"Equations Improve C_P^o Predictions," *Hydrocarbon Process.*, **50**, No. 1, 98 (1971).
Thompson, W. H., "A Molecular Association Factor for Use in the Extended Theorem of Corresponding States," Ph.D. thesis, Pa. State Univ., University Park (1966).
Yuan, Tran-Fu, and L. I. Stiel, "Heat Capacity of Saturated Nonpolar and Polar Liquids," *Ind. Eng. Chem. Fundamentals*, **9**, 393 (1970).

Manuscript received January 3, 1975; revision received March 25 and accepted April 2, 1976.

Particle Attrition in Shear Flow of Concentrated Slurries

A first order kinetic formulation of brittle particle attrition is suggested. Experimental data show that it applies to coal particle attrition in Couette flow. These data reveal that particles are reduced by loss of surface protuberances, which are much smaller than their mean diameter. It is also shown how changes of the size spectrum, due to shearing, can be predicted.

A. J. KARABELAS
Westhollow Research Center
Shell Development Company
Houston, Texas 77077

SCOPE

Concentrated slurries made of ~1 to ~10^3 μ particles are currently studied in connection with long distance pipeline transportation of commodities such as coal and iron ore, usually with water or oil as the liquid carrier. Particle attrition can affect the slurry rheological properties and can present difficulties in the solid/liquid separation at the pipeline terminal.

Attrition is caused by particle-particle collisions and particle impingement on solid boundaries. A statistical description of this process, involving a distribution of particle sizes and associated kinematic properties, although very desirable, is almost impossible at present. A more direct and fruitful approach is to study attrition in a well-defined flow field and to relate observed changes of an initial particle size distribution to some characteristic bulk flow properties, for example, the shear rate. This approach requires an appropriate mathematical formulation of the attrition process.

The problem of particle attrition in slurry flow has not been adequately studied. Only a few exploratory studies on this subject have been published so far (for example, Worster and Denny, 1955; Bjorklund and Dygert, 1968). In the case of coal, for instance, there is essentially no published information about the rate at which small particles degrade in slurry flow, or about the size distribution of the resulting fragments. This lack of information is partly due to difficulties encountered in doing meaningful laboratory experiments, especially with settling suspensions.

The main objective of this study is to suggest a kinetic type of formulation of particle diminution in suspension flow which can serve as the framework for interpreting experimental data and for modeling particle attrition in slurry transportation and processing systems. Another objective is to develop techniques for accurate measurement of attrition and to demonstrate how changes of a wide particle size distribution (PSD) can be predicted (as a function of initial PSD, flow conditions, and time) on the basis of a few experimentally determined parameters.

CONCLUSIONS AND SIGNIFICANCE

Size diminution of brittle, irregular in shape, particles due to slurry flow is described as a rate process, similar to a first-order chemical reaction. This formulation involves two sets of parameters, that is, the coefficients k_i representing the rate of material loss of a particular size fraction, of mean diameter d_i, and the parameters $b_{i,j}$ describing the manner in which the attrition products from fraction i are distributed into various smaller size fractions j. At present, these parameters can only be determined experimentally. The above formulation is fairly general and can provide the basis for attrition studies in any slurry flow field. It is often used in grinding studies, as discussed in an excellent review paper by Austin (1971).

Experiments have been performed with bituminous coal particles of two very narrow size fractions (d = 210 to 250 μ and 150 to 210 μ) and one rather wide continuous distribution ($d \simeq 1$ to 300μ). The laminar Couette flow field, characterized by a nearly uniform shear rate, has been employed in these tests. The results have been interpreted in accordance with the previously described formulation, and the parameters k_i and $b_{i,j}$ have been estimated. It has been found that coal particle attrition generally proceeds rather slowly; for example, k is of order 10^{-4} hr^{-1} for $\dot{\gamma} \simeq 100$ s^{-1} and $d \simeq 200$ μ. Also, the measured distribution of attrition products (parameters $b_{i,j}$, Table 4) provides strong evidence that size diminution is caused by loss of particle surface protuberances (surface abrasion) and not by particle breakage into nearly equal parts.

As expected, the rate of size reduction (k_i) increases with particle diameter d_i and shear rate $\dot{\gamma}$. Equation (19), relating k_i to d_i and $\dot{\gamma}$, has been obtained on the basis of limited data only to demonstrate how the attrition formulation suggested here can be used to predict changes (with time of shearing) of a wide particle size distribution. Satisfactory agreement has been obtained between predicted and measured changes.

In the design of processes involving solid-liquid flow, it is usually desirable to know the effect of slurry properties and flow conditions on particle size reduction, or attrition. It is also of particular interest, at present, to know the rate at which particle attrition takes place in long distance pipelines carrying concentrated slurries, such as coal in water. This problem provided the main motivation for the work presented in this paper. Particle size change during long distance pipeline transportation is important for two main reasons. First, it can affect the slurry rheological properties and consequently the pressure gradient in the line. Second, an overall reduction of particle sizes and especially a substantial increase in the percentage of very fine particles, due to attrition, can present difficulties in the solid/liquid separation, which is usually required at the pipeline terminal.

Most of the work on particle attrition in fluid streams has been performed with process catalyst particles in gas/solid systems; for example, Gwyn (1969). A bench scale apparatus, in which solid particles are kept in suspension by a gas stream (Forsythe and Hertwig, 1949) is commonly employed in these experiments. Such tests are only useful in making comparative evaluations of particle resistance to attrition, but they are inapplicable to the problem under consideration, that is, particle diminution in concentrated solid/liquid suspensions. On this topic, very few studies have been reported in the open literature. This is to a large extent due to the difficulties encountered in performing meaningful laboratory experiments. For example, particle attrition in pipe flow cannot be studied in a short experimental pipe loop because particle breakage caused by the pump proceeds much faster than attrition taking place in the pipe itself.

In order to avoid this problem, Worster and Denny (1955) used a rotating wheel type of apparatus, half filled with slurry. The wheel (of a square cross section) was rotated about an axis normal to the direction of gravity, while the slurry occupied only the lower half of the closed, rotating pipe. This motion of the pipe relative to the fluid bears some resemblance to the fluid flow in the usual straight pipes. However, there is not sufficient information available, about the rotating wheel flow field, to permit proper data interpretation and development of scale-up rules. Bjorklund and Dygert (1968) carried out small scale attrition tests in a concentric cylinder type of apparatus. An inverted cylindrical cup was rotated in a large annulus filled with slurry, creating two separately sheared annular spaces. Useful information was obtained about the attrition characteristics of brittle silica gel and molecular sieve particles, but no attempt was made to correlate the results and to systematically study the effect of flow conditions on attrition. The complexity of the flow field (that is, Taylor vortices in the outer annulus and different mean shear rate in each annular space) did not permit such studies.

Experiments with concentrated coal slurries are reported in this paper. The tests were run in a concentric cylinder, Couette type, device under laminar bulk flow conditions. This flow field is often used for slurry rheological measurements and has the advantage that the shear rate is nearly uniform throughout the narrow annulus, which greatly simplifies data interpretation. Additionally, operation, control, and data acquisition are relatively easy and reliable with a Couette flow apparatus.

Previous attrition experiments with slurries (Berkowitz et al., 1963, Bjorklund and Dygert, 1968; Worster and Denny, 1955) indicate that the size of a particle is reduced by loss of edges and corners which are usually much smaller than its initial mean diameter. This suggests that particle-particle collisions and/or particle impingement on equipment boundaries are not energetic enough to cause particle breakage into nearly equal fragments. Some theoretical remarks made by Rumpf (1959) lead essentially to the same conclusion. It was, therefore, expected at the outset of this investigation that the process of particle diminution in slurry flow would be relatively slow and that experiments of long duration would be necessary to obtain accurate data. The Couette flow apparatus employed in this study is very convenient for such well-controlled experiments. A mathematical formulation of attrition is presented in the next section and is subsequently used to analyze and interpret the experimental data.

DESCRIPTION OF ATTRITION AS A RATE PROCESS

Rate of Particle Size Reduction

Particle weight fractions w_j are defined as

$$w_j = P_j - P_{j+1} \tag{1}$$

where P_j is the cumulative fraction of particles smaller than d_j, and $P_1 = 1.0$. We consider particle size reduction with no recombination or agglomeration. Let us assume that a certain volume of slurry containing W pounds of solids, is subjected to steady shear flow which results in particle size reduction. The size distribution at time t_1 is given as $w_j(t_1)$, $j = 1, 2, \ldots n$, and

$$\sum_{j=1}^{n} w_j = 1.0 \tag{2}$$

The largest size fraction $j = 1$ at time t_2 is $w_1(t_2)$, and the total loss of material from size 1 over the period $\Delta t = t_2 - t_1$ is $W[w_1(t_1) - w_1(t_2)]$. The corresponding mean rate of material loss is

$$Q_1 = \frac{W[w_1(t_1) - w_1(t_2)]}{\Delta t} = - \frac{W[w_1(t_2) - w_1(t_1)]}{\Delta t} \tag{3}$$

As was discussed, particle attrition in common flow fields, such as pipe flow, usually proceeds rather slowly. Therefore, it is very convenient to describe it as a rate process, similar, for example, to the chemical decomposition of certain compounds. The rate of loss of material in interval 1 will be expressed as

$$Q_1 = k_1 W w_1(t_1) \tag{4}$$

where k_1 is a rate coefficient with dimensions $(\text{time})^{-1}$. It will be assumed that this kinetic parameter is constant, over the period Δt, for a given set of system variables (mainly particle size and flow conditions). This formulation is often used in grinding studies (Reid, 1965; Austin, 1971) and Equation (4) with $k = \text{const}$ is usually called first-order law of size reduction or chemical decomposition.

In the limit as $\Delta t \rightarrow 0$, Equation (4) becomes

$$- \frac{d[W w_1(t)]}{dt} = k_1 W w_1(t) \tag{5}$$

If W and k_1 remain constant

$$\frac{dw_1}{w_1} = - k_1 dt \tag{6}$$

and upon integration

$$w_1(t) = w_1(0) \exp [- k_1 t] \tag{7}$$

where $w_1(0)$ is the initial weight fraction. In general, the rate at which material is lost by breakage from any in-

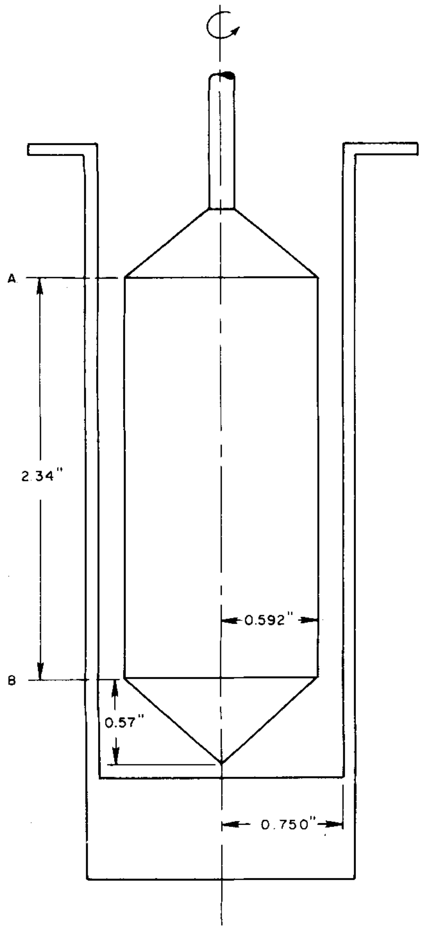

Fig. 1. Schematic of Couette device.

terval i is given as

$$\left.\frac{dw_i(t)}{dt}\right|_{\text{loss}} = -k_i w_i(t) \quad (8)$$

The validity of the above first-order assumption should be tested by plotting ($\ln w_1$) vs. time. Experiments performed in this study show that it is satisfactory for attrition of bituminous coal particles. Furthermore, the rate coefficient k is in general a function of material properties, particle size and shape, solids concentration in the slurry, and flow conditions (for example, shear rate). The significance of all these variables must be also established experimentally. However, in practical applications the important variables may be reduced to 2 or 3, and it is expected that limited bench scale experiments will be sufficient to obtain reliable correlations for k, applicable over a rather wide range of system variables.

Overall Rate of Particle Size Change

In order to complete this formulation, one must take into account not only the loss of material from a certain size interval, but also the products of the size reduction process and their distribution in other size intervals. This can be accomplished by determining the distribution function or matrix $B_{i,j}$ as the cumulative fraction of attrition products from size interval j, which can be found in all size intervals i, where $i > j$; that is, in intervals i, $i+1$, $\ldots$, $n-1$, n. The index j in $B_{i,j}$ is associated with an interval of larger particle sizes whose products fall into intervals i of smaller particles. Obviously, when $j = i = m$

$$B_{m,m} = 1.0; \quad m = 1, 2, \ldots n \quad (9)$$

The distribution of attrition products can be also represented by the following useful parameters:

$$b_{i,j} = B_{i,j} - B_{i+1,j}, \quad i > j \quad (10)$$

This set of distribution parameters $b_{i,j}$ designates the weight fraction of attrition products from size j which fall into size interval i. Therefore

$$\sum_{i=j+1}^{n} b_{i,j} = 1.0 \quad (11)$$

It can be easily shown that the rate of weight increase in size interval i and below, due to attrition products from all size intervals $j < i$, is as follows:

$$\frac{dP_i(t)}{dt} = \sum_{j=1}^{i-1} B_{i,j}k_j[P_j(t) - P_{j+1}(t)] \quad (12)$$

A simplified version of this equation will be used in subsequent sections to analyze the data and to compute the parameters $B_{i,j}$ and $b_{i,j}$. Obviously, the rate of gain in size i due to products from all larger sizes is

$$\left.\frac{dw_i(t)}{dt}\right|_{\text{gain}} = \sum_{j=1}^{i-1} b_{i,j}k_j w_j(t); \quad i > 1 \quad (13)$$

By combining Equations (8) and (13) we obtain the net rate of change of each size fraction w_i during the attrition process; that is

$$\frac{dw_i(t)}{dt} = \sum_{j=1}^{i-1} b_{i,j}k_j w_j(t) - k_i w_i(t); \quad i > 1 \quad (14)$$

The change of weight fraction, $i = 1$, has already been given in closed form [see Equation (7)].

DESCRIPTION OF EXPERIMENTS

Experiments were performed in a modified Epprecht Rheomat 15 Contraves (type RM15D) viscometer with the inner cylinder rotating. Figure 1 shows the basic dimensions of this apparatus. The slurry was sheared in an annular gap 4.0 mm wide. Fluid filled the annulus up to and slightly above level A. The maximum shear rate that could be attained with this device was 195.7 s^{-1}, corresponding to $\Omega = 352$ rev/min for the bob. The cup was immersed in a constant temperature bath, which allowed a long, almost unattended, operation under constant conditions.

Coal was employed in the tests because of its practical significance. It was bituminous (Balmer Seam, Canadian) with inherent moisture ~3% and density ~1.39 g cm^{-3}. Settling of coal particles in water, which is used as a carrier in most commercial slurries, does not permit experimentation in a vertical Couette device. Therefore, the coal particles were made neutrally buoyant by using a zinc chloride solution as the carrier liquid.

In order to minimize particle size effects on the shear field, the maximum particle diameter d_{max} was at least ten times smaller than the instrument gap (4.00 mm). Thus, no particles larger than ~300 μ (50 mesh) were employed in the tests. The following five basic size fractions were selected for particle classification: −60/+70, −70/+100, −100/+200, −200/+325, and −325 mesh, which correspond to arithmetic mean diameters $d_1 = 230$ μ, $d_2 = 180$ μ, $d_3 = 112$ μ, $d_4 = 60$ μ, and $d_5 \simeq 25$ μ, respectively. The experimental conditions are summarized in Table 1. Basically, two types of tests were performed, one with narrow size fractions (experiments 1, 2, 4, 6, 7) and another with a relatively wide size distribution represented by a Rosin-Rammler type of function (experiments 5, 8, and 9).

In most experiments, 2 ml samples were withdrawn

Table 1. Summary of Experimental Conditions, Temperature 77 ± 0.2°F Throughout the Tests

Experiment number	Volume concentration, $\overline{C}$	Initial particle sizes, sieve number	Shear rate, s^{-1}	Duration of experiment, hr	Remarks
1	0.30	−60/+70	111.2	62	
2	0.15	−60/+70	111.2	68	
3	0.40	−60/+70	84.5	~5	Equipment malfunctioning, no data
4	0.30	−70/+100	111.2	50	
5	0.30	15% −50/+70 25% +100 40% +200 15% +325 5% −325	111.2	50	Size distribution following closely equation $1 - P = \exp[-ad^c]$ (Rosin-Rammler)
6	0.30	−60/+70	195.7	53	
7	0.30	−70/+100	195.7	46	
8	0.30	As in No. 5	148.3	55	
9	0.40	As in No. 5	195.7	53	

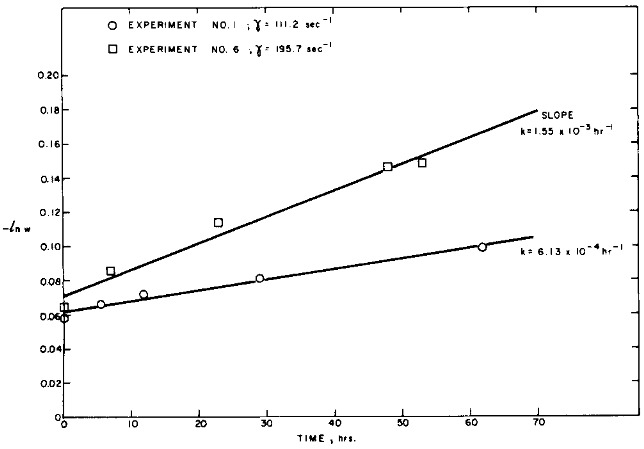

Fig. 2. Effect of shear rate on size reduction coefficient, *k*.

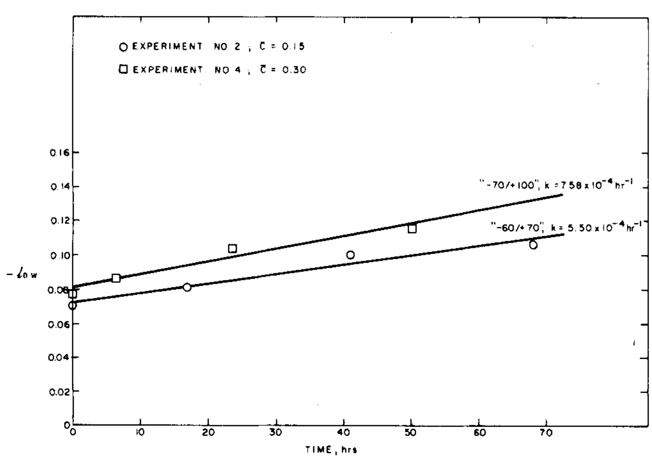

Fig. 3. Size reduction coefficients *k* at shear rate $\dot{\gamma} = 111.2\ s^{-1}$.

after 5 to 7 hr, 23 to 29 hr, and 50 to 55 hr of shearing. The slurry in the cup was mixed well before sample withdrawal. Slurry of the same concentration was used to replace the sample. Standard 3 in. sieves were employed for particle size analyses. Owing to the dead space at the bottom of the cup, approximately 25% of the slurry was not sheared during the tests, and correction of the data was necessary. The formula

$$w_i(t_n)\big|_{cor} = w_i(t_n) + \frac{1}{3}\left[w_i(t_n) - w_i(t_{n-1})\right] \quad (15)$$

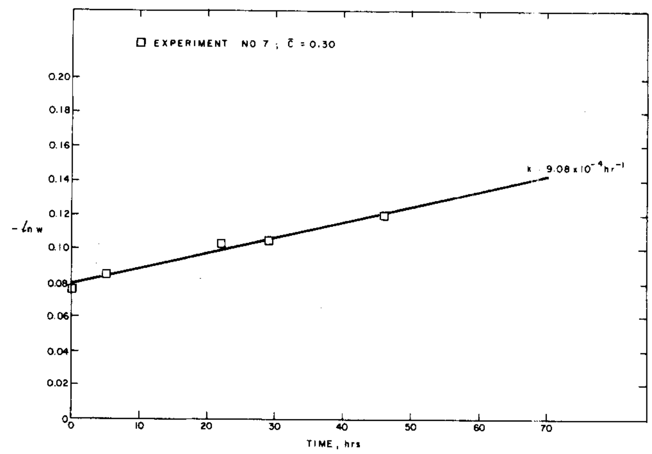

Fig. 4. Size reduction of fraction −70/+100 mesh at shear rate $\dot{\gamma} = 195.7\ s^{-1}$

gives the corrected fraction at time t_n from the measured fractions at times t_n and t_{n-1}. Equation (15) can be easily derived by using simple mass balance considerations. The coefficient $1/3 = 0.25/0.75$ is the relative fraction of slurry which is not sheared between times t_{n-1} and t_n.

DATA INTERPRETATION

Particle Size Reduction Rates

In order to evaluate the coefficient k_i for the size interval of mean diameter d_i, it is convenient to use an initial size distribution with little or no material larger than d_i. By measuring the change of the corresponding weight fraction w_i with time, one can obtain k_i. Figures 2, 3, and 4 show top fraction w variations with time t plotted as $-\ln w$ vs. t. The main fractions characterized as −60/+70 and −70/+100 mesh, with ~85% of material on size, contain also a small percentage (5 to 10%) of −50/+60 and −60/+70 mesh particles, respectively. This small percentage has been included in the weight fractions plotted in Figures 2 to 4 in order to facilitate interpretation of data and to minimize the effect of size analyses errors.

Despite some scatter, the data shown in Figures 2, 3, and 4 exhibit a linear variation, that is, essentially conform to a first-order kinetic formulation. It will be also noticed that the data points at time $t = 0$ show a small consistent deviation and give the impression of a nonlinear variation, at small times. This deviation, however, may be due to a systematic error resulting from sampling or from the correction [Equation (15)] applied to all data points, except

TABLE 2. DISTRIBUTION PARAMETERS $B_{i,1}$ AND $b_{i,1}$ CORRESPONDING TO TOP SIZE "−60/+70", EXPERIMENT NO. 6

Fraction number	Mesh size	Parameters	$t = 0$	Time of shearing $t = 23$ hr	$t = 48$ hr	$t = 53$ hr
1	−60/+70	$B_{1,1} = 1.0$				
		$b_{1,1} = 0.0$				
2	−70/+100	R_2	0.939	0.892	0.871	0.864
		$B_{2,1} = 1.00$				
		$b_{2,1}$		0.510	0.525	0.549
3	−100/+200	R_3	0.985	0.961	0.951	0.949
		$B_{3,1}$		0.490	0.475	0.451
		$b_{3,1}$		0.192	0.214	0.221
4	−200/+325	R_4	0.994	0.979	0.974	0.975
		$B_{4,1}$		0.298	0.260	0.229
		$b_{4,1}$		0.043	0.062	0.031
5	−325	R_5	0.996	0.983	0.981	0.979
		$B_{5,1}$		0.254	0.198	0.198
		$b_{5,1}$		0.254	0.198	0.198

those at $t = 0$. The slopes k in Figures 2 to 4 have been computed by a least-squares fitting of the data.

Comparison of k from experiments 1 and 2 (see Figures 2 and 3) indicates that concentration effects, under the conditions of these experiments, are not very important. The rate coefficient k for $\overline{C} = 0.15$ is slightly smaller than that for $\overline{C} = 0.30$. Also, k tends to increase with mean particle size and, of course, shear rate.

Distribution of Attrition Products

The set of distribution parameters $b_{i,j}$ or $B_{i,j}$ can be determined from the data obtained with narrow size fractions (experiments 1, 4, 6, and 7). An approximate method, suggested by Austin and Luckie (1971) for grinding studies is employed for this purpose. It is assumed that the product $B_{i,j}k_j$ in Equation (12) is a function of i only. Integration of this equation between time 0 and t leads to

$$1 - P_i(t) = [1 - P_i(0)] \cdot \exp[-B_{i,j} \cdot k_j t]; \quad i > j \tag{16}$$

In order to compute the distribution parameters corresponding to the top size fraction $B_{i,1}$, we first recognize that $B_{1,1} = B_{2,1} = 1.0$. Then we apply the above equation twice, to fractions $i = 2$ and $i > 2$, and combine the results to obtain

$$B_{i,1} = \frac{\ln[R_i(0)/R_i(t)]}{\ln[R_2(0)/R_2(t)]} \tag{17}$$

where $R_i(t) \equiv 1 - P_i(t)$. This equation is employed to compute the sets $B_{i,j}$ for top size fractions −60/+70 and −70/+100 mesh. Equation (10) is then used to compute the sets $b_{i,j}$ for each of the above fractions.

The distribution parameters from experiment 6, for three periods of shearing, are listed in Table 2. The practically constant value of each parameter $b_{i,1}$ is evidence that time of shearing does not influence the manner in which the attrition products from size interval −60/+70 are distributed to smaller size fractions. Similar trends are observed in the other experiments, although a few samples give inconsistent distribution parameters.

Table 3 provides a summary of the time average distribution parameters $B_{i,1}$, $b_{i,1}$ from experiments 1 and 6 and $B_{i,2}$, $b_{i,2}$ from experiments 4 and 7. The following interesting observations can be made on the basis of these results. About 50% of the attrition products from a certain size interval j are transferred to the next size range $j + 1$ (compare values of $b_{2,1}$ and $b_{3,2}$). Some products fall into the following range $j + 2$ and the rest (~30%) to the smallest size interval (−325 mesh in this case). Practically no attrition products are transferred to an intermediate size interval, as concluded from the very small value of the parameter $b_{4,1}$ in experiments 1 and 6. These results provide additional evidence that the type of attrition studied here is due to loss of protuberances of a particle and not due to its breakage into several fragments. If the latter took place, the distribution of attrition products would have been more uniform, and the amount of material found in the finest size fraction would have been much smaller.

The results listed in Table 3 have been computed by taking the arithmetic average of values for different times, and some inconsistent sets have been excluded. It is ob-

TABLE 3. AVERAGE DISTRIBUTION PARAMETERS CORRESPONDING TO TOP SIZES "−60/+70" (EXPERIMENT NO. 1 AND 6) AND "−70/+100" (EXPERIMENT NO. 4 AND 7)

Fraction number	Parameters	Experiment No. 1	Experiment No. 6	Parameters	Experiment No. 4	Experiment No. 7
1	$B_{1,1}$	1.0	1.0			
	$b_{1,1}$	0.0	0.0			
2	$B_{2,1}$	1.0	1.0	$B_{2,2}$	1.0	1.0
	$b_{2,1}$	0.340	0.528	$b_{2,2}$	0.0	0.0
3	$B_{3,1}$	0.660	0.472	$B_{3,2}$	1.0	1.0
	$b_{3,1}$	0.326	0.209	$b_{3,2}$	0.551	0.554
4	$B_{4,1}$	0.334	0.262	$B_{4,2}$	0.450	0.446
	$b_{4,1}$	0.005	0.046	$b_{4,2}$	0.149	0.037
5	$B_{5,1}$	0.330	0.217	$B_{5,2}$	0.300	0.409
	$b_{5,1}$	0.330	0.217	$b_{5,2}$	0.300	0.409

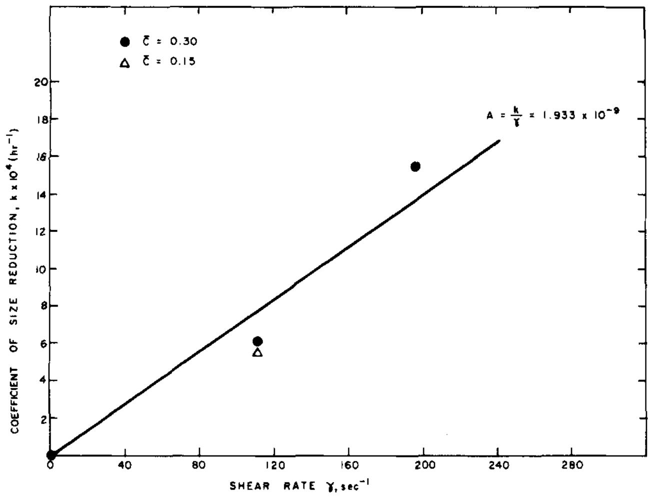

Fig. 5. Approximate variation of size reduction coefficient, k at small shear rates; data for size interval $-60/+70$ mesh.

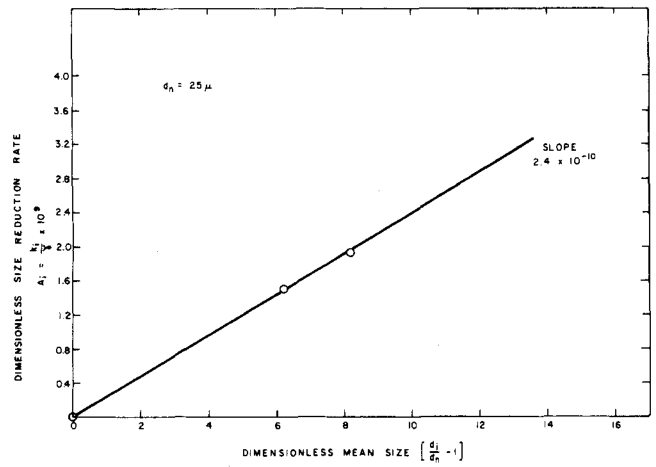

Fig. 6. Effect of particle size on dimensionless size reduction rate A.

vious that additional data with larger particle sizes are needed in order to draw more definite conclusions about the distribution of attrition products.

PREDICTION OF CHANGES OF WIDE PARTICLE SIZE DISTRIBUTIONS DUE TO ATTRITION

In this section it will be demonstrated how the data on k_i and $b_{i,j}$ can be used to predict changes of wide particle size distributions due to attrition. Figure 5 shows the approximate variation of k_i with shear rate for the size interval $-60/+70$ mesh; that is, $d = 250$ to $210\ \mu$. A similar variation of k_i with $\dot{\gamma}$ is obtained with size interval $-70/+100$ mesh. The linear variation assumed here may not be accurate, in general. The slope of the line in Figure 5

$$A \equiv \frac{k}{\dot{\gamma}} \tag{18}$$

will be called dimensionless size reduction rate.

The attrition rate tends to zero at small particle diameters. In practice we often consider particles smaller than $-44\ \mu$ as very fine because they approach dimensions characteristic of colloidal suspensions. We assume, therefore, that the reduction rate of fines, with mean diameter $d_n \simeq 25\ \mu$, is zero. By defining the dimensionless mean particle size as $(d_i - d_n)/d_n$ and by using the previously determined values of A, we obtain the linear expression (see Figure 6)

$$A_i \equiv \frac{k_i}{\dot{\gamma}} = 2.4 \times 10^{-10} \times \left[\frac{d_i}{d_n} - 1\right] \tag{19}$$

relating the size reduction rate k_i to the mean particle diameter d_i and shear rate $\dot{\gamma}$.

The results for the distribution parameters $b_{i,j}$ obtained in the previous section can be used to develop some fairly general rules for estimating these parameters. The data listed in Table 3 suggest that as a first approximation we can consider the $B_{i,j}$ values as normalized (Austin and Luckie, 1971). This property is expressed as follows:

$$B_{i,j} = B_{i+1-j,1} \quad ; \quad b_{i,j} = b_{i+1-j,1} \tag{20}$$

and describes a similarity in the distribution pattern of attrition products from various fractions. The obvious practical advantage of having normalized $B_{i,j}$ (or $b_{i,j}$) values is that the set $B_{i,1}$ (or $b_{i,1}$) is sufficient to determine all the parameters $B_{i,j}$ (or $b_{i,j}$). For example, $b_{3,1} = b_{4,2} = b_{5,3} = b_{6,4} = \ldots$. It should be pointed out that the last row ($i = n$) of the matrix $b_{i,j}$ is computed as

$$b_{n,j} = 1.0 - \sum_{i=j}^{n-1} b_{i,j} \quad ; \quad j = 1, 2, \ldots n-1 \tag{21}$$

in order to preserve the mass balance of the attrition products.

Table 4 includes the average values of all equivalent $b_{i,j}$ parameters obtained in our experiments (see Table 3). In order to predict particle size changes in the problem under study, we round off these numbers and use the approximate values of $b_{i,1}$ shown in Table 4. In a problem involving a wider spectrum of sizes, that is, more than five size intervals, we may use the set

$$b_{2,1} = 0.5, \quad b_{3,1} = 0.2, \quad b_{4,1} = 0, \ldots, \quad b_{n-1,1} = 0, \quad b_{n,1} = 0.30$$

We have now available all the necessary information for computing the change of a wide particle size distribution, with time, due to attrition. The system of Equations (14) can be solved by using either the closed-form solution of Reid (1965) or well-known numerical techniques such as the Runge-Kutta method or a modified Euler method. The latter was employed in our computer calculations. In Table 5 predictions are compared with data from experiments 5, 8, and 9 with relatively wide particle size distributions. The changes due to attrition are small, but even so the agreement between measured and predicted distributions, for 50 to 55 hr of shearing, is good. For most of the cumulative size fractions, the absolute error, expressed as the ratio [R_i (measured) $-$ R_i (predicted)]/[R_i (initial) $-$ R_i (measured)], is less than 30%. The differences between data points and predictions may be partly due to errors in the particle size analyses at time $t = 0$, which are used as initial conditions in the calculations.

TABLE 4. NORMALIZED DISTRIBUTION PARAMETERS; $b_{i,j} = b_{i+1-j,1}$

Data (arithmetic average from Table 3)	Approximate values of $b_{i,1}$
$b_{2,1} = b_{3,2} = 0.493$	$b_{2,1} = 0.50$
$b_{3,1} = b_{4,2} = 0.180$	$b_{3,1} = 0.20$
$b_{4,1} = 0.013$	$b_{4,1} = 0$
$b_{5,1} = b_{5,2}^{*} = 0.314$	$b_{5,1} = 0.30$
1.000	1.00

* In general, $b_{5,1} \neq b_{5,2}$. They are equated here because in our study $b_{5,2}$ is the last element of the array $b_{i,2}$ [see also Equation (21)].

TABLE 5. COMPARISON BETWEEN MEASURED AND PREDICTED CUMULATIVE WEIGHT FRACTIONS, R

Particle size, μ	Experiment No. 5 Measured initial	Measured* $t = 50$ hr	Predicted $t = 50$ hr	Experiment No. 8 Measured initial	Measured $t = 55$ hr	Predicted $t = 55$ hr	Experiment No. 9 Measured initial	Measured $t = 52$ hr	Predicted $t = 52$ hr
−297/+210	0.145	0.140	0.139	0.142	0.140	0.134	0.143	0.137	0.133
+149	0.389	0.381	0.379	0.387	0.382	0.373	0.388	0.377	0.370
+125	0.501	0.491	0.493	0.492	0.485	0.481	0.490	0.477	0.475
+105	0.585	0.581	0.578	0.586	0.576	0.576	0.576	0.564	0.564
+74	0.770	0.769	0.762	0.783	0.772	0.772	0.778	0.756	0.764
+44	0.893	0.883	0.886	0.896	0.881	0.886	0.890	0.875	0.878
−44	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

* Average of two PSD analyses.

DISCUSSION OF RESULTS

The first-order law of particle diminution was shown to describe satisfactorily the process of coal attrition in shear flow of concentrated suspensions. Indeed, the kinetic parameters k_i and $b_{i,j}$ were found to be practically independent of time of shearing. Additional experiments will be required to examine the applicability of this model to other suspensions and at much higher shear rates than those employed in the present study. However, the successful application of similar models to particle size reduction in grinding equipment (see, for example, Austin, 1971; Austin and Luckie, 1971), where the forces on the particles are much greater than in flowing slurries, suggests that the basic formulation given here may also describe attrition in other flow fields of practical interest.

Equation (19) relating the rate coefficient k_i to particle size d_i and shear rate $\dot{\gamma}$ is based on limited data and is expected to provide only rough estimates of k_i. We should also hasten to point out that the effect of concentration on k_i has not been adequately examined in this study, although the experiments with 15 and 30% vol. solids have indicated that it is of secondary importance at high concentrations.

Data analyses show that the size distribution of attrition products can be described by normalized $b_{i,j}$ parameters, that is, $b_{i,j} = b_{i+1-j,1}$, in conjunction with the set of values $b_{2,1} = 0.50$, $b_{3,1} = 0.20$, $b_{4,1} = 0, \ldots, b_{n,1} = 0.30$. The influence of shear rate on this distribution was not apparent in our experiments.

The very low values of the rate coefficient k_i in connection with the above distribution of attrition products, characterized by a high percentage of very fine particles and no intermediate fractions, provide solid evidence that the size diminution studied here is due to particle surface abrasion. It would be of interest to examine in future studies whether this process continues almost indefinitely, which implies that surface roughness is not reduced despite the overall size reduction, or whether it tends to create a more regular particle shape with rounded edges. Some observations made by Berkowitz et al. (1963) suggest that the latter mode prevails in coal slurries under extreme conditions, such as repeated passage through pumps in short pipe loops.

Several important questions regarding attrition have not been dealt with in this paper, for example, the effect of particle physical properties (initial particle shape, density, strength, etc.) on size reduction rate or the significance of particle-particle collisions as compared to particle impact on solid boundaries, especially in turbulent flow. Answers to such questions require basic information, about the flow field and the attrition mechanism, which is not available at present. It is hoped, however, that this paper will stimulate some interest and that subsequent studies will shed more light on this problem.

ACKNOWLEDGMENT

The author is grateful to ShelPac Research and Development, Ltd., Toronto, Canada, for supporting this work and to Shell Development Company for permission to publish it.

NOTATION

A_i = dimensionless size reduction rate, $k_i/\dot{\gamma}$
$B_{i,j}$ = breakage distribution function (matrix); represents the cumulative fraction of attrition products from size j falling into all size intervals smaller than, and including, i
$b_{i,j}$ = distribution parameters, defined by Equation (10); represents fraction of attrition products from size j falling into size i
$\overline{C}$ = mean particle concentration by volume
d_i = average particle diameter
k_i = kinetic or rate coefficient, corresponding to particle size d_i
P_i = cumulative fraction of particles of size smaller than d_i
R_i = cumulative fraction of particles of size larger than d_i
w_i = weight fraction corresponding to particle diameter d_i

LITERATURE CITED

Austin, L. G., "A Review Introduction to the Mathematical Description of Grinding as a Rate Process," *Powder Technol.*, **5**, 1-17 (1971-72).

———, and P. T. Luckie, "Methods for Determination of Breakage Distribution Parameters," *ibid.*, 215-222 (1971/72).

Berkowitz, N., et al., "The Pipeline Flow of Coal-in-Oil Suspensions," *C. J. Chem. Eng.*, **41**, 116-121 (1963).

Bjorklund, I. S., and J. C. Dygert, "Small Scale Tests for Attrition Resistance of Solids in Slurry Systems," *AIChE J.*, **14**, No. 4, 553-557 (1968).

Forsythe, W. L., Jr., and W. R. Hertwig, "Attrition Characteristics of Fluid Cracking Catalysts. Laboratory Studies," *Ind. Eng. Chem.*, **41**, No. 6, 1200-1206 (1949).

Gwyn, J. E., "On the Particle Size Distribution Function and the Attrition of Cracking Catalysts," *AIChE J.*, **15**, No. 1, 35-39 (1969).

Reid, K. J., "A Solution to the Batch Grinding Equation," *Chem. Eng. Sci.*, **20**, 953-963 (1965).

Rumpf, H., "Beanspruchungstheorie der Prallzerkleinerung," *Chem.-Ing. Technik*, **31**, 323-337 (1959).

Worster, R. C., and D. F. Denny, "Hydraulic Transport of Solid Material in Pipes," *Proc. Inst. Mech. Engrs.*, **169**, No. 32, 563 (1955).

Manuscript received November 12, 1975; revision received and accepted May 3, 1976.