Ultrafine Grinding and Separation of Industrial Minerals

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Editor

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Three sessions were held at the 112th AIME meeting as a joint effort between the Minerals Processing Division (Crushing and Grinding Committee) and Industrial Minerals Division. This volume was originated based on the papers presented at these sessions.

Published by
Society of Mining Engineers
of the
American Institute of Mining, Metallurgical and
Petroleum Engineers, Inc.
New York, NY • 1983

Printed in the United States of America
by Guinn Printing Co., Hoboken, New Jersey

Library of Congress Catalog Card Number 83-82078
ISBN 0-89520-419-3

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Preface

The growing demand of ultrafine industrial minerals is due to their important role as fillers, extenders and coatings in the plastic, paint, and paper industries. With the ever increasing cost of energy and depleting sources of high grade ores, development of improved methods of grinding and separation of ultrafine particles has gained considerable importance. Research and development and commercial testing of new methods have experienced rapid growth in the last few decades. This volume has been published by the joint effort of Minerals Processing (Crushing and Grinding Committee) and Industrial Minerals Divisions of the Society of Mining Engineers of AIME in order to recognize the developments and to provide a forum for the exchange of information on the subject of ultrafine grinding and separation of industrial minerals. This volume contains 15 papers presented at the 112th AIME meeting in Atlanta, Georgia in three sessions. These have been combined in the book in two sections, "Ultrafine Grinding of Industrial Minerals" and "Separation of Ultrafine Industrial Minerals."

The primary objective of this volume is to serve as a unique source of information on ultrafine grinding and separation of industrial minerals. The papers include not only state-of-the-art reviews in the production of ultrafines but also recent advances that have been made in dealing with the industrial minerals ultrafines. The major areas covered are ultrafine grinding equipment based on attrition, fluid energy, and fine media; mathematical description of size distribution of ultrafines; mechanochemical effects during ultrafines grinding; separation of ultrafines by pneumatic classification, high gradient magnetic separation, carrier flotation, selective flocculation, and hydrocyclones; and size and surface characterization.

This volume and the proceedings are the result of enthusiastic support and work by many colleagues. I wish to express my sincere thanks to Mr. Bruce H. Mason and Dr. Nikil C. Trivedi for their help in organizing the sessions. Most of all, this volume would not have been published without the fine contributions from authors who generously donated their time and energy. The valuable assistance by Marianne Snedeker of the Society of Mining Engineers of AIME is very much appreciated.

Subhas G. Malghan
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July 15, 1983
Houston, Texas

Contents

1
Ultrafine Grinding of Industrial Minerals

Chapter 1

Ultrafine Grinding Equipment Types, Capabilities, and Choices

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ABSTRACT

Equipment choices for ultrafine grinding encompass several different types of dry and wet size-reduction devices. These need to be put into functional perspective for systematic analysis of capabilities and limitations versus processing requirements of the materials to be satisfactorily ground.

Particle strengths plus maximum and average sizes are the primary variables controlling grinding action requirements and equipment options for efficient processing. These are fairly well understood and provide the starting point for decisions.

Particle space requirements under dynamic processing conditions vary with particle shapes and size-distributions by as much as 30X. This additional major variable is not widely appreciated and does need adequate description to provide a firm basis for selecting processing compositions and procedures.

ULTRAFINE GRINDING
EQUIPMENT TYPES, CAPABILITIES, AND CHOICES

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ABSTRACT

Equipment choices for ultrafine grinding encompass several different types of dry and wet size-reduction devices. These need to be put into functional perspective for systematic analysis of capabilities and limitations versus processing requirements of the materials to be satisfactorily ground.

Particle strengths plus maximum and average sizes are the primary variables controlling grinding action requirements and equipment options for efficient processing. These are fairly well understood and provide the starting point for decisions.

Particle space requirements under dynamic processing conditions vary with particle shapes and size-distributions by as much as 30X. This additional major variable is not widely appreciated and does need adequate description to provide a firm basis for selecting processing compositions and procedures.

EQUIPMENT CAPABILITIES AND LIMITATIONS

Working ranges of typical equipment for dry and wet grinding have been aligned on the basis of average particle sizes in the combined Figures 1 and 2. This graphical comparison shows that either method or some combination of both can be employed to make ultrafine products.

Energy requirements for dry or wet grinding do not differ substantially when using suitable equipment and operating procedures. The energy requirement is proportional to the surface area, as indicated on the second corresponding scale. The cumulative energy required for grinding of medium strength materials to a given average particles size with an efficient equipment is;

Avg.μm =	16	8	4	2	1	[Max.μm = 5X to 20X]
kWh/ton =	20	40	80	160	320	[Usual range $\pm$ 50%]

Consequently, the principal reasons for equipment choices lie elsewhere. The primary constraints are the particle sizes of the available feedstocks, the desired products and the dry or wet state of each. Common secondary constraints are the type of existing equipment, if usable, and new equipment prices.

Within these constraints, sound decisions without unnecessary survey and test work; hinge on ones understanding of the equipment grinding action and related classification requirements for efficiency.

Dry Grinding Methods: Starting with a moderately coarse material, three basic types of mechanisms are employed to grind down into the ultrafine range. In sequence, they are pressure-crushing, mechanical-impact, and direct particle-attrition at velocities exceeding 300 fps (900 cm/sec). All mechanisms require more or less continuous removal of the accumulated "fines' to maintain efficiency.

Devices such as ring-roller mills function via a pressure-crushing action on a compact particle mass. This is the main action in heavy-duty rod and ball mills which also produce modest amounts of low-velocity mechanical impact.

The classification process used with pressure-crushing devices for dry materials, is not difficult down to 10 um average particle size. At about this point, the possible contacts between particles begin to exceed 6 million/inch^2 and the grinding action becomes limited by particle recompaction problems.

Ordinary hammer mills function via high-speed impacts with various sorts of rotating bars and stationary grids or screens, at fairly low particle concentrations. Some internal classification occurs but external units are needed to grind down into the upper half of the ultrafine range.

Very high velocity impact mills, such as the Raymond Vertical or Mikro-Pulverizer, with good continuous internal classifying action; can provide additional reduction. These, however, are functionally hybrids with rotor velocities exceeding 300 fps which produce substantial amounts of direct particle-attrition.

Straight fluid-energy type mills, such as the "Wheeler" and "Micronizer", are generally employed to grind on down through the lower half of the ultrafine range to average particle sizes of 1 um or less. These function almost entirely via particle-particle attrition with excellent internal classification.

In assessing all such high velocity grinding devices, two basic points need recognition: (1) Grinding action depends on particle concentration which should be optimized. (2) Classification capability generally sets the lower average size limit.

The future dry-grinding equipment developments seem to be primarily arising in the area of fine media devices. This has been long retarded by difficulties with media-wear and, for continuous units, by problems with media-separation for classification. Some progress in resolving these problems is being made.

Wet Grinding Methods: All commercial type wet grinding equipment, for other than break-up of relatively weak agglomerates or aggregates, utilize one or the other kind of media to apply sufficient force to particles suspended in liquids.

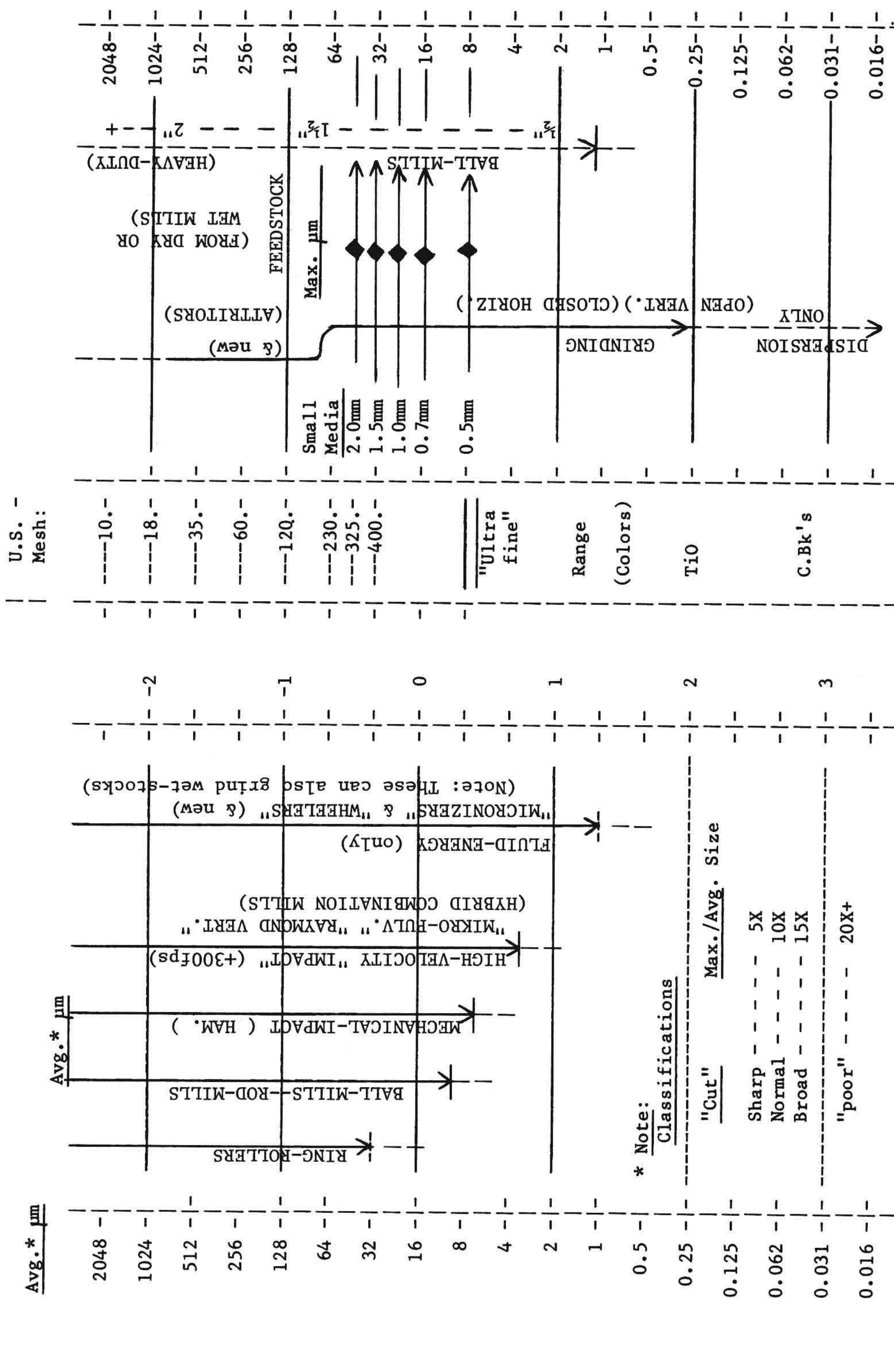


Figure 1: DRY MILLING EQUIPMENT

Figure 2: WET MILLING EQUIPMENT

In the coarser grinding stages, efficiency is increased by external classification and recycling. But wet-classification is more difficult than dry-classification and becomes extremely so as the average particle size decreases below 10 µm. Under these conditions efficient size reduction is obtained via mill design, multiple grind stages and progressive reductions in media size.

Media sizes for coarse grinding in heavy-duty ball mills range from about 80 mm maximum to 20 mm and for medium to fine grinding mill on down to about a minimum of 8 mm. Below about 16 mm media size, removal of the ground mixture becomes increasingly difficult and the practical media size limit is around 12 mm.

Maximum particle size sets the lower limit on media sizes for adequate force application to obtain satisfactory grinding action. Hence for coarse feed particles fewer media contacts per unit mill volume results in poor statistical efficiency--and vice versa in small media type mills employed for efficient fine and ultrafine wet grinding.

In the still growing series of "stirred-mills" that utilize the smaller media is the Segvari Attritor (still being marketed by Union Process Inc.). These are batch processing units using media in the 10 to 3 mm range. Removal of the ground mixture is the principal operating problem.

Second in this small-media mill series was the "Sand Grinder" using 0.7 mm quartz sand as the principal low cost media. Developments in the late 1940's (S. Hochberg Pat. 1952) through 1958 (D. Bosse equipment Pat. 1958), resulted in a highly efficient continuous milling unit then licensed internationally by DuPont. At this media size, however, the primary use was for dispersion and actual grinding uses were limited to particles under 15 µm.

From the Attritor with long rod-agitator and the continuous "Sand Grinder" with multiple high-speed (about 35 fps) disc agitators, the present assortment of vertical and horizontal small-media mills has evolved, including a continuous type Attritor.

Grinding capabilities of all these small-media mills is controlled by their particular combination of (a) shear-stress applied by the agitator rotors to the mixture-media mass and (b) force-multiplication via the specific media on particles caught between. The applied shear stress ranges from about 1/2 psi for open vertical mills to 1 psi in closed pressurized mills, which are largely horizontal units for somewhat better action, and upwards to several psi with rotor element designs for lower speed. Force-multiplication factors, $(D_m/D_p)^2$, are given in Table 1:

TABLE 1:
MEDIA DIAMETER vs CONTACT POINTS
and RELATIVE FORCE

MEDIA Dia, mm	NUMBER* /cm^3	FORCE MULTIPLICATION FACTORS 50 µm Particle	25 µm Particle
4.00	16	6,400	25,600
3.00	37	3,600	14,400
2.00	125	1,600	6,400
1.00	296	900	3,600
0.75	1,000	400	1,600
0.50	8,000	100	400

* At dynamic packing under high shear rates

Statistical efficiency of small-media grinding units can be increased by reducing the maximum particle size in the feed mixture and corresponding reductions in the media size. This is a question of crossover-point selection from either a dry or wet preliminary grinding operation. Maximum particle strength and particle size are the two variables to be considered.

The new and future equipment development needed is principally in the large continuous small-media category that will permit economical high volume production. The assortment of media sizes and media material available at present should be adequate. The problem is one of improved designs to permit sufficient heat removal.

Grinding efficiency in all wet-milling units is also highly dependent on particle concentration in the processing mixtures. And this key variable needs to be examined in some detail.

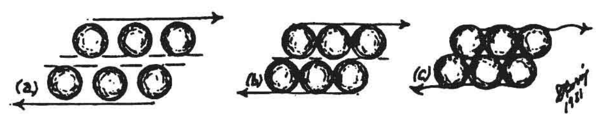
PARTICLE VARIABLES and FLOW-MECHANICS

The behavior of particulate materials in the processing equipment depends on their volumetric concentration and resulting clearances under flow conditions which cause them to rotate. This relationship between the solids volume/gas volume ratio (SV/GV) in dry grinding, or solids volume/liquids volume (SV/LV) in wet grinding, and the effective particle clearances; needs to be defined, understood, and utilized to control the grinding action in the mills.

Uniform spheres provide the primary reference system for relating particle concentrations and clearances during flow. The clearances, which tend to equalize, can be readily calculated for any given SV/GV or SV/LV. This numerical relationship that is directly appliable to spherical grinding media is further translatable to asymmetrical particles.

Particle concentrations at which their clearances have been reduced to zero under high shear rates can be directly or indirectly measured in solid-liquid mixtures. The SV/LV at this critical point numerically defines the "true dilatent point" (TPD) of the specific particulate material. This is shown using uniform spheres in Figure 3.

Figure 3 PARTICLE CLEARANCES vs. SV/LV and TDP

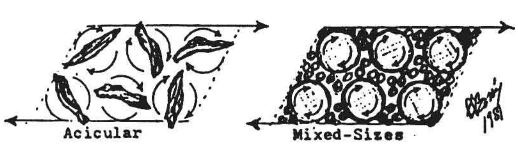


(a) SV/LV TDP (b) SV/LV = TDP (c) SV/LV TDP

For uniform spheres, the mixture SV/LV at TDP is 1.1 and as it is reduced the clearances increase rapidly with corresponding reductions in flow resistance. Conversely, raising the mixture SV/LV results in particle overlapping, oscillatory movement to permit flow a lower shear rates and mechanical locking when the shear rate is increased sufficiently. If the SV/LV is raised 40% above that at TDP, the mixture becomes totally locked.

Asymmetrical particles shapes reduce the TDP and, in turn, the SV/LV or SV/GV for equivalent mixture flow behavior by as much as 10X. The opposite effect is produced by size distributions whereby smaller particles can fit between the larger and the combined effects of both variables cause the TDP of particulate materials to vary from about 0.1 to 3.0 SV/LV (See Fig. 4).

Figure 4: SHAPE vs SIZE-DISTRIBUTION and TDP's



Dry Grinding Considerations: Particle shapes and size distributions alter the number of possible contact points at a given average particle size. Consequently, the lower limit on grinding via pressure crushing action occurs at higher average particle sizes for fairly symmetrical particles with broad size distributions and vice versa. These variables have corresponding effects on adhesion to the equipment surfaces, agglomeration, etc.

At relatively low particle concentrations, as in mechanical impact or fluid-energy type equipment; particle shapes become a less important variable in terms of grinding actions. But size distribution remains important because the finer particle fraction can effectively "cushion" and reduce this type of grinding action.

As yet, the specific relationships between these two variables and particle concentrations needed for maximum grinding efficiencies, to the writers knowledge, have not, been established on a numerical basis. But they can be established in much the same fashion as has been done for wet grinding mixtures.

Wet Grinding Considerations: Mixture compositions for any type of wet grinding equipment must be carefully adjusted to obtain efficient action. Particle concentrations need to be as high as possible, without creating excessive flow-resistance or too much hydraulic "cushioning" at the media contact points. The functional goals are to place a substantial number of particles between media contact points, prevent them from being "flushed" into the surrounding spaces and concentrate media action primarily on the large particles for uniform size reduction.

Particle concentrations required for best grinding actions depend on the type of equipment and the media size being used. But for any particular unit and media, the optimum concentrations will be directly proportional to the TDP of the material being ground. The latter data are not difficult to obtain and they serve to greatly reduce the necessary experimental testing.

Where small media mills are used for the final wet grinding operation, the relatively low driving force on these media must be considered. Because it is transmitted to the media by the liquid phase in units with disc type rotors, the viscosity of the liquid phase must not be too low at operating temperatures. But short of this point, lower liquid viscosity allows higher particle concentrations and generally better efficiency.

Flocculation of particles and formation of agglomerates can also impede grinding if not adequately controlled via mixture compositions. This may further limit the particle concentrations in some cases. But some amount of such structure can aid grinding by helping to retain particles between the media contact points as they close. In coping with flocculation problems, the fact that only a small weight fraction of extremely fine particles can make large differences in flocs must not be overlooked.

There are, of course, many other important fluid flow-mechanics details which could not be included here. Consequently, it is hoped that those presented prove helpful.

SUMMARY

A large number of equipment types are available for wet and dry ultrafine grinding. Depending on the grinding mechanism employed in a particular equipment, limitations exist for achieving final size of the ultrafine particles. Grinding process variables--media size and density, type of movement of the media, solid/ liquid or solid/air ratio, ratio of maximum particle size to media size, etc. play an important role in determining the ultimate efficiency of fine particles production. The future equipment developments will principally have to come from manufacture of large continuous small-media mills that will permit economical high volume production of ultrafines.

Chapter 2

Breakage Rates and Size Distributions in Dry Ball Milling for Fine Sizes

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ABSTRACT

A method for quantitative investigation of the phenomena involved in fine grinding of materials that follows the changes in the breakage rates of fine particles has been presented. For relatively hard, brittle, non-coating material like quartz, the slowing down effect of breakage rates starts to be significant at relatively coarse sizes, which goes often undetected in closed circuit grinding systems, producing relatively coarse product, say $P_{80} = 75\ \mu m$. However, for fine grinding systems, as the $-10\ \mu m$ fractions begin to build-up, and classification becomes more difficult, the build-up of fine sizes causes a slowing down effect. Compounding this problem is the difficulty of obtaining accurate cumulative weight size distributions in the fine size region.

Introduction

It has long been known[1] that dry grinding of brittle materials in tumbling ball mills to ultrafine sizes departs from the "normal" behaviour[2] found for less fine grinding. This has been attributed to the build-up of an adherent coating of compacted fines on the balls[3,4], to reforming of strong larger particles by pelletizing of fines[4,5], or to greatly increased strength of fine particles due to the elimination of Griffith flaws as particles become smaller by fracture[6]. It is also well-known [7] that ductile materials can be caused to interact to form alloys by prolonged ball milling, and if very fine particles exhibit non-brittle characteristics it would appear possible for plastic flow to cause refusion of surfaces during ball milling. The effect of surface active agents (grinding aids)[8] on fine dry grinding has been attributed to their effects on these mechanisms.

The quantitative investigation of the phenomena involved has been hampered by the lack of a methodology to follow the changes in breakage rates of fine sizes, and the imprecise definition of "normal" versus "abnormal" behavior. Austin and Bagga[9] performed an analysis of the variation of specific rates of breakage[10] during the batch grinding of several materials to fine sizes. They found that a normal region could be defined by first-order breakage, defined by

$$\text{rate of breakage of size } j = S_j w_j(t)W \qquad (1)$$

where the size intervals are the $\sqrt{2}$ screen sequence, S_j is the specific rate of breakage of size j and $w_j(t)$ is the mass fraction of total charge W which is of size j at time t of grinding. However, at long grinding times, they found a slowing-down of breakage rate, that is, S_j decreased as fine material accumulated. It was difficult to extend the treatment to long grinding times because the major mass of charge then became less than 38 μm (400 mesh), and precise conclusions could not be drawn on the basis of sieve size analysis.

They tentatively concluded, however, that the slowing-down of the rates of breakage was uniform for all sizes, that is, all sizes have their specific breakage rates reduced by a constant factor, $S_j(t) = \kappa S_j(0)$, where κ is a function of the fineness of grind. They also concluded that the primary daughter fragment distributions[10], $B_{i,j}$, did not change in the slowing-down region.

The present paper is a continuation of their work, with the objective of extending the treatment to ultrafine dry grinding.

Theoretical Background

Equation 1 becomes

$$-\frac{dw_1(t)W}{dt} = S_1 w_1(t)W$$

for the top size interval of the charge. For first-order breakage this integrates to

$$\log[w_1(t)/w_1(0)] = -S_1 t/2.3 \qquad (2)$$

For the general size interval i, a size-mass balance for batch grinding gives[10]

$$\frac{dw_i(t)}{dt} = -S_i t + \sum_{\substack{j=1 \\ i>1}}^{i-1} b_{i,j} S_j w_j(t) \quad , n \geq i \geq j \geq 1 \qquad (3)$$

where $b_{i,j}$ is the fraction of material broken from larger size j which reports to smaller size i on primary fracture, and n is the "sink" size interval defined by the lowest measureable size. Computer programs exist[11,12] for the solution of this batch grinding equation set. The accumulation of $w_i(t)$ values gives the fraction of charge below the top size of size j, $P_j(t) = \sum_n^j w_i(t)$.

The cumulative primary daughter fragment distribution $B_{i,j}$ is defined by $B_{i,j} = \sum_n^i b_{k,j}$, and it has been shown that it often fits the empirical form[13]

$$B_{i,j} = \Phi_j \left(\frac{x_{i-1}}{x_j}\right)^{\gamma} + (1-\Phi_j)\left(\frac{x_{i-1}}{x_j}\right)^{\beta} \quad , n \geq i > j \qquad (4)$$

If Φ_j, γ and β do not change with the breaking size j, the primary daughter fragment distribution is dimensionally normalized, that is, $B_{i,j}$ is constant for a given ratio of x_i/x_j. The parameters Φ, γ and β define the distribution, and, hence, the values of $b_{i,j}$ used in the solution of Eqn. 3. Experimentally, the values of $B_{i,j}$ can be estimated from[13]

$$B_{i,j} = \frac{\log[(1-P_i(0))/(1-P_i(t))]}{\log[(1-P_{j+1}(0))/(1-P_{j+1}(t))]} \quad , i > j+1 \qquad (5)$$

where j is the top size of the charge, the starting feed is almost entirely of this top size, and $P_i(t)$ is for a short grinding time which gives no more than about 30% broken out of the top size interval.

If the breakage process slows down, the solution of equation 3 can still give the correct size distribution but a false time (Θ) has to be used in the computation[9]. This is defined as the grinding time necessary to give the size distribution at time t if grinding stayed first-order. Austin and Bagga have shown that a slowing-down factor κ, defined by $\kappa = S_i(t)/S_i(0)$, is related to Θ and t by

$$\kappa = d\Theta/dt \qquad (6)$$

The value of κ is 1 as long as grinding stays first-order, then decreases as the grinding rate slows down.

Experimental Results

The material investigated was a crystalline quartz from North Carolina (Castastone Products Company, Raleigh, NC) with a Bond Work Index of 19 kWh/metric ton. The mill used was a laboratory tumbling ball mill with the specifications given in Table 1, fitted with six lifters of semi-circular cross-section to avoid slippage of the charge. The material and