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A QUANTITATIVE TREATMENT OF SIZE REDUCTION IN WET BALL MILLINGS.

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The decrease in geometric mean particle size during wet ball milling follows a reciprocal relationship, which predicts an initial rapid rate of comminution, followed by a slow rate of reduction which develops into a situation where the mean particle size virtually remains constant. The initial rate is directly dependent on the weight of the balls, but the final particle size is an inverse function of ball size. Under these conditions the size distributions follow the Gaudin-Schumann equation. The patterns of behaviour breaks down when the process is limited by the viscosity of the charge, preventing the balls from moving within the mill. This occurs when either the solid to liquid ratio of the charge is high or when the balls are small.

INTRODUCTION

The process of wet ball milling can be varied to produce suspensions having different particle size distributions and rheological properties, these being dependent upon the magnitude of the variables involved, such as mill speed, mill load, ball size, time of milling and the viscosity of the suspending fluid. With any one standard set of conditions there is a decrease in mean particle size with time to a characteristic minimum value[1], which means that the process will be a self limiting one with respect to the amount of size reduction that can be achieved.

The prime concern of most investigators has been in the commercial aspects of large scale ball milling processes, for example Gow et al[2] studied the viscosity of the charge only in relation the amount of power and energy demanded to produce efficient milling. Their work has been extended by Kelsall et al[3] in their studies on continuously operating ball mills. The relationships between particle size distribution and the mill variables have not been considered in detail. A review on milling by Parrott[4] reported no new advances in ball milling techniques. The present study considers the effects of the time of milling, the ball size (grinding media), the ball density and the solid

to liquid ratio in the mill, on the geometric mean particle size and the limiting particle size of the product.

EXPERIMENTAL

Potassium hydrogen tartrate (B.D.H.) was recrystallised and sieved to obtain a constant starting material. Crystals which passed a B.S. 16 sieve and were retained on a B.S. 22 sieve were selected. The suspending fluid used was an equal parts mixture of glycerol and methanol, in which the solubility of the potassium hydrogen tartrate, determined gravimetrically, was 0.0005 per cent and could therefore be ignored.

Ball Mills

All milling experiments were carried out in stainless steel mills of $5.46 \times 10^{-4} m^3$, total capacity, internal height 9.4cm and internal diameter 8.5cm. The grinding media employed were 0.952cm (3/8") and 1.27cm (½") stainless steel or phosphor bronze balls. The mills and their contents were rotated on a pair of rollers whose speed could be varied by a transformer placed in series with an electric motor (Pascall Engineering Co Ltd). The critical speed of the mill was determined with the aid of a sensitive microphone and a decibel meter. The microphone was clamped as near as possible to the rotating surface of the mill where it could

sense the noise caused by the cascading or cataracting ball charge. The decibel meter registered a high and fairly constant noise level whilst rotational speed was being increased, but when critical speed was attained a sudden drop in the meter reading occurred. The rotational speed was then determined using a stroboscope, and was found to be 150 revolutions per minute.

All millings were carried out at 65 per cent of the critical milling speed[5]. The experimentally determined critical speed (Nc) was found to be within 0.6 per cent of the value calculated using the equation of Rose and Sullivan[6].

$$N_c = 76.6 \frac{1}{D} \times \frac{1 + 0.5d}{D} \quad \ldots\ldots\ldots (1)$$

where d is the diameter of the ball in inches and D the diameter of the mill in feet.

The grinding medium charge (ball charge) filled an apparent 50% per cent of the volume of the mill and the total solid + liquid charge was always constant at an apparent 60% of the volume of the mill i.e. sufficient to fill the void spaces and cover the ball charge. The ratio of solid to liquid in the charge was varied, three ratios being used, 0.35, 0.40, and 0.45, by weight.

The various combinations of ball charge, solids concentrations and milling times used in the experimental work are shown in Table 1.

Size Analysis

Particle size distributions were determined with a Coulter Counter Model ZB. fitted with a 70μm or 100μm aperture tube. Methanol containing 2% lithium chloride was the non-aqueous electrolyte solution, and it was saturated with potassium hydrogen tartrate to avoid solubility problems during analysis. Samples were taken from the mill at hourly intervals, dispersed in the electrolyte by gentle ultrasonic agitation and diluted for analysis. The data reduction and weight

TABLE 1.
SUMMARY OF BALL SIZES, SOLID CONCENTRATIONS AND MILLING TIMES

Ball size and type	Milling times in hours for solid phase ratios of		
	0.35	0.40	0.45
3/8inch stainless steel	2 to 12	3 to 12	3 to 12
1/2inch stainless steel	3 to 12	4 to 10	4 to 10
3/8inch phosphor bronze	3 to 12	3 to 12	3 to 12
1/2inch phosphor bronze	3 to 12	3 to 10	3 to 10

conversion were carried out on an I.C.L. 1900 computer, using an Eckoff[7] extrapolation to determine the 100% value by weight.

RESULTS AND DISCUSSION

Particle size distributions were plotted on logarithmic probability paper as cumulative weight oversize against particle size. A typical set of graphs is given in Fig. 1. and shows that the distributions are log normally distributed. Geometric mean diameters $(d)_w$ were read directly from the graphs.

Typical plots of geometric mean diameter against milling time are shown in Fig 2. No mean diameters were recorded for times less than 3 hrs because in these short periods samples exhibited a wide spread of sizes. All plots were curved initially, but flattened out with increasing time to a limiting diameter. The results therefore suggest that all the various combinations of conditions used in these experiments gave rise to a self-limiting process. Geometric mean diameters obtained after 11 hrs, the longest period recorded in all runs, are given as an indication of the relative limiting diameters in Table 2. Selection of 11 hrs is not as arbitrary as might be imagined, because all plots have levelled out by this time, and diameters selected after 10 or 12hrs for example, would give virtually the same result..

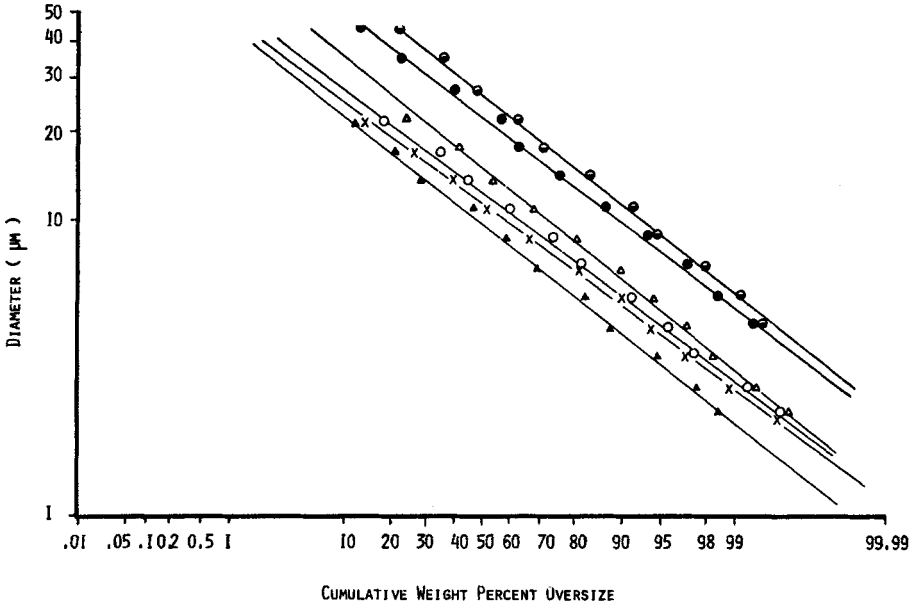

Figure 1. Cumulative size distribution of milled products using 3/8 inch stainless steel balls.

◒ 3 hours milling
● 4
△ 5
○ 6
× 7
▲ 8

Solid liquid ratio = 0.45

The relative values of the limiting diameters are mainly in accord with a process of attrition, in which the limiting factor is the size of the interstices

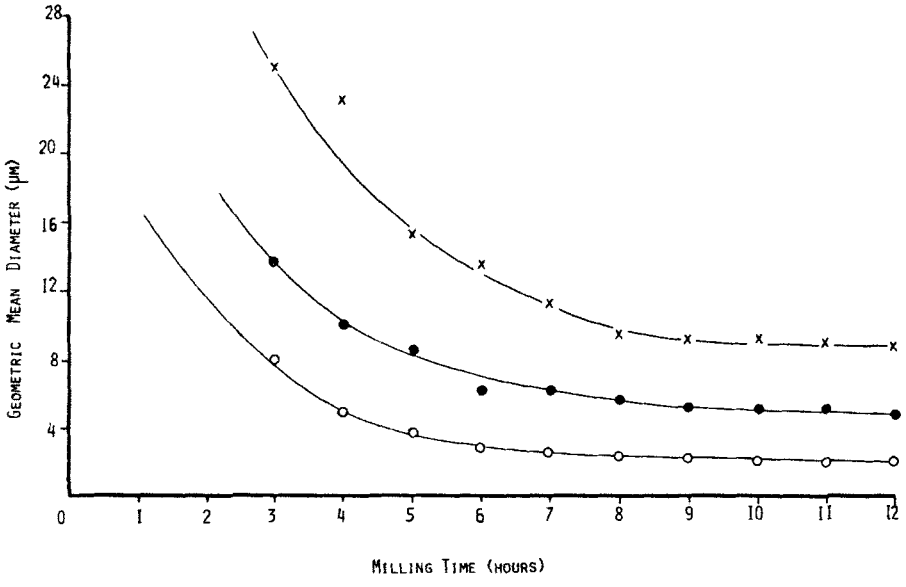

Figure 2 Variation of geometric mean diameter with time of milling using 3/8inch stainless steel balls

X 0.45 solid phase

● 0.40 " "

○ 0.35 " "

between the balls, so that the smaller the ball, the smaller the resultant limiting particle size. There is a limit to this theory, in that 1/4" balls used in preliminary experiments, failed to bring about effective size reduction, even with extended milling times.

TABLE 2.

VARIATION OF LIMITING DIAMETERS WITH MILLING CONDITIONS

Solid/Liquid ratio	Limiting Diameter (μm)			
	Stainless Steel Balls		Phosphor Bronze Balls	
	3/8"	1/2"	3/8"	1/2"
0.45	9.0	8.8	6.2	6.1
0.40	5.1	7.2	3.0	5.5
0.35	2.0	6.8	2.8	4.8

Comparison between limiting diameters produced by 3/8" and 1/2" balls, under otherwise identical conditions, reveals that in 4 of the 6 pairs of results, the 3/8" ball gave the finer product. The relevant results are shown in Table 2. Each of the four pairs of results involved suspensions that were dilute and hence highly mobile even after prolonged milling, so that the balls could be kept in motion indefinitely. The particles are small enough to move into the interstices between the balls and therefore any further size reduction that takes place, due to particle to particle attrition, will be slow and almost undetectable. The two exceptions, when the 1/2" balls gave the finer products, both involve a high solid/liquid ratio (0.45). Since

the solids concentration was high, the apparent viscosity of the suspension increased with time of milling, until a critical point was reached, when the 3/8" balls no longer fell freely, but remained embedded in the suspension mass, and rotated with the mill. The exceptions were therefore probably due to the charge holding the 3/8" balls, before their potential limit of comminution was reached under the conditions of these experiments. The 1/2" balls with their increased mass, would provide more resistance to the viscosity of the charge. This suggestion is supported by the fact that the phosphor bronze balls, which have a higher density than the corresponding steel ones, gave a finer particle size in every case. This also explains the behaviour of 1/4" balls.

We can only speculate on the shape of the plots of geometric mean diameter against time between commencement of milling and 3 hrs later. A mean diameter of 720μm can be calculated from the sieve range used to grade the starting material, so that all the plots converge to this initial value. A fall in mean diameter of about 700μm during the first three hours, compared with less than 25μm during the subsequent 9hrs suggests that a straight line, close to, and slowly diverging from the ordinate with increasing time would be a reasonable prediction. Furthermore, we can speculate

that this region represents impaction, rather than attrition, since the 1/2" balls produce finer particles during this period.

Since the limiting diameters are small compared with 720 m the results at milling times approaching 11hrs can be considered to form a line perpendicular to the pre-3hrs line close to, and converging with the abscissa. The resulting overall graph is a reciprocal curve, having the general equation.

$$td_w = \text{a constant}$$

where t = time d_w = geometric mean diameter

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The curve portions on the plots obtained with 3/8" balls, in Figure 2, support this hypothesis, since the product of time and observed geometric mean diameter gives a constant value. The mean constant can then be used to predict diameters at milling times less than 3 hrs. A typical set of results is shown in Table 3 and predicted plots are compared with observed diameters in Figure 3.

The same mathematical analysis could not be applied to the 1/2" balls, because the plots of geometric mean diameter against time showed little curvature. It was assumed that the significantly curved portions of these graphs lay in the pre-3 hr. period.

The ball milling system used in these studies could be described as a model one, because only one size of ball was used instead of a mixture of sizes, and all the

TABLE 3

COMPARISON OF OBSERVED AND PREDICTED GEOMETRIC MEAN DIAMETERS FOR 3/8 INCH STAINLESS STEEL BALLS AND A SOLID PHASE OF 0.40

Time in hours	0	0.06	3	4	5	6	7	8	9
d_{w} observed (μm)	720	-	13.6	10.0	8.5	6.2	5.9	5.4	5.1
d_{w} predicted (μm)		720	13.9	10.4	8.3	6.9	5.9	5.2	4.6

parameters were closely controlled. It is considered necessary to demonstrate the relationship between this model system and some of the practical systems previously reported in the literature. To this end, size distribution data from the millings were fitted to the Gaudin-Schumann equation as expressed by Schumann[8] and by Charles[9] for homogeneous materials.

$$y = \left(\frac{x}{k}\right)^{\alpha}$$

where y = weight percent finer than size x, k is the size modulus and describes the theoretical maximum size particles in the system and α is the distribution modulus which has been defined by Crabtree[10] and by Kapur[11] as the slope of the line obtained when the cumulative weight fraction finer than a given size is plotted against

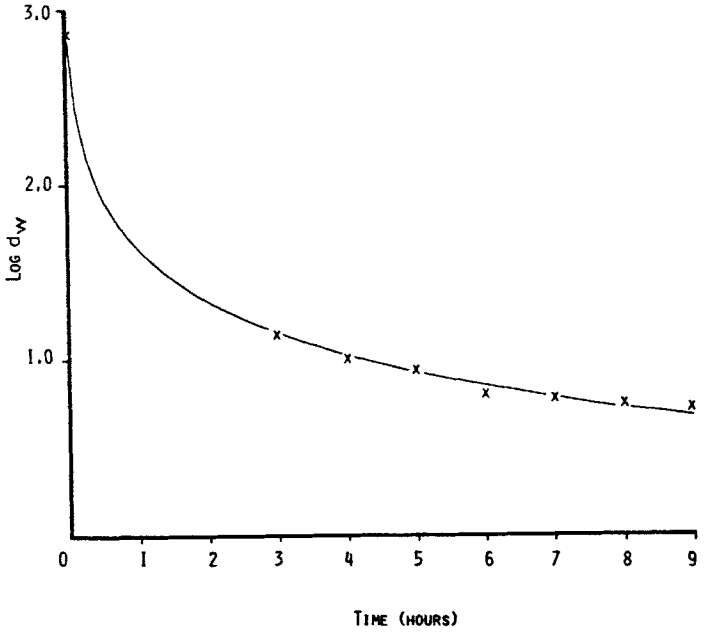

Figure 3 Correlation between observed and predicted values of geometric mean diameters from Table 3.

× Observed

—— Predicted

that size, on double logarithmic graph paper. These authors indicated that the most commonly found value in ball milling operations is 0.8. Using this value the Gaudin-Schumann equation becomes

$$y = \frac{x}{y^{0.8}} \qquad (2)$$

$$\text{or} \quad 0.8 \log k = 0.8 \log x - \log y \qquad (3)$$

The values of k obtained by using data from two typical milling experiments showed good agreement with the values published in the literature and it can therefore be inferred that the patterns of size reduction obtained using the model system are similar to those produced in these less ideal practical systems.

The implications of the results given above are that the initial rate of comminution is controlled by the weight of the balls, and that a practical limiting particle size distribution is reached, when the balls are still moving freely within the mill. In contrast, the degree of comminution is inversely dependent on ball size, in other words, the smaller the balls, the finer the particles. Both objectives can be assisted by using balls made of a denser material. These predictions assume that the viscosity of the charge does not increase to a value at which its resistance to the motion of the balls within the mill becomes significant.

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