, an excessive amount of the dispersant is unnecessary extravagance and can even cause slurry destabilization (He et al., 2006a). Therefore, it is important to determine an optimal dosage of Dispersant S40 in wet ultra-fine grinding of limestone in order to enhance energy efficiency.

Figures 28 and 29 show the effect of addition amount of Dispersant S40 into 70 wt. % of solid concentration on the grinding results at 74 vol. % of bead load. Clearly, the energy efficiency increases first and then decreases with increasing the addition amount of the dispersant from 0.04 to 0.6 wt. % in the first pass. The addition amount of 0.1 wt. % gives the best energy efficiency and the smallest median size of the ground product. The difference of rheological properties of the feeds for pass 1 is marginal for 70 wt. % of solid concentration with different dosages of the dispersant when the dosage is larger than 0.04 wt. % (Figure 30 (a)). When the addition amount is below 0.1 wt. % (i.e., 0.04 wt. %), the energy efficiency is reduced due to a rapid increase in the viscosity of the ground slurry during pass 1 (Figure 30 (b)). The rheological property of the discharge slurry with 0.04 wt. % of the dispersant for pass 1 exhibits a pseudoplastic flow with a high yield stress. Therefore, the stress intensity from the collision of milling beads is rapidly weakened due to the poor flowability of the slurry. After pass 1, the grinding operation automatically ceased due to the poor flowability of the slurry.

At an addition dosage of 0.1 wt.% of Dispersant S40 or more, the rheological differences of the feed and the discharge slurries are both insignificant for pass 1 for 70 wt.% of solid concentration with different dosages of Dispersant S40 (Figure 30). But in a region of small cumulative specific energy input (less pass number), a smaller addition amount of the dispersant gives a higher energy efficiency and a smaller median size at a given specific energy input (Figure 29). However, the addition amount of Dispersant S40 up to 0.6 wt. % causes an inefficient grinding in the initial stage. The reason could be that the excessive Dispersant S40 exists in the slurry, but does not adsorb onto the suspended limestone particles for 70 wt. % of solid concentration with 0.6 wt. % of Dispersant S40. When the slurry is pumped
through the mill, the excessive dispersant not adsorbed by limestone particles could possibly adsorb onto grinding beads surface, and also some carboxylic groups on the dispersant molecules absorbed onto the beads can simultaneously adsorb some fine limestone particles. This forms a cushion layer on the bead surfaces, which results in a lower stress intensity from the collision of the beads and thus gives inefficient grinding action. With the cumulative specific energy input increasing, the specific surface area of the ground limestone particles increases and some excessive dispersant molecules immigrate onto the surface of the particles from that of the beads. The cushion layers on the bead surfaces become thinner and thinner and even disappear. Thus, the energy efficiency increases (Figure 29 (a)). Similar grinding phenomenon was observed by Bernhardt et al. (1999). The particle size is reduced with increasing the cumulative specific energy input, and thus causes a smaller stress zone (or active volume) between two approaching milling beads (Figure 4). The possibility of a particle captured is reduced, thus the energy efficiency gradually lowers, as is interpreted by the grinding mechanism in stirred media mills described in detail in “Introduction” section. Before the grinding operation automatically ceases, the energy efficiency quickly reduces, especially for a smaller addition dosage of Dispersant S40. This is due to a rapid increase in the apparent viscosity of the slurry, causing lower stress intensities. However, the slurry with 70 wt.% of solid concentration can be ground for one pass at 0.04 wt.% of Dispersant S40, two passes at 0.1 wt.%, four passes at 0.2 wt.% and twelve passes at 0.6 wt.%. For 70 wt. % of solid concentration with whatever addition dosage of Dispersant S40 and pass number, the grinding operation automatically stop when a slurry discharged from the mill displays a pseudoplastic flow with an evident yield stress.
Figure 28 Effect of various addition dosages of Dispersant S40 into 70 wt. % of solid concentration on the grinding energy efficiency at 74 vol. % of bead load

Figure 29 Effect of three different addition dosages of Dispersant S40 into 70 wt.% of solid concentration on the grinding results at 74 vol. % of bead load
4.2.1.4 Effect of addition method of Dispersant S40

The achievement of a specific product fineness needs a certain addition amount of a suitable dispersant for a ground limestone slurry at a given solid concentration (paper 5). For instance, at 70 wt. % of solid concentration, at least 0.5 wt. % of Dispersant S40 is indispensable for the achievement of the product fineness of 90% passing 2 μm. To avoid the detrimental effect of excessive Dispersant S40 in a ground limestone slurry, the multi-point addition of the dispersant was adopted (Wang and Forssberg, 1995). Figure 31 shows the effect of multi-point and single-point additions of Dispersant S40 on wet ultra-fine grinding of the limestone. It is evident that an insignificant difference exists between three-point and one-point additions for 70 wt. % of solid concentration at an addition level of 0.2 wt. % of Dispersant S40 at 74 vol. % of bead load. This is because the existence of a small addition amount (i.e., 0.2 wt. %) in the limestone slurry cannot form a cushion layer on the milling bead surfaces. However, in the case of 75 wt. % of solid concentration, the multi-point addition of 0.6 wt. % Dispersant S40 gives a higher energy efficiency in a range of lower specific energy input (i.e., < 200 kWh/t). While at a higher level of the specific energy input > 300 kWh/t, the difference in cumulative energy efficiency resulting from different addition methods of Dispersant S40 is marginal. For an addition amount of 0.6 wt.% of the dispersant, a multi-point addition avoids the existence of the excessive dispersant, and thus the formation of a cushion layer on milling bead surfaces in the lower specific energy input.
4.2.1.5 Effect of bead load

For wet ultra-fine grinding in stirred media mills, the milling bead load is also an important parameter in terms of energy efficiency (Gao and Forssberg, 1992). Figures 32 and 33 show the effect of bead load on the grinding results for 70 wt. % of solid concentration at 0.2 wt. % and 0.6 wt. % of Dispersant S40, respectively. The higher the bead load, the higher the cumulative energy efficiency, and the finer the product fineness is at a given specific energy consumption. However, it is interesting to note that for a lower bead load (≤ 74 vol. %) and a higher addition dosage of Dispersant S40 (e.g., 0.6 wt. %) at a given solid concentration (i.e., 70 wt. %), the cumulative energy efficiency exhibits a maximum in a range of lower specific energy input. This phenomenon cannot occur in the case of a higher bead load (i.e., 83 vol. %). This indicates a higher bead load (≥ 83 vol.% can eliminate the detrimental effect of the excessive dispersant on the wet ultra-fine grinding of limestone (see Figures 29 and 34). In the case of 83 vol. % of bead load, the differences in grinding results are insignificant between 70 wt. % of solid concentration in the presence of 0.2 wt. % and 0.6 wt. % of Dispersant S40 in a region of low specific energy input (Figure 34).
Figure 32 Effect of various bead loads on the grinding results for 70 wt.% of solid concentration in the presence of 0.2 wt.% of Dispersant S40

Figure 33 Effect of various bead loads on the grinding results for 70 wt.% of solid concentration in the presence of 0.6 wt.% of Dispersant S40
4.2.2 Quartzite (Paper 4)

4.2.2.1 Effect of media bead density

Figure 35 shows the effect of media bead density on the median size of a product at 65 wt.% solid concentration at three stirrer rotational speeds. It is seen that a higher density media bead (i.e., 5.4 g/ml) results in a smaller median size at a lower stirrer rotational speed (< 1808 rpm) (Figure 35 (a)), as opposed at a higher stirrer rotational speed (i.e., 2255 rpm) (Figure 35 (c)) except for SiO₂ beads with a density of 2.5 g/ml. However, the change of cumulative energy efficiency with media bead density at a certain stirrer speed is opposite to that of median size, as shown in Figure 36. However, they both give consistent grinding results. This is because high density beads (i.e., 5.4 g/ml) have higher stress intensities than low density beads (i.e., 3.7
g/ml) at a lower stirrer speed (see Equ.(8)) and can more effectively grind the captured quartzite particles.

![Figure 35 Effect of media bead (1.6-2.0 mm in diameter) density on the median size of a product at 65 wt. % of solid concentration at three stirrer rotational speeds.](image)

With increasing stirrer rotational speed, stress intensities of beads rise (Blecher et al., 1996; Kwade et al., 1996). At a stirrer rotational speed up to 2255 rpm, the stress intensity of beads with a higher density (i.e., 5.4 g/ml) exceeds the required one for
pulverizing quartzite particles, resulting in the waste of energy in stress events. SiO₂ beads (density: 2.5 g/ml) used as grinding media give larger median size for a ground product at a given energy consumption. It could be due to the very serious wear of SiO₂ beads observed during grinding, leading to an increasingly decrease in filling rate of media beads. Thus, the SiO₂ beads used as grinding media for quartzite are unsuitable and uneconomical. For 70 wt.% solid concentration with 0.04 wt.% Dispersant S40 at 2255 rpm stirrer speed, similar phenomena were observed, as shown in Figure 37 (b).

However, at 1204 rpm stirrer speed (Figure 37 (a)), 3.7 g/ml beads result in a higher cumulative energy efficiency than 5.4 g/ml beads, as is contradictory to that at 65 wt.% solid concentration. The possible reason could be that at 70 wt.% solid concentration, the grinding beads may not effectively be stirred up to produce effective impact breakage at 1204 rpm due to higher viscosities between 100 s⁻¹ and 1200 s⁻¹ (Figure 38), which is within the range of shear rate distribution in the stirred
media mill (Lane, 1999). Furthermore, more energy is needed to stir the heavier bead-slurry mixture containing higher density grinding beads (i.e., 5.4 g/ml) in the milling chamber. Thus the heavy grinding beads with 5.4 g/ml density give a lower energy efficiency.

Figure 37 Effect of media bead (1.6-2.0 mm in diameter) density on the cumulative energy efficiency at 70 wt. % of solid concentration with 0.04 wt.% Dispersant S40 at two stirrer rotational speeds

Figure 38 Comparison of rheological behaviours for 70 wt.% solid concentration with 0.04 wt.% Dispersant S40 with 65 wt.% without dispersant. (by Bohlin viscometer)
4.2.2.2 Effect of chemical

Chemicals have an important impact on wet ultra-fine grinding in stirred media mills since the addition of chemicals can modify the rheology of a ground slurry (He et al, 2006a and b). The effect of addition of Flotigam P or Dispersant S40 on wet ultrafine grinding of quartzite was investigated. Figure 39 shows the grinding results at 65 wt.% solid concentration using 1.6-2.0 mm media beads with 3.7 g/ml density.

![Effect of chemicals on grinding results at 65 wt.% of solid concentration with 1.6-2.0 mm media beads with a density of 3.7 g/ml.](image)

Clearly, Dispersant S40 leads to better grinding results (i.e., a higher energy efficiency and a smaller median size) when quartzite is ground in the stirred bead mill. The reason is that Dispersant S40 maintains lower viscosities at shear rates studied for 65 wt.% solid concentration during the grinding (see Figure 40). However, 65 wt. % of solid concentration with 0.04 wt.% Flotigam P exhibits higher viscosities at shear rates studied during the grinding, which damp the motion of grinding beads in the mill and significantly increase the attenuation of the velocity and kinetic energy of the beads. This brings about lower stress intensities of collisions among
beads/particles/chamber inner wall. Thus, the presence of 0.04 wt.% Flotigam P leads to a lower energy efficiency and a larger median size. Similar result was obtained in the case of ZrO₂ beads with 5.4 g/ml density. Therefore, Dispersant S40 is suitable to be used as a grinding aid because it can lower the slurry viscosity and eliminate the shear yield stress. This enhances the product fineness and the energy efficiency in wet ultra-fine grinding of quartzite.

4.2.2.3 Effect of solid concentration

Figure 41 shows the effect of solid concentration on grinding results in the presence of 0.04 wt.% Dispersant S40 using 1.6-2.0 mm beads with 3.7 g/ml density. It is seen that a lower solid concentration has a positive effect on the grinding results at a given stirrer rotational speed (i.e., 1808 rpm), and thus results in a higher cumulative energy efficiency and a smaller median size. Similar result was also achieved in the case of ZrO₂ beads with 5.4 g/ml density.

Figure 40 Change of rheological behaviours for 65 wt.% solid concentration with different chemicals with pass number (grinding time) increasing at 70 vol. % of bead load (bead size: 1.6-2.0 mm, bead density: 3.7 g/ml) ; a: feed; b: after pass 1; c: after pass 2; d: after pass 3. (by Bohlin viscometer)
Although a higher solid concentration (i.e. 70 wt. %) gives a smaller average interparticle distance, which leads to a larger average number of stress events of each particle, 70 wt. % of solid concentration with 0.04 wt.% Dispersant S40 exhibits a larger viscosity than 65 wt.% in the range of shear rates studied during the grinding (Figure 42). It retards the motion of grinding beads in the mill and significantly attenuates the velocity of the beads, which results in lower stress intensities of collisions between beads and beads or chamber inner wall. Therefore, the captured particles cannot be effectively ground, which causes a lower cumulative energy efficiency and a larger median size at a given specific energy consumption.

![Figure 41](image_url)

**Figure 41** Effect of solid concentration with 0.04 wt.% Dispersant S40 on grinding results at 1808 rpm stirrer rotational speed with 1.6-2.0 mm media beads with a density of 3.7 g/ml.
4.2.2.4 Effect of stirrer rotational speed

Stirrer rotational speed is believed to be one of the most important factors in wet ultrafine grinding since it is directly related to the stress intensity of individual grinding beads. Three stirrer rotational speeds, i.e., 1204 rpm, 1808 rpm and 2255 rpm, were selected in the study. The corresponding peripheral speeds of the stirrer disks were 7.56 m/s, 11.36 m/s and 14.17 m/s, respectively. The effect of stirrer speed on grinding results at two solid concentrations with various types of grinding beads are shown in Figures 43 and 44, respectively. For 65 wt.% solid concentration, the cumulative energy efficiency first increase and then decrease with increasing stirrer rotational speed under the grinding conditions investigated. The stirrer speed of 1808 rpm gives the best energy efficiency. This indicates that for 65 wt.% solid concentration, the stress intensity of individual media beads is sufficient to break the caught particles at 1808 rpm, below which the stress intensity is insufficient for breakage or above which some energy is excessive and wasted.

Figure 42 Change of rheological behaviours for two solid concentrations with 0.04 wt.% Dispersant S40 with pass number (grinding time) increasing at 70 vol. % of bead load (bead size: 1.6-2.0 mm, bead density: 3.7 g/ml); a: feed; b: after pass 1; c: after pass 2; d: after pass 3. (by Bohlin viscometer)
Figure 43 Effect of stirrer rotational speed on the cumulative energy efficiency at 65 wt. % of solid concentration with various media beads
However, for 70 wt.% solid concentration with 0.04 wt.% Dispersant S40, a higher energy efficiency was obtained at a higher stirrer speed in the range of stirrer speeds studied. This is because 70 wt.% of the quartzite slurry with 0.04 wt.% Dispersant S40 exhibits a higher viscosity than 65 wt.% without chemical in the range of shear rates from 100 to 1200 s\(^{-1}\) (Figure 38), which is within the range of shear rate distribution in the stirred media mill (Lane, 1999). It damps the motion of grinding beads in the mill, and more energy is used to counteract the viscous resistance. The increase of stirrer speed can improve the stress intensity of individual beads (see Equ.(8)), and thus results in a better energy efficiency in the range of stirrer speeds studied. It is expected that a higher optimum stirrer speed would exist for the denser slurry.

![Graphs showing energy efficiency and specific energy input](image)

Figure 44 Effect of stirrer rotational speed on the cumulative energy efficiency at 70 wt. % of solid concentration with 0.04 wt.% of Dispersant S40 with two different media beads.

### 4.3 Rheological behaviour in wet ultra-fine grinding (Paper 5)

Because the product fineness significantly increases with grinding time in wet ultra-fine grinding operations characterized by a high solid concentration and the
presence of excessive fines, the surface properties tend to be predominate in the system (Bernhardt et al., 1999; Klimpel 1999; Klein and Hallbom, 2002; He et al., 2004). Enhanced inter-particle forces, such as van der Waals forces (Greenwood et al., 2002) lead to the formation of more agglomeration or aggregation. This results in changes in the rheological behaviour in wet ultra-fine grinding operations.

In addition, there was no effort to control the temperature of a ground slurry for each grinding test except for keeping cooling water circulating continuously at 0.5 L/s. The slurry temperature evidently varied during grinding due to the release of lattice energy of ground particles from comminution and the heat energy from the friction between milling media beads and the ground particles in the slurry. Previous studies have shown that an increase in slurry temperature reduces the viscosity of the slurry (He et al., 2006a; Yang et al., 2001). To take into account the effect of temperature, all rheological measurements were carried out at a required temperature corresponding to that of a discharge slurry.

4.3.1 Effect of solid concentration

Limestone was chosen to investigate the rheological behaviour during grinding as it is not too hard and shows a good grindability, and the produced fines leads to a quicker rheological change comparing with quartzite.

Figure 45 shows the evolution of rheological behaviour of limestone slurries with grinding at 70 wt. % and 75 wt. % of solid concentrations in the presence of 0.2 wt. % of Dispersant S40. As can be seen, the initial feed slurries exhibit a dilatant flow, suggesting the particles in the slurries could not be subjected to interparticle attractive forces but free to move as individuals. Initially, the viscosities of the ground slurries at shear rates studied decrease with increasing pass number (i.e., grinding time or specific energy consumption) and the fineness of the ground product until the pass number is up to 2. Similar phenomenon was observed by previous work (Tangsathitkulchai and Austin 1989). The reason could be due to an increase in packing efficiency of particles. Further increase in pass number leads to the viscosities of the ground slurries reverting. At pass number up to 4 or more for 70 wt.% of solid concentration, or 3 or more for 75 wt.% of solid concentration, the slurries are transformed into a pseudoplastic flow with an evident Casson yield stress. This indicates that with prolonging grinding time and the particle size finer and finer, there are strong inter-particle interactions to hold the particles together in the slurry.
The grinding operation for 70 wt.% of solid concentration with 0.2 wt.% of Dispersant S40 automatically ceases at pass 5 but stops at pass 4 for 75 wt.% of solid concentration with 0.2 wt.% of Dispersant S40 by a safety control device due to high pressure inside the mill chamber. A pseudoplastic slurry with a high extrapolated Casson yield stress could be the reason because the more viscous the slurry, the more power is needed to make the slurry flow when the slurry is circulated through the mill by a pump. This increases the pressure in the mill up to the limit.

Figure 45 Variation of the rheological behaviours of limestone slurry at two different solid concentrations in the presence of 0.2 wt.% Dispersant S40 at 74 vol.% bead load with grinding: a and b, Apparent viscosity; c, Extrapolated Casson yield stress. (by Bohlin viscometer).
If the point, where a grinding operation automatically terminates by a safety control device due to high pressure inside the mill chamber resulting from a pseudoplastic slurry with a high Casson yield stress, is defined as a reference terminal, where the final discharge product is called an FP product. The FP product has a quite similar specific surface area and particle size distribution for a given solid concentration at a specific addition level of Dispersant S40 (Table 8 and Figure 46). For instance, 70 wt.% of solid concentration with 0.2 wt.% of Dispersant S40 can be ground to an FP product with a specific surface area of $9.979 \pm 0.043 \text{ m}^2/\text{g}$ and a quite similar particle size distribution with a median size of $1.167\pm0.05 \mu\text{m}$. For 65 wt.% and 75 wt.% solid concentrations, the similar results were obtained. Figure 47 shows the effect of solid concentration on the specific surface area and particle size distribution of an FP product in the presence of 0.2 wt.% of Dispersant S40. Obviously, the specific surface area of an FP product is inversely proportional to solid concentration at a given addition amount of Dispersant S40 (Figure 47 (a)), whereas the particle size distribution parallelly moves towards a range of smaller particle size with decreasing solid concentration (Figure 47 (b)). Thus, for a given suspension system, it is possible to maintain a certain rheological behaviour when the amount of water is proportional to the specific surface area. A high solid concentration means a small amount of water per unit volume, which is indispensable to flow, and thus results in a small specific surface area of a product.

Table 8: Characteristic parameter values of an FP product obtained for 70 wt.% of solid concentration with 0.2 wt.% and 0.6 wt.% Dispersant S40 under other different grinding conditions

<table>
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<tr>
<th>Addition of S40</th>
<th>FP product number</th>
<th>Media bead load (vol.%)</th>
<th>Pass number</th>
<th>Specific energy consumption (kWh/t)</th>
<th>Median size ($X_{50}, \mu\text{m}$)</th>
<th>Specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 wt.% S40</td>
<td>1</td>
<td>65</td>
<td>9</td>
<td>215</td>
<td>1.169</td>
<td>9.975</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>74</td>
<td>5</td>
<td>180</td>
<td>1.108</td>
<td>10.04</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>77</td>
<td>4</td>
<td>174</td>
<td>1.159</td>
<td>9.959</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>83</td>
<td>3</td>
<td>163</td>
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<tr>
<td>Mean</td>
<td></td>
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<td></td>
<td></td>
<td>1.167±0.05</td>
<td>9.979±0.043</td>
</tr>
<tr>
<td>0.6 wt.% S40</td>
<td>5</td>
<td>74</td>
<td>12</td>
<td>432.66</td>
<td>0.584</td>
<td>17.911</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>80</td>
<td>10</td>
<td>405.91</td>
<td>0.557</td>
<td>18.147</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>83</td>
<td>8</td>
<td>372.39</td>
<td>0.52</td>
<td>18.113</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.554±0.032</td>
<td>18.057±0.128</td>
</tr>
</tbody>
</table>
4.3.2 Effect of addition amount of Dispersant S40

For a certain solid concentration at different addition levels of Dispersant S40, the evolution of rheological behaviour of limestone slurries with grinding time appears to be similar to that for different solid concentrations with a given addition amount of Dispersant S40, as shown in Figure 48. At the addition dosage of Dispersant S40 ≤ 0.1 wt.%, the apparent viscosity of a ground slurry at a given shear rate increases with pass number whereas the apparent viscosity first decreases and then increases at the addition dosage of Dispersant S40 ≥ 0.2 wt.%. Tangsathitkulchai and Austin (1989) also observed the similar phenomenon. For 70 wt.% of solid concentration with whatever addition dosage of Dispersant S40, the grinding operation automatically stop when a discharge slurry from the mill displays a pseudoplastic flow with an evident extrapolated Casson yield stress, where the discharged slurry is defined as an
FP product. The slurry with 70 wt.% of solid concentration can not smoothly be ground without Dispersant S40, but 2 passes with 0.1 wt.%, 4 passes with 0.2 wt.% and 12 passes with 0.6 wt.%. It is interesting to note that the specific surface area and median size of an FP product are correlated to the addition amount of Dispersant S40 for a given solid concentration (Table 8). Figure 49 shows the effect of the addition dosage of Dispersant S40 on the specific surface area and particle size distribution of an FP product. Evidently, the specific surface area of an FP product at a certain solid concentration (i.e., 70 wt.%) is directly proportional to the addition amount of Dispersant S40 (Figure 49 (a)). The particle size distribution parallelly moves towards a range of smaller particle size with increasing the addition amount of Dispersant S40 when the addition amount of the dispersant is up to 0.2 wt. %. At the addition amount above 0.4 wt.%, the finer particles (< 0.4 μm) increase more evidently, and the increase in specific surface area is mainly dependent on the created finer particles.

Figure 48 Variation of the slurry rheology of a ground limestone slurry at 70 wt. % of solid concentration with various dosages of Dispersant S40 with grinding. (by Bohlin viscometer)
In addition, the slurry also exhibits a time-dependent rheological behaviour when a discharge slurry from the mill displays a pseudoplastic flow with an evident extrapolated Casson yield stress. Figures 50 and 51 show the rheological behaviour of a ground slurry with a given characteristic size and specific surface area at 70 wt.% of solid concentration with 0.2 wt.% and 0.6 wt.% Dispersant S40, respectively. It is seen that the appearance of thixotropy is related to the particle size and specific surface area of ground product as well as the addition amount of Dispersant S40. For instance, when the slurry of 70 wt.% solid concentration with 0.2 wt.% Dispersant S40 is ground to a product with a median size (x₅₀) of 1.331 μm and a specific surface area of 10.04 m²/g, the “up” and “down” rheological curves do not coincide (see Figure 50(b)). This hysteresis loop is caused by a decrease in viscosity with increasing shearing time, which is defined as the thixotropic flowability. This is typical character of agglomerated or flocculated suspensions (Papo et al., 2002; Hackly 1998). This demonstrates that the attractive inter-particle forces are dominant due to the existence of a large amount of fine particles (< 1 μm), which attract each other by van der Waals attractive forces to form aggregates or flocs. At a higher addition of Dispersant S40, a ground slurry showing thixotropic property has a smaller particle size and a larger specific surface area (Figure 51(b)). For different solid concentrations with a certain addition amount of Dispersant S40, the similar phenomena were observed. The higher the solid concentration, the larger the particle size for a thixotropic slurry is and the smaller the specific surface area is.
4.4 Comparison of rheological results obtained by two viscometers

By comparison of rheological results obtained by Bohlin rotational viscometer and TA Instruments CSL 2 500 rheometer, it is found that these two instruments give the consistent results for time-independent slurries (Figures 50 (a) and 51 (a)). For time-dependent slurries, there exist differences in rheological results obtained from the two instruments in the range of shear rates studied, but the flowability from the two instruments follows the same tendency (Figures 50 (b) and 51(b)). This is because the time-dependent rheological properties are generally irreversible. Different configurations of rheometers, or shear intensities or shear time lead to various deformations or damages of flocs for time-dependent suspensions and thus give
distinct rheological results. The two instruments can produce consistent results with respect to flow type for a given slurry, but the accurate rheological characterization of time-dependent fluids is dependent upon the viscometer or rheometer used and operation conditions.

4.5 Empirical prediction

In classical grinding theory, the particle size of a ground product reduces with increasing net specific energy input in the form of a power-law function. The differential form of the power-law relationship between an infinitesimal specific energy input and an infinitesimal increase in the overall fineness of the product can be described by the following equation (Austin et al., 1984):

\[ dE = -k \cdot \frac{dx}{x^n} \]  

(18)

where \( E \) is the net specific energy input (kWh/t) to a mill, \( x \) is the particle size, \( k \) is a proportionality coefficient depending on the grindability of a material and the efficiency of the mill, and \( n \) is a variable related to the particle size regime. Since a ground product does not consist of particles with one size, \( x \), the product fineness has to be described by an appropriate characteristic particle size, \( x_p \), such as \( x_{50} \) (the 80 wt.% passing size) or \( x_{50} \) (the median size) of its cumulative particle size distribution, which is convenient characteristic value for a particle size distribution (Kwade et al., 1996; Gao and Forssberg, 1995). Integration of Eq. (18) for \( n \neq 1 \) gives the following equation for the specific energy consumption, \( E \):

\[ E = \frac{k}{n-1} \left( \frac{1}{x_{m,p}^{n-1}} - \frac{1}{x_{m,F}^{n-1}} \right) \]  

(19)

where \( x_{m,p} \) is a characteristic size of the particle size distribution of a ground product and \( x_{m,F} \) is the characteristic size of the particle size distribution of the feed. In this study, the median size, \( x_{50} \), of a product was chosen as the characteristic size, \( x_{m,p} \). It is found that the relationship between the median size (\( x_{50} \)) and the specific energy consumption can be well described by the following power-law function, which can be derived for \( x_F \gg x_p \), which is valid for ultra-fine grinding, from Eq. (19):
\[ x_{50} = C \cdot E^m \]  \tag{20} 

where \( C = \left( \frac{k}{n-1} \right)^{\frac{1}{n-1}} \), \( m = -\frac{1}{n-1} \).

Figures 22(b), 25(b), 29(b), 32(b), 34(b), 35, 39(a) and 41(a) present the experimental (dots) and predicted (lines) results for all grinding experiments under various grinding conditions. Clearly, the particle size-energy model of Equation (20) provides a good fit to the experimental results for both limestone and quartzite with a high regression coefficient (> 0.904) under grinding conditions investigated. This is in agreement with a previous conclusion for dolomite (Gao and Forssberg, 1995).

5 Conclusions

This thesis investigated the slurry rheology of industrial minerals (limestone and quartzite) and its effects on the wet ultra-fine grinding. The following conclusions were drawn:

(1) The rheological behaviour of a limestone slurry (< 100 \( \mu \)m) is transformed from a weakly dilatant characteristic to a pseudoplastic one with a yield stress, which is in combination with a thixotropic property at a higher solid concentration (i.e., \( \geq 75 \) wt.%), when the solid concentration is increased from 60 wt.% (35.71 vol.%) to 78.5 wt.% (57.49 vol.%). At a certain shear rate, the apparent viscosity and the relative viscosity of the slurry increase exponentially with increasing solid concentration. The extrapolated Casson yield stress increases in a power-law form with increasing solid concentration when the solid concentration of the slurry is larger than 70 wt.% (i.e., 46.36 vol.%). The attainable maximum packing solid fraction (\( \phi_m \)) is predicted as \( \phi_m = 64.6 \) vol.% at the certain limestone-water slurry.

For control of slurry rheology, the mostly used dispersant is polyacrylic acid or its salts. The effect of sodium polyacrylate salts with various molecular weights on the rheological behaviour of a limestone slurry (<100 \( \mu \)m) at a given solid concentration appears to be similar. With increasing the addition amount of a sodium polyacrylate, the apparent viscosity of the slurry first increases, and decreases, then reverts after reaching a minimum. Also, the yield stress is eliminated when the addition amount
exceeds a certain value. Sodium polyacrylate called Dispersant S40 with a molecular weight of 5500 Da appears to be most effective for reduction of the apparent viscosity and maintenance of stable flowability.

For a given solid concentration of limestone slurry, the smaller the particle size, the more evident the pseudoplastic property is with a larger yield stress and a larger apparent viscosity at a given shear rate. However, a sufficient addition dosage of the dispersant called Dispersant S40 significantly decreases or even eliminates the effect of particle size and distribution on the slurry rheology.

(2) Wet ultra-fine grinding of a limestone powder (< 100 μm) has been investigated in a stirred media mill with respect to the effect of slurry rheology. A polymeric dispersant called Dispersant S40 with a molecular weight of 5,500 Da gives a higher energy efficiency and a smaller product size for wet ultra-fine grinding of the limestone due to its maintenance of a lower viscosity during grinding. For a certain media bead load, an optimal solid concentration exists for the effective grinding. At an addition dosage of 0.1 wt. % of Dispersant S40 or more, a smaller addition amount leads to a higher energy efficiency and a smaller product size at a given specific energy consumption in a lower level of specific energy input. However, the excessive amount of the dispersant causes the grinding less efficient. This can be avoided by the multi-point addition of the dispersant or by a higher bead load (≥ 83 vol. %).

(3) The effect of slurry rheology on stirred media milling of quartzite has been studied as well. Media bead density has an evident but complex effect on stirred milling performance, depending on stirrer rotational speed and solid concentration. Addition of Dispersant S40 or a lower solid concentration results in better grinding results (i.e., a higher energy efficiency and a smaller median size) due to maintenance of lower viscosities at shear rates investigated during grinding. The combined effect of stirrer rotational speed and solid concentration is evident. For a given solid concentration, an optimal stirrer speed exists. The observed phenomena can be explained by the effect of slurry rheology on the stress intensity of individual grinding beads.

(4) The rheological behaviour of ground limestone slurries vary with grinding from a starting dilatant flowability to a resulting pseudoplastic one with an evident Casson yield stress in combination with a thixotropic character. The appearance of pseudoplastic flowability combining thixotropy is related to solid concentration and the addition amount of Dispersant S40. The less the dispersant amount is for a given
solid concentration, the earlier a pseudoplastic flowability accompanying a thixotropic character appears. The lower the solid concentration with a specific addition amount of the dispersant, the later a pseudoplastic fluid with a thixotropic character displays. Regardless of whatever grinding conditions, the grinding operation automatically ceases when a discharge slurry from the mill shows a pseudoplastic flow with an evident extrapolated Casson yield stress, where the discharged slurry is defined as an FP product. The specific surface area and particle size distribution of an FP product are correlated to solid concentration and the addition level of Dispersant S40. The specific surface area of an FP product is inversely and directly proportional to solid concentration and the addition amount of Dispersant S40, respectively, whereas the particle size distribution of an FP product parallelly moves towards a range of smaller particle size with decreasing solid concentration or increasing the addition amount of Dispersant S40. Besides, the accurate rheological characterization of time-dependent fluids is dependent upon the instruments used and operation conditions.

(5) In addition, an empirical particle size-energy model provides a good fit to the wet ultra-fine grinding results for both limestone and quartzite under the experimental conditions investigated.

**Recommendations for future work**

Interfacial chemistry of industrial minerals should be performed by zeta potential measurements in a concentrated suspension. Polymeric dispersant adsorption onto industrial minerals should also be investigated by means of some effective characterization methods such as attenuated total reflection Fourier transform infrared spectrometry (ATR-FTIR) and x-ray photoelectron energy spectrometry (XPS). It would be interesting to draw a link between interfacial chemistry / polymer adsorption and slurry rheology for industrial minerals.

Motion of grinding beads, flow filed and shear rate distributions are not well understood in a stirred media mill. Modelling of motion of grinding beads, flow filed and shear rate distributions in a stirred media mill is a challenge using Computational Fluid Dynamics (CFD). This can provide scientific understanding of the role of slurry rheology in stirred media milling and grinding mechanisms in a stirred media mill. It
would be desirable to build up a quantitative grinding mechanism involving grinding operation parameters and slurry rheology.

References


Kwade, Arno, 1999 b. Determination of the most important grinding mechanism in stirred media mills by calculating stress intensity and stress number. Powder Technology 105, 382-388.


Appendix
Paper 1

Slurry rheology in wet ultrafine grinding of industrial minerals: A review


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Slurry rheology in wet ultrafine grinding of industrial minerals: a review

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Abstract

Wet ultrafine grinding has been increasingly used for production of ultrafine powders in various industries. It has been known that slurry rheology significantly influences the grindability of industrial minerals in wet ultrafine grinding. This review represents some previous work with respect to slurry rheology in ultrafine grinding. In this review, some methods for the characterization of the slurry rheology and some empirical equations modelling rheological behaviours of slurries were presented. The semiempirical model incorporating slurry rheology, solids concentration, particle size and slurry temperature was described. In addition, on-line measurement for the slurry rheology control was also discussed. In the case of ultrafine grinding, various parameters (such as solid concentration, particle size and distribution, particle shape, temperature, rotation and pH, use of dispersants), which affect the slurry rheology, have been described. It was revealed that the optimization of the rheological behaviours of slurry in ultrafine grinding could increase throughput, energy efficiency and product fineness as well. It is suggested to further study the mechanisms of slurry rheology in the presence of chemical dispersants in wet ultrafine grinding. It is desired to develop a model, which can represent a relation among slurry rheology, comminution parameters, amount of dispersant, energy efficiency and particle size characterization.

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Keywords: Rheology; Wet ultrafine grinding; Slurry; Fine particles; Industrial minerals; Dispersants

1. Introduction

With an increasing demand for ultrafine powders for industries [1–3], wet ultrafine grinding has been increasingly used in various fields, such as minerals [4–6], ceramic materials [7–9], pigments [10], chemical products [2,11], microorganisms [12], pharmaceutics [13,14] and paper-making [15]. It has well been known that slurry rheology affects the wet comminution of materials [16–30]. From a diagnostic point of view, the rheological behaviour of mineral slurries is indicative of the level of interparticle interaction or aggregation in a slurry and therefore it is an important variable of the processing control [31]. The influence of rheological behaviour of mineral slurries on their grindabilities has attracted more and more interests and attention, especially on ultrafine grinding performance [8,10,29,30,32–37]. Most of the mills used in ultrafine grinding are stirred media mills, rather than conventional tumbling ball mills [3]. Although many studies [16–26,28,38–43] on the slurry rheology in tumbling ball mills have been published, there is still little understanding on the slurry rheology relevant to ultrafine grinding at high slurry densities [29,36]. This is because the breakage mechanism of ultrafine comminution in stirred media mills is rather different from that of tumbling ball mills. In the case of tumbling ball milling, the size reduction is mainly dependent on the cataracting and cascading motions of charge balls, leading to striking charge particles nipped against other balls, and rubbing charge particles between balls in the bed on the bottom of cylinder [40,44]. The impact stress from cataracting and cascading is far larger than shear stress from rubbing [40]. However, the fragment in stirred media mills for ultrafine grinding is mainly subject to shear stress [3]. The predominant comminution mechanisms are dependent...
on shear, compressional and torsional stresses, which are invoked by stirring the particles–grinding media mixture at a very high velocity [45–48]. The effective motion of the mixture is much related to the flow field in the grinding chamber. Therefore, the effect of the slurry flowabilities or slurry rheology in wet ultrafine comminution in stirred media mills becomes of particular importance. In addition, in the case of the requirements of product fineness, cylinder ball mills are suitable for coarse comminution and can efficiently achieve the aim that $X_{80}$ (the particle size at which 80 wt.% particles pass) is not larger than 75 $\mu m$ [35]; however, the objective of ultrafine grinding in stirred media mills is at least the median size ($X_{50}$) less than 2 $\mu m$ [32] or 90 wt.% particles below 10 $\mu m$ [3,29].

Since the product fineness significantly increases with grinding time in wet ultrafine grinding characterized by a very fine product size and a high slurry concentration, the surface properties tend to predominate in the system [3,29,30,32,36,37]. This results in changes in the rheological properties in wet ultrafine grinding operations due to the agglomeration and aggregation resulting from the interparticle forces, such as van der Waals forces [3,49] and electrostatic forces [31,32,50]. Therefore, the investigations of the slurry rheology for the process of ultrafine grinding are important and necessary for the scientific understanding and the industrial application. Much work in this aspect has been carried out. This review is thus to represent some previous work with respect to the slurry rheology in wet ultrafine grinding of industrial minerals during the last 20 years.

2. Rheological characterization of mineral slurry

2.1. Types of rheological behaviour

Rheology is a science of deformation and flow of materials [51,52]. The principal theoretical concepts are kinematics, dealing with geometrical aspects of deformation and flow; conservation laws, forces, stress and energy interchanges; constitutive relations special to classes of bodies. The constitutive relations, namely, the relations between stress, strain and time for a given test sample, serve to link motion and forces to complete the description of the flow process, which may then be applied to solve the engineering problems. There are the Newtonian and non-Newtonian fluids based on the constitutive relations. For the fluids, the viscosity, $\eta$, defined by [30,52]

$$\eta = \frac{\text{Shear stress}}{\text{Rate of shear strain}},$$  \hspace{1cm} (1)

is a useful parameter. In the case of Newtonian fluids, $\eta$ is constant. For non-Newtonian fluids, $\eta$ is variable, which means that the shear stress ($\tau$) varies with the rate of shear strain ($\dot{\gamma}$). As known, most semisolids, such as mineral slurries, which are either found in nature or synthesized in laboratory, exhibit non-Newtonian fluids [30,35,36]. The information for characterization of the rheology of non-Newtonian mineral slurries is outlined in Fig. 1.

2.2. Rheological characterization of mineral slurry

Rheological characterization of a mineral slurry is to measure the relationship between shear stress and rate of shear strain varying harmonically with time, indicating the level of interparticle force or flocculation in the mineral slurry. However, the charge (media and slurry) motion inside a grinding vessel is very complex [23,32,39–42], especially for stirred bead mills [1,3,12,32,37,46,48,53]. In addition, the surface properties of mineral particles are easily changeable, such as increase of specific surface area [54], enhancement of surface reactivity [54], increase of solubility of the fine particle due to its high surface energy [3], extensively heterogeneous surface chemistry controlled by electrochemical oxidation process [55]. Therefore, it is rather difficult to measure or predict accurately the slurry rheology during the grinding process. Klimpel [54] has been involved with 30 different industrial examples of fine grinding in the last three decades and found each example so unique that it was difficult to generalize the specific learning experience. However, many efforts have been exerted in this aspect. According to different measurement parameters and methods used, the methods of rheological characterization of mineral slurries include as follows.

2.2.1. Direct characterization by the use of viscometers or rheometers

Direct characterization using viscometers or rheometers is of direct measurement of the relationship between shear rate and shear stress or apparent viscosity, which characterizes the time-independent rheology of slurry [56]. At present, among the commercially available rheometers and
viscometers, three basic types have been tried for slurry applications [57]:

1. Coaxial cylinder viscometers or rheometers (Bohlin Instruments [58], Brookfield Viscometers [30,56–61], Haake viscometers [29,30,55,62,63], TA Instruments [49], Debex viscometers [38–42]) can be used to measure at a particular shear rate, which can be varied by changing the rotational speed of the spindle. Because of this control in shear rate, coaxial cylinder viscometers have been popular for many applications. However, the settling of solid particles causes serious problems in the case of coaxial cylinder viscometers or rheometers. In order to overcome this problem, Kawatra et al. [57,58] developed a Brookfield setup including a slurry presentation system and a UL adaptor assembly, consisting of a UL adaptor spindle and a UL adaptor tube (see Fig. 2). Slurry is mixed in an overhead tank and passes continuously through the annular space between the UL adaptor spindle and the tube. Then, the viscosity is determined by measuring the torque required to rotate the spindle at a constant rotational speed. The Brookfield viscometer setup can eliminate any swirling motion caused by the flow at the inlet and display a steady reading before the settling of particles occurs. In addition, it is suitable for the measurement of apparent viscosity at low and different shear rates and can measure a viscosity as low as 0.001 Pa s. Another modified viscometer, Debex, is shown in Fig. 3 [39]. A sample of slurry is presented to the bobbin for measurement. The feed slurry flows upwards in an annulus around the measuring cup, overflows into the cup and into an outer annulus, and drains after viscosity measurement. Slurry collected from the drain and overflow is returned to the circuit. The measuring cup thus provides a constant level of flowing slurry in which the bobbin rotates. The flow through the cup is sufficient to maintain the slurry in a homogeneous suspension. In addition, in order to eliminate a rotational movement of the fluid, to assist mixing and to allow the free passage of coarse particles, the measuring cup is fitted with six radial baffles.

2. Capillary tube viscometers or rheometers (pressure vessel rheometers [56], a capillary rheometer system designed and constructed [60], balanced beam tube viscometer [64]) are mechanically simple and rather sensible to low viscosity. A capillary viscometer can operate at high shear rates but at a fixed value [56,65]. Besides, during the measurement of a capillary rheometer, a test sample is not subject to a sustain flow but varying shear rate and shear stress over the tube cross section, allowing to measure time-dependent effects, such as thixotropy flow. These two parameters are generally calculated at the wall [65]. Hence, this kind of rheometers cannot be directly used as the accurate measurement of slurry rheology. In order to avoid the disadvantages of capillary tube viscometers or rheometers, a pressure vessel rheometer, which is a capillary rheometer (see Fig. 4), has been developed [56]. The inlet tube of this rheometer is attached to a recirculating fluid line and the other end is connected to a conical sealed chamber. An automatic ball valve is attached to the base of the vessel to drain fluids or slurries after each test. An absolute pressure transducer measures the pressure of the air inside the vessel, and a differential pressure transducer does the pressure difference across the tube. Data from both pressure transducers are collected by a digital computer. The pressure vessel rheometer varying continuously the shear rate can measure the
viscosity at different shear rates, the rheological types, and the yield stresses for a wide range of fluids and slurries with high precision and complete shear stress vs. shear rate curves.

(3) Vibrating sphere viscometers or rheometers (Nametre viscometer [56–58,66,67]) operate at a very high shear rate, and cannot operate at a specific shear rate but average the shear rates from zero to the maximum value. The maximum shear rate is not a definite constant for the instrument but varies according to the velocity of propagation of the shear wave in a fluid, which in turn depends upon the fluid viscosity. This instrument is insensitive to most turbulence, and can easily measure the viscosity of well-mixed slurries. In order to avoid solids settling during measurement by the use of a Nametre viscometer, the Nametre setup containing a Nametre viscometer and a special slurry presentation system (see Fig. 5) was developed by Kawatra et al. [57,58,66]. The Nametre viscometer consists of a spherical probe, which oscillates along a vertical shaft at its resonant frequency with a constant amplitude. The special slurry presentation system is composed of a vessel of two concentric cylinders. The bottom of the inner cylinder is made conical to avoid solids settling and has an inlet opening through which the slurry from the pump enters the vessel. The outer cylinder is 1 in. taller than the inner one and has a discharge opening on its side. The viscometer is suspended from the top by a cable and the probe of the viscometer is immersed inside the inner cylinder. This arrangement prevents problems with vibration and excessive fluid drag on the sensor. A thermocouple is also placed inside the sump, so that both the viscosity and the temperature of a test sample are recorded simultaneously. The Nametre setup can measure the apparent viscosity of rapidly settling mineral suspensions, such as coal slurries [67] and silica slurries [57,58,66], at a high shear rate and a viscosity as low as 0.001 Pa·s.

Much rheological data [29,30,33,35,55,58,68,69] were obtained by off-line measurements. However, the rheological properties of ground slurries vary continuously with grinding time in the case of wet grinding, the on-line measurement is thus far more important for plant-scale production and control. Shi and Napier-Munn [39,41,42] used the single bobbin Debex viscometer (see Fig. 3) as an online measurements of unstable slurries, such as gold, copper and lead/zinc on 16 full-scale industrial grinding mills. A sample of the suspension of interest is taken continuously from process and presented to the bobbin for measurement. Feed to the viscometer can be degritted by a screen fixed inside a constant-head tank, or by some other appropriate methods. In addition, a turbulence correction procedure obtaining a full shear rate–shear stress flow curve was developed. Another viscometry system involving a coaxial cylinder rotational viscometer (see Fig. 2) and a vibrating sphere viscometer (see Fig. 5) has been developed for the on-line measurement of viscosity, and for rheological characterization of mineral slurries into either Newtonian or non-Newtonian flow curves [57,58]. Both of the viscometers are combined respectively with a slurry presentation system to avoid settling of solids particles during a viscosity measurement. It uses a rotating-type viscometer to measure apparent viscosities at a low shear rate and a vibrating sphere-type viscometer, at a high shear rate. The two instruments together can accurately determine the shear-rate dependency of the viscosity. In addition, Kawatra et al. [56] developed an on-line pressure vessel rheometer (see Fig. 4), which is a capillary viscometer with continuously various shear rates. It can be used for on-line measurement of viscosity at different shear rates, the rheological types, and the yield stresses for a wide range of fluids and slurries with high precision and complete shear stress vs. shear rate curves.

Fig. 4. Schematic diagram of the pressure vessel rheometer modified [56]. The instrument is directly connected to the process line to tap a sample for measurement. Legend: (1) process line, (2) vessel, (3) stainless steel tube, (4) differential pressure transducer, (5) absolute pressure transducer, (6) drain valve, (7) water valve.

Fig. 5. Nametre viscometer setup, sample is placed in the sump and is circulated through the system by a centrifugal pump. This arrangement is very suitable for suspensions with rapidly settling particles [57,58,66].
measurements of both Newtonian and non-Newtonian slurries, and produces complete shear stress–shear rate curves, which can characterize the time-independent rheology of the slurry.

On-line measurements of rheological behaviour in wet ultrafine grinding have not been reported in any literature. The following reasons can contribute to the fact (23,29,33,39,41,42): (a) In wet ultrafine grinding, slurry rheology is extremely complex and is affected by many factors, such as particle size and shape, temperature, solid content, interparticle force, media hardness and density, and stirred velocity; (b) It is rather difficult to measure the unstable mineral suspension, especially on-line in wet ultrafine grinding process, and to unequivocally explain what is measured; (c) More formidable is the reproduction of the real shear rates in a running mill for a measurement; for instance, it is difficult to accurately evaluate the real shear rates in a stirred media mill with the similarity rule due to the complexity of a slurry flow field and the easy variation of a shear rate from point to point in a stirred media mill.

2.2.2. Indirect characterization by measuring zeta potential (ζ)

The indirect characterization of slurry rheology by measuring zeta potential (ζ) is feasible because the relationship between zeta potential (ζ) and apparent viscosity (η) is valid for a lot of solid/additive system [32,70]. The state of dispersion in a slurry, namely, the rheological behaviour, is closely related to the zeta potential of the particles [49,61], which represents the potential difference between the surface of the particles and the external plane of Helmholtz, illustrated by use of a model for the electric double layer in Fig. 6. The zeta potential of a suspension is an indication of the magnitude of the repulsive force between the particles. The higher the zeta potential with the identical polarity is, the more predominant the electrostatic repulsion between particles. On the contrary, when the zeta potential is close to the isoelectric point (ζ=0), the particles tend to flocculate, as illustrated in Fig. 7. The electrical double layer develops [36,71] when a particle is immersed in the continuous fluid (i.e., water). Once the immersion occurs, charged species will start to migrate across the solid/liquid interface until an equilibrium is reached. Ions that directly increase the charge on the particle surface are called as potential determining ions and are unique to each type of particle system [36]. With many types of solid particle suspensions, especially oxide [33,34,36,61,69] and sulfide [31,55,68] mineral slurries, the potential determining ions are H⁺ or OH⁻. In this case, the change in the pH of a liquid can cause a change in the particle surface charge. Hence, for a given mineral slurry, zeta potential is directly dependent on the pH value. The relationship between zeta potential and pH value in slurries can characterize rheological behaviours of slurries that conforms well to the results obtained using rheometers or viscometers, as seen in Figs. 8 (a and b) and 9.

Fig. 6. Model for the electric double layer at the solid–solution interface. The surface going through the centers of ions which are specially adsorbed on the solid surface is the so-called ‘Inner Helmholtz Plane’ (IHP). The ‘Outer Helmholtz Plane’ (OHP) indicates the closest distance of approach of hydrated ions in solution [36,61].

Fig. 7. Slurry stability versus zeta potential [61].
2.2.3. Indirect characterization by measurements of the torque drawn by mills

The slurry viscosity is directly proportional to the torque drawn by mills under a given grinding condition. Therefore, the indirect characterization of slurry rheology by measurements of the torque drawn by mills during the operation period cannot obtain the accurate rheological behaviours of slurry, but give a relative indication of the slurry rheology under different milling conditions. The characterization of slurry rheology using average torque drawn by tumbling ball mills has been reported [26,72]. Zheng et al. [37] measured the relationship of the torque of a stirred media mill versus grinding time to characterize slurry rheology in wet ultrafine grinding in order to reveal the effect of grinding aids on the slurry rheology.

2.3. Modelling of the rheology of mineral suspensions

Modelling of the rheology of mineral suspension is to use mathematic methods describing the constitutive relations between shear stress and shear rate for a given test slurry. The empirical rheological models describing the shear stress (τ)–shear rate (γ) dependence of non-Newtonian mineral slurries are the two-parameter power-law [35,73], Bingham plastic [31,43,55,68,74,75] and Casson [69,76,77], and the three-parameter Herschel–Bulkley [31,55,62,68,69] and Sisko models [60,78]. These models are given as follows:

- Power law model: \( \tau = K_p\gamma^n \) \( \quad (2) \)
- Bingham plastic model: \( \tau = \tau_0 + \eta_p\gamma \) \( \quad (3) \)
- Casson model: \( \sqrt[1/2]{\tau} = \sqrt[1/2]{\tau_0} + \left(\eta_p\gamma\right)^{1/2} \) \( \quad (4) \)
- Herschel–Bulkley model: \( \tau = \tau_0 + K_h\gamma^n \) \( \quad (5) \)
- Sisko model: \( \tau = \eta_p\gamma + K_s\gamma^n \) \( \quad (6) \)

where \(\tau_0\) is the yield stress; \(\eta_p\) is the plastic viscosity; \(n_p, n_h\) and \(n_s\) are the power-law indexes for various models, respectively; \(K_p, K_h\) and \(K_s\) are the consistencies, with the dimension of time, for various models, respectively.

![Fig. 8.](image-url) (a) Zeta potential of the mixed slurry (involving TiO₂, SnO₂, ZrO₂, NiO and La₂O₃) versus pH. (b) Rheogramms for the mixed slurries (40 wt.% density) for two different pH [61].

![Fig. 9.](image-url) The influence of pH on the rheological behaviour and zeta potential of ultrafine galena particles: (a) extrapolated yield values for slurries of 45.5% solid content; (b) viscosity for slurries of 45.5% solids content; (c) zeta potentials [68].
In addition, Shi and Napier-Munn [38,39,42] have developed a semiempirical model to predict the slurry rheology from easily measured slurry properties. The model first predicted machine output readings of the on-line Debex slurry viscometer at various bobbin rotational speeds, from solids concentration, solids size distribution and temperature. The machine readings and the bobbin rotational velocity per minute are then converted to shear stress and shear rate using the turbulence correction method.

The relationship between the Debex readings (mV) and the bobbin angular velocity (Ω) is

\[ mV = a_0 + a_1Ω + a_2Ω^2 + a_3Ω^3 \]  

(7)

where \( a_0 \)—the coefficient related to the yield stress of slurry; \( a_1 \)—the coefficient related to a combined effect from the bobbin shear action and the particle hydrodynamics; \( a_2 \)—the coefficient as a function of solids volume fraction and particle size; and \( a_3 \)—the coefficient mainly reflecting the bobbin mechanical action.

The equation determining the actual torque on the bobbin, \( M_b \), from the Debex voltage output is

\[ M_b = (2.0657 mV - 0.4831) \times 9.81 \times 10^{-5} \text{ N} \cdot \text{m} \]  

(8)

The measured shear stress, \( S_b \), can then be calculated as follows:

\[ S_b = \frac{M_b}{2\pi h R_b^4} \]  

(9)

where \( h \)—the effective height of bobbin; \( R_b \)—the bobbin radius.

In the case of non-Newtonian mineral slurry with a yield stress, the calculation of shear rate, \( γ \), is

\[ γ = \frac{\Omega}{\ln e} \left( 1 + \frac{\ln(\ln e)}{3} + \frac{\ln(e)}{3} + \frac{\ln(S_b - ψ)}{3} \right) \]  

(10)

where \( ψ \)—yield stress; \( m = (\ln(\ln e))/\ln(S_b - ψ); e \)—the ratio of cup to bobbin radii.

Although the model was developed from the on-line Debex slurry viscometer, Shi and Napier-Munn [39] have revealed that as long as the parameters used in any particular application are appropriate, the method that has been constructed with reference to one particular instrument type becomes irrelevant. In addition, a turbulence correction procedure was developed to obtain a full and accurate shear rate–shear stress flow curve, which is in good agreement with that measured. The model is a semiempirical model incorporating solids concentration, particle size and slurry temperature, but does not take explicitly into consideration of other variables, such as particle shape, specific surface area, electrochemical conditions, or complex interactions of these variables. It provides a method for the modelling of slurry rheology.

3. Major parameters influencing the slurry rheology

As mentioned above, the rheology of a mineral suspension is highly complicated and there is no single parameter that can solely explain it [23,29,30,37,79]. Physical and chemical properties of slurry, such as solids content, particle size, particle size distribution, particle shape, pH value, shear rate, slurry temperature, have a significant influence on the rheology of slurry in wet ultrafine grinding.

3.1. Effect of solid concentration

Qualitatively, the rheological behaviour of a time-independent suspension has the following characteristics. At low concentrations, it may be Newtonian with the viscosity \( \eta \) independent of the shear rate. As the concentration increases, it will become progressively more strongly non-Newtonian with a steeply increasing viscosity as the shear rate decreases (see Fig. 10), signifying the possible appearance of a yield stress (see Fig. 11) and a remarkable shear-thinning characteristic over the intermediate shear rates (see Fig. 12(a)). The rheological behaviours, for dolomite slurries [29,30], galena slurries [55,68], quartz slurries [43], coal slurries [74], respectively, with respect to the effect of solids concentration, are similar to Figs. 10–12(a).

Gao and Forsberg [29] have investigated the influence of various slurry densities of dolomite on the slurry rheology and ultrafine grinding performance. It was found that by increasing the slurry density from 65 to 75 wt.%, the slurry viscosity exponentially increased (see Fig. 13). This phenomenon was also observed by other researchers in the cases with and without dispersants [27,74]. The slurry viscosities at different slurry densities did not change (see Fig. 14(a)) much as the milling proceeded. It has been concluded [29] that the slurry viscosity caused by the difference in slurry density should be as low as possible, leading to a better grinding result in terms of increasing the
specific surface area per unit of energy consumption (energy efficiency), as was consistent with that by Zheng et al. [37] in the cases with and without the dispersant of PAA. It was found that a higher slurry density allowed fewer numbers of milling passes because of the yield stress jumped up from zero (see Fig. 14).

Bernhardt et al. [32] have studied the effect of the solid concentration of limestone on the slurry rheology for the effective wet ultrafine grinding and the energy utilization. The curves in Fig. 12(a) showed the typical non-Newtonian behaviour with a yield stress value and remarkable shear-thinning characterization, both strongly dependent on the solid concentration. Fig. 12(b) revealed that the energy utilization was nearly independent of the energy consumption for low solid concentrations, but for high solid concentrations, it showed a clear maximum, which was shifted to lower energy consumption with increasing solid concentrations. The reason is that in the region of low specific energy input (or short grinding time), the number of particles increases with grinding time, and the stressing conditions become better, and the energy efficiency increases. However, there is a point where the ground particles increase the viscosity of the suspension to such an extent that they increase the attenuation of the velocity and kinetic energy of the grinding media ball. Besides, they found that the earlier the maximum shift occurs, the higher the solids concentration.

Fig. 11. The maximum yield stress of alumina A16 and zirconia Unitec suspensions, respectively, as a function of solid loading [80].

Fig. 13. Variation in the slurry viscosity at different slurry densities of dolomite in size less than 30 µm in the presence of 1.0 wt.% Dispex N40 [29].

Fig. 12. The influences of various slurry concentration of limestone on slurry rheology (a) and on energy utilization (b), respectively, parameter \(c_m\)=solid concentration [32].

Fig. 14. Influence of the slurry density on the viscosity (a) and the yield stress (b) during milling process for dolomite below 30 µm in the presence of 1.0 wt.% Dispex N40 [29].
3.2. Effects of particle size and particle size distribution

Tangsathitkulchai and Austin [74] investigated the influence of natural size distributions of ground coal and quartz on the rheological properties of concentrated slurries. They found that the strong influence of characteristic particle size on the slurry rheology was not due to packing or adsorbed layers on the particles. In addition, it was deduced that any rheological theory of concentrated slurries, which does not include a strong dependence of viscosity on particle size, could not be correct. A similar investigation was reported by Logos and Nguyen [63] that by adding a narrow-sized coarse coal fraction (208–279 \(\mu m\)) to the fine (<45 \(\mu m\)) coal slurry, the flow characteristics of the slurry, at a fixed total solids concentration, could be changed significantly with a substantial reduction in the slurry viscosity. It was also found that an optimum coarse-to-fine particle ratio of 40:60 existed at which the slurry containing only the fine particles at the same solids concentration. Another similar work [76] has presented that the titanium dioxide suspensions with a broad size distribution exhibited a lower yield stress and a smaller viscosity than those with a narrow size distribution at the same solid volume fraction (see Fig. 15). Other several researchers have reported the effect of particle size and distribution on the flow patterns of the slurries of iron ore [35], quartz [43] and metal [38]. Although these reported results are not in complete agreement with each other, the influence of particle size and distribution on the rheological behaviour of slurry is significant (see Fig. 16).

3.3. Effect of pH value of slurries

Some literature shows that the pH value greatly influenced the rheological behaviours of ultrafine sulphide mineral slurries in size below 5 \(\mu m\), such as sphalerite [31] and galena [55,68]. It was found that the yield stress was strongly dependent on the pH value due to the significant dependence of the surface properties of ultrafine sulphide mineral particles in slurries on the pH value (see Fig. 17). Furthermore, the maximum yield stress value occurred in the region of pH values corresponding closely to the isoelectric points (IEP) of various minerals, as is in agreement with the results from the slurry of oxides [61,69,76,81–86], and kaolin [85]. Besides, Prestidge [55,68] studied the effect of pH on the viscosity of galena slurry. The results showed that the plastic viscosity of the slurry was insignificantly dependent on pH, which is similar to the experimental results for alumina suspensions in the pH ranges from 7.3 to 10.8 by Zhou et al. [84]. However, some studies on the slurries of titanium dioxide [69,76,86] and of ZST (\((Zr,Sn)TiO_4\)) and Nb_2O_5 [61] have shown that the pH of slurry could change the flow pattern of slurry and thus varied the viscosity of slurry (see Figs. 8(b) and 18). These results are not free from contradictions due to the complexity of the factors influencing slurry rheology, such as particle size/shape and particle surface properties. Besides, the effect of the interactions between or among the pH value and other factors on slurry rheology is unclear.

3.4. Effect of shear rate (rotation)

Viscometric investigations of concentrated aqueous alumina suspensions with particle size smaller than 5 \(\mu m\) have been investigated [62]. In the shear rate interval between 20 and 640 \(s^{-1}\), the experimental flow curves indicated thixotropy, which exhibited a pseudoplastic flow behaviour in the range smaller than 200 \(s^{-1}\) and a dilatant flow behaviour in the higher range. The shear rate in a stirred bead mill is closely pertinent to its rotational speed. Thus, the effect of rotational speeds on slurry rheology is important to characterize correctly the flow behaviour of slurry and to provide reasonable data for commercial production. However, no methods can accurately predict a real shear rate in a stirred media mill at present. Therefore, the precise evaluation of the shear rate distribution at different points in a stirred media mill with respect to the slurry rheology should be studied by means of computational fluid dynamics [87].

Fig. 15. Effects of particle size distribution on yield stress (a) and viscosity at a solid volume fraction of 0.28 (b) [76].
3.5. Effect of temperature

Temperature is another important factor that strongly affects the apparent viscosity and yield stress of slurries by varying the viscosity of a carrier solvent. Yang et al. [76] have investigated the temperature dependences of viscosity and yield stress for titanium dioxide suspensions. The viscosity decreased with increasing temperature (see Fig. 19), as is consistent with results reported by Mikulášek et al. [69], and the yield stress decreased with increasing temperature in the lower temperature ranges and increased in the high temperature (see Fig. 20). It was also noted that the suspensions underwent a flow transition from shear thinning to shear thickening at a shear rate of about 10 s⁻¹ around 50 °C (see Fig. 19). The onset of shear thickening was dependent on the balance of hydrodynamic and Brownian contributions. In wet ultrafine grinding, the temperature of ground slurries changes significantly during grinding. For instance, the temperature of various ground slurries fluctuated from 14 to 60 °C under different conditions in a stirred media mill [29]. It is necessary to take into account the effect of temperature when evaluating the slurry rheology.

![Fig. 16. Effect of characteristic particle size on flow curves of Hellyer grinding slurries at various solids concentrations [38].](image1)

![Fig. 17. Extrapolated yield values for ultrafine sphalerite slurry as a function of pH at the solids content of 42 wt.% [31].](image2)

![Fig. 18. Effect of pH on the flow properties of 30 vol.% titanium dioxide dispersions at temperature 20 °C [69].](image3)
3.6. Effect of particle shape (crystal morphology)

The effect of particle shape on the rheological behaviour of slurry for wet ultrafine grinding was seldom reported. Yuan and Murray [88] only studied the effect of particle morphology on the rheological behaviour of high-solids kaolin suspensions. It was revealed that the spherical halloysite showed the lowest viscosity, followed by the platy kaolinite and the tubular halloysite (see Fig. 21). These results clearly demonstrated the importance of particle shape affecting the slurry rheology.

4. Use of dispersants into the slurry for the rheology control

4.1. Selection of dispersants

Most of the effective dispersants identified in the literature are low-molecular-weight, water-soluble polymers, in addition to well-known inorganic dispersants, such as sodium silicate, sodium metaphosphate, sodium tripolyphosphate, NaOH or KOH, etc. [30,35,36]. Table 1 shows some water-soluble polymeric dispersants commonly used as grinding additives for the control of the slurry rheology.

In aqueous solutions or slurries, nonionic dispersants, usually containing –O/CO and –OH functionality, are relatively insensitive to pH but are most effective as dispersants on near-neutral particle surfaces. The most common anionic dispersants contain carboxylic acids or their salts. Such organic acids dissociate in aqueous solutions into negatively charged carboxylate ions [36],

\[RCOOH(\text{aqueous}) \rightarrow H^+ + RCOO^-\]

at a pH of 5 and above. Thus, such chemicals are not generally effective as dispersants at pH less than 5. With carboxylic acids, the presence of multivalent ions (i.e., Ca\(^{2+}\)) from hard water or lime being added as a part of the slurry is quite detrimental since insoluble carboxylic salts are formed. Therefore, comminution under such conditions can cause a higher consumption of dispersant to be used since much of the initial dosage must be used to remove the water hardness. Sulfonic acid based dispersants, RS(=O)\(_2\)OH, are often used as dispersants for a lower range of pH as they dissociate at a pH of approximately 2 by

\[RS(=O)\_2OH(\text{aqueous}) \rightarrow H^+ + RS(=O)\_2O^-\]

In addition, the cationic dispersants used are generally amines. Amines ionize as follows [36],

\[RNH_2(\text{aqueous}) + H_2O \rightarrow RNH_3^+ + OH^-\]

The actual form of the amines used can be quite variable and includes primary, secondary, tertiary, and quaternary forms. Quaternary amines are strong bases so are ionized essentially over the complete range of pH, while the ionization of the remaining forms is dependent on pH. Typically for a primary amine, the ionization starts to fall off in the range of pH 10 or greater, thus its practical use window is defined as being less than pH 10.
With regard to the selection of an appropriate dispersant for a given ground slurry, it is important to have some fundamental knowledge of the effects of dispersants on wet ultrafine grinding, product characteristics and energy consumption, in addition to the type and the magnitude of electrical charge existing on the surfaces of particles in a slurry [30,36,37,89]. The additional attention is the side effects of dispersants. For instance, complexation by the polymer during ultrafine grinding in stirred media mills was recently found to cause extraction of yttrium from the milling beads of yttria-stabilized zirconia into the solution, leading to significant changes in the composition of the product [89].

In the case of the identification of suitable viscosity control chemicals acting as dispersants, it is necessary to satisfy some required conditions as follows [30,36]: (a) the dispersants must adsorb on enough of the solid surfaces available in an industrial mineral being ground so as to affect slurry viscosity; (b) the slurry viscosity must be so high that the utilization of the dispersant can detectably help reduce or control slurry viscosity; (c) the dispersants must be consistent in its ability to lower viscosity as a function of changing dispersant concentrations, pH value, water quality, and amount of shear present; (d) the dispersants must be nontoxic and degradable; (e) the dispersants must not adversely affect downstream operations, such as flotation, thickening, and pelletization, or contaminate the resultant products; (f) the use of dispersant must be economically viable in grinding operations.

4.2. Disperse mechanisms of dispersants

From the viewpoint of slurry rheology, the role of chemical dispersants or grinding aids is primarily to minimize or to completely eliminate the yield stress of a ground slurry [36]. In general, interparticle forces in an aqueous suspension of minerals consist of a van der Waals force and an electrostatic force. A steric force is included if a polymeric dispersant is added. The attractive van der Waals forces occurring in all particles decay to the second and third power of the interparticle distances with respect to the shape and the contact geometry. A liquid dispersion medium diminishes their power and adsorbed layers in general cause a removal of their reach. As known, the fine particles below 1 \( \mu m \) attract each other by van der Waals attractive forces to form aggregates or flocs [49]. Furthermore, in the case of wet ultrafine grinding, especially at the end, the fraction of particles less than 1 \( \mu m \) is very high; hence, the van der Waals force is significant. The electrostatic repulsive force is due to the surface charge of particle and the formation of an electric double layer on particle surface (see Fig. 6). Similarly charged particles repel one another as soon as they break through the diffuse ranges of electric double layers. The measurable evidence of surface charges is the zeta potential. The steric force is caused by the long-tail interference of absorbed polymeric molecules [36,90], resulting in repulsive forces when sufficiently short distances between particles are

![Fig. 22. Steric stabilization of particles due to adsorption of polymeric dispersants [36,90].](image-url)
given. A simple illustration of the steric repulsion force of particles by adsorbed polymers is given in Fig. 22. When the steric interaction does not exist due to the absence of adsorbed dispersants, the stabilization mechanisms of suspensions can be quantificationally explained by the DLVO (Derjaguin–Landau–Verwey–Overbeck) theory [32,33,91].

By the utilization of polymeric dispersants, the electrostatic and steric forces can be essentially influenced [91]. An increase in particle charge, which leads to a reinforcement in electrostatic force, can be achieved through the changes in pH or the adsorption of multivalued cations or anions. A reinforcement of the steric force is fulfilled through hydrophilic macromolecules with the molecular weight ranging from several thousand to 100,000 [33,36], such as polyphilic macromolecules with the molecular weight ranging in distance. For suspensions that are stabilized by polyacrylamide or polyacrylate [33,49] and Dispex N40 (sodium salt of a polycarboxylic acid) [29,30], PAA (polyacrylic acid) [37]. The steric force involving polymeric dispersants is the primary mechanism involved with chemical dispersants [36,49]. The repulsive force is caused by the interference of adsorbed chemical molecules so that the particles cannot come close enough with one another. This in turn weakens the van der Waals force due to the increase in distance. For suspensions that are stabilized by poly-electrolytes, there is still no quantitative theory to account for the stabilization, but the behaviour of the suspensions can be explained qualitatively as a combined effect of electrostatic and steric interactions [91].

### 4.3. Influence of dispersants on slurry rheology in ultrafine grinding

Most ultrafine grinding processes are characterized by a high solids content and the presence of excessive fines [29,36], which are two of the primary factors leading to the formation of agglomerations or flocculations and hence the development of a yield stress of slurry. The use of an optimal dispersant can change the surface nature of particles in a ground slurry, resulting in interparticle forces being entirely repulsive. Thus, the slurry rheology is improved by the reduction or elimination of yield stress. This can increase the fineness of products and enhance the ultrafine grinding efficiency and throughput. For instance, in the absence of any dispersant, the typical maximum percentage of solids by weight in a suspension is approximately 50% for ultrafine grinding in a stirred ball mill while an upper limit of solid concentration is up to 80% in the presence of an optimum dispersant [49]. The effects of different dispersants, quantities of dispersants, molecular weights of dispersants and methods of introducing dispersants on slurry rheology control in wet ultrafine grinding performance are discussed in the following aspects:

#### 4.3.1. Effect of different dispersants

Efforts have been made in developing and searching grinding aids for wet ultrafine grinding system [30,32–34,36,37,49]. Wang and Forssberg [30] have studied the influence of five different dispersants [namely, Dispex CP (sodium salt of an acrylic copolymer), Dispex N40 (sodium salt of a polycarboxylic acid), DP6-3437 (sodium salt of polyacrylic acid), Calgon (sodium hexametaphosphate) and TSPOP (Tetrasodiumpyrophosphate)] used as grinding aids in wet ultrafine grinding of dolomite by a stirred bead mill. It was shown that the organic dispersants exerted a more favourable grinding action than the inorganic ones and the difference was more pronounced at the fine ends (see Fig. 23). In addition, it was found that the dispersant of Dispex N40 gave the most excellent performance in grinding energy efficiency (m²/kWh), resulting from its ability of a controlled amount of weak flocculation and producing the desired rheological properties of ground slurry. Similar work by Zheng et al. [37] involved an investigation of the effects of additions of sodium hydroxide, sodium carbonate, sodium oleate, oleic acid, and poly (acrylic) acid (PAA) on wet ultrafine grinding of limestone in a stirred bead mill. It was found that PAA, which is similar to Dispex N40, was best among selected grinding aids for the improvement of the energy efficiency in grinding, resulting from the beneficial fluidity of slurry obtained in the presence of PAA. This is because PAA can modify the surface properties of limestone and produce the moderate interaction presented between media and particles. It is qualitatively interpreted by adsorption density and zeta potential, respectively, as a function of PAA concentration, as seen in Fig. 24. Other similar investigations reported [32–34,36,49] are in good agreement with those referred to above. The polyacrylic acids or its salts as advanced dispersants for wet ultrafine grinding of some industrial minerals are identified.

#### 4.3.2. Effect of the quantities of dispersants

Of the numerous dispersants commercially available, it can be difficult to determine the most appropriate one and its correct dosage for a certain ground slurry. An insufficient amount of dispersant is a problem since some particles will be flocculated by bridging mechanisms [49,92], or electrostatic patch, or mosaic flocculation [50], which increases the viscosity of slurry. However, an excessive amount of dispersant is an unnecessary extravagance and can even
cause slurry destabilization [29]. Therefore, it is important to determine an optimal dosage of dispersant in wet ultrafine grinding of a given raw material. Gao and Forssberg [29] have studied the influences of different quantities of Dispex N40 (sodium salt of a polycarboxylic acid) on the viscosity of dolomite slurry in a stirred media mill. It was found that the presence of different quantities of Dispex N40 transformed the slurry through different rheological behaviours (see Fig. 25). It was desirable for the ultrafine grinding from the energy efficiency point of view that the addition of the optimum amount (0.5 wt.%) of the dispersant could eliminate a yield stress and make a slurry as viscous as possible (see Fig. 26) at a fixed solids concentration, resulting in more intense friction between particles and milling beads without the formation of flocculation and thus a high grinding efficiency.

Another work by Bernhardt et al. [32] involved a study of the concentration of sodium polyacrylate (SPA) on the slurry rheology of a limestone (\( \tau_{\text{0}} \)). It was concluded that the amount of 0.5% SPA by weight of solids was sufficient to obtain the optimum slurry rheology of the limestone for wet ultrafine grinding in a stirred bead mill. In addition, by the comparison of the dependences of the energy utilization on the solids concentration without and with SPA at a fixed value of energy consumption (see Fig. 27), it was found that for the solids concentration above 40 wt.%, a better grinding efficiency and a higher achievable product fineness were attained in the presence of the optimal...
dosage of SPA. The reason is that the limestone suspensions with solid concentrations more than 40 wt.% showed pseudoplastic flow behaviour (see Fig. 12(a)). The addition of SPA led to an increase in negative charges of particle (see Fig. 28) and thus increased repulsive interparticle forces, resulting in the decrease or elimination of yield stress and the suitable rheological behaviour for the ultrafine grinding. This made the bead energy lower attenuation in the presence of SPA than in the absence of SPA. This phenomenon is in good agreement with previous results [29,35,36]. In the case of solid concentration less than 40 wt.%, the energy utilization became lower in the presence of SPA than in the absence of it. This is because the viscosity is lower with SPA and some particles can evade the stressing zone between the approaching beads. Thus, it is important to take into account the influence of other factors (i.e., solids concentration) on the rheology of a given slurry when interpreting the effect of additive amount. Reinisch et al. [33,34] have done some similar work and obtained the consistent conclusions with Bernhardt’s [32]. It was deduced [33,34] that the additive amount of a selected dispersant, which was proportional to the growth of resulting surface area, was necessary for the optimum rheological behaviour of slurry, leading to the best comminution results.

Zheng et al. [37] investigated the effect of the concentration of poly (acrylic) acid (PAA) on wet ultrafine grinding of a limestone slurry. It was found that the best energy efficiency and the excellent product fineness are obtained at an additive dosage of 0.1% by weight of the feed limestone, below or above which resulted in both a lower product surface area and a lower energy efficiency. Fig. 24 shows the changes of the slurry fluidity in the presence of different amounts of PAA. In addition, an excessively high fluidity could result in less contact or interaction between media and particles, and thus in a lower grinding efficiency.

These above conclusions regarding an optimal dosage often seem to be not free of contradictions, for which the following facts may be responsible. The slurry rheology in wet ultrafine grinding depends as well as on many other parameters, such as particle size, particle shape and particle charge, and viscosity of the fluid and solids concentration. In the case of wet ultrafine grinding, the rheological behaviour inside the grinding vessel is highly complex and significantly varies from point to point. In addition, the methods to determine an optimum dosage of a dispersant are different and include sedimentation tests, adsorption isotherms, rheological experiments or electrophoresis [49]. The first two are extremely time consuming, while the electrophoresis method can only measure zeta potentials under very dilute conditions. Hence, there are significant errors in extrapolating the results to the high solids loading that are used in many industrial processes. Until fairly recently, the only quick and reliable way of measuring the optimum amount of a dispersant was rheology. Besides, Greenwood et al. [49] developed a technique, so-called electroacoustics, which allows zeta potentials to be measured in concentrated suspensions and determines the optimum dosage of a dispersant used.

4.3.3. Effect of the molecular weights of dispersants

The use of adsorbed dispersants can cause a steric stabilization of particles [36,49,71,90,91,93], which is caused by the interference of adsorbed molecules of dispersant (see Fig. 22). The steric force involving polymers is the primary mechanism involved with chemical grinding aids [36,49]. Therefore, it is important to select a suitable long chain (molecular weight) of polymeric dispersant in order to obtain a desirable rheology of slurry for wet ultrafine grinding. Generally, the most widely used dispersant as a grinding aid is polyacrylic acid or its salts, whose molecular weights in the region of 5000–20,000 appear to be optimal depending on the application [36]. Zheng et al. [37] investigated the effect of the molecular weights of poly (acrylic) acid (PAA) on wet ultrafine grinding of a limestone. The product fineness and the energy efficiency both increased with increasing molecular weights from 2000 to 5000 Da at a solids content of either 65 or 75 wt.%. The optimal molecular weight of PAA for the best energy efficiency and the best product fineness at both solids concentrations was found to be 5000 Da due to an improvement of the slurry rheology (see Fig. 24).

![Fig. 28. Zeta-potential and apparent viscosity in dependence on the specific surface area newly produced [32].](image)

![Fig. 29. The variations in the median sizes and the yield stress during milling process at the slurry density of 75 wt.% with 1.0 wt.% Dispex N40 [29].](image)
higher molecular weight resulted in a higher energy input in the both cases possibly due to increasing the particle flocculation caused by the polymer. However, the mechanisms of action of the dispersants with various molecular weights on the slurry rheology in a stirred media mill are sufficiently unclear. Therefore, further studies on this aspect should be carried out.

4.3.4. Effect of the methods of introducing the dispersants

The fineness of ground products would increase significantly with grinding time, leading to predominantly increasing the yield stress (see Fig. 29) and the apparent viscosity of ground slurry [29,30,32,33] (see Fig. 28). This can markedly decrease the fineness of resulting products and lower the grinding energy efficiency; and even stop a grinding operation due to high yield stress and poor slurry fluidity (see Fig. 30(a) and (b)) [29]. Wang and Forssberg [30] have found the effects of periodic and instantaneous additions of dispersants of Dispex N40 or DP6-3437, respectively, on wet ultrafine grinding of a dolomite based on the slurry rheology control in a stirred media mill. The periodic addition led to an increased grinding rate and a decreased specific energy input (kWh/t). They deduced that the procedure of periodic addition could keep the viscosity of slurry suitable for the attrition and impact of the particles and media. An excessively high viscosity makes handling impossible due to the poor fluidity of the slurry without or with only a very small amount of dispersant. Too low a viscosity gives a reduced grinding rate and an increased specific energy input. The periodic addition can optimize the slurry rheology until the final product is achieved. Gao and Forsberg [29] also reported that the best results in terms of the increase in the specific surface area per unit of energy consumption (m²/Wh) were obtained by the addition of 0.5 wt.% Dispex N40 in the case of the ultrafine grinding 70 wt.% dolomite in a stirred media mill. The operation was stopped at the fourth pass due to the sudden increase in yield stress, while the grinding operation could last at least nine passes with a yield stress of zero or a small value and a nearly constant viscosity with the number of passes if 1.5 wt.% Dispex N40 was added into the ground slurry of dolomite (see Fig. 30). Provided that 1.5 wt.% Dispex N40 was separated into three parts and periodically added three times, it was not reported whether or not the optimal slurry rheology could be maintained and the excellent grinding performance could be achieved. A further work related to this aspect should be expected.

5. Summary

Most of mineral suspensions exhibit non-Newtonian fluids. The characterization methods for non-Newtonian mineral slurries include the direct measurement of rheological relationship with a viscometer or a rheometer and indirect characterizations by measurements of zeta potential or torque drawn by mills. Several modified viscometers or rheometers with special setups, which can avoid the settling of solids particles and turbulent flow occurring in slurry, were described. It will be desirable to develop a rheometer or a viscometer system that can be used to be on-line measurement of rheological behaviour in wet ultrafine grinding.

The slurry rheology in wet ultrafine grinding is highly complex and is influenced by many parameters, like solid concentration, particle size and distribution, particle shape, slurry temperature, pH and the use of dispersant. Interpretation of the rheological behaviours of slurry must essentially take into account the identification of the respective effects of these main factors and their interactions. The optimization of the rheological behaviours of slurry in wet ultrafine grinding can significantly increase throughput, energy efficiency and product fineness as well. The optimal rheological behaviour of slurry for wet ultrafine grinding need further be ascertained.

The effect of a dispersant on wet ultrafine grinding performance is crucial since the solids content of a ground material with an appropriate dispersant in a stirred media mill increases by about 30 wt.% and the fineness of the final product significantly enhances. For the slurry rheology control, the mostly used dispersant as a grinding aid is polyacrylic acid or its salts with a molecular weight in the range of 5000 to 20,000, which appears to be optimal depending on the application. However, there is still little understanding on the mechanism for the effect of molecular weights of a dispersant on the slurry rheology control. The methods to determine the optimum dosage of a dispersant need further be optimized to accurately control a slurry
rheology by the use of a dispersant. The influence of the periodic addition of dispersant on slurry rheology is still lack of reasonable experimental explanation. These relevant investigations should be studied by means of some effective characterization methods, such as X-ray photoelectron energy spectrometry (XPS), infrared spectrometry (FT-IR), atomic force microscopy (AFM), and the measurements of rheology with a suitable rheometer and of zeta potential in a concentrated suspension with a reliable technique as well.

In addition, some empirical equations, which can model the slurry rheology of minerals, have been investigated. However, a semiempirical model incorporating solids concentration, particle size and slurry temperature could be of commercial interest. The relationships among rheological properties, composition parameters, amount of suitable dispersant, energy efficiency and particle size characterization are of particular interests for wet ultrafine grinding.

Acknowledgements

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References


Parameter studies on the rheology of limestone slurries


Parameter studies on the rheology of limestone slurries

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Abstract

The influences of solids concentration, molecular weight of dispersant, particle size and distribution, and temperature on the rheological behaviour of limestone slurries have been investigated. The results reveal that when the solids concentration of a limestone slurry is increased from 60 wt.% (35.71 vol.%) to 78.5 wt.% (57.49 vol.%), the rheological behaviour of the slurry is transformed from a weakly dilatant characteristic to a pseudoplastic one with a yield stress, which is in combination with a thixotropic property at a higher solids concentration (i.e., ≥75 wt.% or 52.63 vol.%). At a certain shear rate, the apparent viscosity and the relative viscosity of the slurry increase exponentially with solids concentration. The extrapolated Bingham yield stress increases rather sharply in a power-law form with increasing solids concentration when the solids concentration of the slurry is larger than 70 wt.% (i.e., 46.36 vol.%). An attainable maximum packing solids fraction (\(\phi_m\)) is predicted as \(\phi_m=64.6\) vol.% at the certain limestone–water suspension system. A polymeric dispersant named Dispersant S40 with a molecular weight of 5500 appears most effective for the reduction of the apparent viscosity of limestone slurry due to its good electrosteric stabilization and effective avoidance of depletion flocculation. The smaller the particle size and the narrower the size distribution, the more evident the pseudoplastic property of limestone slurry is with a larger yield stress and a larger apparent viscosity at a given shear rate in the range of 12 to 1200 s\(^{-1}\). Also, a statistic model describes a relationship between the particle size and distribution and the apparent viscosity of the slurries at a given solids concentration (i.e., 70 wt.% or 46.36 vol.%). However, a sufficient additive dosage of Dispersant S40 (i.e., ≥0.1 wt.%) significantly decreases or even eliminates the rheological differences of limestone slurries (apparent viscosities and extrapolated yield stresses) resulting from the difference in particle size and distribution. Besides, the apparent viscosity of limestone slurries decreases with increasing temperature in the range of 13 to 55 °C, regardless of the absence or the presence of Dispersant S40.

Keywords: limestone; slurry rheology; solids concentration; molecular weight; fine particle; temperature

1. Introduction

From a diagnostic point of view, the rheological behaviour of a mineral slurry is indicative of the level of interparticle interaction or aggregation in the slurry and therefore it is a useful variable to be controlled in industrial processes such as transportation of slurries, dewatering and wet grinding (Master and Prestidge, 1995). However, the rheological property of a mineral suspension is complicated and there is no single parameter that can solely explain it. Physical and chemical properties of a slurry, such as solids concentration, use of dispersants, particle size and distribution, particle shape, pH value, shear rate, slurry temperature, have a significant influence on the slurry rheology due to the change or modification in surface property (He et al., 2004). As known, the fine particles below 1 μm in a suspension attract each other by van der Waals attrac-
the result of van der Waals forces (Greenwood et al., 2002; Reinisch et al., 2001a) and electrostatic forces (Bernhardt et al., 1999; Muster and Prestidge, 1995; Gregory, 1987). Therefore, the effect of the slurry flowabilities or slurry rheology in wet ultra-fine grinding becomes of particular importance. It is known that an optimised rheological behaviour of a ground slurry can enhance energy efficiency and throughput in wet ultrafine grinding operation. For instance, the addition of an optimum dispersant to a given feed slurry can result in a drastic reduction or even the elimination of yield stress and permits a higher solids concentration of the ground slurry (Kapur et al., 1996; Klimpel, 1999; Greenwood et al., 2002; Reinisch et al., 2001a,b). In the absence of any dispersant, the typical maximum percentage solids by weight in a slurry is approximately 50% for a feed of wet ultra-fine grinding in stirred media mills while an upper limitation of solids concentration is up to 80 wt.% in the presence of an optimal dispersant (Greenwood et al., 2002). Therefore, the improvement of the rheological behaviour of a feed slurry with a suitable dispersant can enhance the productivity and throughput for wet ultra-fine grinding.

The objective of this work is to investigate the effects of solids concentration, molecular weight of dispersant, particle size and distribution, and temperature on the rheology and flowability of limestone slurries.

2. Experimental set-up and procedures

2.1. Materials

A limestone material (93.7% CaCO₃) provided by SMA Karbonater AB in Sweden was used for the rheological experiments. The chemical analysis and physical characteristics of the limestone material are listed in Tables 1 and 2, respectively. The samples of the material with three various particle sizes and distributions were prepared for the tests. The first sample is the original sample provided with a size of <100 μm, as designated as raw 1; the second is a sieved sample with a size of <74 μm from the raw 1 by the use of a U.S. Standard sieve (0–74 μm), as designated as raw 2; and the third, with a size of <40 μm from the raw 1 by a sieve of Retsch DIN 4188 type (0–40 μm), as designated as raw 3. Fig. 1 shows the particle sizes and distributions of these samples, which were determined by an X-ray Sedimentometer Sedigraph 5100D (Micromeritics Co. Ltd., USA). Raw 1 has the characteristic sizes of d₅₀ (the median size) of 24.68 μm and d₉₀ (the 90% passing size) of 97.3 μm, and raw 2, d₅₀ of 17.48 μm and d₉₀ of 45 μm, and raw 3, d₅₀ of 10.04 μm and d₉₀ of 23.5 μm.

Three polymeric dispersants with various molecular weights, i.e., BCX-476, Dispersant S40 and BCX-552 (CDM AB, Sweden) were used in this study. Table 3 lists the physical and chemical properties of these dispersants.

Table 1
Chemical analysis of composition of the limestone

<table>
<thead>
<tr>
<th>Main chemical composition</th>
<th>Percent (%)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO ASTM C-602</td>
<td>52.5</td>
<td>0.7</td>
</tr>
<tr>
<td>CaCO₃ ASTM C-602</td>
<td>93.7</td>
<td>1.3</td>
</tr>
<tr>
<td>MgO</td>
<td>4.50</td>
<td>1</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.70</td>
<td>0.2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3.50</td>
<td>1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.85</td>
<td>0.2</td>
</tr>
<tr>
<td>MnO</td>
<td>0.15</td>
<td>0.03</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>40</td>
<td>0.6</td>
</tr>
<tr>
<td>Moisture</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

Table 2
Physical characteristics of the limestone

<table>
<thead>
<tr>
<th>Real density (kg/m³)</th>
<th>Volume density (kg/m³)</th>
<th>Moh’s hardness</th>
<th>Whiteness (ISO 457)</th>
<th>pH</th>
<th>Particle shape</th>
<th>Specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2700</td>
<td>1000</td>
<td>3</td>
<td>77%</td>
<td>9</td>
<td>Nodular</td>
<td>1.174</td>
</tr>
</tbody>
</table>
each slurry sample. The slurry was stirred as the limestone powder was added into water, and the stirring was continued for 15 min to make the slurry uniform after the completion of adding limestone powder. If a chemical with a given amount was added, the slurry was stirred for 15 min again after the addition of the chemical to make the chemical disperse uniformly in the slurry. About 200 ml slurry was taken from each sample, which was used to analyse the particle size and distribution and to measure the rheological behaviour of the slurry. The slurry samples were aged for 4 hr, and then were shaken at an intensity of 225 min⁻¹ with a shaker of Model TH-30 (Edmund Bühler Co., Germany) for 1 hr to re-disperse the samples prior to the rheological measurement.

2.2.2. Viscometer

A rotational viscometer was used for the determination of slurry viscosities and shear stress–shear rate curves. The viscometer is the Bohlin Visco 88 BV (Bohlin Reologi UK Ltd., UK). It employs a concentric cylinder geometry with a rotating inner cylinder and a stationary outer cylinder. The concentric cylinder system can be configured in 8 different measurement systems (3 DIN, 2 ‘Wide Gap’, 3 ‘Infinite Sea’), corresponding to SYSTEM knob 1 to 8 on the instrument, and its design allows the measurement of samples to be made in situ (e.g., in a container) as well as on the laboratory bench. Any inner cylinder has 8 different rotation speeds to be chosen, which is from 20 to 1000 rpm (in agreement with a SPEED setting value 1 to 8 on the instrument), corresponding to a shear-rate range of 4 to 1200 s⁻¹. The torque developed on the inner cylinder due to a sample is directly related to the sample viscosity and should be in the range of 0.5 to 9.5 mNm for the accurateness. In this study, all samples were measured by the use of C30 system (C30 DIN), which has a gap width of 1.5 mm between the inner and outer cylinders and can provide a viscosity range of 0.007 to 6.18 Pas. A thermal jacket allows the use of an external fluids circulator to control or regulate the temperature of a measured sample. Prior to the measurement, each slurry sample was pre-sheared for 3 min at the highest shear rate (corresponding to the SPEED setting value 8 on the instrument), and then the measurement started from this highest shear rate. The shear rate was stepped down one by one until the torque reading was less than 0.5 mNm, and the measurement was finished. The digital readings (viscosity, shear rate, shear stress, torque) were recorded at each shear rate. About 25 ml of slurry sample was required for each measurement. Each sample was measured thrice and the mean values of shear stress, shear rate and viscosity were used for analysis.

Table 3

<table>
<thead>
<tr>
<th>Physical and chemical properties</th>
<th>BCX-476</th>
<th>Dispersant S40</th>
<th>BCX-552</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid content (wt.%)</td>
<td>45%</td>
<td>45%</td>
<td>30%</td>
</tr>
<tr>
<td>Active content (wt.%)</td>
<td>40%</td>
<td>40%</td>
<td>26%</td>
</tr>
<tr>
<td>pH</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Density at 20 °C</td>
<td>1.30</td>
<td>1.30</td>
<td>1.315</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>2000</td>
<td>5500</td>
<td>85,000</td>
</tr>
<tr>
<td>Sodium polyacrylate content (wt.%)</td>
<td>40%</td>
<td>40%</td>
<td>26%</td>
</tr>
<tr>
<td>Water content (wt.%)</td>
<td>55%</td>
<td>55%</td>
<td>70%</td>
</tr>
<tr>
<td>Solubility (in water)</td>
<td>Very soluble</td>
<td>Very soluble</td>
<td>Very soluble</td>
</tr>
</tbody>
</table>

Fig. 1. Particle size distributions of three limestone samples.
2.3. Evaluation procedures

The viscometer (Bohlin Visco 88 BV), which is widely used for industrials, including coatings, foods and pharmaceuticals, directly measures the rotational speed of a rotor (a rotating inner cylinder), \( V \) (rpm), and the shear stress-related torque, \( M \) (mNm). Shear rate (\( \gamma \), 1/s), shear stress (\( \tau \), Pa) and apparent viscosity (\( \eta_p \), Pas) are calculated by the following formulas,

\[
\tau = C_1 M \\
\gamma = C_2 V \\
\eta_p = \frac{\tau}{\gamma}
\]

where \( C_1 \) and \( C_2 \) are constants related to a measurement system. The viscometer employs a so-called “viscosoft” computation program so the digital readings or measurement parameters such as shear rate, shear stress, viscosity, torque are directly displayed on the screen of the viscometer. In this work, the accuracy of this viscometer was examined by the reproducibility of the rheological measurements of a limestone slurry (<100 \( \mu \)m, i.e., raw 1) over a wide range of shear rate. The results are shown in Table 4. It is evident that the viscometer exhibits a very good reproducibility with a rather small standard deviation for all the measurement parameters. The sample standard deviation of viscosity is less than 0.0013 Pas when the torque is larger than 0.5 mNm. Even though the measured torque is less than 0.5 mNm, the sample standard deviation of viscosity is still less than 0.0018 Pas. Thus, the viscometer accurately gives a resolution of 0.001 Pas at a torque larger than 0.5 mNm.

Table 4
Reproducibility of the rheological data for 70 wt.% of a limestone slurry (i.e., raw 1) without chemicals

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Time</th>
<th>Measurement data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear rate (1/s)</td>
<td>1</td>
<td>37.1</td>
</tr>
<tr>
<td>2</td>
<td>37.2</td>
<td>91.3</td>
</tr>
<tr>
<td>3</td>
<td>36.7</td>
<td>91.2</td>
</tr>
<tr>
<td>4</td>
<td>43.4</td>
<td>96.5</td>
</tr>
<tr>
<td>5</td>
<td>43.6</td>
<td>96.5</td>
</tr>
<tr>
<td>6</td>
<td>42.3</td>
<td>94.7</td>
</tr>
<tr>
<td>7</td>
<td>42.1</td>
<td>95.1</td>
</tr>
<tr>
<td>Mean value</td>
<td>40.34</td>
<td>93.83</td>
</tr>
<tr>
<td>Sample standard deviation</td>
<td>3.18</td>
<td>2.43</td>
</tr>
<tr>
<td>Shear stress (Pa)</td>
<td>1</td>
<td>3.7</td>
</tr>
<tr>
<td>2</td>
<td>3.7</td>
<td>5.7</td>
</tr>
<tr>
<td>3</td>
<td>3.7</td>
<td>5.6</td>
</tr>
<tr>
<td>4</td>
<td>4.4</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>4.4</td>
<td>6.2</td>
</tr>
<tr>
<td>6</td>
<td>4.3</td>
<td>6.4</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>5.8</td>
</tr>
<tr>
<td>Mean value</td>
<td>4.03</td>
<td>5.91</td>
</tr>
<tr>
<td>Sample standard deviation</td>
<td>0.34</td>
<td>0.3</td>
</tr>
<tr>
<td>Viscosity (Pas)</td>
<td>1</td>
<td>0.102</td>
</tr>
<tr>
<td>2</td>
<td>0.101</td>
<td>0.063</td>
</tr>
<tr>
<td>3</td>
<td>0.103</td>
<td>0.063</td>
</tr>
<tr>
<td>4</td>
<td>0.102</td>
<td>0.062</td>
</tr>
<tr>
<td>5</td>
<td>0.102</td>
<td>0.064</td>
</tr>
<tr>
<td>6</td>
<td>0.101</td>
<td>0.066</td>
</tr>
<tr>
<td>7</td>
<td>0.098</td>
<td>0.061</td>
</tr>
<tr>
<td>Mean value</td>
<td>0.1013</td>
<td>0.0629</td>
</tr>
<tr>
<td>Sample standard deviation</td>
<td>0.0016</td>
<td>0.0018</td>
</tr>
<tr>
<td>Torque (mNm)</td>
<td>1</td>
<td>0.24</td>
</tr>
<tr>
<td>2</td>
<td>0.23</td>
<td>0.38</td>
</tr>
<tr>
<td>3</td>
<td>0.24</td>
<td>0.36</td>
</tr>
<tr>
<td>4</td>
<td>0.28</td>
<td>0.38</td>
</tr>
<tr>
<td>5</td>
<td>0.28</td>
<td>0.39</td>
</tr>
<tr>
<td>6</td>
<td>0.27</td>
<td>0.39</td>
</tr>
<tr>
<td>7</td>
<td>0.25</td>
<td>0.36</td>
</tr>
<tr>
<td>Mean value</td>
<td>0.256</td>
<td>0.374</td>
</tr>
<tr>
<td>Sample standard deviation</td>
<td>0.021</td>
<td>0.014</td>
</tr>
</tbody>
</table>
Fig. 2. Effect of solids concentrations on the rheological properties of the limestone slurry in the absence of chemicals at the temperature of 25 ± 0.2 °C.
3. Results and discussion

3.1. Effect of solids concentration

The influence of solids concentration on slurry rheology is significant since various ranges of solids concentrations can lead to different types of flow curves, as shown in Fig. 2. The result shows the rheological properties of seven different solids concentrations of a limestone slurry (<100 μm, i.e., raw 1: \(d_{50}=24.68 \mu m\); \(d_{90}=97.3 \mu m\)) without any dispersant at a temperature of 25 ± 0.2 °C.

Clearly, the slurry rheological behaviour is transformed from a weakly dilatant characteristic (shear-thickening) to an evidently pseudoplastic (shear-thinning) one with a yield stress when the solids concentration is increased from 60 wt.% (35.71 vol.%) to 78.5 wt.% (57.49 vol.%). At a solids concentration ≤65 wt.% (40.75 vol.%), the slurry presents a weakly dilatant (shear-thickening) flow. This is because in a dilute slurry (i.e., ≤65 wt.% or 40.75 vol.%), the inter-particle distance is so large that the limestone particles in the slurry are not subjected to the attractive van der Waals forces between the particles but free to move as individuals. At lower shear rates, the particles have enough opportunities to slip over each other. At higher shear rates, the shearing process is more and more rapid so that the particles cannot move around freely any longer. The local accumulation of solid particles causes the slurry to behave like a solid system. In a dilatant system, however, this state is not stable. As long as the external force is removed, the particles without any tendency to adhere are distributed more uniformly in the suspension. At the solids concentration up to 67 wt.% or 42.92 vol.%, the flowability of the slurry exhibits a pseudoplastic (shear-thinning) characteristic without a definite yield stress at shear rates less than 663 s\(^{-1}\) and a weakly dilatant (shear-thickening) one at shear rates larger than 663 s\(^{-1}\). This indicates that in a lower range of shear rates, the attractive interparticle force is predominant over the hydrodynamic force exerted by a flow field at 67 wt.% of solids concentration, as opposed to shear rates larger than 663 s\(^{-1}\). With further increasing the solids concentration to 70 wt.% (i.e., 46.36 vol.%) or more, the slurry rheology is changed into a pseudoplastic flow with an evident shear yield stress at shear rates below 362 s\(^{-1}\), followed by a transition to a Bingham plastic flow (with a higher extrapolated Bingham yield stress) at shear rates above 362 s\(^{-1}\). Furthermore, the degree of pseudoplasticity and the shear yield stress increase with increasing solids concentration when the solids concentration is larger than 70 wt.% (Fig. 2 (a)). Similar phenomena were observed for various slurries of materials such as coal and quartz (Tangsathitkulchai and Austin, 1988), titania pigment (Morris et al., 1999), galena (Prestidge, 1997) and sphalerite (Muster and Prestidge, 1995). In addition, the extrapolated Bingham yield stress, \(\tau_B\), is obtained by fitting the experimental data in a higher range of shear rates (i.e., >362 s\(^{-1}\)) into the Bingham model (Gao and Forsberg, 1993; Morris et al., 1999; Prestidge, 1997; Muster and Prestidge, 1995; Hackley, 1998):

\[
\tau = \eta_p g + \eta_p N \frac{\dot{\gamma}}{C}
\]

where \(\eta_p\) is the plastic viscosity. The extrapolated yield stress values for the slurries as a function of solids concentration are plotted in Fig. 3. The extrapolated yield stress increases rather sharply in a power-law form with increasing solids concentration when the solids concentration is larger than 70 wt.% or 46.36 vol.%. This is similar to a previous conclusion (Tseng and Chen, 2003; Leong et al., 1995). This indicates that there are strong interactions between the particles to hold the particles together in the slurry and form loosely packed flocs, immobilizing some water within them, which is indispensable to flow. This is because a smaller interparticle distance in a denser slurry produces an increased attractive potential and a larger probability of collisions between the particles, resulting in more particles attracting each other. A shearing force over a certain shear yield stress has to be exerted on the slurry to overcome the internal friction among the particles constituting the flocs and to make it flow again. Once the slurry flows, the flocs are broken down into smaller flow units and the water entrapped within them is gradually released with increasing shear rate. This facilitates the slurry to flow and leads to a
decrease of the slurry viscosity. In addition, it is interesting to see that the slurry of 75 wt.% of solids concentration or more presents a thixotropic characteristic (Fig. 4). For a given solids concentration, the viscosity of the slurry decreases with shear time at a certain shear rate. The time to reach a stable viscosity is about 3 min for 75 wt.% of solids concentration at the shear rate of 1191 s$^{-1}$ and 4 min for 77 wt.% at 663 s$^{-1}$. The shear-thinning behaviours with a definite yield stress associated with thixotropic characteristics are typical of agglomerated or flocculated suspensions (Muster and Prestidge, 1995; Papo et al., 2002; Hackley, 1998). A similar conclusion was drawn for kaolin suspensions with sodium tripolyphosphate (Papo et al., 2002), for concentrated alumina suspensions (Lemke et al., 1999), for sphalerite slurries (Muster and Prestidge, 1995) and for galena slurries (Prestidge, 1997).

Besides, the viscosity of the limestone slurry increases exponentially with increasing the solids concentration at a certain shear rate (Fig. 5), as is in agreement with previous conclusions for dolomite (Velamakanni and Fuerstenau, 1993) and for quartz slurries (Tangsathitkulchai and Austin, 1988). By fitting the experimental data, it is found that a relation between the apparent viscosity of limestone slurry and the solids concentration at a given shear rate can be described by

$$\eta_a = a(\gamma)e^{b(\phi)}$$

where $\eta_a$ designates the apparent viscosity; $\phi$ is the solids concentration by volume; $a(\gamma)$ and $b(\gamma)$ are the coefficients related to a used shear rate, and the higher the shear rate is, the larger $a(\gamma)$, and the less $b(\gamma)$. This model gives a good accurateness in the investigated range of solids concentration, as shown in Fig. 5. The errors between the experimental and predicted viscosities at a certain solids concentration are less than 14.28% at a shear rate of 1191 s$^{-1}$, 26.08% at 663 s$^{-1}$, 19.39% at 362 s$^{-1}$, or 19.94% at 194 s$^{-1}$. It is evident that in the case of solids concentration over 75 wt.% or 52.63 vol.%, the slurry viscosity increases rather sharply in the range of shear rate investigated, tending towards infinity at a limiting solids concentration. The similar phenomenon is observed when the apparent viscosity ($\eta_a$) of the suspensions is substituted by the relative viscosity ($\eta_r$, defined as the viscosity of the suspension, $\eta_a$ with respect to the viscosity of the suspending fluid, $\eta_0$ at a given shear rate). Fig. 6 shows a relation between the relative viscosity of the slurries and solids volume fraction at a shear rate of 663 s$^{-1}$. The viscosity

![Fig. 4. Change in the viscosity of limestone slurry with shearing time at the temperature of 25 ± 0.2 °C.](image-url)

![Fig. 5. Effect of solids concentration on the viscosity at the temperature of 25 ± 0.2 °C: solid points, experimental; lines, modeling.](image-url)
of the suspending fluid, $\eta_0$, was determined separately as 0.004 Pas at the given shear rate. Besides, the relation between the relative viscosity ($\eta_r$) and the volume fraction of solids in the suspension ($\phi$) allows to calculate the theoretical, maximum solids volume fraction ($\phi_{m}$, at which the relative viscosity approaches toward infinity and the slurry ceases from flowing) attainable in the limestone–water suspension according to (Tseng and Chen, 2003):

$$1 - \eta_r^{-1/n} = a\phi + b$$

where $a$ and $b$ are constants, which can be determined from the $(1 - \eta_r^{-1/n})$ relationship, and $n$ is an integer in the range of 2 to 4 (Tseng and Chen, 2003). Table 5 lists the values of parameters obtained by fitting experimental data into Eq. (6) with three different $n$-values, i.e., 2, 3, and 4. The experimentally determined $\eta_r$ derivative, i.e. $(1 - \eta_r^{-1/n})$ appears to be linearly proportional to $\phi$ with a reasonable correlation factor for all three $n$-values. The theoretical, maximum solids concentration can hence be obtained from the fitted equation by extrapolating the linear line to $1 - \eta_r^{-1/n} = 1$. The corresponding $\phi_{m}$ is given in Table 5. The calculated $\phi_{m}$ compares with the $\tau_{W-\phi}$, $\eta_r-\phi$ and $\eta_{p-\phi}$ relations, which are shown in Figs. 3, 5 and 6, respectively. The apparent viscosity, relative viscosity and extrapolated Bingham yield stress approach infinity at the solids concentration of 65 vol.% or 83.37 wt.%. Thus, the exponent $n=2$ in Eq. (6) is applicable to the limestone slurry at a high shear rate of 663 s$^{-1}$, and gives a good correlation factor (Fig. 7) and a reasonable maximum packing volume fraction of 0.646, which closely approaches the random close packing ($\phi=0.64$) for spheres.

### 3.2. Effect of the molecular weight of dispersant

These are two primary factors in wet ultrafine grinding operation, i.e., a high solids concentration and the presence of excessive fines, leading to the formation of agglomerations or flocculations and hence the development of a yield stress of slurry. This causes an increase in energy consumption for the operation (Bernhardt et al., 1999; Gao and Forsberg, 1993; Klimpel, 1999; Greenwood et al., 2002). It is known that a small addition of a suitable dispersant is indispensable for wet ultra-fine grinding. The polyacrylic acids or their salts as advanced dispersants for wet ultra-fine grinding are identified (He et al., 2004). The use of a polyacrylic acid or its salt with an optimal molecular weight as a grinding aid can change the surface nature of particles in a ground slurry, resulting in inter-particle forces being entirely repulsive to improve the slurry fluidity by decreasing the slurry viscosity and by reducing or eliminating the shear yield stress (He et al., 2004). This can increase the fineness of products and enhance the energy efficiency and throughput in wet ultra-fine grinding.

Figs. 8–10 present the results on the effect of the concentration of sodium polyacrylate salts with various molecular weights on the rheological behaviour of 70 wt.% of a limestone slurry below 100 µm (i.e., raw 1). It is seen that the apparent viscosity of the slurry first

### Table 5

Parameter values obtained by fitting experimental data into Eq. (6)

<table>
<thead>
<tr>
<th>$n$</th>
<th>$a$</th>
<th>$b$</th>
<th>$\phi_{m}$ (vol.%)</th>
<th>$R^2$ (correlation factor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.0195</td>
<td>-0.2597</td>
<td>64.6</td>
<td>0.9925</td>
</tr>
<tr>
<td>3</td>
<td>0.0191</td>
<td>-0.3771</td>
<td>72.1</td>
<td>0.9879</td>
</tr>
<tr>
<td>4</td>
<td>0.0174</td>
<td>-0.3909</td>
<td>79.94</td>
<td>0.9839</td>
</tr>
</tbody>
</table>


![Fig. 6. Effect of solids concentration on the relative viscosity at the shear rate of 663 s$^{-1}$ at the temperature of 25±0.2°C.](image6.png)

![Fig. 7. The $1 - \eta_r^{-1/2} - \phi$ relationship at the shear rate of 663 s$^{-1}$ at the temperature of 25±0.2°C.](image7.png)
increases, and then decreases, and reverts after reaching a minimum. Clearly, the slurry with less than 0.01 wt.% of BCX-476, or Dispersant S40 or BCX-552 shows a pseudoplastic characteristics with a yield stress and possesses a higher apparent viscosity than that without dispersants at a given shear rate. This reason is that an insufficient dispersant causes the flocculation of particles in the slurry by bridging attraction forces, leading to larger flow units (Zhou et al., 2001; Johnson et al., 2000). At the addition amount of dispersants up to 0.02 wt.%, the apparent viscosity of the slurry is lower than that without dispersants. The slurry exhibits a pseudoplastic property without a yield stress at shear rates below 663 s\(^{-1}\) and a weakly dilatant one at shear rates above 663 s\(^{-1}\) for BCX-476 or BCX-552, and a Newtonian flow with a viscosity of 0.021 Pas at shear rates less than 663 s\(^{-1}\) and a weakly dilatant one at shear rates larger than 663 s\(^{-1}\) for Dispersant S40. The gradual increase in the addition amount of a dispersant leads to a complete transition to a weakly dilatant flow and a further slight decrease of the apparent viscosity in the range of shear rates investigated, and to a minimum at an addition level of 0.1 wt.% for BCX-476 or Dispersant S40 (Figs. 8 (c) and 9 (c)), or 0.04 wt.% for BCX-552 (Fig. 10 (c)). In these cases, the saturation adsorption of the dispersants on the particle surface has been attained, and electrostatic and steric

![Fig. 8. Flowability of 70 wt.% solids concentration with various dosages of BCX-476 at the temperature of 25 ± 0.2 °C.](image)

![Fig. 9. Flowability of 70 wt.% solids concentration with various dosages of Dispersant S40 at the temperature of 25 ± 0.2 °C.](image)
stabilizations (electrosteric stabilizations) occur. By further adding the dispersants, the apparent viscosity at a given shear rate reverts insignificantly for BCX-476 or Dispersant S40 (Figs. 8 (c) and 9 (c)), but evidently returns for BCX-552 (Fig. 10 (c)). In the case of BCX-476 or Dispersant S40, the excessive dispersant above the adsorption saturation exists in the slurry but not adsorb on the suspended particles, which causes a depletion flocculation (Papo et al., 2002; Zhou et al., 2001; Johnson et al., 2000). In addition, the excessive dispersant can increase the ion strength of the slurry, resulting in a compression of the electrical double layers around the particles and a reduction of the range and magnitude of the electrostatic repulsive force between the particles, that is, the electrosteric forces are decreased (Papo et al., 2002; Zhou et al., 2001; Banash and Croll, 1999; Einarson and Berg, 1993; Ewais et al., 2002). In the case of BCX-552, it possesses a larger molecular weight (i.e., 85,000) with a longer molecular chain, so the depletion flocculation is more significant besides the reduction of electrosteric force (Banash and Croll, 1999; Kiratzis et al., 1999). Therefore, above the adsorption saturation, a further addition of BCX-552 evidently raises the apparent viscosity of the slurry at a given shear rate (Fig. 10 (c)). Fig. 11 shows the results.

Clearly, the yield stress is eliminated when the addition amount of dispersants with three different molecular weights exceeds 0.02 wt.%. In the case of BCX-476 and Dispersant S40, the viscosity of the slurry at a given shear rate almost stays constant in a wide range of dispersants concentration (about 0.1–0.8 wt.%) for 70 wt.% of the limestone slurry. A similar phenomenon was observed for kaolin suspensions with sodium tripolyphosphate and sodium polyphosphate (Papo et al., 2002) and zirconia with tri-ammonium citrate (Ewais et al., 2002). For 75 wt.% of the limestone slurry, the similar phenomenon was also observed. The apparent viscosity of 75 wt.% of the limestone slurry reaches a minimum at an addition level of 0.2 wt.% for BCX-476, 0.1 wt.% for Dispersant S40 or 0.04 wt.% for BCX-552. Figs. 12 and 13 show the accessible minimum viscosity for 70 and 75 wt.% of the limestone slurry with a given addition amount for each dispersant, respectively. In the case of the reduction of viscosity of the limestone slurry, Dispersant S40 and BCX-476 are better than BCX-552. Dispersant S40 and BCX-476 present almost the same effect for 70 wt.% of the limestone slurry, while the former is better than the latter for 75 wt.% of the slurry. This is because Dispersant S40 gives a better steric stabilization than BCX-476 in a denser limestone slurry due to its relatively larger molecular weight with respect to BCX-476.

3.3. Effect of particle size and distribution

Tangsathitkulchai and Austin (1988) have indicated that the rheological theory of concentrated slurries is strongly related to the viscosity-dependence on the particle size. Furthermore, a prolonged grinding time will give a higher fineness of a ground product. The investigation of the rheological behaviour of limestone slurries with respect to particle size and distribution is necessary. In this work, the limestone materials with three particle sizes and distributions (Fig. 1) were used to study the effect of particle size and distribution on the slurry rheology in the
absence of any dispersant. It was found that the particle size distributions of these materials could be fitted by the Rosin–Rammler equation over the size range:

$$P(x) = 1 - \exp\left(-\frac{x}{k}\right)^m$$

(7)

where $P(x)$ is the cumulative fraction less than a sieve size $x$, $k$ is the fineness modulus (i.e., the 63.21%-passing size) and $m$ is the distribution modulus. Table 6 lists the results obtained by fitting, which present a good correlation.

Figs. 14 and 15 show the rheological properties of the limestone slurries with three different particle size distributions for 70 wt.% of solids concentration at a temperature of 25 ± 0.2 °C.

The slurries exhibit a pseudoplastic flow with an evident shear yield stress in a lower range of shear.
rate, followed by a transition to an approximate Bingham plastic flow (with a higher extrapolated Bingham yield stress) in a higher range of shear rate. Furthermore, the degree of pseudoplasticity is more evident, the viscosity at a given shear rate and the yield stress of the slurries increase, and the onset of the Bingham plastic flow shifts to a higher shear rate at a finer particle size with a narrower size distribution. The extrapolated Bingham yield stress exponentially increases and decreases with increasing the distribution modulus \((m)\) and the characteristic sizes (i.e., \(d_{50}\) and \(k\)), respectively (Fig. 15). Some researchers have also drawn a similar conclusion for titanium dioxide (Yang et al., 2001), for coal (Tangsathitkulchai and Austin, 1988; Logos and Nguyen, 1996) and for quartz slurries (Tangsathitkulchai and Austin, 1988). This is because the interparticle attractions become stronger in a slurry with finer particles. Also, the packing efficiency reduces in a material with a narrower particle size distribution at a fixed solids concentration, and more water is required to fill the inter-particle voids. In the cases of various shear rates, the non-linear relation between the particle size and distribution and the apparent viscosity at 70 wt.% of the limestone slurries can be found:

$$\eta_p = 0.5 \left[ \frac{1}{1 + \frac{(3 \times 10^{-8} \gamma + 0.0005) \exp \left( -0.5191 \ln(\gamma) + 7.4223 \right)}{0.1778 \ln(\gamma) - 2.4801}} \right]$$

When \(\gamma < 362 \text{ (1/s)}\):

$$\eta_p = 0.5 \left[ \frac{1}{1 + \frac{(5 \times 10^{-7} \gamma + 0.0003) \exp \left( -0.5191 \ln(\gamma) + 7.4223 \right)}{0.1778 \ln(\gamma) - 2.4801}} \right]$$

where \(\eta_p\) is the apparent viscosity at a shear rate, \(\gamma\); \(m\) and \(k\) are the distribution modulus and the fineness modulus, respectively. The prediction by the models is shown in Fig. 14 (b). The models give a high

<table>
<thead>
<tr>
<th>Test samples</th>
<th>(m)</th>
<th>(k)</th>
<th>(R^2) (correlation factor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw 1</td>
<td>0.9658</td>
<td>37.2</td>
<td>0.9955</td>
</tr>
<tr>
<td>Raw 2</td>
<td>1.0967</td>
<td>22.14</td>
<td>0.9981</td>
</tr>
<tr>
<td>Raw 3</td>
<td>1.3137</td>
<td>13.01</td>
<td>0.9951</td>
</tr>
</tbody>
</table>

Fig. 14. Effect of particle size and distribution on the flowability of 70 wt.% of solids concentration in the absence of chemicals at the temperature of 25 ± 0.2 °C.

Fig. 15. Effect of particle size and distribution on the extrapolated Bingham yield stress for 70 wt.% of solids concentration in the absence of chemicals at the temperature of 25 ± 0.2 °C.
accurateness. The predicted viscosities are slightly higher than the experimental values in the shear-rate range of 94 to 1200 s$^{-1}$ for raw 2. The errors between the experimental and predicted viscosities at a certain shear rate are 0.00% to 9.06% for raw 1, 3.27% to 20.00% for raw 2, and 2.41% to 7.94% for raw 3.

In addition, when 0.04 wt.% of Dispersant S40 is added into these three slurries, the rheological behaviours of the slurries are transformed from pseudoplastic flows with a yield stress to dilatant ones (Fig. 16 (a)). The difference in viscosity resulting from the particle size and distribution decreases with increasing the addition amount of the dispersant. At an addition dosage of the dispersant up to 0.1 wt.%, the difference becomes smaller and the difference in viscosity between raw 1 and raw 2 is insignificant (Fig. 16 (c)), as can be attributed to the dispersion effect of Dispersant S40. This is consistent with a previous observation for dolomite slurries with Dispex N40 (Gao and Forsberg, 1993).

3.4. Effect of slurry temperature

The slurry temperature varies during milling tests due to the release of lattice energy of ground minerals.
from comminution and the heat energy from the friction between milling media and a ground slurry. In a stirred media mill, the temperature of a ground slurry fluctuates from 14 to 60 °C depending on various grinding conditions (Gao and Forssberg, 1993). The influence of slurry temperature on slurry rheology is also evident. Figs. 17 and 18 present the influence of temperature on slurry rheology is also evident. Figs. 17 and 18 present the influence of temperature on the rheological behaviour of 70 wt.% of limestone slurries with three different particle size distributions in the absence of dispersants (Fig. 17) and 70 wt.% of a limestone slurry below 100 μm (i.e., raw 1) in the presence of 0.2 wt.% of Dispersant S40 (Fig. 18), respectively. It is evident that the change in the temperature studied does not change the flow type of the slurries without or with Dispersant S40. However, the viscosities of the slurries decrease with increasing temperature in the range of temperature studied regardless of the absence and the presence of the dispersant, and the extrapolated Bingham yield stresses also reduce without any dispersant (Fig. 17 (c)). In the case of 70 wt.% of the limestone slurry with 0.2 wt.% of Dispersant S40, the slurry temperature rises from 13 to 55 °C, the viscosity of the slurry reduces from the range of 0.0215 to 0.0365 Pas to the range of 0.01 to 0.019 Pas, i.e., about 1 time in the range of shear rate studied (Fig. 18). This is similar to a previous conclusion for titanium dioxide suspensions (Yang et al., 2001; Mikulášek et al., 1997).

4. Conclusions

The influences of solids concentration, molecular weight of dispersant, particle size and distribution, and temperature on the rheological behaviour of limestone slurries with various particle sizes have been investigated systematically. The rheological behaviour of a limestone slurry with a size of <100 μm is transformed from a weakly dilatant characteristic to a pseudoplastic one with a yield stress, which is in combination with a thixotropic property at a higher solids concentration (i.e., ≥75 wt.%) when the solids concentration is increased from 60 wt.% (35.71 vol.%) to 78.5 wt.% (57.49 vol.%). At a given shear rate, the apparent viscosity and the relative viscosity of the limestone slurry increase exponentially with increasing solids concentration. The extrapolated Bingham yield stress increases in a power-law form with increasing solids concentration when the solids concentration is larger than 70 wt.%(or 46.36 vol.%). The attainable maximum packing solids fraction (ϕ_m) is predicted as ϕ_m = 64.6 vol.% at the certain limestone–water suspension system. Dispersant S40 (Mw: 5500) and BCX-476 (Mw: 2000) are superior to BCX-552 (Mw: 85,000) for the reduction of the slurry viscosity. BCX-552 readily leads to an evident depletion flocculation due to its higher molecular weight. For a denser limestone slurry (i.e., 75 wt.%), Dispersant S40 prevails over BCX-476. The smaller the particle size and the narrower the size distribution, the more evident the pseudoplastic property of limestone slurry is with a larger yield stress and a larger apparent viscosity at a given range of shear rate. Also, an empirical relation between the particle size and distribution and the apparent viscosity of the slurries at a given solids concentration (i.e., 70 wt.% or 46.36 vol.%) is given. A sufficient addition of Dispersant S40 (i.e., ≥0.1 wt.%) significantly decreases or even eliminates the rheological differences of limestone slurries (apparent viscosities and extrapolated yield stresses) resulting from the particle size and distribution. Besides, the viscosity and the yield stress of limestone slurries decrease with increasing temperature in the range of temperature studied regardless of Dispersant S40. In the case of 70 wt.% of limestone slurry with a size below 100 μm in the presence of 0.2 wt.% of Dispersant S40, the slurry viscosity reduces by about 1 time with the temperature rising from 13 to 55 °C.

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References


Parameter effects on wet ultrafine grinding of limestone through slurry rheology in a stirred media mill


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Parameter effects on wet ultrafine grinding of limestone through slurry rheology in a stirred media mill

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Abstract

Wet ultra-fine grinding of a limestone powder (<100 μm) has been investigated in a stirred media mill with respect to the effect of slurry rheology. The grinding results obtained by various parameters (i.e., molecular weight of a dispersant, solids concentration, additive dosage, addition method and beads load) are evaluated in terms of energy efficiency and the fineness of a product. A polymeric dispersant called Dispersant S40 with a molecular weight of 5500 gives the best grinding results. For a certain level of beads load, an optimal solids concentration exists. In the case of the additive dosage of Dispersant S40 at 0.1 wt.% or more, a smaller additive amount of Dispersant S40 gives a higher energy efficiency and a smaller median size at a lower level of specific energy input. However, the excessive amount of the dispersant could cause a cushion layer formed on milling beads and thus lowers stress intensities from the collisions of milling beads, leading to an inefficient milling operation. This can be avoided by either the multi-point addition of the dispersant or a higher beads load (>83 vol.%). In addition, it was found that the higher the beads load, the better the cumulative energy efficiency, and the smaller the product size at the same specific energy consumption. For a given solids concentration, the relationships between the specific surface area and the particle size of an FP product and the additive amount of Dispersant S40 are explored, respectively. Furthermore, an empirical particle size-energy model provides a good fit ($R^2 > 0.991$) to the grinding results under the experimental conditions investigated.

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Keywords: Wet ultra-fine grinding; Stirred media mills; Slurry rheology; Limestone; Dispersants; Ultra-fine particles

1. Introduction

Due to some advanced properties of ultra-fine powders such as surface chemistry, packing characteristics, strength, optical properties and reaction kinetics and an increasing demand for ultra-fine powders for industries, wet ultra-fine grinding has found increased use in many fields such as minerals [1,2], ceramic materials [3,4], pigments [5], chemical products [6,7], microorganisms [8], pharmaceuticals [9,10], papermaking [11].

Ultrafine ground limestone powder is widely used in paints, pigments, food, plastics and pharmaceuticals industries as fillers [5,11,12]. For instance, this powder is employed as fillers in plastics to improve heat resistance, hardness, colour fastness and stability of materials. It is also utilised in papermaking as coatings and fillers to produce highly bright paper with a good resistance to yellowing and ageing and to provide large opacity, printability, ink receptivity and smoothness to paper [12].

Most of the mills used in wet ultra-fine grinding are stirred media mills due to their high unit outputs and high-energy efficiencies [13–16]. The stirred media mills are equipped with a stationary grinding chamber and a high-speed stirrer (disks or pins) fixed on a drive shaft. The grinding chamber is filled with small grinding media (normally spherical annealed glass, steel, or ceramic beads) at a high beads load. By stirring a slurry-bead mixture at a high stirring speed, a characteristic flow pattern and a grinding action are generated in the chamber. The respective kind of flow determines the spatial distribution of zones with high grinding intensities and the predominant types of grinding mechanisms as well as their composition [16,17]. Thus, the predominant grinding mechanisms in stirred media mills are dependent on...
compression, shear and torsional stresses, which are invoked by stirring the slurry-bead mixture at a very high velocity [16–21]. The effective grinding motions of the mixture are correlated to its flow behaviour in the grinding chamber. The optimization of the rheological behaviour of a ground slurry can enhance energy efficiency and throughput in wet ultra-fine grinding operation.

From a diagnostic point of view, the rheological behaviour of a mineral slurry is indicative of the level of interparticle interaction or aggregation in the slurry. Therefore, it is a useful variable to be controlled in industrial processes such as transportation of slurries, dewatering and wet grinding [22]. Since the product fineness significantly increases with grinding time in wet ultra-fine grinding operation characterized by a very fine product size and a high solids concentration, the surface properties tend to predominate in the system [13,14,23,24]. Inter-particle forces, such as van der Waals forces [25,26] and electrostatic forces [13,22], lead to the formation of agglomeration and aggregation. This results in changes in rheological property in wet ultra-fine grinding operations. The effect of slurry flowability or slurry rheology in wet ultra-fine grinding becomes of particular importance. For instance, the addition of an optimum dispersant to a given feed slurry can result in a drastic reduction or even elimination of yield stress and permits a higher solids concentration of a ground slurry [15,23,25–27]. In the absence of any dispersant, the typical maximum percentage solids by weight in a slurry is approximately 50% for the feed of ultra-fine grinding in stirred media mills, whereas an upper limitation of solids concentration is up to 80 wt.% in the presence of an optimal dispersant [25]. Therefore, the improvement of rheological behaviours of a feed slurry with the addition of a suitable dispersant can enhance the productivity and throughput for wet ultra-fine grinding.

Many studies related to slurry rheology in conventional tumbling ball mills have been published, but there is still little understanding of slurry rheology relevant to wet ultrafine grinding characterized by a very fine product size and a high slurry concentration due to the complex slurry rheological behaviours in stirred media mills [24,28]. Also, findings from tumbling ball mills involving the role of slurry rheology on the grinding results cannot be completely applicable to the stirred media milling case due to their different breakage mechanisms [18,19,29,30]. Therefore, it is necessary for scientific understanding and industrial application to systematically investigate the effect of slurry rheology on wet ultra-fine grinding performance by varying grinding conditions.

The objective of this paper is to investigate the effect of the rheological behaviours of limestone slurries ground in a stirred media mill on the energy efficiency and the product fineness obtained by varying the grinding parameters such as molecular weight of a dispersant, solids concentration, additive dosage, addition method, beads load. The grinding results were evaluated by energy efficiency and the median size of a ground product with respect to specific energy consumption.

2. Experimental set-up and procedures

2.1. Materials

A limestone powder <100 μm (93.7% CaCO₃) provided by SMA Karbonater AB in Sweden was used for grinding experiments in this study. Sodium polyacrylates with a range of molecular weights such as BCX-476, Dispersant S40 and BCX-552 obtained from CDM AB in Sweden were selected as dispersants. Table 1 shows the physical and chemical properties of the sodium polyacrylates including the molecular weights. In this investigation, the additive amount of a dispersant is the percent of the pure dispersant (i.e., active content) by weight relative to the weight of solids in a limestone slurry.

2.2. Stirred media mill

A stirred media mill utilized for the grinding experiments is the PMH 5 TEX Drais mill (Draiswerk GmbH, Germany). It consists of a Φ150 × 420 mm stainless steel cylinder chamber (5.6 l of net grinding chamber volume) and a stirrer with six Φ120 × 10 perforated discs installed on a horizontal driven shaft. The grinding chamber is equipped with a water jacket for cooling. The discs rotate at 1808 rpm (corresponding to a peripheral speed of 11.36 m/s). The flowrate of the slurry was controlled by a feeding pump at 1.5 l/min. Discharge of the product was facilitated by means of two specially designed screen cartridges inserted at the end of the cylinder. Zircon beads with diameters of 1.6–2.0 mm and a density of 3700 kg/m³ were used as the grinding media. The grinding operation in the PMH 5 TEX is the mode of circulation pass by pass. A limestone–water slurry was prepared at a pre-determined solids concentration by mixing 40 to 50 kg of limestone powder with water to make up about 35 l of the slurry. 14.1 l of the slurry were fed through the mill first and then thrown away in order to attain a steady milling state with regard to the solids concentration. The remaining about 20 l of the slurry were circulated through the mill pass by pass. Around 200 ml of slurry sample was taken after each pass. The samples were then analysed for particle size, rheological property and specific surface area, respectively. The grinding operation was stopped either when the

<table>
<thead>
<tr>
<th>Physical and chemical properties of three sodium polyacrylates</th>
<th>BCX-476</th>
<th>Dispersant S40</th>
<th>BCX-552</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid content (wt.%)</td>
<td>45%</td>
<td>45%</td>
<td>39%</td>
</tr>
<tr>
<td>Active content (wt.%)</td>
<td>40%</td>
<td>40%</td>
<td>26%</td>
</tr>
<tr>
<td>pH</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Density at 20 °C</td>
<td>1.30</td>
<td>1.30</td>
<td>1.315</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>2000</td>
<td>5500</td>
<td>85,000</td>
</tr>
<tr>
<td>Sodium polyacrylate content (wt.%)</td>
<td>40%</td>
<td>40%</td>
<td>26%</td>
</tr>
<tr>
<td>Water content (wt.%)</td>
<td>55%</td>
<td>55%</td>
<td>70%</td>
</tr>
<tr>
<td>Solubility (in water)</td>
<td>Very soluble</td>
<td>Very soluble</td>
<td>Very soluble</td>
</tr>
</tbody>
</table>

(1)molecular weight determined by gel permeation chromatography (GPC).
2.3. Measurements and evaluation

2.3.1. Energy consumption

The energy consumed by the mill was measured by an electrical meter called a Micro VIP (Elcontrol Co., Italy). In this study, only the active power (kW) was recorded and used by considering the power factor. The active power of the mill is sensitive to the current change at all levels up to the rated power of the motor. An active power reading was recorded every minute during each grinding pass, and about 10 readings were done for each pass. The mean active power of each pass is regarded as its real one. The mean active power, \( P_{mn} \), of the \( n \)th pass for a grinding experiment was determined by

\[
P_{mn} = \frac{\sum_{i=1}^{n} P_{ni}}{m}
\]

(1)

where \( P_{ni} \) is the \( i \)th discrete power reading of the \( n \)th pass, and \( m \), the number of readings of the \( n \)th pass. The milling energy of the \( n \)th pass was calculated by taking away the idle power draw of the mill, \( P_0 \) (kW) (without grinding media or ground material) from the mean active power, \( P_{mn} \) (kW) at the given rotation speed of 1808 rpm. Only the power adsorbed by the mill chamber was accounted in all the tests in this study. In order to evaluate the net energy consumption of the Drais mill, the mass specific energy consumption, \( E_m \) (kW h/t), was determined by [32]:

\[
E_m = \frac{P_{mn} - P_0}{3600 M_s C_0 \rho}
\]

(2)

where \( M_s \) (kg/s) is the mass flowrate of a slurry suspension fed to a mill, and \( C_0 \) is the solids concentration by weight. Due to the volume flowrate of a limestone slurry being controlled and measured in this study, the Eq. (2) is modified as

\[
E_m = \frac{P_{mn} - P_0}{3600 M_s C_0 \rho}
\]

(3)

where \( M_s \) (m³/s) is the volume flowrate of the slurry suspension fed to the mill, and \( C_0 \), the volume concentration of the slurry suspension, and \( \rho \) (kg/m³), the density of solid.

2.3.2. Specific surface area

The specific surface area of a sample was measured by Flow Sorb II 2300 (Micromeritics Co. Ltd., USA), which is an instrument designed to take the measurements on bone-dried powders by N₂ gas adsorption and desorption in liquid nitrogen temperature and room temperature (BET), respectively. A representative amount of sample was taken from each sample, and then was dried in an oven at 110 °C for 24 h in order to remove the residual moisture of the sample prior to the measurement. The mean value of the adsorption and desorption specific surface areas of a sample was regarded as its real one.

2.3.3. Calculation of energy efficiency

Energy efficiency or energy utilization, \( E_f \) (m²·Wh), which is defined as the increment of specific surface area per unit of specific energy consumption [14, 33], was calculated by

\[
E_f = \frac{1000 \Delta S}{E_m}
\]

(4)

where \( \Delta S = S - S_0 \), \( S \) and \( S_0 \) are the specific surface areas (m²/g) of a ground product and its feed by BET, respectively.

2.3.4. Particle size and distribution and slurry rheology

An X-ray Sedimentometer Sedigraph 5100D (Micromeritics Co. Ltd., USA) was used to analyze the particle size and distribution of samples. Its measurement range of particle size ranges from 0.1 to 300 μm, which is suitable for the samples in the study. A representative amount of sample was directly dispersed in aqueous solution of 0.1 wt.% of Calgon for the measurement.

2.3.5. Slurry rheology

A rotational viscometer (Bohlin Visco 88 BV (Bohlin Reologi UK Ltd., UK)) was utilized to determine the rheological property of the slurry. It employs a concentric cylinder geometry with a rotating inner cylinder and a stationary outer cylinder. The concentric cylinder system can be configured in 8 different measurement systems (3 DIN, 2 ‘Wide Gap’, 3 ‘Infinite Sea’), corresponding to SYSTEM knob 1 to 8 on the instrument, and their design allows the measurement of samples to be made in-situ (e.g. in a container) as well as on the laboratory bench. Any inner cylinder has 8 different rotation speeds from 20 to 1000 rpm (in agreement with a SPEED setting value 1 to 8 on the instrument), corresponding to a shear-rate range of 4 to 1200 s⁻¹. The torque developed on the inner cylinder due to a sample is directly related to the sample viscosity and should be in the range of 0.5 to 9.5 mN m for accuracy. In this study, all samples were measured by the use of C30 system (C30 DIN), which has a gap width of 1.5 mm between the inner and outer cylinders and can provide a viscosity range of 0.007 to 6.18 Pa s. A thermal jacket allows the use of an external fluids circulator to control or regulate the temperature of a sample measured. The viscometer employs a so-called “viscosoft” computation program so the digital readings or measurement parameters such as shear rate, shear stress, viscosity, torque are directly displayed on the screen of the viscometer.

The slurry samples were aged for 2 h, then were shaken at an intensity of 225 min⁻¹ with a shaker of Model TH-30 (Edmund Bühler Co., Germany) for 1 h to re-disperse the samples prior to rheological measurement. Each slurry sample was first pre-sheared for 3 min at the highest shear rate.
(corresponding to the SPEED setting value 8 on the instrument), then the measurement started from this highest shear rate. The shear rate was stepped down one by one until the torque reading was less than 0.5 mN m. The digital readings (viscosity, shear rate, shear stress, torque) were recorded at each shear rate. About 25 ml of slurry sample was required for each measurement. Each sample was measured three times and the mean values of shear stress, shear rate and viscosity were used for analysis. In addition, the extrapolated Bingham yield stress was utilized for analysis in this study.

2.3.6. Reproducibility of rheological data

The accuracy of this viscometer was examined by the reproducibility of the rheological measurements of a limestone slurry (<100 μm) over a wide range of shear rate. The results are shown in Table 2. It is evident that the viscometer exhibits good reproducibility with a rather small standard deviation for all the measurement parameters. The sample standard deviation of viscosity is less than 0.0013 Pa s when the torque is larger than 0.5 mN m. Even though the measured torque is less than 0.5 mN m, the sample standard deviation of viscosity is still less than 0.0018 Pa s. Thus, the viscometer accurately gives a resolution of 0.001 Pa s at a torque larger than 0.5 mN m.

2.3.7. Reproducibility of grinding results

Table 3 shows the mean value and the standard deviation for the measured values from three grinding tests, which were performed under the same conditions. It is evident that the grinding results with the stirred media mill (PMH 5 TEX)
exhibit good reproducibility with a rather small sample standard deviation for all the measurement parameters, as was confirmed and emphasized in Ref. [26].

3. Results and discussion

3.1. Effect of molecular weight of a dispersant

The ultra-fine grinding process is characterized by a high solids concentration and the presence of excessive fines, which are two of the primary factors leading to the formation of agglomerations or flocculations and hence the development of a yield stress of slurry. This results in an increase in the energy consumption for ultra-fine grinding and even makes the operation impossible [13,23–25]. It is known that a small addition of a suitable dispersant is indispensable for wet ultra-fine grinding. The polycrylic acids or its salts as efficient dispersants for wet ultra-fine grinding have been identified [34]. The use of a polycrylic acid or its salt with an optimal molecular weight as grinding aids can change the surface nature of particles in a ground slurry, resulting in inter-particle forces being entirely repulsive to improve the slurry flowability by decreasing the slurry viscosity and by reducing or eliminating the shear yield stress. This can enhance the fineness of products, energy efficiency and throughput in wet ultra-fine grinding.

Fig. 1 shows the effect of three sodium polycrylates with different molecular weights on the grinding results for 75 wt.% of solids concentration with 0.2 wt.% of each dispersant.

3.2. Effect of solids concentration

A small addition of a suitable dispersant is indispensable for the wet ultra-fine grinding of limestone [13,26,27]. It can change the surface nature of limestone particles in a ground slurry, resulting in inter-particle forces being entirely repulsive to improve the slurry flowability [31]. This decreases the energy consumption and increases throughput for the ultra-fine grinding. Based on the previous results, Dispersant S40 is selected as a grinding aid. Fig. 4 shows the grinding results of limestone slurries with three different solids concentrations with 0.2 wt.% of Dispersant S40 at 74 vol.% of beads load. The cumulative energy efficiency increases first and then decreases with increasing solids concentration from 65 to 75 wt.% at a given specific energy input. The median size of the product varies with solids concentration in an opposite way from the cumulative energy efficiency. This is in agreement with previous conclusion [13]. The best grinding results are obtained at 70 wt.% of solids concentration with 0.2 wt.% of Dispersant S40 at 74 vol.% of beads load. The reason is that the slurry of 70 wt.% of solids concentration with 0.2 wt.% of the dispersant exhibits proper viscosities in a wide range of shear rate (Fig. 5) and produces better stress conditions (i.e., a higher stress intensity and a larger average number of stress events for each particle). In the case of 65 wt.% of solids concentration with 0.2 wt.% of the dispersant, a lower
viscosity and a larger average interparticle distance make grinding beads difficult to effectively capture the particles. This increases the possibility of the direct collision between the beads, resulting in higher energy loss. A higher solids concentration (i.e. 75 wt.%) gives a smaller average interparticle distance, which leads to a larger average number of stress events of each particle. However, at 75 wt.% of solids concentration, the larger viscosity damps the motion of the grinding beads in the mill and significantly increases the attenuation of the velocity and kinetic energy of the beads, which bring about lower stress intensities of collisions among beads/particles/chamber inner wall. The decrease in stress intensity is dominant, compared with the increase in the number of stress events. Therefore, the captured particles cannot be effectively ground, which causes an ineffective milling operation. However, the grinding operation at a solids concentration from 65 to 75 wt.% with a given amount of
Dispersant S40 (i.e., 0.2 wt.%) automatically ceases when a ground slurry exhibits a pseudoplastic flow with an evident extrapolated Bingham yield stress (Figs. 5(d) and 6).

3.3. Effect of additive dosage of Dispersant S40

A small addition of a suitable dispersant is indispensable, and decreases energy consumption and increases throughput for wet ultra-fine grinding processes. An insufficient amount of the dispersant is a problem since some particles will be flocculated by bridging mechanisms, which increases the viscosity of a ground slurry. However, an excessive amount of the dispersant is unnecessary extravagance and can even cause slurry destabilization [31]. Therefore, it is important to determine an optimal dosage of Dispersant S40 in wet ultra-fine grinding of limestone in order to enhance energy efficiency.

Figs. 7 and 8 show the effect of various additive amounts of Dispersant S40 into 70 wt.% of solids concentration on the grinding results at 74 vol.% of beads load. Clearly, the energy efficiency increases first and then reduces with increasing the additive amount of the dispersant from 0.04 to 0.6 wt.% in the first pass. The additive amount of 0.1 wt.% gives a best grinding energy efficiency and a smallest median size of the ground product. The difference of rheological properties of the feeds for pass 1 is insignificant for 70 wt.% of solids concentrations with different dosages of the dispersant when the dosage is larger than 0.04 wt.% (Fig. 9 (a)). When the
additive amount is below 0.1 wt.% (i.e., 0.04 wt.%), the energy efficiency is reduced due to a rapid increase in the viscosity of the ground slurry during pass 1 (Fig. 9 (b)). The rheological property of the discharge slurry with 0.04 wt.% of the dispersant for pass 1 exhibits a pseudoplastic flow with a high extrapolated Bingham yield stress of 45.8 Pa. Therefore, the stress intensity from the collision of milling beads is rapidly weakened due to the poor flowability of the slurry. After pass 1, the grinding operation automatically ceased due to the poor flowability of the slurry. At an additive dosage of 0.1 wt.% of Dispersant S40 or more, the rheological differences of the feed and the discharge slurries are both insignificant for pass 1 for 70 wt.% of solids concentration with different dosages of Dispersant S40 (Fig. 9). But in a region of small cumulative specific energy input (less pass number), a smaller addition amount of the dispersant gives a higher energy efficiency and a smaller median size at a given specific energy input (Fig. 8). However, the additive amount of Dispersant S40 up to 0.6 wt.% causes an inefficient grinding in the initial stage. This is because the excessive Dispersant S40 exists in the slurry, but does not adsorb on the suspended limestone particles for 70 wt.% of solids concentration with 0.6 wt.% of Dispersant S40 [31]. When the slurry is pumped through the mill, the excessive dispersant not adsorbed by limestone particles could possibly adsorb on the grinding beads surface, and also some carboxylic groups on the dispersant molecules adsorbed on the grinding beads can simultaneously adsorb some fine limestone particles. This forms a cushion layer on the beads surface, which results in a lower stress intensity from the collision of the beads and thus gives the inefficient grinding action. With the cumulative specific energy input increasing, the specific surface area of the ground limestone particles increases and some excessive dispersant molecules immigrate onto the surface of the particles from that of the beads. The cushion layers on the beads become thinner and thinner and even disappear. Thus, the energy efficiency increases (Fig. 8 (a)). Similar phenomenon was observed by Bernhardt et al. [13]. The particle size is reduced with increasing the cumulative specific energy input, which causes a smaller stress zone (or active volume) between two approaching milling beads [19]. The possibility of a particle captured is reduced, thus the energy efficiency gradually lowers, as is interpreted by the grinding mechanism in stirred media mills, which has been described in detail by Kwade [18,19]. Before the grinding operation automatically ceases, the energy efficiency quickly reduces, especially for a smaller additive dosage of the dispersant. This is due to the rapid increase in the viscosity of the slurry, causing lower stress intensities. However, the slurry with 70 wt.% of solids concentration can be ground for one pass at 0.04 wt.% of Dispersant S40, two passes at 0.1 wt.% four passes at 0.2 wt.% and twelve passes at 0.6 wt.% For 70 wt.% of solids concentration with whatever additive dosages of Dispersant S40 and pass number, the grinding operation automatically stop when a discharge slurry from the mill displays a pseudoplastic flow with an evident extrapolated Bingham yield stress (Fig. 10), where the discharged slurry is defined as an FP product or FP slurry. In addition, it is interesting to observe the

Fig. 8. Effect of three different additive dosages of Dispersant S40 into 70 wt.% of solids concentration on the grinding results at 74% vol.% of beads load.

Fig. 9. Rheological properties of the feed and discharge slurries for 70 wt.% of solids concentration with various additive dosages of Dispersant S40 for pass 1: (a) Feeds; (b) Discharges.
influences of the additive amount of Dispersant S40 on the particle size distribution and the specific surface area of an FP product at the same solids concentration regardless of other grinding conditions (Figs. 11 and 12), respectively. This indicates that the limestone slurry with a given solids concentration is ground to an FP product with approximately the same particle size and specific surface area in the presence of the same additive amount of Dispersant S40. Obviously, the specific surface area of the FP product is directly proportional to the additive amount of Dispersant S40 (Fig. 12). The particle size distribution parallelly moves towards a range of smaller particle size with increasing the additive amount of Dispersant S40 when the additive amount is up to 0.2 wt.%. At the additive amount above 0.4 wt.%, the finer particles (<0.4 μm) increase more evidently, and the increase in specific surface area is mainly dependent on the created finer particles.

3.4. Effect of addition method of Dispersant S40

A product fineness of 90% passing 2 μm is required in industrials such as papermaking. The achievement of the product fineness needs a certain addition of a suitable dispersant for the limestone powder at a given solids concentration (Fig. 11). It is obvious that for 70 wt.% of solids concentration, at least 0.5 wt.% of Dispersant S40 is indispensable for the achievement of a product fineness of 90% passing 2 μm. To avoid the detrimental effect of the existence of excessive Dispersant S40 in a limestone slurry, the multi-point addition of the dispersant was adopted [35]. Fig. 13 shows the effect of multi-point and one-point additions of Dispersant S40 on wet ultra-fine grinding of the limestone. It is evident that an insignificant difference exists between three-point and one-point additions of Dispersant S40 on wet ultra-fine grinding of the limestone. It is because the existence of a small
additive amount (i.e., 0.2 wt.%) in the limestone slurry cannot form an effective cushion layer on the milling beads. However, in the case of 75 wt.% of solids concentration with 0.6 wt.% Dispersant S40, the multi-point addition of the dispersant gives a better energy efficiency in a range of lower specific energy input (i.e., <200 kW h/t). While in a higher level of the specific energy input above 300 kW h/t, the difference in cumulative energy efficiency resulting from different addition methods of Dispersant S40 is marginal. For an additive amount of 0.6 wt.% of the dispersant, a multi-point addition avoids the existence of the excessive dispersant, and thus the formation of a cushion layer on the milling beads in the lower specific energy input.

3.5. Effect of beads load

For wet ultra-fine grinding in stirred beads mills, the milling beads load is the most important parameter in terms of energy efficiency [36]. Fig. 14 shows the effect of various beads loads on the grinding results for 70 wt.% of solids concentration with 0.2 wt.% of Dispersant S40. The higher the beads load, the better the cumulative energy efficiency, the finer the product fineness at the same specific energy consumption. Besides, a higher beads load causes a less pass number under the same other grinding conditions before the grinding operation automatically stops when a discharge slurry from the mill displays a pseudoplastic flow with an evident extrapolated Bingham yield stress. For 65 vol.% beads load, the ground slurry of 70 wt.% of solids concentration with 0.2 wt.% of the dispersant can be circulated at least 7 passes, but can be circulated only 3 passes for 83 vol.% of beads load. This means less time needed at a constant feed flowrate of the slurry (1.5 l per min). This shows that a higher beads load gives a better energy efficiency and a higher milling rate (m²/g/min), which is defined as the increase in the specific surface area per unit of mean residence time [33]. For 70 wt.% of solids concentration with 0.6 wt.% of the dispersant, the consistent conclusion is drawn (Fig. 15). Also, it is interesting to see that for a lower beads load (≤ 74 vol.%) and a higher additive dosage of the dispersant (e.g., 0.6 wt.%) at a given solids concentration (i.e., 70 wt.%), the cumulative energy efficiency exhibits a maximum in a range of lower specific energy input. This phenomenon cannot occur in the case of a higher beads load (i.e., 83 vol.%). This indicates a higher beads load (≥ 83 vol.%) can eliminate the detrimental effect of the excessive...
dispersant in a limestone slurry on the wet ultrafine grinding, as is confirmed by comparing Figs. 8 with 16. In the case of 83 vol.% of beads load, the differences in grinding results are insignificant for 70 wt.% of solids concentration in the presences of 0.2 and 0.6 wt.% of the dispersant in a region of low specific energy input (Fig. 16).

4. Empirical prediction

In classical grinding theory, the particle size of a ground product reduces with increasing net specific energy input in the form of a power–law function. The differential form of the power–law relationship between an infinitesimal specific energy input and an infinitesimal increase in the overall fineness of the product can be described by the following equation [30]:

\[ dE = -k \frac{dx}{x^n} \quad (5) \]

where \( E \) is the net specific energy input (kW h/t) to a mill, \( x \) is the particle size, \( k \) is a proportionality coefficient depending on the grindability of a material and the efficiency of a mill, and \( n \) is a variant related to the particle size regime. Since a ground product does not consist of particles with one size, \( x \), the product fineness has to be described by an appropriate characteristic particle size, \( x_P \), such as \( x_{50} \) (the 80 wt.% passing size) and \( x_{10} \) (the median size) of its cumulative particle size distribution, which are convenient characteristic values for a particle size distribution [17,21]. Integration of Eq. (5) for \( n \neq 1 \) gives the following equation for the specific energy consumption, \( E \):

\[ E = \frac{k}{n-1} \left( \frac{1}{x_P} - \frac{1}{x_{50}} \right) \quad (6) \]

where \( x_{50} \) is a characteristic size of the particle size distribution of a ground product and \( x_P \) is the characteristic size of the particle size distribution of the feed. In this study, the median size, \( x_{50} \), of a product was chosen as the characteristic size, \( x_P \). It is found that the relationship between the median size (\( x_{50} \)) and the specific energy consumption can be well described by the following power–law function, which can be derived for \( x_P \geq x_{50} \), which is valid for ultra-fine grinding, from Eq. (6):

\[ x_{50} = \frac{C}{E^m} \quad (7) \]

where

\[ C = \left( \frac{k}{n-1} \right)^{\frac{1}{n-1}}, m = -\frac{1}{n-1} \]

Figs. 1(b), 4(b), 8(b), 14(b) and 16(b) present the experimental (dots) and predicted (lines) results for the grinding results under various conditions. Clearly, the particle size-energy model of Eq. (7) provides a good fit to the experimental results with a high regression coefficient (>0.991), regardless of whatever grinding conditions. This is in agreement with a previous conclusion for dolomite [21].

5. Conclusions

Wet ultra-fine grinding of a limestone powder (<100 μm) has been investigated in a stirred media mill with respect to the effect of slurry rheology. The results were evaluated in terms of energy efficiency and the fineness of a product as functions of various parameters such as molecular weight of a dispersant, solids concentration, additive dosage, addition method and beads load.

A polymeric dispersant, Dispersant S40, with a molecular weight of 5500 gave a higher energy efficiency and a smaller product size for wet ultra-fine grinding of the limestone due to its maintenance of a lower viscosity during grinding. For a certain media beads load, an optimal solids concentration existed for the effective grinding. The higher the beads load, the better the cumulative energy efficiency, the higher the milling rate, the finer the product fineness at the same specific energy consumption. At an additive dosage of 0.1 wt.% of Dispersant S40 or more, a smaller additive amount gave a higher energy efficiency and a smaller product size at a given specific energy consumption in a lower level of specific energy input. The excessive additive could cause a cushion layer formed on the surface of the milling beads and thus lowered stress intensities from the collisions of the beads, causing the ineffective grinding operation. This could be avoided by the multi-point addition of the dispersant or by a higher beads load (>83 vol.%). The wet ultra-fine grinding operation in the stirred media mill ceased when a discharge slurry from the mill displayed a pseudoplastic flow with an evident extrapolated Bingham yield stress. For a given solids concentration of limestone slurry, the relationships between the specific surface area and the particle size of an FP product and the additive amount of Dispersant S40 were explored, respectively. For a given solids concentration, the particle size and the specific surface area of an FP product were only related to the additive amount of Dispersant S40 regardless of other grinding conditions. Furthermore, a particle size-energy model provided a good fit (\( R^2 \approx 0.991 \)) to the grinding results under the experimental conditions studied.

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References

Paper 4

Influence of slurry rheology on stirred media milling of quartzite


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Influence of slurry rheology on stirred media milling of quartzite

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Abstract

The role of slurry rheology in stirred media milling of quartzite has been investigated by varying important grinding parameters such as media bead density and size, addition of chemicals, solids concentration, stirrer rotational speed as well as the combined effect of these factors. Media bead density has an evident but complex effect on stirred milling performance, depending on stirrer rotational speed and solids concentration. The effect of media bead size on the ultra-fine grinding of quartzite is relevant to the feed size. Optimal ratio of media bead size to the median size of a feed is between 150 and 200. The combined effect of grinding bead size and stirrer speed or solids concentration is insignificant. The addition of Dispersant S40 or a lower solids concentration results in better grinding performance (i.e., a higher energy efficiency and a smaller median size) due to the maintenance of lower viscosities at shear rates investigated during grinding. Stirrer rotational speed interacts with solids concentration. For a given solids concentration, an optimal stirrer speed exists. The observed phenomena can be explained by the interaction of slurry rheology and the stress intensity of individual grinding bead.

In addition, an empirical particle size-energy model provides a good fit ($R^2 > 0.904$) to the grinding results under the experimental conditions investigated. Furthermore, the wear of grinding media beads is involved. ZrO$_2$ beads have a lowest wear rate whereas the wear of SiO$_2$ beads is most serious. The wear rate of Al$_2$O$_3$ beads is related to bead size.

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Keywords: Wet ultra-fine grinding; Stirred media mill; Slurry rheology; Quartzite; Chemicals; Ultra-fine particle

1. Introduction

Due to some advanced properties of ultra-fine powders, such as surface chemistry, packing characteristics, strength, optical properties and reaction kinetics, and an increasing demand for ultra-fine powders for industries, wet ultra-fine grinding has found increased use in many fields such as minerals, ceramic materials, pigments, chemical products, microorganisms, pharmaceuticals, papermaking. Most of the mills used in wet ultra-fine grinding are stirred media mills due to their high unit throughput and energy efficiency (Bernhardt et al., 1999; Zheng et al., 1997; Kapur et al., 1996; Blecher et al., 1996). The stirred media mills are equipped with a stationary grinding chamber and a high-speed stirrer (disks or pins) fixed on a drive shaft. The grinding chamber is filled with small grinding media (normally spherical annealed glass, steel, or ceramic beads) at a high bead load. By stirring a slurry-bead mixture at a high stirring speed, a characteristic flow pattern and a grinding action are generated in the...
chamber. The respective kind of flow determines the spatial distribution of zones with high grinding intensity and the predominant types of grinding mechanisms as well as their composition (Blecher et al., 1996; Kwade et al., 1996). Thus, the predominant grinding mechanisms in stirred media mills are dependent on compressional, shear and torsional stresses, which are invoked by stirring the slurry-bead mixture at a very high velocity (Blecher et al., 1996; Kwade et al., 1996; Theuerkauf and Schwedes, 1999; Gao and Forsberg, 1995). The effective grinding motions of the mixture are correlated to its flow behaviour in the grinding chamber.

From a diagnostic point of view, the rheological behaviour of a mineral slurry is indicative of the level of interparticle interaction or aggregation in the slurry. Therefore, it is a useful variable to be controlled in industrial processes such as transportation of slurries, dewatering and wet grinding (Muster and Prestidge, 1995). Physical and chemical properties of a slurry, such as solids concentration, use of dispersants, particle size and distribution, particle shape, pH value, shear rate, and slurry temperature, have a significant influence on the slurry rheology due to the change or modification in surface property (He et al., 2004).

Since the product fineness significantly increases with grinding time in wet ultra-fine grinding operation characterized by a very fine product size and a high solids concentration, the surface properties tend to predominate in the system (Bernhardt et al., 1999; Zheng et al., 1997; Klimpel, 1999). Inter-particle forces, such as van der Waals forces (Greenwood et al., 2002; Reinisch et al., 2001) and electrostatic forces (Bernhardt et al., 1999; Muster and Prestidge, 1995), lead to the formation of agglomeration and aggregation. This results in changes in rheological property in wet ultra-fine grinding operations. The effect of slurry flowability in wet ultra-fine grinding becomes particularly important. The optimization of the rheological behaviour of a ground slurry can enhance the energy efficiency and throughput in wet ultra-fine grinding operations. For instance, the addition of an optimum dispersant to a given feed slurry can result in a drastic reduction or even elimination of yield stress and permits a higher solids concentration of a ground slurry (He et al., 2006b; Klimpel, 1999; Greenwood et al., 2002; Reinisch et al., 2001). In the absence of any dispersant, the typical maximum percentage solids in a slurry is approximately 27.4% by volume for the feed of ultra-fine grinding in stirred media mills, whereas an upper limitation of solids concentration is up to 60.15 vol.% in the presence of an optimal dispersant (Greenwood et al., 2002). Therefore, the improvement of rheological behaviours of a feed slurry with the addition of a suitable dispersant can enhance the productivity and throughput for wet ultra-fine grinding.

However there is still little understanding of slurry rheology relevant to wet ultra-fine grinding characterized by the presence of excessive fineness and a high slurry concentration due to the complex slurry rheological behaviours in stirred media mills (Gao and Forsberg, 1993a; Blecher and Schwedes, 1996). The objective of this work is to study the role of slurry rheology in stirred media milling of quartzite by varying important grinding parameters such as media bead density and size, addition of chemicals, solids concentration, stirrer rotational speed as well as the combined effect of some factors. The grinding results were evaluated by energy efficiency and the median size of a ground product with respect to specific energy consumption.

2. Materials and experimental procedures

2.1. Materials

A quartzite material (94.52% SiO₂) with a real density of 2710 kg/m³ (Density meter called Multivolume Pycnometer 1305, Micromeritics Instrument Corporation, USA) was provided by LKAB, Sweden and was used for grinding experiments in this study. The chemical analysis and particle size distribution of the quartzite material are presented in Table 1 and Fig. 1, respectively. Dispersant S40 (Sodium polyacrylate) from CDM AB, Sweden and Genamin CC 100 (C8–C18 amine, alias: Flotigam P) from Clariant GmbH, Germany were selected as dispersants.

2.2. Experimental procedures

2.2.1. Mix-up

A quartzite-water slurry was prepared at a predetermined solids concentration by the addition of 40 to 50 kg of quartzite powder into a certain amount of water to

| Table 1  |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Chemical analysis of quartzite composition |
| Main chemical composition | SiO₂ | Al₂O₃ | TiO₂ | MnO | MgO | CaO | Na₂O | K₂O | V₂O₅ |
| Percent (%) | 94.52 | 0.65 | 0.04 | 0.01 | 0.53 | 0.24 | <0.001 | 0.132 | 0.01 | 0.041 | 3.71 |
make up about 35 l of the slurry. The slurry was stirred as the quartzite powder was added to the water, and the stirring continued for 15 min after the completion of adding the quartzite powder to make the slurry uniform. If a given dispersant was necessary, the slurry was stirred again for 15 min after its addition to make the chemical disperse uniformly in the slurry. About 200 ml slurry was taken for each sample, which was used to analyse the particle size and distribution and to measure the rheological behaviour of the slurry. The rest of the quartzite slurry was used for grinding experiments.

2.2.2. Stirred media mill

A stirred media mill utilized for the grinding experiments is PMH 5 TEX Drais mill (Draiswerk GmbH, Germany). It consists of a Φ150×420 mm stainless steel cylinder chamber (5.6 l of net grinding chamber volume) and a stirrer with six Φ120×10 mm perforated discs installed on a horizontal driven shaft. The grinding chamber is equipped with a water jacket for cooling. The feed flowrate of the slurry was controlled by a feeding pump. Discharge of the product was facilitated by means of two specially designed screen cartridges inserted at the end of the cylinder. The grinding operation in the PMH 5 TEX is the mode of circulation pass by pass. 15 of 35 l of the slurry prepared previously were fed through the mill first and then discarded in order to attain a steady milling state with regard to solids concentration. The remaining about 20 l of the slurry were circulated through the mill pass by pass for several passes. This means that the entire 20 l of slurry was passed through the mill, collected at the discharge outlet and then passed through again. About 200 ml of slurry sample was taken after each pass. The samples were then analysed for particle size, rheological property and specific surface area, respectively. The grinding results with the stirred media mill (PMH 5 TEX) exhibit good reproducibility (He et al., 2006a). The experimental conditions for grinding tests are summarized in Table 2.

2.2.3. Measurements and evaluation

2.2.3.1. Energy consumption. The energy consumed by the mill was measured by an electrical meter named Micro VIP (Elcontrol Co., Italy). In this study, only the active power (kW) was recorded and used by considering the power factor. An active power reading was recorded every minute during each grinding pass, and about 10 readings were done for each pass. The mean active power of each pass is regarded as its real one. The mean active power, \( P_{\text{mn}} \), of the \( n \)th pass for a grinding experiment was determined by

\[
P_{\text{mn}} = \frac{\sum_{i=1}^{m} P_{ni}}{m}
\]

where \( P_{ni} \) is the \( i \)th discrete power reading of the \( n \)th pass, and \( m \), the number of readings of the \( n \)th pass. The milling energy of the \( n \)th pass was calculated by taking away the idle power draw of the mill, \( P_0 \) (kW) (without grinding media or ground material) from the mean active power, \( P_{\text{mn}} \) (kW) at a given rotation speed. And only the power adsorbed by the mill chamber was accounted in all the tests. In order to evaluate the net energy consumption of the mill, the mass specific energy consumption, \( E_m \) (kWh/kg), was determined by (He et al., 2006a):

\[
E_m = \frac{P_{\text{mn}} - P_0}{3600 M_v C_v \rho} \tag{2}
\]

where \( M_v \) (m³/s) is the volume flowrate of the slurry suspension fed to the mill, and \( C_v \), the volume

<table>
<thead>
<tr>
<th>Experimental conditions for grinding tests</th>
<th></th>
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<tbody>
<tr>
<td><strong>Constants:</strong></td>
<td></td>
</tr>
<tr>
<td>Filling rate of grinding media (vol.%)</td>
<td>70</td>
</tr>
<tr>
<td>Feed flowrate (l/min):</td>
<td>1.5</td>
</tr>
<tr>
<td>Variables:</td>
<td></td>
</tr>
<tr>
<td>(1) Solids concentration (wt.%)</td>
<td>65, 70</td>
</tr>
<tr>
<td>(2) Grinding media type, size and density:</td>
<td></td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 ) beads:</td>
<td>0.5–0.75 mm, 3.7 g/ml</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 ) beads:</td>
<td>0.75–1.0 mm, 3.7 g/ml</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 ) beads:</td>
<td>1.0–1.5 mm, 3.7 g/ml</td>
</tr>
<tr>
<td>( \text{ZrSiO}_4 ) beads:</td>
<td>1.6–2.0 mm, 3.7 g/ml</td>
</tr>
<tr>
<td>( \text{SiO}_2 ) beads:</td>
<td>1.6–2.0 mm, 2.5 g/ml</td>
</tr>
<tr>
<td>( \text{ZrO}_2 ) beads:</td>
<td>1.6–2.0 mm, 5.4 g/ml</td>
</tr>
<tr>
<td>(3) Stirrer speed (rpm):</td>
<td>1204, 1808, 2255</td>
</tr>
<tr>
<td>(4) Chemicals: Dispersant S40, Flotigam P</td>
<td></td>
</tr>
</tbody>
</table>
concentration of the slurry suspension, and $\rho$ (kg/m$^3$), the density of solids.

The specific surface area of a sample was measured by Flow Sorb II 2300 (Micromeritics Co. Ltd., USA), which is an instrument designed to take the measurements on bone-dried powders by N$_2$ gas adsorption and desorption at liquid nitrogen temperature and room temperature (BET), respectively. A representative amount of sample was taken from each sample, and then was dried in an oven at 110 °C for 24 h in order to remove the residual moisture of the sample prior to the measurement. The mean value of the adsorption and desorption specific surface areas of a sample was regarded as its real one.

2.2.3.3. Calculation of energy efficiency. Energy efficiency or energy utilization, $E_f$ (m$^2$/Wh), which is defined as the increment of specific surface area per unit of specific energy consumption (Gao and Forssberg, 1993b; He et al., 2006a), was calculated by

$$E_f = \frac{1000\Delta S}{E_m}$$

where $\Delta S = S - S_0$, $S$ and $S_0$ are the specific surface areas (m$^2$/g) of a ground product and its feed by BET, respectively.

2.2.3.4. Particle size and distribution. An X-ray Sedimentometer Sedigraph 5100D (Micromeritics Co. Ltd., USA) was used to analyze the particle size and distribution of samples. Its measurement range of particle size ranges from 0.1 to 300 $\mu$m, which is suitable for the samples in the study.

2.2.3.5. Slurry rheology. A rotational viscometer called a Bohlin Visco 88 BV (Bohlin Reologi UK
Ltd., United Kingdom) was used for the determination of slurry viscosities and shear stress–shear rate curves. It employs a concentric cylinder geometry with a rotating inner cylinder and a stationary outer cylinder. In this study, all samples were measured by the use of C30 system (C30 DIN), which has a gap width of 1.5 mm between the inner and outer cylinders and can provide a viscosity range of 0.007 to 6.18 Pa s. The inner cylinder has 8 different rotation speeds, from 20 to 1000 rpm, corresponding to a shear-rate range of 4 to 1200 s⁻¹. The torque developed on the inner cylinder due to a sample is directly related to the sample viscosity and should be in the range of 0.5 to 9.5 mN m for accuracy. A thermal jacket allows the use of an external fluid circulator to control or regulate the temperature of a sample measured. The viscometer employs a so-called “viscous” computation program so the digital readings, or measurement parameters, such as shear rate, shear stress, viscosity, and torque, are directly displayed on the screen of the viscometer. The viscometer exhibits

Fig. 4. Effect of media bead (1.6–2.0 mm in diameter) density on cumulative energy efficiency at 70 wt.% of solids concentration with 0.04 wt.% Dispersant S40 at two stirrer rotational speeds.

Fig. 5. Comparison of rheological behaviours for 70 wt.% solids concentration in the presence of 0.04 wt.% Dispersant S40 with 65 wt. % without chemicals.

Fig. 6. Effect of media bead (3.7 g/ml in density) size on the median size of a product at 65 wt. % of solids concentration at three stirrer rotational speeds.
good reproducibility with a rather small standard deviation for all the measurement parameters and accurately gives a resolution of 0.001 Pa s at a torque greater than 0.5 mN m (He et al., 2006b).

Slurry samples were aged for 4 h and then were shaken at an intensity of 225 min\(^{-1}\) (TH-30 shaker from Edmund Bühler, Germany) for 1 h to redispers the samples prior to rheological measurement. Each slurry sample was first presheared for 2 min at the highest shear rate of the viscometer (i.e., 1200 s\(^{-1}\)) prior to the measurement; then the measurement started from this highest shear rate. The shear rate was stepped down one by one until the torque reading was less than 0.5 mN m. The digital readings (viscosity, shear rate, shear stress, and torque) were recorded at each shear rate. About 25 ml of slurry sample was required for each measurement. Each sample was measured three times, and the mean values of shear stress, shear rate, and viscosity were used for analysis.

3. Results and discussion

3.1. Effect of media bead density

The effect of media bead density on the median size of a product at 65 wt.% solids concentration at three stirrer rotational speeds is shown in Fig. 2. It is seen that a higher density media bead (i.e., 5.4 g/ml) results in a smaller median size at a lower stirrer rotational speed (<1808 rpm) (Fig. 2a), as opposed at a higher stirrer rotational speed (i.e., 2255 rpm) (Fig. 2c) except for SiO\(_2\) beads with a density of 2.5 g/ml. However, the change of cumulative energy efficiency with media bead density at a certain stirrer speed is opposite from that of median size, as shown in Fig. 3. But they both give consistent grinding results. This is because high density beads (i.e., 5.4 g/ml) have higher stress intensities than low density beads (i.e., 3.7 g/ml) at a lower stirrer speed and can more effectively grind the captured quartzite.

![Fig. 7. Effect of media bead (3.7 g/ml in density) size on cumulative energy efficiency at 65 wt.% of solids concentration at three stirrer rotational speeds.](image)

![Fig. 8. Effect of chemicals on grinding results at 65 wt.% of solids concentration with 1.6–2.0 mm media beads with a density of 3.7 g/ml.](image)
particles. With stirrer rotational speed increasing, stress intensities of beads rise (Blecher et al., 1996; Kwade et al., 1996). At a stirrer rotational speed up to 2255 rpm, the stress intensity of beads with a higher density (i.e., 5.4 g/ml) exceeds the required one for pulverizing quartzite particles, resulting in the waste of energy in stress events. SiO₂ beads (density: 2.5 g/ml) used as grinding media give far larger median size for a ground product at a given energy consumption. It could be due to the very serious wear of SiO₂ beads observed during grinding, leading to an increasingly decrease in filling rate of media beads. Thus, the SiO₂ beads used as grinding media for quartzite are unsuitable and uneconomical. For 70 wt.% solids concentration with 0.04 wt.% Dispersant S40 at 2255 rpm stirrer speed, similar phenomena were observed, as shown in Fig. 4b. However, at 1204 rpm stirrer speed (Fig. 4a), 3.7 g/ml beads result in a higher cumulative energy efficiency than 5.4 g/ml beads, as is contradictory to that at 65 wt. % solids concentration. The possible reason could be that at 70 wt.% solids concentration, the grinding beads may not effectively be stirred up to produce effective impact breakage at 1204 rpm due to higher viscosities between 100 s⁻¹ and 1200 s⁻¹ (Fig. 5), which is within the range of shear rate distribution in the stirred media mill (Lane, 1999). Furthermore, more energy is needed to stir the heavier bead-slurry mixture containing higher density grinding beads (i.e., 5.4 g/ml) in the milling chamber. Thus 5.4 g/ml grinding beads give lower energy efficiency.

### 3.2. Effect of media bead size

Media bead size is claimed to be a crucial operating parameter for ultra-fine grinding in stirred media mills, and determines the probability that particles are captured and sufficiently stressed for a given feed size. Figs. 6 and 7 present the influence of several media sizes on the median size of a product and energy efficiency for 65 wt.% solids concentration at three stirrer rotational speeds, respectively. As can be seen, for a given bead load, a larger bead gives a smaller median size and a higher energy efficiency at specific energy consumption below 150 kWh/t regardless of stirrer speed. The 1.6–2.0 mm grinding beads lead to best grinding results (i.e., a smaller median size and a higher energy efficiency) under the experimental conditions studied. At specific energy consumption up to 40 kWh/t, corresponding to a median size larger than 10 μm, the difference in the median size of ground products by different media sizes rises at a certain cumulative specific energy input (Fig. 6a and b), indicating that coarse media beads (i.e., 1.6–2.0 mm) are more advantageous for the grinding. At specific energy consumption above 75 kWh/t, as the

---

Fig. 9. Change of rheological behaviours for 65 wt.% solids concentration with different chemicals with pass number (grinding time) increasing at 70 vol.% of bead load (bead size: 1.6–2.0 mm, bead density: 3.7 g/ml); a: feed; b: after pass 1; c: after pass 2; d: after pass 3.
product size becomes finer, the difference in the median size of ground products by different bead sizes decreases (Fig. 6c), suggesting that smaller media beads become more and more efficient for finer products. Similar conclusion was reached for zinc concentrations (Jankovic, 2003). For instance, at specific energy consumption above 150 kWh/t, corresponding to a median size less than about 5 \( \mu m \), the 0.75–1.00 mm bead size appears to be more efficient for finer products. For a certain feed size, a grinding bead is too small to capture ground particles effectively and break them due to lower stress intensity. With the media bead size increasing, the possibility of a particle caught by grinding beads and the stress intensity of individual bead both rise, and grinding performance is improved. However, it is expected that an optimum media bead size exists for most effective grinding, above which further increases in media bead size will have a detrimental effect on grinding. This is because the captured possibility of particles will not increase but decrease for a given feed size as a media bead size is over the optimum value, causing the decrease in the number of grinding beads per unit volume. Also, the stress intensity of individual media bead exceeds the required one for single breakage event, causing some energy wasted.

The median size of a product is regarded as a characteristic size and is used to calculate the ratio of media bead to feed sizes. The optimal ratio of media bead size to the median size of a feed is between 150 and 200 for 65 wt.% solids concentration. This ratio is far larger than 12:1 suggested by Zheng et al. (1996) for glass beads grinding limestone and than 20:1 recommended by Mankosa et al. (1986) for steel beads grinding coal. The difference is possibly due to different minerals, media types and densities, measurement and evaluation methods. For 70 wt.% quartzite slurry with 0.04 wt.% Dispersant S40, similar conclusion was obtained at 1204 rpm and 2255 rpm stirrer speeds.

### 3.3. Effect of chemicals

Chemicals have an important effect on wet ultra-fine grinding in stirred media mills since the addition of chemicals can modify the slurry rheology of ground slurry (He et al., 2006a). The effect of the addition of Flotigam P or Dispersant S40 on the ultra-fine grinding of quartzite was investigated. Fig. 8 shows the grinding results at 65 wt.% solids concentration using 1.6–2.0 mm media beads with a density of 3.7 g/ml.

![Fig. 10](image)

**Fig. 10.** Effect of solids concentration with 0.04 wt.% Dispersant S40 on grinding results at 1808 rpm stirrer rotational speed with 1.6–2.0 mm media beads with a density of 3.7 g/ml.

For 70 wt.% quartzite slurry with 0.04 wt.% Flotigam P, Dispersant S40 gives better grinding results (i.e., a higher energy efficiency and a smaller median size) in wet ultra-fine grinding of quartzite. The reason is that Dispersant S40 maintains lower viscosities at shear rates studied for 65 wt.% solids concentration during the grinding, as seen in Fig. 9. Whereas 65 wt.% of solids concentration with 0.04 wt.% Flotigam P exhibits higher viscosities at shear rates studied during the grinding, which damps the motion of the grinding beads in the mill and significantly increases the attenuation of the velocity and kinetic energy of the beads. This brings about lower stress intensities of collisions among beads/particles/chamber inner wall, and thus gives a lower energy efficiency and a larger median size. Consistent phenomena were also observed in the case of 5.4 g/ml media beads. Therefore, Dispersant S 40 is suitable to be used as a grinding aid because it can lower the slurry viscosity and eliminate the shear yield stress. This can enhance the fineness of products, energy efficiency and throughput in wet ultra-fine grinding, as consistent with a previous conclusion (He et al., 2006a).

### 3.4. Effect of solids concentration

A small addition of a suitable dispersant is indispensable for wet ultra-fine grinding (He et al., 2004). It can change the surface nature of particles in a ground slurry, resulting in inter-particle forces being
entirely repulsive to improve the slurry flowability (He et al., 2006b). This decreases the energy consumption and increases throughput for wet ultra-fine grinding. Based on the above results, Dispersant S40 is selected as a grinding aid. Fig. 10 shows the effect of solids concentration on grinding results in the presence of 0.04 wt.% Dispersant S40 using 1.6–2.0 mm media beads with 3.7 g/ml density. It is seen that a lower solids concentration has a positive effect on the grinding results at a given stirrer rotational speed (i.e., 1808 rpm), and thus results in a higher cumulative energy efficiency and a smaller median size. Consistent phenomena were also observed in the case of 5.4 g/ml media beads.

Although a higher solids concentration (i.e., 70 wt.%) gives a smaller average interparticle distance, which leads to a larger average number of stress events of each particle, 70 wt.% of solids concentration with 0.04 wt.% Dispersant S40 exhibits a larger viscosity than 65 wt.% in the range of shear rates studied during grinding (Fig. 11). It retards the motion of the grinding beads in the mill and significantly attenuates the velocity of the beads, which results in lower stress intensities of collisions between beads and beads or chamber inner wall. Therefore, the captured particles cannot be effectively ground, which causes a lower cumulative energy efficiency and a larger median size at a given specific energy consumption.

3.5. Effect of stirrer rotational speed

Stirrer rotational speed is believed to be one of the most important factors in ultra-fine grinding, which is directly related to the stress intensity of individual grinding bead. Three stirrer rotational speeds were selected in the study by changing the pulley with different diameters on the motor shaft or the mill shaft. The speed was varied at 1204 rpm, 1808 rpm and 2255 rpm, and the corresponding peripheral speeds of the stirrer disks were 7.56 m/s, 11.36 m/s and 14.17 m/s, respectively. The effect of stirrer speed on grinding results at two solids concentrations with various types of grinding beads are shown in Figs. 12 and 13, respectively. For 65 wt.% solids concentration, the cumulative energy efficiency first increase and then decrease with stirrer rotational speed rising under the grinding conditions investigated. 1808 rpm stirrer speed gives the best energy efficiency. This indicates that for 65 wt.% solids concentration, the stress intensity of individual media bead is sufficient to break the caught particles at 1808 rpm, below which the stress intensity is insufficient for breakage and above which some energy is excessive and wasted. For 70 wt.% solids concentration with 0.04 wt.% Dispersant S40, a different phenomenon was observed that a higher energy efficiency was obtained at a higher stirrer speed in the range of
stirrer speeds studied. This is because 70 wt.% of solids concentration with 0.04 wt.% Dispersant S40 exhibits a higher viscosity than 65 wt.% in the range of shear rates from 100 s\(^{-1}\) to 1200 s\(^{-1}\) (Fig. 5), which is within the range of shear rate distribution in the stirred media mill (Lane, 1999). It damps the motion of the grinding beads in the mill, and more energy is used to counteract the viscous resistance. Increasing stirrer speed improves the stress intensity of individual bead, and thus results in a better energy efficiency in the range of stirrer speeds studied. It is expected that a higher optimum stirrer speed would exist for a denser slurry.

4. Empirical prediction

In classical grinding theory, the particle size of a ground product reduces with increasing net specific energy input in the form of a power-law function. The differential form of the power-law relationship between an infinitesimal specific energy input and an infinitesimal increase in the overall fineness of the product can be described by the following equation (Austin et al., 1984):

\[
\frac{dE}{dx} = -k \frac{dx}{x^n}
\]

where \(E\) is the net specific energy input (kWh/t) to a mill, \(x\) is the particle size, \(k\) is a proportionality coefficient depending on the grindability of a material and the efficiency of a mill, and \(n\) is a variant related to the particle size regime. Since a ground product does not consist of particles of only one size, \(x\), the product fineness has to be described by an appropriate characteristic particle size, \(x_m\), such as \(x_{80}\) (the 80 wt.% passing size) or \(x_{50}\) (the median size) of its cumulative

![Fig. 12. Effect of stirrer rotational speed on cumulative energy efficiency at 65 wt.% of solids concentration with various media beads.](image)

![Fig. 13. Effect of stirrer rotational speed on cumulative energy efficiency at 70 wt.% of solids concentration with 0.04 wt.% of Dispersant S40 with two different media beads.](image)
particle size distribution, which is a convenient characteristic value for a particle size distribution (Kwade et al., 1996; Gao and Forssberg, 1995). Integration of Eq. (4) for \( n \neq 1 \) gives the following equation for the specific energy consumption, \( E \):

\[
E = \frac{k}{n-1} \left( \frac{1}{x_{m,F}^{-1}} - \frac{1}{x_{m,P}^{-1}} \right)
\]

where \( x_{m,P} \) is a characteristic size of the particle size distribution of a ground product and \( x_{m,F} \) is the characteristic size of the particle size distribution of the feed. In this study, the median size, \( x_{50} \), of a product was chosen as the characteristic size, \( x_m \). It is found that the relationship between the median size (\( x_{50} \)) and the specific energy consumption can be well described by the following power-law function, which can be derived from Eq. (5):

\[
x_{50} = C \cdot E^m
\]

where \( C = \left( \frac{1}{x_{m,F}^{-1}} \right)^{1/m} \), \( m = -\frac{1}{n-1} \).

Figs. 2, 6, 8a, and 10a present the experimental (dots) and predicted (lines) results for the grinding results under various conditions investigated. Clearly, the particle size-energy model of Eq. (6) provides a good fit to the experimental results with a high regression coefficient (> 0.904), regardless of whatever grinding conditions. This is in agreement with previous conclusions for dolomite (Gao and Forssberg, 1995) and limestone (He et al., 2006a).

5. Wear of grinding media beads

During the grinding in stirred media mills, not only the product particles are comminuted but also the surface of grinding beads is stressed and abraded, causing the mass of grinding beads decreased. To evaluate the wear of grinding beads, the mass of grinding beads is weighed before and after each grinding test, respectively, and the mass difference, \( \Delta m_{gb} \), is regarded as the wear of grinding beads. A dimensionless wear rate, \( \sigma \) is

\[
\sigma = \frac{\Delta m_{gb}}{m_{gb}} \times 100\%
\]

where \( m_{gb} \) is the mass of grinding beads before each grinding test. The wear percent is used as an evaluation parameter. In Fig. 14, the dimensionless wear rate for different types of grinding beads is plotted against specific energy consumption (kWh/t). It is shown that ZrO₂ beads have a lowest wear rate while the wear of SiO₂ beads is most serious and about 100 times as much as ZrO₂ beads. The ZrSiO₄ beads and 1.0–1.5 mm Al₂O₃ beads are similar in wear, which is higher than 0.75–1.0 mm and 0.5–0.75 mm Al₂O₃ beads. The wear mechanisms of grinding media beads are complex and consist of impact, abrasion, corrosion wear (Chenje and Radziszewski, 2004). The wear mechanisms are dependent on many factors such as the surface roughness of grinding beads, the microstructure, the shape, the hardness as well as the shape and the hardness of ground particles (Becker and Schwedes, 1999; Sepúlveda, 2004; Chenje and Radziszewski, 2004). Further work would be done to seek scientific understanding.

6. Conclusions

The effect of slurry rheology on stirred media milling of quartzite has been studied by varying important grinding parameters such as media bead density and size, addition of chemicals, solids concentration, stirrer rotational speed as well as the combined effect of these factors. Media bead density has an evident but complex effect on stirred milling performance, depending on stirrer rotational speed and solids concentration. The effect of media bead size on the ultra-fine grinding of quartzite is relevant to the feed size. Optimal ratio of media bead size to the median size of a feed is between 150 and 200. Grinding bead size insignificantly interacts with stirrer speed and solids concentration. The addition of Dispersant S40 or a lower solids concentration results in better grinding performance (i.e., a higher energy efficiency and a smaller median size) due to the maintenance of lower viscosities at shear rates investigated during grinding. The combined effect of stirrer rotational speed and solids concentration is evident. For a given solids concentration, an optimal stirrer speed exists.
In addition, an empirical particle size-energy model provides a good fit ($R^2$ > 0.904) to the grinding results under the experimental conditions investigated. Furthermore, the wear of grinding media beads is involved. ZrO$_2$ beads have a lowest wear rate whereas the wear of SiO$_2$ beads is most serious. The wear rate of Al$_2$O$_3$ beads is related to the bead size.

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References


Paper 5

Rheological behaviors in wet ultrafine grinding of limestone


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Rheological behaviors in wet ultrafine grinding of limestone

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Abstract
This paper investigates the effects of solids concentration and the addition of Dispersant S40 on the flowability of original and ground limestone slurries. A rotational viscometer with a cone-and-plate geometry was used to characterize the rheological behaviors of limestone slurries. The rheological behavior of original limestone slurries (<100 μm) is transformed through different types of flows with increasing solids concentration. The use of Dispersant S40 can improve the slurry flowability by decreasing viscosity and eliminating Casson yield stress. It is therefore used as a grinding aid for the wet ultrafine grinding of limestone. The rheological behaviors of ground limestone slurries vary with grinding from a starting dilatant flowability to a resulting pseudoplastic one with an evident Casson yield stress in combination with a thixotropic character. The appearance of pseudoplastic flowability combining thixotropy is related to the fineness of a ground product and its specific surface area, which are both correlated to solids concentration and the additive amount of Dispersant S40. In addition, the accurate rheological characterization of time-dependent fluids is dependent on the instruments used and operation conditions.

Keywords: Carbonates; Stirred media mills; Wet ultra-fine grinding; Slurry rheology

Introduction
From a diagnostic point of view, the rheological behavior of a mineral slurry is indicative of the level of interparticle interaction or aggregation in the slurry. It is therefore a useful processing control variable (Muster and Prestidge 1995). Because the product fineness and the specific surface area significantly increase with grinding time in wet ultrafine grinding characterized by a high solids concentration and the presence of excessive fines, the surface properties tend to predominate in the slurry system (Gao and Forssberg, 1993; Bernhardt et al., 1999; Klimpel, 1999; Klein and Hallbom, 2002; He et al., 2004). This results in evident changes in the rheological properties in wet ultrafine grinding operations due to the agglomeration and aggregation resulting from the inter-particle forces, such as van der Waals forces (Greenwood et al., 2002) and electrostatic forces (Muster and Prestidge, 1995; Bernhardt et al., 1999; Klein and Hallbom, 2002).

Slurry rheology in wet ultrafine grinding plays an important role. There is substantial literature on the qualitative and quantitative investigation of the influence of rheological behaviors of a ground slurry on ultrafine grinding results (Gao and Forssberg, 1993; Bernhardt et al., 1999; Greenwood et al., 2002; Yue and Klein, 2004; He et al., 2006a). However, there is still a poor understanding of changes in the rheological properties of the slurry in wet ultrafine grading. The aim of this work is to study the effects of solids concentration and the addition of a dispersant called Dispersant S40 on the rheological behaviors of original and ground limestone slurries in a stirred media mill. The work explores the dependence of slurry rheology on solids concentration, the addition of dispersant, the particle size and the specific surface area of a product. The slurry rheology is expected to act as a useful process-control variable for wet ultrafine grinding.

Materials and experimental methods
Materials. A limestone powder sample (93.7% by weight CaCO₃, 2,700 kg/m³) provided by the SMA Karbonater AB, Sweden, was used for the grinding experiments. The particle size distribution of the powder is shown in Fig. 1. Limestone was selected because it is not too hard and exhibits good grindability, which means the contamination of the mill by wear is small and also the produced size fineness leads to an evident change of the apparent viscosity of a ground slurry. The chemical analysis and physical characteristics of the limestone powder are presented elsewhere (He et al., 2006b).

A polymeric dispersant called Dispersant S40, provided by CDMAB, Sweden, was used as a dispersant or grinding aid.

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Table 1 — Experimental conditions for grinding tests.

<table>
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<tr>
<td>Filling rate of grinding media</td>
<td>70% (by volume)</td>
</tr>
<tr>
<td>Feed flow rate</td>
<td>1.5 L/min</td>
</tr>
<tr>
<td>Stirrer speed</td>
<td>1,808 rpm (11.36 m/s)</td>
</tr>
<tr>
<td>ZrSiO₄ milling beads</td>
<td>1.6-2.0 mm, 3.7 g/mL</td>
</tr>
</tbody>
</table>

| Variables:                                     |          |
| Solids concentration                           | 65%, 70%, 75% (by weight) |
| Addition of Dispersant S40                     | 0% - 0.6% (by weight) |

Experimental methods.

Mixing: Limestone–water slurry was prepared at a predetermined solids concentration by the addition of 40 to 50 kg of limestone powder into a certain amount of water to make up about 35 L of the slurry. The slurry was stirred as the limestone powder was added into water, and the stirring continued for 15 min after the completion of adding the limestone powder to make the slurry uniform.

If a given amount of Dispersant S40 were added, the slurry was stirred again for 15 min after its addition to make the chemical disperse uniformly in the slurry. About 200 mL slurry was taken for each sample, which was used to analyze the particle size and distribution and to measure the rheological behavior of the slurry. The remaining limestone slurry was used for grinding experiments.

Stirred media milling: A stirred-media mill utilized for the grinding experiments was a commercial laboratory mill called a PMH5 TEX Drais mill (Draiswerk GmbH, Germany). Figure 2 (a) and (b) schematically shows the mill set-up and the grinding chamber. It consists of a Ø150×420-mm stainless steel cylinder chamber (5.6 L of net grinding chamber volume) and a stirrer with six Ø120×10 perforated discs installed on a horizontal driven shaft. The grinding chamber is equipped with a water jacket for cooling. The grinding operation conditions are listed in Table 1. The grinding operation in the PMH 5 TEX is the mode of circulation pass by pass. Fifteen of the 35-L portions of the slurry were fed through the mill first and then thrown away to attain a steady milling state with respect to solids concentration. The remaining about 20 L of slurry was circulated through the mill pass by pass. About 200 mL of slurry sample was taken after each pass. The samples were then analyzed for particle size, rheological property and specific surface area, respectively.

Rheological measurements: Slurry samples were aged for four hours and then shaken at an intensity of 225 min⁻¹ (TH-30 shaker from Edmund Bühler, Germany) for one hour to redisperse the samples prior to rheological measurement.

A rotoviscometer called a Bohlin Visco 88 BV (Bohlin Reologik UK Ltd., United Kingdom) was used for the determination of slurry viscosities and shear stress–shear rate curves. In this study, all samples were measured by the use of C30 system (C30 DIN). It employs a concentric cylinder geometry with a rotating inner cylinder and a stationary outer cylinder between which a gap width is 1.5 mm. The inner cylinder has eight different rotation speeds, from 20 to 1,000 rpm, corresponding to a shear-rate range of 4 to 1,200 sec⁻¹.

The torque developed on the inner cylinder due to a sample is directly related to the sample viscosity and should be in the range of 0.5 to 9.5 mN·m for accuracy, during which the viscometer exhibits good reproducibility with a resolution of 0.001 Pa·sec (He et al., 2006b). A thermal jacket allows the use of an external fluid circulator to control or regulate the temperature of a sample measured.

The sedimentation of particles has always been a major problem in measuring the rheology of mineral slurries (Kawatra and Bakshi, 1996; Kawatra et al., 1999), but unfortunately, no modification to the viscometer was done to prevent particle from settling in this study. The viscometer employs a so-called "viscosoft" computation program, so the digital readings (measurement parameters) such as shear rate, shear stress, viscosity and torque are directly displayed on the screen of the viscometer. Each slurry sample was first presheared for 3 min at 1,000 rpm (i.e., 1,200 sec⁻¹) prior to measurements. The measurement were then started from this highest shear rate.

The shear rate was stepped down one by one until the torque reading was less than 0.5 mN·m. The digital readings (viscosity, shear rate, shear stress and torque) were recorded at each shear rate. About 25 mL of slurry sample was required for each measurement. Each sample was measured three times, and the mean values of shear stress, shear rate and viscosity were used for analysis.

A controlled-stress rheometer called a TA Instruments CSL² 500 (TA Instruments, Leatherhead, United Kingdom) was used to characterize the time-dependent flowability of a ground slurry because it can give far more shear rate–viscosity points than Bohlin Visco 88 BV viscometer. According to measurement requirements, a TA Instruments CSL² 500 can calibrate and optimize parameter options itself through an auxiliary computer software called TA Instruments Rheology Solutions. Also, the rheometer can accurately maintain a given temperature varying in the range of ± 0.1°C by the use of a heating-refrigerating bath and circulator system.

Samples were measured in the shear-rate range of 20 to 600 sec⁻¹ using a cone-and-plate geometry with a cone of a
A sample was first presheared at 800 sec\(^{-1}\) for 5 sec rather than 3 min to avoid evaporation, and then it was subjected to a varying shear rate, which was first increased from 20 to 600 sec\(^{-1}\) ("up") in 2 min and then decreased to 20 sec\(^{-1}\) ("down") in 2 min.

In addition, the rheological data were fitted using both Bingham plastic (Gao and Forsberg, 1993b; Muster and Prestidge, 1995; Prestidge, 1997) and Casson (Yang et al., 2001; Yue and Klein, 2004) models (Eqs. (1) and (2), respectively), as these two models are simple two-parameter equations as follows

\[
\tau = \tau_y + \eta_s \gamma \\
\tau^{\frac{1}{2}} = (\tau_y)^{\frac{1}{2}} + (\eta_s)^{\frac{1}{2}}
\]

where

- \(\tau\) is the shear stress,
- \(\gamma\) is the shear rate,
- \(\tau_y\) and \(\eta_s\) are yield stress terms and
- \(\eta_b\) and \(\eta_q\) are the viscosity terms.

Figure 3 shows the fits of rheological data at various solids concentration into the (a) Bingham and (b) Casson equations, respectively. It is revealed that the Casson model (average correlation coefficient, \(R^2 = 0.998\)) fits the data a little bit better than Bingham model (\(R^2 = 0.996\)), as is in agreement with previous results for quartz suspensions (Yue and Klein, 2004). Therefore, the Casson model was used to fit the rheological data to obtain Casson yield stress.

Energy consumption: The energy consumed by the mill was measured by an electrical meter called a Micro VIP (Elcontrol Co., Italy). In this study, only the active power (kilowatts) was recorded and used. An active power reading was recorded every other minute during each grinding pass, and more than ten readings were taken for each pass. The mean active power of each pass is regarded as its real one. The mean active power, \(P_a\) (kW), of the \(n^{th}\) pass for a grinding experiment could be formulated by the equation

\[
P_a(n) = \frac{1}{n} \sum_{i=1}^{n} P_a(i)
\]
Results and discussion

Effect of solids concentration. The influence of solids concentration on slurry rheology is significant because various ranges of solids concentrations can lead to different types of flows, as shown in Fig. 4. The result shows the rheological properties of seven solids concentrations of original limestone slurries without dispersant at a temperature of 25 ± 0.2°C. Clearly, at a solids concentration ≤ 65% by weight (40.75% by volume), the slurry appears to be a weakly dilatant flow when the effect of particle settling is neglected. This is because in a dilute slurry (i.e., ≤ 65% by weight or 40.75% by volume), the interparticle distance is so large that the limestone particles in the slurry are not subjected to the attractive forces between the particles.

At lower shear rates, the particles have enough opportunities to slip over each other and are free to move as individuals. Increasing shear rate increases the degree of shear-induced aggregation, leading to an increase in viscosity (Klein and Hallbom, 2002). Alternatively, the slurry at a solids concentration ≤ 65% (by weight) may present Newtonian fluid if particle sedimentation is eliminated, as observed during measuring.

A decrease in apparent viscosity with reducing shear rate may arise from particle settling. Unfortunately, no effort was made to overcome the issue of particle settling in the study. At solids concentrations of up to 67% by weight (42.92% by volume), the flowability of the slurry exhibits a pseudoplastic characteristic without a definite yield stress at shear rates less than 663 sec⁻¹ and a weakly dilatant or Newtonian one at shear rates larger than 663 sec⁻¹. This indicates that in a lower range of shear rates the interparticle attractive force is predominant over the hydrodynamic one exerted by a flow field at 67% (by weight) of solids concentration, as opposite in a range of shear rates larger than 663 sec⁻¹.

With further increasing the solids concentration to 70% by weight (46.36% by volume) or more, the slurry rheology is changed into a pseudoplastic flow with an evident shear yield stress at low shear rates, followed by a transition to a Casson plastic flow (with a higher extrapolated Casson yield stress) at high shear rates. Furthermore, the degree of pseudoplasticity and the shear yield stress increase with increasing solids concentration when the solids concentration is larger than 70% (by weight) (Fig. 4 (a)).

Similar phenomena were observed for quartz (Yue and Klein, 2004) and titanium dioxide suspensions (Yang et al., 2001). The effect of solids concentration on the apparent viscosity at a given shear rate and the extrapolated Casson yield stress for the slurries is shown in Fig. 5. The viscosity and the yield stress rather sharply increase in exponential and power-law forms with increasing solids concentration when the solids concentration is larger than 70% by weight (46.36% by volume), respectively.

This is similar to a previous conclusion (Tseng and Chen, 2003). This indicates that there are strong interactions between the particles to hold the particles together in the slurry and form loosely packed flocs, immobilizing some water within them, which is indispensable to flow. This is because a smaller
produces an increased interparticle distance in a denser slurry produces an increased attractive potential and a larger probability of collisions between the particles, resulting in more particles attracting each other. A shearing force over a certain shear yield stress has to be exerted on the slurry to overcome the internal friction among the particles constituting the flocs and to make it flow again. Once the slurry flows, the flocs are broken down into smaller flow fragments with increasing flow intensity (i.e., shear rate for a given suspension system).

The fragment size is determined mainly by the balance between the strength of the aggregate structure and the flow intensity (Higashitani et al., 2001). An increase in shear rate (flow intensity) gives smaller flow units and thus decreases viscosity of the slurry.

A small addition of a suitable dispersant is indispensable for the wet ultrafine grinding of limestone at a higher solids concentration (> 70% by weight) due to the rapid increases in viscosity and yield stress, which result in an increase in the energy consumption for wet ultrafine grinding and even make the operation impossible (Gao and Forssberg, 1993; Greenwood et al., 2002).

Figure 5 — Effect of solids concentration on the (a) apparent viscosity and (b) the Casson yield stress at the temperature of 25 ± 0.2°C (by Bohlin viscometer).

Effect of Dispersant S40. Figure 6 shows the effect of the additive dosage of a sodium polyacrylate called Dispersant S40 on the flowability of original limestone slurry at 75% (by weight) solids concentration. The slurry with less than 0.01% (by weight) Dispersant S40 shows a pseudoplastic characteristic with a yield stress and possesses a higher apparent viscosity than that without the dispersant at a given shear rate. This reason is that an insufficient dispersant causes the flocculation of particles in the slurry by bridging attraction forces, leading to larger flow units (Johnson et al., 2000). At the additive amount of Dispersant S40 up to 0.015% (by weight), the apparent viscosity of the slurry is lower than that without the dispersant, and the slurry still exhibits a pseudoplastic flow with a smaller yield stress. When the additive dosage of Dispersant S40 is up to 0.03% (by weight) or more, the slurry is transformed into a weakly dilatant flow when the effect of particle settling is neglected, and the apparent viscosity in the range of shear rates investigated slightly decreases with the further addition of Dispersant S40 and is up to a minimum at the addition level of 0.1% (by weight). In this case, it is expected that the saturation adsorption of the dispersant on

Figure 6 — Flowability of original limestone slurry at 75% (by weight) solids concentration with various dosages of Dispersant S40 at the temperature of 25 ± 0.2°C (by Bohlin viscometer).
the particle surface has been attained, and electrostatic and steric stabilizations (i.e., electrosteric stabilizations) occur. By further adding the dispersant, the apparent viscosity at a given shear rate insignificantly reverts. The excessive dispersant can increase the ion strength of the slurry. This results in a reduction of the magnitude of zeta potential (electrostatic repulsive) around the particles and a compression of the adsorption layer of the dispersant producing a lower steric force, that is, the electrosteric forces are decreased (Banush and Cooll, 1999; Ewais et al., 2002; Papo et al., 2002). In addition, the excessive dispersant above the adsorption saturation exists in the slurry but not adsorb on the suspended particles and can cause a depletion flocculation. (Depletion flocculation results from the approach of particle surfaces in a concentrated solution of nonadsorbing polymers. When the interparticle distance is less than the dimensions of the polymer molecules, the polymers are excluded from the gap due to an osmotic pressure gradient between the colloidal particles and surrounding solution. As a result, an effective attractive force is produced between the colloidal particles, [Hunter, 1987; Milling and Biggs, 1995; Johnson et al., 2000]).

For 70% (by weight) solids concentration, similar phenomena were also observed with the addition of Dispersant S40. Figure 7 shows the results. Clearly, the Casson yield stress is eliminated at 0.02% (by weight) of the dispersant for 70% (by weight) solids concentration and at 0.03% (by weight) for 75% (by weight) solids concentration (Fig. 7 (a)). The apparent viscosity of the slurry at a given shear rate first increases and then decreases. It then reverts after reaching a minimum with increasing the additive dosage of Dispersant S40. Similar phenomena were observed for kaolin suspensions with sodium tripolyphosphate and sodium polyphosphate (Papo et al., 2002), for zirconia slurries with tri-ammonium citrate (Ewais et al., 2002) and for silica suspensions with polyethylene oxide (Zaman et al., 2000). In the case of the limestone slurry at 70% and 75% (by weight) solids concentrations, the apparent viscosity at a certain shear rate reaches a maximum at the additive amount of 0.004% (by weight) Dispersant S40 and decreases to a minimum at 0.1% (by weight) (Fig. 7 (b) and (c)).

The use of a sodium polyacrylate with a given molecular weight (i.e., 5,500) called Dispersant S40 can change the surface nature of particles in limestone slurries, resulting in repulsive interparticle forces to improve the slurry flowability by decreasing viscosity and eliminating yield stress. Thus, Dispersant S40 is suitable to be used as a grinding aid for wet ultrafine grinding of limestone.

**Rheological behaviors during grinding.** Because the fineness of a product significantly increases with grinding in wet ultrafine grinding operations characterized by a high solids concentration and the presence of excessive fines, the surface properties tend to predominate in the system (Bernhardt et al., 1999; Klimp, 1999; Klein and Hallbom, 2002; He et al., 2004). Inter-particle forces, such as van der Waals (Greenwood et al., 2002) and electrostatic force (Muster and Prestdige, 1995; Bernhardt et al., 1999; Klein and Hallbom, 2002), lead to the formation of agglomerations or aggregations. This results in changes in the rheological behaviors in wet ultrafine grinding operations. Besides, there was no effort to control the temperature of a ground slurry for each grinding test except for keeping cooling water circulating continuously at 0.5 L/s. The slurry temperature evidently varied during grinding due to the release of lattice energy of ground particles from commination and the heat energy from the friction between milling media and the ground particles in the slurry.

Previous studies have shown that an increase in slurry temperature reduces viscosities of slurries (Yang et al., 2001; He et al., 2006b). To take into account the effect of temperature, all rheological measurements were carried out at a required temperature corresponding to that of a discharge slurry.

Figure 8 shows the evolution of rheological behaviors of limestone slurries with grinding at 70% and 75% (by weight) solids concentrations in the presence of 0.2% (by weight) Dispersant S40. As can be seen, the initial feed slurries ex-
habit dilatant flows, suggesting the particles in the slurries not subjected to interparticle attractive forces but free to move as individuals. Initially, the viscosities of the ground slurries at shear rates studied do not increase but decrease with increasing pass number (i.e., grinding time or specific energy consumption) and the fineness of the ground particles until the pass number is up to 2.

A similar phenomenon was observed by previous work (Tangsathitkulchai and Austin, 1989). A further increase in pass number leads to the viscosities of the ground slurries revert-

Figure 8 — Variation of the rheological behaviors of limestone slurry at two different solids concentrations in the presence of 0.2% (by weight) Dispersant S40 at 74% (by volume) bead load with grinding: (a) and (b) apparent viscosity and (c) extrapolated Casson yield stress (by Bohlin viscometer).

Figure 8

![Variation of the rheological behaviors of limestone slurry](image)

- **a** 70 wt.% solids concentration
- **b** 75 wt.% solids concentration
- **c** Extrapolated Casson yield stress (Pa)

Shear rate (1/sec)

Apparent viscosity (Pa•sec)

0 500 1000 1500

0 0.1 0.2 0.3

0 5 10 15

At pass numbers of up to 4 or more for 70% (by weight) solids concentration or pass numbers of 3 or more for 75% (by weight) solids concentration, the slurries are transformed into a pseudoplastic flow with an evident Casson yield stress. This indicates that increasing grinding time with increasingly finer particle sizes, there are strong interparticle interactions to hold the particles together in the slurry.

The grinding operation for 70% (by weight) solids concentration with 0.2% (by weight) Dispersant S40 automatically ceases at Pass 5 but stops at Pass 4 for 75% (by weight) solids concentration with 0.2% (by weight) Dispersant S40 by a safety control device due to high pressure inside the mill chamber. A pseudoplastic slurry with a high extrapolated Casson yield stress could be the reason for this, because the more viscous the slurry, the more power is needed to make the slurry flow when the slurry is circulated through the mill by a pump. This increases the pressure in the mill up to the limit.

The point where a grinding operation automatically terminates by a safety control device due to high pressure inside the mill chamber resulting from a pseudoplastic slurry with a high Casson yield stress is defined as a reference terminal, where the final discharge product is called an FP product.

The FP product has a quite similar specific surface area and particle size distribution for a given solids concentration at a specific addition level of Dispersant S40 (Table 2 and Fig. 9). For instance, 70% (by weight) solids concentration with 0.2% (by weight) Dispersant S40 can be ground to an FP product with a specific surface area of 9.979 ± 0.043 m²/g and a quite similar particle size distribution with a median size of 1.167 ± 0.05 μm.

Similar phenomena were observed for 65% and 75% (by weight) solids concentrations. Figure 10 shows the effects of solids concentration on the specific surface area and particle size distribution of an FP product in the presence of 0.2% (by weight) Dispersant S40. Obviously, the specific surface area of an FP product is inversely proportional to solids concentration with a specific addition of Dispersant S40 (Fig. 10(a)), whereas the particle size distribution moves parallel towards a range of smaller particle size with decreasing solids concentration (Fig. 10(b)).

For a given suspension system, it is possible to maintain
Table 2 — Characteristic parameter values of an FP product obtained for 70% (by weight) of solids concentration with 0.2% and 0.6% (by weight) Dispersant S40 under other different grinding conditions.

<table>
<thead>
<tr>
<th>Addition of S40</th>
<th>Media beads number</th>
<th>FP product loads vol. %</th>
<th>Pass number</th>
<th>Specific energy consumption, kWh/t</th>
<th>Median size, μm</th>
<th>Specific surface area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2% by weight</td>
<td>1</td>
<td>65</td>
<td>9</td>
<td>215</td>
<td>1.169</td>
<td>9.975</td>
</tr>
<tr>
<td>2</td>
<td>74</td>
<td>5</td>
<td></td>
<td>180</td>
<td>1.108</td>
<td>10.04</td>
</tr>
<tr>
<td>3</td>
<td>77</td>
<td>4</td>
<td></td>
<td>174</td>
<td>1.159</td>
<td>9.959</td>
</tr>
<tr>
<td>4</td>
<td>83</td>
<td>3</td>
<td></td>
<td>163</td>
<td>1.231</td>
<td>9.94</td>
</tr>
<tr>
<td>Mean: 1.167±0.05</td>
<td></td>
<td></td>
<td></td>
<td>9.979±0.043</td>
<td></td>
<td>9.979±0.043</td>
</tr>
<tr>
<td>0.6% by weight</td>
<td>5</td>
<td>74</td>
<td>12</td>
<td>432.66</td>
<td>0.584</td>
<td>17.911</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>10</td>
<td></td>
<td>405.91</td>
<td>0.557</td>
<td>18.147</td>
</tr>
<tr>
<td>7</td>
<td>83</td>
<td>8</td>
<td></td>
<td>372.39</td>
<td>0.52</td>
<td>18.113</td>
</tr>
<tr>
<td>Mean: 0.554±0.032</td>
<td></td>
<td></td>
<td></td>
<td>18.057±0.128</td>
<td></td>
<td>18.057±0.128</td>
</tr>
</tbody>
</table>

Figure 10 — Effect of solids concentration on the specific surface area and particle size distribution of an FP product in the presence of 0.2% (by weight) Dispersant S40: (a) specific surface area and (b) particle size distribution.

Figure 11 — Variation of the slurry rheology of ground limestone slurry at 70% (by weight) of solids concentration with various dosages of Dispersant S40 with grinding (by Bohlin viscometer).

A certain rheological behavior when the amount of water is proportional to the specific surface area. A high solids concentration means a small amount of water per unit volume, which is indispensable to flow and thus results in a small specific surface area of a product.

For a certain solids concentration at different addition levels of Dispersant S40, the evolution of rheological behaviors of limestone slurries with grinding appears similar to that for different solids concentrations with a given addition of Dispersant S40, as shown in Fig. 11. At the additive dosage of Dispersant S40 ≤ 0.1% (by weight), the apparent viscosity of a ground slurry at a given shear rate increases with pass number, whereas the apparent viscosity first decreases and then increases at the addition dosage of Dispersant S40 ≥ 0.2% (by weight). For 70% (by weight) solids concentration with whatever additive dosages of Dispersant S40, the grinding operation automatically stop when a discharge slurry from the mill displays a
pseudoplastic flow with an evident extrapolated Casson yield stress, where the discharged slurry is defined as an FP product. The slurry with 70% (by weight) solids concentration cannot smoothly be ground without Dispersant S40 (two passes with 0.1% by weight, four passes with 0.2% by weight and 12 passes with 0.6% by weight). It is interesting to observe that the specific surface area and median size of an FP product are correlated to the addition of Dispersant S40 for a given solids concentration (Table 2).

Figure 12 shows the effect of the additive dosage of Dispersant S40 on the specific surface area and particle size distribution of an FP product. Evidently, the specific surface area of an FP product at a certain solids concentration is directly proportional to the additive amount of Dispersant S40 (Fig. 12 a). The particle size distribution moves parallel towards a range of smaller particle size with increasing the additive amount of Dispersant S40 when the additive amount of the dispersant is up to 0.2% (by weight). At the additive amount above 0.4% (by weight), the finer particles (<0.4 μm) increase more evidently, and the increase in specific surface area is mainly dependent on the created finer particles.

In addition, the slurry also exhibits a time-dependent rheological behavior when a discharge slurry from the mill displays a pseudoplastic flow with an evident extrapolated Casson yield stress. Figures 13 and 14 show the rheological behaviors of a ground slurry with characteristic sizes and specific surface area for 70% (by weight) solids concentration with 0.2% and 0.6% (by weight) Dispersant S40, respectively. It is seen that the appearance of thixotropy is related to the particle size and specific surface area of ground particles as well as the additive amount of Dispersant S40. For instance, when the slurry of 70% (by weight) solids concentration with 0.2% (by weight) Dispersant S40 is ground to a product with a median size (x50) of 1.331 μm and a specific surface area of 10.04 m²/g, the “up” and “down” rheological curves do not coincide (see Fig. 13 b). This hysteresis loop is caused by a decrease in viscosity with increasing time of shearing, which is defined as the thixotropic flowability. This is typical character of agglomerated or flocculated suspensions (Hackly, 1998; Papo et al., 2002). This demonstrates that the attractive interparticle forces are dominant due to the existence of a large amount of fine particles (<1 μm), which attract each other by van der Waals attractive forces to form aggregates or flocs. At a higher addition level of Dispersant S40, a ground slurry product appearing thixotropic has a smaller particle size and a larger specific surface area (Fig. 14 b). For different solids concentrations with a certain additive amount of Dispersant S40, similar phenomena were observed. The higher the solids concentration, the larger the particle size for a thixotropic slurry is and the smaller the specific surface area is.
Comparison of rheological results obtained by different viscometers. By comparison of rheological results obtained using a Bohlin rotational viscometer and a TA Instruments CSL® 500 rheometer, it is found that these two instruments give consistent results for time-independent slurries (Figs. 13 (a) and 14 (a)). For time-dependent slurries, there exist differences in rheological results obtained from the two instruments in the range of shear rates studied, but the flowability from the two instruments follows the same tendency (Figs. 13 (b) and 14 (b)). This is because the time-dependent rheological properties are generally irreversible. Different configurations of rheometers, or shear intensities or shear time lead to various deformations or damages of flocs for time-dependent suspensions, giving distinct rheological results. The two instruments can produce consistent results with respect to flow type for a given slurry, but the accurate rheological characterization of time-dependent fluids is dependent upon the viscometer or rheometer used and operation conditions.

Conclusions

The rheological behavior of limestone slurries was transformed from a weakly dilatant or Newtonian characteristic to an evidently pseudoplastic one with a Casson yield stress when the solids concentration was increased from 60% to 78.5% by weight (35.7% to 57.49% by volume). At solids concentration above 70% by weight (46.36% by volume), the apparent viscosity at a given shear rate and the extrapolated Casson yield stress rather sharply increased with increasing solids concentration, respectively. The use of a sodium polycarboxylate with a given molecular weight (i.e., 5,500), called Dispersant S40, improved the slurry flowability by decreasing viscosity and eliminating Casson yield stress. Thus, Dispersant S40 was suitable to be used as a grinding aid for wet ultrafine grinding of limestone.

The rheological behaviors of ground limestone slurries varied with grinding from a starting dilatant flowability to a resulting pseudoplastic one with an evident Casson yield stress in combination with a thixotropic character. The appearance of pseudoplastic flowability combined with thixotropy was related to solids concentration and the additive amount of Dispersant S40. The less the dispersant amount was for a given solids concentration, the earlier a pseudoplastic flowability accompanying a thixotropic character appeared; the lower the solids concentration with a specific addition of the dispersant, the later a pseudoplastic fluid with a thixotropic character appeared to be. Regardless of whatever grinding conditions, the grinding operation automatically ceased when a discharge slurry from the mill displayed a pseudoplastic flow with an evident extrapolated Casson yield stress, where the discharged slurry was defined as an FP product. The specific surface area and particle size distribution of an FP product were correlated to solids concentration and the additive level of Dispersant S40. The specific surface area of an FP product was inversely and directly proportional to solids concentration and the additive amount of Dispersant S40, respectively, whereas the particle size distribution of an FP product moved parallel towards a range of smaller particle size with decreasing solids concentration or increasing the additive amount of Dispersant S40. In addition, the accurate rheological characterization of time-dependent fluids was dependent upon the instruments used and operation conditions.

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References


