A Review of Breakage Behavior in Fine Grinding by Stirred-Media Milling

R. Hogg
Department of Energy and Geo-Environmental Engineering
The Pennsylvania State University*

H. Cho
Department of Civil, Urban & Geosystems Engineering
Seoul National University**

Abstract

The use of stirred-media mills for grinding into the micron and submicron size range is reviewed. Mill performance and energy efficiency are discussed in the context of mill mechanics as related to mill power, material transport and flow, and particle breakage mechanisms. The development and adaptation of general size-mass balance models to fine grinding in stirred-media mills is evaluated. Specific problems in the application of the process models and, especially, in parameter estimation are described. Comparison of breakage rates and breakage distributions with those observed in coarser grinding systems reveals several similarities but some differences, particularly with respect to size-dependence. It is shown that the approach to a grinding limit can have significant effects on grinding rates and product size distributions.

Introduction

The purpose of the grinding process is to reduce particle size. In doing so, we are concerned about how to meet the objective with the minimum energy input. Obviously, a finer product requires more energy input, but the same energy input does not necessarily produce the same degree of size reduction. Grinding processes operate by applying stress to individual particles so as to induce breakage. This requires that particles first be appropriately located to receive the stress. Particle placement is relatively simple at large sizes—in jaw crushing for example—where individuals can be directly placed between the jaws. In such systems, the placement and stress application functions can be separated, with placement controlled by the feeding mechanism and stressing supplied by the motion of the jaws. This ideal approach is, unfortunately, quite impractical in fine grinding and the energy input to the mill is required to provide both functions. In the case of media milling, energy is supplied to the mill so as to agitate the media. Collisions between the media elements provide the stressing action while random motion of media and particles is relied upon to effect proper particle placement. To a considerable extent, these two functions present conflicting requirements, especially with respect to media size. Increasing media size increases the breakage stresses available per collision but decreases the number of media elements in the mill, thereby reducing the collision frequency. The best operating conditions generally involve a compromise between these requirements. An important consequence is that the process is highly inefficient in terms of energy utilization.

There are many variables that determine the ultimate outcome of the grinding process. These include material properties such as strength, hardness, brittleness, etc. The other variables are mostly related to the conditions under which particles are subjected to breakage. In the case of media milling, these include the particle loading, the feed particle size, the rotational speed, the media size, the media loading, the solids concentration, etc. In principle, operating the mill using the proper selection of these variables should ensure the production of a desired product with minimum expenditure at the desired capacity.

Energy Efficiency

As noted above, grinding processes in general are well known for their energy inefficiency. In most grind-
stresses on the particles; compression, impact, or shear. However, the fraction of the energy input actually used for breakage is extremely low. In tumbling media mills, this percentage is said to be around 1%, with most of energy being wasted as heat. Nevertheless, the total energy input to grinding mills can often be related to the fineness of grinding. In the classical work on grinding, the fineness of the ground product, represented by some characteristic size x, has been correlated to the specific energy input E through a relationship of the form:

$$E = ax^b$$  \( (1) \)

where a and b are constants. Equation 1 is generally known as the Charles' Energy-Size relationship (1). In several studies on stirred ball milling [2,3,4], it was reported that the fineness of the product remains the same for a given energy input, regardless of the mill size and the operating conditions. If this is true, scale up of a stirred ball mill should be quite straightforward. However, in recent studies, this appears not to be the case and the energy efficiency is found to depend upon various operating conditions such as media size, media density, media load, slurry density, stirrer speed, and feed rate. Gao and Forssberg [5,6] investigated the effect of the above operating parameters on energy efficiency in stirred media milling. It was found that the energy utilization increases with increasing media load up to 83% of the available volume. Higher speeds naturally pulled more power and thus a higher degree of grinding could be achieved in a shorter time. But in the context of energy efficiency, lower speeds were found to be more energy efficient. In studies using media of varying density (2.5, 3.7, and 5.4 g/cm³), the efficiency was found to increase for densities up to 3.7 g/cm, but then decreased at 5.4 g/cm³, probably because the density was too high for the media to be fully stirred up. Also, it was found that the energy utilization decreased at a higher slurry density. The media size was found to be optimum at 0.8-1.0 mm for the grinding the particles smaller than 70 μm. Smaller media gave bimodal size distributions with coarser particles remaining unbroken. With the larger media, the particles were broken efficiently over the whole size range, giving a steeper size distribution. Overall, the authors suggested that stirred ball mills were best operated at high media loading (over 80%) using sufficiently large, but not too dense media and high rotational speed to obtain a high throughput. However, in a subsequent study [6], it was claimed that the energy efficiency was not affected significantly by the rotational speed and media load, but was most affected by the media size.

Zheng et al. [8] studied the energy efficiency of stirred media mills with pin-type stirrers in the grinding of limestone with glass beads. It was found that as the impeller speed was increased, the product surface area and energy input increased, but energy efficiency declined. The best energy efficiency and product fineness were obtained when the particles just filled the interstices between the media. As seen frequently in conventional tumbling ball mills, better grinding is achieved using smaller media size as long as they are large enough to cause particle fracture. The maximum rates of grinding were achieved when the media to feed size ratio was 12:1. However, in contrast to observations for ball milling, higher density media resulted in much higher energy consumption but did not increase the milling rate significantly. Thus, the energy efficiency was greatly reduced. Overall, the specific area increase was found to correlate with energy input through a power equation:

$$A_s = 9.27E^{0.54}$$  \( (2) \)

which implies that the energy efficiency was less for the higher energy input.

It is clear that there are numerous apparent inconsistencies in the literature on the energy-efficiency of stirred-media milling. For the most part, these arise from interactions among many material, equipment, and operating variables. It is generally agreed, however, that there is a clear link between energy input and product fineness. Also it is known that operating conditions play an important role. Powder and media loading and the media to particle size ratio seem to be primary factors in determining energy efficiency.

**Mill Mechanics**

**Mill Power**

The studies described above suggest that the energy input alone can not correctly predict mill performance, i.e. size reduction. Nonetheless, the power requirement for stirred ball milling is important and has been the subject of many investigations, especially aimed at scale-up. The standard treatment for the power P necessary to drive a stirrer in a Newtonian liquid operating in the turbulent regime starts with (9)

$$P = N_s N_d^2 D^5 \rho$$  \( (3) \)

where N is the rotational speed, D is the diameter of the stirrer, and \( \rho \) is the density of the liquid. \( N_s \) is the power number which depends on flow conditions and
In stirred ball milling, the mill contains the solids being ground, the liquid (in wet grinding) and, more importantly, the grinding media. It is extremely unlikely, therefore, that the behavior would be Newtonian. Furthermore, the density in Equation 3 is no longer clearly defined. Since there is a considerable difference in the densities of the liquid and the media, there is a tendency for segregation of the media in the mill. At a low rotational speed, the media tend to settle, leading to an inhomogeneous distribution of media. On the other hand, at higher rotational speeds, a vortex is formed and the media are concentrated at the wall due to centrifugal forces. Therefore, the dependency of the power draw on the rotational speed can vary significantly. Also, the movement of the media is highly dependent upon the media loading. It might be expected that the movement of the media would be more rapid at high loading, since the higher portion of media could be in direct contact with stirrers and among themselves. Therefore, it is very difficult to analyze the mill power theoretically, and it is often necessary to resort to empirical equations based on experiment. The problem with empirical equations is that they may be valid only for the particular design of the rotor. The values of the parameters, for the range of rotational speeds of interest, may depend on media loading, size, and density and slurry concentration, density, and viscosity.

Herbst and Sepulveda [2] measured power consumption for a pin-type stirred ball mill of 1 to 5 gallons, operated at 100–500 rpm, with a media size of 1/8" to 1/4" and density of 2.74 to 8 g/cm³. Multiple regression of the data points resulted in

\[ P = 2.55 \times 10^{-5} N^{1.37} V^{1.75} d_b^{-0.48} \rho^{-1.09} \]  

where \( P \) is shaft power (kw), \( N \) is rotational speed (rpm), \( V \) is mill volume (gallons), \( d_b \) is diameter of media (in.), and \( \rho \) is media density (g/cm³). A similar equation was given by Gao et al. [8], based on experiments using a 6-liter, horizontal, disk-type stirred ball mill using operating conditions of media density: 2.5–5.4 g/cm³, slurry density: 65–75 wt.%, and stirrer speed: 805–2253 rpm. A dispersant was used at a level of 0.5–1.5% of the solids. Their equation for power consumption, obtained by regression, was

\[ P = 1.95 \times 10^{-5} N^{1.20} \rho_s^{-0.90} \rho_b^{0.16} c_d^{-0.096} \]  

where \( \rho_s \) is slurry density (weight %), \( \rho_b \) is media density (g/cm³), and \( c_d \) is dispersant concentration (%).

Zeng et al. [8,10] developed a method for predicting the power consumption of stirred ball milling in terms of power number and Reynolds Number. The correlation between the power number and Reynolds number was determined for various conditions. This relationship was then used to estimate the effective viscosity of the mill contents. The suggested equation for the power consumption was

\[ P = C \mu N^{2} D^{3} \]  

where \( C \) is an impeller geometry constant and \( \mu \) is the effective viscosity of the mill contents.

It should be recognized that none of these relationships take explicit account of the effects of charge segregation, etc. More realistic models will require a more detailed, quantitative understanding of the complex motion of the mill contents.

**Transport and Flow**

The motion of the charge, media plus powder plus liquid, in a stirred-media mill is complex and depends on mill geometry, rotational speed and the characteristics of the charge (solids/media content, density, fluid viscosity, etc.). Empirical and semi-theoretical investigations have been reported in the literature and are said to be in general agreement [12]. A detailed numerical analysis of laminar flow in a mill vessel of typical geometry with disk-type agitators indicates a relatively uniform flow field except close to the disk surfaces and the grinding chamber walls where there are high velocity gradients and, correspondingly, high energy dissipation [13]. Blecher and Schwedes [13] evaluated the motion of a single grinding bead entrained in the fluid, but the extension to a concentrated media bed has not been reported. While such studies provide some insight into the mechanics of media milling, so far they are of limited value in the analysis and prediction of mill performance. To our knowledge, discrete-element analysis, analogous to recent studies on tumbling and centrifugal ball mills [14,15], has not been attempted for stirred-media mills.

**Particle Breakage**

Breakage of particles occurs as a result of applied stress, which originates from energy input to the grinding device. However, as shown above, the effectiveness of the breakage action does not depend on the level of energy input alone. The nature of the energy input also plays an important role. Kwade et al. [16] have introduced the concept of energy intensity as a critical factor in determining whether or not stress application actually leads to breakage. At low stress intensities, several stressing events may be required to cause fracture. As the stress intensity increases, a
Critical value is reached above which further increase does not lead to additional breakage. In any grinding process, particles are exposed to a distribution of stress intensities. The effectiveness of the process depends on the fraction of stressing events for which the stress intensity exceeds this critical level. On the other hand, excessive stress intensities, well above the critical value, lead to reduced grinding efficiency, i.e., increased specific energy.

Breakage rates are determined by the stress frequency, modified by the stress intensity, i.e., by the frequency of adequate stress applications. Relationships between the stress intensity and frequency and the operating conditions in stirred-media milling have been proposed [13,17]. The stress frequency $f_s$ clearly depends on mill geometry and agitator speed and a general relationship can be expected with the form:

$$f_s \propto N \left( \frac{d_4}{d_8} \right)^2$$

(6)

where $N$ is the rotational speed and $d_4$ and $d_8$ are the respective diameters of the grinding chamber and the grinding beads. The stress intensity $I_s$ can be expected to depend on agitation speed, grinding media size and density, and on the elasticity of the media and the material being ground. The latter determines the effectiveness of energy transfer between media and particles. The following specific relationship has been proposed [12,16]:

$$I_s = d_8^3 \rho_b v_t^2 \left( 1 + \frac{Y_1}{Y_b} \right)^{-1}$$

(7)

where $\rho_b$ is the grinding bead density, $v_t$ is the agitator tip speed, and $Y_1$ and $Y_b$ are the respective elastic moduli for the solid and the grinding media.

The specific grinding energy depends on the product of the stress frequency and the stress intensity, both of which vary with grinding conditions. Becker et al. [17] showed that, for a fixed energy input, there is an optimum stress intensity that provides the most size reduction. By varying the energy input using different combinations of speed, media size, and media density, they demonstrated that the optimum stress intensity decreased with increased energy input. The optimum intensity presumably reflects the critical intensity for fracture discussed above. Equation 7 indicates how it varies with media size. It would be of particular interest to establish its dependence on the size of the particles being broken. Unfortunately, the experimental procedure used in this work provides only very limited information on particle size effects, since many different sizes are being broken simultaneously.

### Process Modeling

#### Size-Mass Balance Models

During the last three decades, mathematical modeling of grinding processes has been developed to the extent that the performance of grinding circuits can often be predicted with a reasonably high degree of precision. The models use two basic model parameters: the breakage rate function and the breakage distribution function. The breakage rate reflects the rates at which different kinds (sizes etc.) of particles are broken. The breakage distribution describes the size distribution of the fragments produced by breakage. If the breakage rates and breakage distributions are known, the product size distributions can be predicted by means of mass balances. The generalized size-mass balance model can be expressed by

$$\frac{dm_i}{dt} = -S_i m_i + \Sigma b_{ij} S_j m_j$$

(8)

where $m_i$ is the mass of material in size class $i$, $S_i$ and $b_{ij}$ are, respectively, the breakage rate and breakage distribution for size $i$. Unfortunately, the determination of the breakage parameters $S_i$ and $b_{ij}$ is difficult, especially for the subsieve size range, which has somewhat limited the application of this approach in studies of stirred media milling.

Experimentally, the rate and distribution functions are usually determined by the so-called one-size-fraction method [18]. In this method, a narrowly sized fraction (e.g., one sieve size fraction) is prepared and subjected to grinding for various times. The fraction remaining unbroken in the starting size is used to determine the breakage rate, and the size distribution obtained for very short grinding times is used to estimate the breakage distribution. The variations in the breakage parameters with particle size are evaluated using different feed sizes. It is the difficulty of preparing precise, narrow size fractions in the sub-sieve size range that seriously limits direct estimation of the breakage parameters in ultrafine grinding.

In many cases, the specific rate of breakage for any size is found to be independent of time and the extent of grinding, i.e., the process follows first-order kinetics. There are, however, many instances of rates that either increase or decrease with time. Acceleration of breakage has been observed in wet grinding tests in tumbling ball mills and is probably due to changes in the environment inside the mill. Deceleration of the breakage rate is often encountered in prolonged grinding and appears to result from the accumulation of fine particles, which produce some...
kind of cushioning effect.

Generally, the specific rate of breakage $S$ increases with size, but decreases as the particles become too large to be broken efficiently by the grinding media. A typical plot of $S$ values against the particle size is shown in Figure 1. This result is entirely consistent with the stress-efficiency/stress-frequency concept discussed by Kwade [12]. The maximum is probably determined by the optimum stress intensity for particle breakage. A more detailed study of the relationship between media size and particle size and critical stress intensity would be invaluable in the optimization of grinding conditions.

The relationship for the particle size range below the maximum can be fitted to a simple power function (18)

$$S_i = S_0 \left( \frac{x_i}{x_0} \right)^\alpha$$

where $S_i$ is the specific rate of breakage for particles of size $x_i$, $x_0$ is a standard particle size, $S_0$ is the specific rate of breakage at size $x_0$, and $\alpha$ is a constant.

The breakage distribution describes the fragments produced by each breakage event. It is somewhat more difficult to determine than the breakage rate because it involves measurement of the fragment size distribution before any rebreakage occurs. The form of the breakage distribution is strongly affected by the breakage mechanism. It is generally considered that there are three breakage mechanisms which are important in media milling: fracture, chipping, and abrasion [19]. Fracture refers to the complete disintegration of a particle, chipping refers to removal of fragments from edges and corners, while abrasion involves the uniform removal of surface material due to wear. Fracture leads to disappearance of the original particle, which is replaced by a complete suite of smaller fragments. Chipping and abrasion both lead to the appearance of fine particles along with the original particle, which slowly decreases in size. The chipping and abrasion mechanisms are sometimes lumped together as attrition. The fragment size distributions resulting from each of these mechanisms have a distinct, characteristic appearance as shown in Figure 2. In any given grinding device, all three mechanisms may take place simultaneously, but the shape of the product size distribution depends on which mechanism dominates. Figure 3 shows a typical breakage distribution observed in a tumbling ball mill operated

![Fig. 1](image1.png) Illustration of the typical variation of the specific rate of breakage with particle size.

![Fig. 2](image2.png) Size distribution of fragments produced by different breakage mechanisms (schematic). Note that the fragments produced by chipping or abrasion include the residual core of the parent particle while, in the case of fracture, the parent disappears completely.

![Fig. 3](image3.png) A typical breakage distribution.
where $B_{ij}$ is the cumulative breakage distribution, i.e. the fraction of the fragments produced by breaking particles of size $x_i$ that are smaller than size $x_j$, and $\phi$, $\alpha$, and $\gamma$ are constants which may vary with the size ($x_i$) being broken.

In several studies, the above grinding model has been shown to be applicable to stirred ball milling [2, 20-23]. Generally, the trends in the breakage parameters were found to be similar to those for conventional, tumbling ball milling. Mankosa et al. [22, 24] determined breakage rates for coals in the size range of 20×140 US mesh ground in a stirred ball mill. The grinding kinetics showed first-order behavior and for a given ball size, the breakage rates followed the trend shown in Figure 1. The maximum breakage rates were observed for particle sizes at about 1/20 of the ball size. The power draw was found to be higher for the larger ball sizes but, for a given energy input, the smaller ball sizes produced finer product size distributions. This indicates that the breakage distribution might be flatter for the smaller ball sizes. In a subsequent study [24], the effects of operating variables were analyzed. It was reported that the lower rotational speeds were more energy efficient. It was concluded that, at lower speeds, the balls move in a somewhat gentle manner, producing a larger effective volume for comminution. For a given specific energy input, the product size distributions were found to be essentially the same over the range of 20 to 50 wt.% solids. However, at 60% solids, the product size distribution became significantly broader than those obtained at the lower solids concentrations. This was attributed to rheological effects. When the slurry becomes too thick, the movement of media does not give proper impact on the particles. Therefore, a good portion of the large pieces still remain unbroken in the ground product, leading to a wider size distribution. It appears that the dominant breakage mechanism changes from fracture to more of an attrition type of breakage as the pulp density increases. Although not directly shown in this study, it also means that the breakage distribution may depend on the pulp density. In tumbling ball milling, grinding of higher pulp density slurries typically produces flatter breakage distributions. This effect often necessitates the use of dispersants when the slurry density and viscosity become too high or the mill contents become too fine. In their study, Mankosa et al.[24] found that the addition of a dispersant significantly improved the grinding efficiency.

Schröder et al. [21] analyzed the breakage parameters for the grinding of a 16×25 mesh coal sample in a stirred ball mill. The breakage distribution was found to have the typical form shown in Figure 3. However, it was considerably broader (smaller $\gamma$) than those generally observed for grinding in ball mills. This suggests that stirred ball milling produces more fines, probably because the attrition type of breakage mechanisms are more dominant in stirred ball milling. The breakage rates, which were obtained by non-linear regression, also showed a form similar to that of Figure 1. However, the slope of the curve was smaller (smaller $\alpha$), i.e. the dependence of the breakage rate on particle size was much reduced. Overall, the experimental results, which agreed well with the kinetics model predictions, showed considerably broader product size distributions than those commonly obtained from tumbling ball mills.

Sadler et al. [3] investigated the breakage rate of 40×50 mesh dolomite ground in an attrition mill with 16×30 mesh Ottawa sand as media. The mill used had a cage-like rotor and stator type of agitation system. The breakage rate exhibited non-first order behavior, showing a decrease in rate after a short period. The initial, rapid breakage was explained by rounding of sharp edges of the particles. However, since the particle size and the media size were not much different, it is quite likely that the particles were simply too large to be crushed in the mill. The breakage rate in the later period appeared to be time independent, and to increase linearly with the cube of the agitation speed. Since the power consumption also increased with the cube of the agitation speed, it was concluded that the grinding efficiency was independent of the power input.

In many respects, the findings given in these studies are analogous to the trends frequently observed in conventional, tumbling ball milling. However, the majority of the results were based on the sieve size range and it does not necessarily follow that the same trends should continue into the sub-sieve and the micron size ranges. As noted previously, there are difficulties in directly determining the grinding kinetics model parameters for particles in the sub-sieve size range. The size-mass balance model generally used for data analysis is itself based on subdivision of the particles into narrow size intervals and determining the changes in the mass fraction in each fraction. In the sub-sieve size range, particles cannot easily be
subdivided into narrow size fractions, which makes it difficult to determine the breakage parameters experimentally. In addition, application of the model requires a consistent definition of size (usually sieve size). Fine grinding results that include size distributions obtained by combining sieve and sub-sieve (e.g., light scattering) data involve more than one size definition so that the applicability of the grinding model itself becomes questionable.

**Breakage Parameters in Fine, Stirred-Media Milling**

It is always possible to make estimates by extrapolating coarse grinding results into the sub-sieve size range. When the amount of the particles in the sub-sieve size range is small, this extrapolation may not produce a noticeable error in the predicted results. However, as grinding proceeds, the particles in the mill will eventually all fall in the sub-sieve size range and the predictions made by extrapolated breakage parameters may deviate substantially from the experimental results. In coarse grinding, the breakage parameters are found to be essentially independent of the extent of grinding and of the environment in the mill. There is considerable evidence, however, that this may not be true for very fine grinding; breakage parameters may change as grinding proceeds and environmental effects, due to changes in slurry rheology, become significant. Alternatively, the breakage characteristics of the particles themselves may be different in the sub-sieve range.

Recently, the authors have made considerable effort to establish reliable procedures for characterizing the model parameters in ultrafine grinding systems [25, 26]. Fine quartz (270 x 400 US mesh) was ground for up to 64 hours at rotational speeds ranging from 2000 to 6000 rpm in a 0.6 liter laboratory mill using 0.8–1.0 mm zirconia/silica beads as media. Examples of the product size distributions are given in Figure 4. Breakage rates for the feed material were obtained by direct measurement of disappearance rates. The corresponding breakage distributions were estimated from short-time product size distributions obtained by combining sieving data (at 400 mesh) with laser scattering/diffraction using an appropriate instrument-to-instrument size conversion procedure [27, 28].

The disappearance plots for the 270 x 400 mesh quartz feed at various rotational speeds indicated that breakage follows first-order kinetics initially, but the rates were found to increase in each case after about 2 minutes of grinding. As expected, breakage rates obtained from the short-time (<2 min) results were found to increase with rotational speed. The accelerated breakage at longer times was attributed to changes in the grinding environment inside the mill. Non-first order behavior of this kind is often observed in conventional ball milling and is generally believed to be caused by the rheological properties of the slurry, which change as the amount of fines present increases. Tangsathitkulchai and Austin [29] reported that increases in the breakage rates often occur when the slurry is rather dilute. On the other hand, breakage rates tend to decrease when the slurry becomes too thick. It appears that the media movement is hindered when the slurry becomes too viscous, suggesting that the breakage rate could decrease as the mill contents become very fine during prolonged grinding. However, this effect could not be observed directly in these tests because the original 270 x 400 mesh fraction disappears completely after a very short grinding time.

The product size distributions obtained for grinding times up to 64 hours at 2000 rpm were found to become progressively narrower as grinding proceeds, with a consistent steepening of the curves at sizes below about 1 μm. This effect is not generally observed in coarse grinding where the product size distributions typically shift to finer sizes in a parallel fashion. Measured surface areas, by gas adsorption and light scattering (Microtrac), were found to correlate well for grinding times up to 8 hours, which suggests that the break in the size distribution is real and is not simply an artifact resulting from the failure of the light scattering system to detect ultra-fine particles [25].

![Fig. 4 Product size distributions from stirred-media milling of 270 x 400 US mesh quartz.](image-url)
The form of the size distribution of the ground products is strongly influenced by the fragmentation process occurring at each fracture event. In coarse grinding, the breakage distributions are usually not influenced by the presence of other particles. Also, the size distributions of the fragments can often be normalized with respect to the size of the particle being broken. Consequently, the shape of the size distribution tends to be conserved even after repeated breakage events, resulting in a self-similar or self-preserving size distribution among the comminuted products [30]. However, for the data shown in Figure 4, the shape of the size distribution is not self-preserving but becomes progressively narrower, which suggests that the breakage distributions are not normalizable but change as a function of the size of the parent particles.

Strazisar and Runovc [31] reported that the product size distributions from grinding into the submicron size range could be represented by the log-normal size distribution and also that the distribution variance decreased for longer grinding times. This may be a consequence of the approach to a “grind limit”, a limiting size below which particles cannot be broken mechanically, nor can they be produced by breakage of coarser material. As particles close to the grinding limit cease to grind, those particles still in the coarse range continue to break and the product size distribution becomes progressively narrower. Liu and Schöner [32] reported that the breakage distribution for particles undergoing bed compression could be described by a truncated log-normal distribution, i.e., one for which there is a maximum limit in particle size. For ultrafine grinding systems, extending into the submicron particle size, there is theoretical and experimental evidence of an approach to a minimum particle size [25, 33]. Thus, the breakage distribution should be bounded at both the upper and lower ends. Such a distribution can be represented by a double-truncated log-normal distribution. The latter can be represented using a transformed size variable \( \eta \) defined by:

\[
\eta = \frac{x - Y}{X - x} \tag{11}
\]

where \( x \) is particle size, \( Y \) is the minimum size (the grind limit), and \( X \) is the maximum size, i.e. that of the parent particle. The form of the distribution is further defined by the median value \( \eta_{\text{50}} \) and the standard deviation \( \sigma \) of the transformed variable.

The breakage distributions shown in Figure 5 were calculated for the 270×400 mesh feed material \((X=37 \, \mu m)\) based on several pairs of the product size distributions from Figure 4 using the so-called BII method [16]. It was found that these distributions could be approximated by the double-truncated log-normal function with \( \sigma = 1.75, \eta_{\text{50}}=1.0 \), and the lower limiting size \( Y \) arbitrarily set at 0.03\( \mu m \).

The progressive steepening of the product size distributions noted previously implies that the standard deviation of the breakage distributions should decrease with decreasing parent size \( X \). It was found, by trial and error, that the general form of the product size distributions shown in Figure 4 was consistent with the pattern of breakage distributions shown in Figure 5. Simulations based on these breakage distributions agreed well with experimental data for grinding times up to 1 hour. For longer times, the simulations appeared to overestimate the extent of grinding.

The approach to a “grind limit” implied by the truncated form of the breakage distribution suggests that breakage rates may also be reduced in the finer sizes. It was postulated that the overestimates noted above were a consequence of reduced breakage rates in the fine sizes corresponding to an increase in the exponent \( \alpha \) (Equation 9) in the submicron range. For the fine quartz particles, it was found that the data could be simulated using an exponent which increased from 1.0 in the coarse size range to 2.0 for the submicron material. This modified breakage rate is illustrated in Figure 6.

Reports of the specific effects of media size and density on the breakage parameters are somewhat scarce, largely due to the experimental difficulties involved in the direct measurement of breakage rates etc. at very fine sizes. In general, it appears that the trend is quite
similar to that observed in tumbling media mills, i.e. breakage rates for a given media size increase with particle size but reach a maximum above which the media are simply too small to provide sufficient impact energy to ensure breakage. Breakage distributions seem to be relatively insensitive to media size.

Based on such data as are available and on indirect evidence from the work of Kwade et al., [11, 15] and others [2, 6, 7, 22, 23, 34], it appears that the trade-off between stress intensity and stress frequency becomes especially critical at ultrafine sizes. Changing media size can lead to enhanced breakage in one range of sizes but simultaneously to reduced rates for slightly coarser material. Staged stirred-media milling using progressively finer media may be a useful option for improving efficiency in ultrafine grinding. The use of a distribution of media sizes, as is the common practice in tumbling ball mills, should also be evaluated.

Conclusions

Stirred-media milling is an effective means of grinding to very fine sizes. While the process is well established commercially, much remains to be learned regarding the fundamental principles involved and the role of equipment and operating variables on grinding performance. Process design remains largely a matter of trial and error. The energy efficiency of the process is recognized to be strongly dependent on operating conditions, but there is a good deal of inconsistency in the literature with respect to the relative importance and specific effects of different variables. There is general agreement that, as with most media milling systems, the highest efficiency is obtained when the powder loading is just sufficient to fill the interstices in the media charge. It is also clear that the media size to particle size ratio is a critical factor; the optimum ratio seems to lie between 10 and 20 to 1.

Understanding of mill mechanics is far from complete. Empirical and semi-empirical relationships for mill power requirements have been presented, but their ability to account for complex flow behavior etc., is questionable.

The concepts of stress intensity and stressing frequency are central to the appropriate design and operation of stirred-media mills and provide a useful way of addressing the question of media size to particle size ratio. While this approach has been shown to be consistent with general observations of product fineness etc., their relationship to breakage rates and breakage distributions has yet to be established.

The size – mass balance models have proved to be invaluable in the design and control of conventional (tumbling ball mill) grinding circuits. Several applications of these models to stirred-media milling have been reported, mostly for relatively coarse grinding. The results and the estimated model parameters are generally similar to those from tumbling mills. Due to problems with reliable parameter estimation, their application at fine (sub-sieve) sizes has been somewhat limited, but some general patterns are being established. The breakage rates and breakage distributions seem to follow the same trends with particle and media size as those observed for tumbling mills, but appear to be affected by the approach to an apparent grind limit at about 0.03–0.05 μm. Breakage rates, which normally decrease with decreasing particle size, do so more abruptly as the grind limit is approached, i.e., in the submicron size range. Breakage distributions are, by definition, bounded at the upper end by the size of the parent particle. The existence of a grind limit imposes a lower bound to the distribution as well, the result being distributions that are not normalizable with respect to the size of the parent but become progressively narrower as the parent size decreases.

Nomenclature

\[ a : \text{Constant in energy-size relationship} \]
\[ \text{[units depend on value of exponent, } a] \]
\[ A_0 : \text{Specific surface area} \]
\[ [\text{m}^2/\text{g}] \]
\[ b : \text{Exponent in energy-size relationship} \]
\[ [-] \]
\[ b_{ii} : \text{Incremental breakage distribution} \]
\[ [-] \]
\[ B_{ii} : \text{Cumulative breakage distribution} \]
\[ [-] \]
\[ c_d : \text{Dispersant concentration} \]
\[ [%]\]
### Table 1

| Symbol | Definition                                      | Unit               |
|--------|-------------------------------------------------|--------------------|
| $d_b$  | Impeller geometry constant                     | [m]                |
| $d_d$  | Grinding media diameter                        | [m]                |
| $D$    | Impeller diameter                              | [m]                |
| $E$    | Specific energy input                          | [kwh/T]            |
| $f_s$  | Stress frequency                               | [s$^{-1}$]         |
| $I_s$  | Stress intensity                               | [N/m$^2$]          |
| $m_i$  | Mass of material in size interval $i$          | [-]                |
| $N_p$  | Power number                                   | [-]                |
| $N$    | Rotational speed                                | [rpm]              |
| $P$    | Mill power                                     | [kw]               |
| $S_i$  | Specific rate of breakage for size class $i$   | [min$^{-1}$]       |
| $S_n$  | Specific rate of breakage for standard size $X_n$ | [min$^{-1}$]  |
| $v_t$  | Agitator tip speed                             | [m/s]              |
| $V$    | Mill volume                                    | [gal.]             |
| $x$    | Characteristic particle size                    | [$\mu$m]           |
| $x_i$  | Particle size in class $i$                     | [$\mu$m]           |
| $x_s$  | Standard particle size                         | [$\mu$m]           |
| $X$    | Size of parent particle                        | [$\mu$m]           |
| $Y$    | Minimum particle size (grind limit)            | [$\mu$m]           |
| $Y_b$  | Elastic modulus of grinding media              | [N/m$^2$]          |
| $Y_s$  | Elastic modulus of solid being ground          | [N/m$^2$]          |
| $\alpha$ | Exponent in relationship between specific rate of breakage and particle size | [-] |
| $\beta$ | Exponent in expression for breakage distribution | [-] |
| $\gamma$ | Exponent in expression for breakage distribution | [-] |
| $\eta$  | Transformed size variable                      | [-]                |
| $\mu$  | Viscosity                                      | [Pa.s]             |
| $\rho$  | Density of mill contents                        | [kg/m$^3$]         |
| $\rho_b$ | Density of grinding media                     | [kg/m$^3$]         |
| $\rho_s$ | Density of solid being ground                  | [kg/m$^3$]         |
| $\phi_j$ | Constant in expression for breakage distribution for size $j$ | [-] |

### References

1. Charles, R.J., “Energy-Size Reduction Relationships in Comminution,” Trans. AIME, 208, pp. 80-88 (1957).
2. Herbst, J.A. and Sepulveda, J.L., “Fundamentals of Fine and Ultrafine Grinding,” Proceedings, The International Powder and Bulk Solids Handling and Processing Conference, Chicago, III, pp. 452-470 (1978).
3. Sadler, L.Y., Stanley, D.A., and Brooks, D.R., “Attrition Mill Operating Parameters,” Powder Technol., 12, pp. 19-28 (1975).
4. Stehr, N. and Schwedes, J., “Investigation of the Grinding Behavior of a Stirred Ball Mill,” Ger. Chem. Eng., 6, pp. 337-343 (1983).
5. Gao, M.W. and Forssberg, E., “Increasing the Specific Surface Area of Dolomite by Stirred Ball Milling,” in Comminution-Theory and Practice Symposium, S.K. Kawatra (ed.), SME/AIME, Littleton, CO (1992).
6. Gao, M.W. and Forssberg, E., “A Study on the Effect of Parameters in Stirred Ball Milling,” Int. J. Miner. Process., 3, pp. 45-59 (1983).
7. Gao, M.W. and Forssberg, E., “Prediction of Product Size Distributions for a Stirred Ball Mill,” Powder Technol., 84, pp. 101-106 (1995).
8. Zheng, J. Harris, C.C. and Somasundaran, P., “A Study on Grinding and Energy Input in Stirred Media Mills,” SME AIME Annual Meeting, Denver, CO, March 1996.
9. Rushion, J.H., Costich, E.W. and Everett, H.J., “Chem. Eng. Progr., 46, pp. 405-409; 467-476 (1950).
10. Gao, M.W., Forssberg, E. and Weller, K.R. “Power Prediction for a Pilot Scale Stirred Ball Mill,” Int. J. Miner. Process., 44-45, pp. 641-652 (1996).
11. Zheng, J., Harris, C.C. and Somasundaran, P., “Power Consumption of Stirred Media Mills,” SME AIME Annual Meeting, Albuquerque, NM, Feb. 1994.
12. Kwaide, A., “Wet Commination in Stirred-Media Mills – Research and Its Practical Application,” Powder Technol., 105, pp. 14-20 (1999).
13. Blecher, L. and Schwedes, J., (1996) “Energy Distribution and Particle Trajectories in a Grinding Chamber of a Stirred Ball Mill,” Int. J. Miner. Process, 44-45, pp. 617-627 (1996).
14. Mishra, B.K. and Rajamani, R., “The Discrete Element Method for the Simulation of Ball Mills,” Appl. Math. Modeling, 16, pp. 598-604 (1992).
15. Inoue, T. and Oyaka, K., “Grinding Mechanism of Centrifugal Mills – A Simulation Study Based on the Discrete Element Method,” Int. J. Miner. Process, 44-45, pp. 425-435 (1996).
16. Kwaide, A., Blecher, L. and Schwedes, J., “Motion and Stress Intensity of Grinding Beads in a Stirred Media Mill. Part 2: Stress Intensity and Its Effects on Comminution,” Powder Technol., 86, pp. 69-79 (1996).
17. Becker, M., Kwaide, A. and Schwedes, J., “Influence of the Stress Intensity on the Commination of Ceramics in Stirred Ball Mills,” in Fine Powder Processing, Eds., R. Hogg, R.G. Cornwall, and C.C. Huang, Penn State University, pp. 51-58 (1997).
18. Austin, L.G., Klimpel, R.R., and Luckie, P.T., Process Engineering of Size Reduction: Ball Milling, AIME, New York, (1984).
19. Crabtree, D.D. et al., “Mechanisms of Size Reduction in Comminution Systems,” Trans. SME/AIME, 229, pp. 202-210 (1964).
20. Heindereich, E. and Kruger, G., “Investigations Concerning the Mathematical Description of Ultra-Grinding Processes,” Preprints, World Congress Particle Technology, Nuremberg, FRG, pp. 695-707 (1986).
21. Stehr, N., Mehta, R.K., and Herbst, J.A., “Comparison of Energy Requirements for Conventional and Stirred Ball Milling of Coal-Water Slurries,” Coal Preparation, 4, pp. 209-226 (1987).
22. Mankosa, M.J., Adel, G.T., and Yoon, R.H., “Effect of Media Size in Stirred Ball Mill Grinding of Coal,” Powder Technol. 49, pp. 75-82 (1986).
23. Rajamani, R.K. and Bourgeois, F., “Energy Efficiency of
Silicon Carbide Grinding in a Stirred Ball Milling,
Preprints, World Congress Particle Technology, Kyoto,
Japan., pp. 369-375 (1990).

24) Mankosa, M.J., Adel, G.T., and Yoon, R.H., “Effect of
Operating Parameters in Stirred Ball Mill Grinding of
Coal,” Powder Technol. 59, pp. 255-260 (1989).

25) Cho, H. and Hogg, R, “Investigation of the Grind Limit
in Stirred-Media Milling,” Int. J. Miner. Process, 44-45,
pp. 607-615 (1996).

26) Cho, H. and Hogg, R, “Breakage Parameters for Ultra­
fine Grinding in Stirred-Media Mills,” Proceedings, XIX
International Mineral Processing Congress, San Fran­
cisco, Ca, Vol. 2 pp. 53-57 (1995).

27) Austin, L.G. and Shah, L, “A Method for Inter-Conver­
sion of Microtrac and Sieve Size Distributions,” Power
Technol. 35, pp. 271-278 (1983).

28) Cho, H, Yildirim, K. and Austin, L.G., “The Conversion
of Sedigraph Size Distributions to Equivalent Sub-sieve
Screen Size Distributions,” Powder Technol. 95, pp. 109­
117 (1998).

29) Tangsathitkulchai, C and Austin, L.G., “The Effect of
Slurry Density on Breakage Parameters of Quartz, Coal
and Copper Ore,” Powder Technol., 42, pp. 287-296
(1985).

30) Kapur, F.C., “Self-Preserving Size Spectra of Commin­
uated Particles,” Chem. Eng. Sci. 27, pp. 425-431 (1972).

31) Strasizar, J. and Runovc, F., “Kinetics of Comminution in
Micro and Sub-micrometer Ranges,” Int. J. Miner. Pro­
cess. 44-45, pp. 673-682 (1996).

32) Liu, J. and Schönter, K. “Modelling of Interparticle
Breakage,” Int. J. Miner. Process, 44-45, pp. 101-115
(1996).

33) Schönter, K, “Advances in the Physical Fundamentals
of Comminution, in Advances in Mineral Processing,
P. Somasundaran (ed.), SME/AIME, Littleton, CO.,
p. 28, 1986.

34) Hogg, R., Hu, S. and Musselman, S.W, (1998) “Breakage
Mechanisms in Stirred-Media Milling,” Proceedings,
World Congress on Particle Technology 3, Institution
of Chemical Engineers, Rugby, Warwickshire, England,
1998.

Richard Hogg

Richard Hogg is Professor of Mineral Processing and GeoEnvironmental Engineer­ing at the Pennsylvania State University. He received a B.Sc. from the Univer­
sity of Leeds and the M.S. and PhD degrees from the University of California at
Berkeley. Dr. Hogg’s research interests include fine particle processing, particle
coloration, and colloid and surface chemistry.

Heechan Cho

Heechan Cho graduated from the Seoul National University with a B.S. degree in
Mineral and Petroleum Engineering. He obtained the M.S. and Ph.D. degrees in
mineral processing from the Pennsylvania State University. He has held research
positions with the U.S. Department of Energy, Penn. State and the Korea Electric
Power Research Institute. He is presently an assistant professor in the School of
Civil, Urban & Geosystem Engineering of the Seoul National University.