Grinding Aids†

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Abstract

The use of chemical additives for improving the efficiency of both wet and dry comminution is reviewed. Although such additives can affect breakage strength under general comminution conditions crack velocities are probably too great to involve adsorption effects. Additives in dry grinding systems appear to function by coating the particles and preventing reagglomeration. In wet grinding systems, their main influence on grinding is through their effect on slurry rheology. Such additives do not affect the specific energy for grinding but only regulate mill power draft and kinetics.

1. Introduction

The large tonnages of mineral raw materials comminuted annually, the low energy efficiency and high energy intensity of grinding operations in conventional tumbling mills together with the depletion of high-grade, coarse-grained ores over the years have all compelled researchers to find ways to improve the overall performance of grinding mills. Of the gross energy input to the mill, perhaps only 1 or 2 percent of it results in the production of new surface area. Most of the input energy ends up as heat, resulting from transmission losses, deformation and wear of crushing media and crushing surfaces, fruitless impacts or stresses, friction, kinetic energy, elastic and plastic deformation, and sound. During some comminution operations, reagglomeration of particles (an energy loss) or de-agglomeration (an energy gain) can occur. In some devices, the kinetic energy of the comminuted fragments might result in secondary breakage. Adding certain chemicals, which are often surface-active, to the mill feed in small quantities (0.1 percent of the feed solids) to improve mill throughput in both dry and wet grinding has been widely reported in the literature (1,2). In the cement grinding industry, grinding aids have now been regularly employed in plants for several decades. Although a large number and variety of chemicals are reported to be efficacious as grinding additives, for the most part their mechanisms have not been precisely delineated (1,2).

There are many reasons why the mechanisms by

which these aids improve mill performance are not well understood. First, only in a few of the more recent studies reported has the energy expended for grinding been taken into account, even though it is well recognized that energy is a rational basis for the analysis of grinding results. In most of the studies, batch grinding experiments with and without additive were performed for a certain length of time, and the energy expended by the mill was assumed to be the same whether the additive was present or absent. This implies identical mill power in both cases. However, in wet grinding, the power drawn by the mill can be significantly influenced by the presence/absence of the additive, particularly in slurries at high solids content.

Second, the surface area of the ground product has generally been measured using air permeability methods. Changes in the specific surface of samples ground in the presence of an additive are very unsatisfactory indicators to deduce the effect of these aids if the surface area is measured by air permeametry. The additives are generally surface-active, and therefore give rise to dispersion/agglomeration effects with powders, which is the actual purpose for their use in industrial dry grinding systems, but the specific surface measured with air permeability methods on such dispersed/agglomerated samples can lead to erroneous inferences.

Under these circumstances, despite a large number of papers available on the subject, a coherent understanding of the mechanism(s) by which additives may improve the performance of tumbling mills has been elusive. Often the first explanation given for the action

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of a grinding aid has been that it reduces the breakage strength of the material being comminuted. However, in his paper on the physical aspects of comminution, Rumpf (3) showed from theoretical considerations that it is very unlikely that changes in the environment brought about by an additive would improve the efficiency of a grinding operation, measured in terms of energy. Perhaps, the most detailed research reported on additives is that of Klimpel and co-workers (4) on the use of polycarboxylates in wet grinding systems; their research clearly points to the action of those additives being the control of slurry rheology.

Comminution involves several subprocesses: 1) the transport of particles to the zone in the mill where they can be stressed, 2) loading or stressing of the particles such that they fracture, 3) prevention of reagglomeration of the fine fragments and 4) the removal of fine broken particles from the grinding zone. Grinding aids potentially can play a role in all four of the subprocesses that occur during comminution. The mechanisms involved in grinding aid action may include 1) the reduction of breakage energy, 2) embrittlement to reduce plastic deformation 3) the flocculation/dispersion of fines, 4) the prevention of reagglomeration, and 5) control of slurry rheology. A useful objective for a grinding aid in ore milling would be to foster breakage along grain boundaries, thereby enhancing liberation. The overall objective of this paper is to review and discuss how various types of chemical additives might or might not affect comminution subprocesses and energy losses.

2. Crack Propagation and Fracture Energy

The production of fine particles involves the propagation of cracks when materials are stressed mechanically above their breakage strength. Both bulk and surface properties of a material determine the energy required for fracture. Any aspect of the chemical environment that can affect breakage energy and crack propagation could be considered to be a grinding aid.

The Griffith theory for the energy balance in crack extension states that a crack will propagate if the loss in elastic strain energy is greater than the increase in surface energy accompanying the formation of new surface. For a crack of length $2a$ inside a specimen, the fracture strength, σ_f , is given by (5):

$$\sigma_f = \frac{2Y\gamma^{1/2}}{\pi a} \quad (1)$$

where Y is the modulus of elasticity and γ is the surface free energy of the solid material. Often the Griffith criterion for fracture is written as:

$$\sigma_f = \frac{YG_c^{1/2}}{\pi a} \quad (2)$$

where G_c is the total work of fracture. Quite early on, fracture researchers recognized that plastic deformation might be occurring in the region around the crack tip so that the energy to form the crack surface may exceed the surface energy of the material. Thus, G_c may involve the energy required not only for the formation of new surface, but also for plastic deformation, chemical reactions, etc.

Controlled cleavage of solid materials has been quite widely used to determine the surface free energy of solids and the results show good agreement with calculated values and with the results from other kinds of measurements. Under controlled cleavage of brittle solids, all of the energy put into the system can be accounted for as either strain energy or surface energy (6). This would be the ultimate in the energy efficiency of comminution.

After detailed consideration of the energies involved in the controlled cleavage of quartz under various experimental environments, Parks (7) has analyzed how stages of water adsorption reduce the surface free energy of quartz. As discussed by him, the presence of water has a major effect on the surface energy of quartz, a phenomenon that must be taken into account when analyzing the results of experimentally fracturing quartz.

How much the surface free energy, γ , is reduced by adsorption is given by the Gibbs adsorption equation:

$$d\gamma = -\sum \Gamma_i d\mu_i \quad (3)$$

where μ_i is the adsorption density of species i and Γ_i is its chemical potential. Parks' estimates of the surface and interfacial free energies of quartz through consideration of its interaction with water are given in **Table 1**. The greatest reduction in the surface-free energy of quartz comes from the chemical reaction of water vapor molecules with $\equiv \text{Si-}$ and $\equiv \text{SiO-}$ sites at the fracture surface to form surface silanol groups, that is $\equiv \text{SiOH}$ surface sites.

Hammond and Ravitz (8) measured the tensile breaking load of annealed fused silica rods in various

Table 1 Estimated Surface and Interfacial Energies of Quartz (7)

Surface or Interface	Free Energy, mJ/m ²
γ_s (quartz/vacuum)	>2000
γ_{sh} (quartz/silanol surface)	480 – 690
γ_{sf} (quartz/saturated water vapor)	406 – 458
γ_{sw} (quartz/liquid water)	335 – 385

saturated vapors and found that the breaking load decreased in accordance with the reduction in surface tension brought about by the adsorption of the vapor. The Gibbs adsorption equation was used to calculate the lowering of the surface tension of the solid. **Table 2** summarizes their results. Although they baked the specimens at 800°C at 10^{-4} torr for 30 minutes, their results indicated that the surface free energy of the fused silica rods was 400 mJ/m², which is a rather low value.

In a study of the effect of dissolved surfactants on the stress required for the propagation of cracks in synthetic quartz crystals, Dunning et al. (9) found the mean values of the crack propagation stress in air (ambient humidity) to be 69.7 MPa, 60.5 MPa in liquid water, 48.6 MPa in 3×10^{-4} M dodecyltrimethylammonium bromide (DTAB) and 45.3 MPa in 1×10^{-3} M DTAB. Cationic organic surfactants, such as DTAB, strongly adsorb on silica from aqueous solutions. In addition, morphological studies showed that the cracks propagated in DTAB environments were often bifurcated. This work provides an indication that adsorption from aqueous solution can affect fracture behavior.

Table 2 Surface Energy Lowering and the Fracture Strength of Silica Rods in Various Saturated Vapors (8).

Saturated Vapor	Surface Free Energy	
	Lowering mJ/m ²	Fracture Strength, MPa
Vacuum	0	91.1 ± 4.8
Dry benzene	52	93.9 ± 6.9
Butyl alcohol	85	82.2 ± 4.1
Propyl alcohol	110	66.3 ± 0.7
Water	244	55.2 ± 3.9
Water*	244	45.6 ± 4.8

(*This series of breakage tests was carried out after 100 minutes of exposure to water vapor, whereas all of the other results were for 10 minutes of exposure).

The results given in **Table 2** indicate that there are time effects involved in the action of an additive on breakage strength. Clearly, since the diffusion of molecules to the crack tip and possible chemical reaction require finite time, the environment can affect crack propagation only if the crack velocity is sufficiently low (as would be the case in controlled cleavage experiments). Schoenert (5) reported the results of crack velocity measurements in glass as a function of crack extension energy, G_c , under different environmental conditions. **Figure 1**, adapted from his paper, shows crack velocities as a function of G_c for glass in vacuum (10^{-4} and 10^{-6} torr), humid air and liquid water at room temperature (20–23° C).

Clearly, water strongly influences and promotes crack propagation at slow rates. As an example, a crack propagates at a velocity of 10^{-4} cm/sec in high vacuum when G_c is 8.5 joule per m² whereas only 2.4 joule per m² is required in liquid water. **Figure 1** shows that at a crack velocity of about 0.05 cm per sec, the presence of water in the vapor has no effect on the system, that is the G_c value is not affected by water-vapor stress corrosion (the formation of surface silanols).

In dry grinding in ball mills, the loading time is less than 1 second and cracks will propagate faster than 10^{-1} cm/sec. Therefore, one must conclude that for dry grinding neither adsorption nor chemical reaction can influence crack propagation in a comminution mill. For wet grinding, however, crack velocities must be greater than 10 cm per sec before the influence of the environment becomes negligible.

3. The Concept of Surface Energy Reduction in Grinding Aid Action

Some of the studies summarized in the previous section showed that the amount of work involved in propagating a slow crack (that is in forming new crack surface) in a brittle material is related to the surface free energy of the material, and that the energy to propagate a crack can be reduced through adsorption at the surface.

Fig. 1 Crack velocity in glass as a function of crack extension energy, G_c , in high vacuum, humid air, and liquid water (after Schoenert, Ref 5).

Since comminution involves the production of new surface, the amount of energy required to produce a given amount of surface should be reduced by decreasing the surface energy of the material being comminuted. This relatively intuitive mechanism was believed to be responsible for the improved efficiency of rock drilling, as suggested by Rehbinder and Kalinkovaskaya (10). Rose and Sullivan (11) extended this concept of adsorption-induced decrease in surface energy to explain the mechanism of grinding aids in tumbling mills. However, crack propagation velocities measured by Schoenert in dry systems are such that adsorption cannot take place rapidly enough to affect dry comminution. Others have also suggested that crack propagation velocities in impact breakage that occurs in grinding mills are much greater than the spreading velocities of the surfactant molecules by diffusion into the cracks. As indicated by the work of Locher and von Seebach (12), even vapors of a (liquid) grinding aid adsorbed on the solid surface cannot improve breakage efficiency by decreasing the surface energy of the solid. It is, therefore, very doubtful that adsorption-induced surface energy changes can be responsible for the mechanism of grinding aid action in dry systems.

Westwood and Goldheim (13) showed that adsorption of surfactants from solution can reduce the strength of materials only when plastic deformation is important in the process of fracture. According to them, the adsorption of the surface-active molecules or ions on the solid surface essentially blocks the motion of dislocations near the surface, rendering their motion under stress gradients very difficult. Material plasticity due to dislocation movement is thus greatly reduced and the solid is rendered brittle. This mechanism applied to tumbling mill grinding is also subject to criticism similar to the foregoing discussion on Rehbinder's effect, namely that the rate of dislocation movement is much lower than crack propagation rates in impact fracture. Locher and von Seebach (12) have also given experimental evidence indicative that Westwood's mechanism is probably inoperative.

It has been suggested that molecules of the grinding aid might penetrate deep into the tips of pre-existing cracks and exert pressure on the crack tips, aiding the fracture process. The role of this in impact fracture is, again, doubtful, since, as pointed out by Somasundaran (14), long-chain organic surfactants which would have limited diffusion owing to their larger size.

A further factor to be considered is that the environment may influence the level of strain energy in the

particle when cracks begin to propagate but may not affect the amount of energy needed to achieve the desired level of size reduction. For example, in a study of the breakage of Pyrex glass cylinders, Sullivan and Fuerstenau (15) found that the relation between breakage energy, E , and product particle size could be expressed by:

$$E = CX_m^{-1} \quad (4)$$

where C is a constant and X_m is the Gaudin-Schuhmann size modulus of the product. Annealed specimens broke at a load of 9500 kg whereas unannealed specimens broke at a much lower load, namely at 4300 kg. However, the product from the annealed specimens was much finer and obeyed the same relation (Eq. 4). These results suggest that even if an adsorbed species lowers the initial breakage strength, the relation between specific energy and the size distribution of the product may not be altered.

4. Grinding Aids in Dry Systems

Historically, considerably more effort has been expended in developing grinding aids for dry grinding systems than for wet grinding systems with most of this work being oriented toward the cement industry, where huge amounts of cement clinker are dry ground in ball mills. Cement clinker is particularly difficult to grind, and the fine grinding of this material is one of the chief problems of that industry. The first commercial use of grinding aids in the cement industry came about 50 years ago. These grinding aids, which are generally organic liquids added in amounts usually not exceeding 0.25% by weight, are used to increase the product fineness at a given production rate or to increase the production rate at a given product size. The benefits of any grinding aid must outweigh its cost; furthermore, the grinding aid should have no detrimental effect on downstream processing or the finished product. Given these constraints, the industrial acceptance of grinding aids in the cement industry that took place over a period of 10 to 15 years must be considered relatively rapid.

Figure 2 shows a typical comparison between the grinding of cement clinker with and without a grinding aid. As recently reviewed (See Reference 17 for sources), 0.1% of di- or tri-ethanolamine increases the rate of clinker grinding by 22-29%, with glycerol and lower alcohols being less effective. A 25-50% increase in the production rate has been reported with glycol as the grinding aid. The use of

Fig. 2 A typical comparison between grinding of cement clinker with and without a grinding aid in a laboratory mill (after Ref. 16).

0.05% propylene glycol in pilot plant grinding tests showed that a 20% increase in production accompanied by a 10% decrease in energy costs is possible. The addition of as little as 0.01-0.05% of organo-silicones has been found to decrease grinding time by 70%. In addition to these, other additives have been shown to have grinding aid characteristics for grinding cement clinker, including resins, cod oil, kojic acid, carbon blacks, wool grease, calcium sulfate, urea, asphaltenes, etc. In general, experience has shown that polar grinding aids are more effective than nonpolar additives. The addition of hydrophilic surface-active substances such as calcium ligno-sulfonates during the comminution of cement clinker allows production of highly effective plasticized cements. In an analogous manner, it is possible to obtain hydrophobic cements by introducing hydrophobic-type additives (acidol-naphthenate soap or sodium abietate) during comminution. These additives comprise about 0.1% of the mass of the pulverized cement.

The effect of grinding aids on the grinding of materials other than cement clinker has also been reported. Some examples (See Ref. 17) include the use of wool grease in the grinding of gypsum, limestone, and quartz, the effect of hydrocarbons in the milling of aluminum powder, the use of silicones in the ball mill grinding of quartz; and the use of acetone, carbon tetrachloride, benzene and nitromethane in the vibratory milling grinding of glass, marble, and quartz.

In view of the inability of theories based on adsorption-induced improvement of the breakage or fracture subprocess to explain the action of grinding aids, it has been postulated by many researchers

that their effect is in controlling the agglomeration and flow characteristics of material in the mill. The idea that grinding aids caused dry dispersion of material was suggested over 50 years ago when a considerable increase in dust was noticed in the early commercial uses of grinding aids in cement grinding (18). Observations like these over a period of time suggested that grinding aids coat the cement particles, shielding them from agglomerating forces and thereby preventing the particle from welding back together again. It has been argued that grinding aids readily satisfy the valence forces produced by material fracture (16, 19). Since grinding aids usually are polar substances, they can preferentially adsorb on specific sites where the breakage of electrovalent or covalent bonds result in residual electrical forces. By the same token, at least part of the improved efficiency in wet grinding over dry grinding may be attributed to the polar nature of water.

It is believed, therefore, that grinding aids which chemisorb on solid particles would most effectively reduce adhesive tendencies between particles and thereby improve grinding efficiency. Since adhesive forces are (particle-size) surface-area dependent, the relative improvement in grinding efficiency is greater, the finer the product size (12, 17). It should be noted that most of the surface area data were obtained by air permeability methods and this tends to magnify the benefits of grinding aids when assessing the results in terms of new surface.

At very fine grinds, the tendency of ground particles to coat the grinding media and mill liner becomes very pronounced and has long been considered to limit the effectiveness of the grinding process. There has been some diversity in opinion as to whether grinding aids are effective only in reducing ball and liner coating but, as Mardulier (16) points out, this can be considered as a special and extreme case of agglomeration.

5. Grinding in Liquids

As pointed out earlier, perhaps water itself can be considered a grinding aid because of the improved efficiency and mill capacity obtained with wet grinding relative to dry grinding. **Figure 3**, plotted from the results from Coghill and DeVaney (20) for the grinding of dolomite in a pilot-scale ball mill, clearly shows better grindability of the material over the entire range of mill holdups in wet grinding as compared to dry grinding. A variety of reasons have been put forth to explain this phenomenon. As discussed earlier, the effect of water is believed by some to

Fig. 3 Comparison between the grindability of dolomite when ground under wet and dry conditions as a function of holdup in a ball mill (data from Ref. 19).

be due to its polar nature and consequent ability to satisfy the surface residual electrical forces created upon fracture, thereby reducing adhesive tendencies between the ground particles (16). In liquid water, the surface energy (7) and the energy to propagate cracks is markedly reduced (5). Also, the cushioning effect of fine particles in wet grinding will be minimal because they become suspended in the liquid. This would lead to increased grinding action on the coarser particles, with improved grinding efficiency.

Meloy and Crabtree (21) proposed that the surface tension of the liquid enables particles to cling to balls and move into the zone of maximum grinding action. Their results indicate that particles are ground more rapidly in liquids of high surface tension. They also found that larger particles are ground more rapidly in a more viscous liquid, while smaller particles show the opposite effects. This they attributed to two competing phenomena: at higher viscosity, the coarser particles tend to be lifted into the grinding zone, while the cushioning effect is enhanced. This implies the existence of an optimum liquid viscosity for grinding. Similar results were reported by Schweyer in 1942 (22). Although grinding in organic liquids is economically prohibitive in most cases, these studies imply that to obtain a narrow size distribution in the product, a high viscosity liquid might be used as the grinding environment if the material to be ground has a high unit value. Kapur et al. in 1965 (23) showed that the specific gravity of the material with respect to the environment is important; if the material is less dense than the environment (the liquid in which it is ground), it tends to float away from the grinding zone in the mill, which reduces comminution. A detailed analysis of the role of fluid density on comminution was recently carried out (24). The study

showed that with different liquid fluids the grinding path remains invariant even though the energy input is throttled significantly with increase in fluid density.

Although organic liquids tend to be economically impractical, it must be mentioned that many of them have been shown on a laboratory scale to provide more efficient grinding environments than water. Several workers observed that grinding in alcohols appears to be more efficient than grinding in water, an example being doubling the surface area per unit of expended energy for grinding quartz in alcohol. The results of Lin and Mitzmager (26) are rather interesting in that grinding in nonpolar carbon tetrachloride and methylcyclohexane actually decreased the rate of fine particle production somewhat compared to the corresponding rate in water. However, this decrease was not observed if only a small amount of water was dissolved in the organics, indicating that polar water molecules in such a system may be acting as a grinding aid.

6. Additives in Wet Grinding Systems

As with grinding aids in dry grinding systems, a fairly large number of investigations on the effectiveness of chemical additives for wet grinding have been reported in the literature mostly for laboratory-scale investigations.

In 1942, Szantho (27) demonstrated that Flotigam P (C12-C14 amine) in concentrations of up to 0.03% produced a 100% increase in surface area of quartzite and limestone. As can be seen from the results given in **Figure 4**, the effectiveness of the grinding aid increases with increasing concentration to a maximum, beyond which further additions cause

Fig. 4 Effect of a commercial flotation reagent (Flotigam P) on the grinding of quartzite and limestone in a rod mill. An optimum Flotigam P concentration of about 0.03% results in a maximum increase in product surface area (After Szantho, 27).

a decrease in the specific surface area of the products. As summarized (Ref. 17), some other reported examples of the beneficial effects of grinding aids in wet grinding include the work of Khodakov and Rehbinder (1961) on the ball milling of quartz; Kokolev et al. who found a four-fold decrease for the time of grinding alumina in the presence of about 0.005% organo-silicones; and Orlava et al. on the grinding of zircon and other minerals with 0.2% triethanolamine, giving a four-fold decrease in grinding time. In some cases (17, 27), the addition of organic liquids to a wet grinding system has been reported to decrease grinding efficiency.

There has also been considerable study of the effects of inorganic electrolytes on grinding performance (14, 17). Although there are some ambiguities, it can be generally concluded that some improvement in grinding results from the addition of an optimum electrolyte concentration and that dispersing agents improve wet comminution performance.

More recently, Somasundaran and El-Shall (28, 29) conducted a detailed experimental investigation of the application of both inorganic and organic additives to wet ball mill grinding, with details of ionic strength and pH control being given. In a study of the wet grinding of quartz in a laboratory ball mill, Somasundaran and El-Shall (29) found that the addition of dodecylammonium chloride (a cationic surfactant) can be either beneficial or detrimental to the grinding process,

depending upon the pH and the concentration of amine. Using the change in the percentage of minus 200-mesh quartz produced as an index of grindability, they found that in neutral or alkaline solutions, the amine is beneficial to the process whereas under acidic conditions, the effects of amine additions are detrimental (29). Plots of their results, have the same general shape as curves showing the effect of pH and amine concentration on contact angles or flotation response of quartz in other words, significant effects occur upon amine adsorption.

In order to delineate what must be responsible for these complex effects, they also conducted single-impact breakage experiments, flocculation/dispersion studies, and measurements of suspension fluidity. The results given in **Figure 5(a)** and **5(b)** show how pH affects all of these properties of quartz in the presence of 10^{-3} M amine additions and 10^{-5} M AlCl_3 , respectively. Both the amine and the aluminum chloride affect the grinding process because of their effect on primary breakage and pulp fluidity. The grindability index for AlCl_3 addition was the change in the production of minus 400-mesh particles. In the case of the AlCl_3 addition, improvement in the acidic pH range results from improved pulp fluidity as well as enhanced primary breakage; at pH 10 decreased pulp fluidity and enhanced dispersion retards grinding rate. Somasundaran and El-Shall (28) have summarized the explanation of their results for a

Fig. 5 (a) Effect of pH and 10^{-3} M dodecylammonium chloride on grindability, particle breakage, suspension fluidity, and degree of flocculation/dispersion of quartz.

(b) The same for 10^{-5} M aluminum chloride solutions (after 28).

number of additives and pH conditions (Table 3). The fluidity (rheology) and degree of dispersion of the suspension appears to have a major role in this system.

7. Polymeric Grinding Aids

Klimpel and coworkers (4, 30, 31) have written an extensive series of papers concerning the use of hydrophobic polymers as grinding aids, including not only extensive laboratory studies but also plant-scale applications. An example of the type of results that Klimpel and coworkers obtained for wet batch ball milling is given in Figure 6, which shows the production of minus 325-mesh taconite as a function of weight percent solids in the slurry. Without any grinding aid, the production of minus 325-mesh product falls off markedly as the slurry density increases above 80 percent solids. With the addition of the grinding aid, (a polycarboxylate designated as XFS 4272 by Dow Chemical Company) the production of minus 325-mesh product increased markedly. Grinding at such high pulp densities in the presence of 0.03 percent of the additive resulted in a higher than average mill torque, a more finely ground product and a pulp of lower viscosity.

From their extensive test work, Klimpel and coworkers conclude that significant advantages can be realized by using grinding aids if 1) the mill is operated in a region of percentage solids high enough so that a further increase produces a large slurry viscosity increase in the absence of the grinding aid, 2) the solids in the slurry have sufficient adsorption capacity for the grinding aid so that it can improve the slurry dispersion characteristics, and 3) the grinding aid has consistently good dispersion characteristics over

Fig. 6 The net amount of fines produced during grinding plotted against the percent solids in the pulp. The number beside the experimental points are the values for pulp viscosity in thousand centipoises (after Ref. 30).

the range of physicochemical conditions (such as slurry pH, intensity of mixing, etc.) encountered in practical operation of the mill.

As a consequence of increasing the solids content of a suspension, the rheological characteristics of a slurry may change from Newtonian to non-Newtonian. This transition is always accompanied by an increase in the viscosity of the suspension. There are three controllable factors which regulate the rheological properties of a pulp or slurry: 1) slurry density, 2) particle size distribution, and 3) chemical environment. Particle shape (which also has a major effect) cannot be controlled in comminution systems. As grinding proceeds, at a given solids concentration, the particle size distribution changes and the produc-

Table 3 Summary of the Various Conditions Leading to Enhancement or to a Reduction in the Rate of Grinding Quartz in Aqueous Systems (after Somasundaran and El-Shall, Ref. 28).

Enhanced Grinding		Reduced Grinding	
Condition	Possible Mechanism	Condition	Possible Mechanism
<u>Water</u>			
low pulp density	higher pulp fluidity	higher pulp density	decreased pulp fluidity
acidic solution	better dispersion of particles	alkaline solution	decreased pulp fluidity
<u>Aluminum Chloride</u>			
acidic solution	improved pulp fluidity and primary breakage	acidic solution	flocculation of particles
neutral solution	better dispersion of particles	neutral solution	decrease in pulp fluidity
<u>Amine</u>			
alkaline solution	improved primary breakage and pulp fluidity balanced partly by increased flocculation.	<u>Sodium Silicate</u>	— —
		<u>Sodium Sulfate</u>	— —
		all pH conditions	— —

tion of fresh surface adsorbs chemicals present in the system and, thus, slurry rheology can change with time. Recently, Velamakanni and Fuerstenau (32) conducted a detailed study of how polycarboxylate polymers affect the viscosity of suspensions of different minerals. The polymers used were polyacrylic acid (PAA), sodium polyacrylate (SPA) and Dow's XFS 4272 and the minerals tested included dolomite, hematite and quartz. The molecular weights of PAA and SPA were 5000 and XFS 4272 is 5000-10000. As can be seen by the results presented in **Figure 7**, the viscosity of a minus 65-mesh dolomite slurry (61 volume percent solids) was reduced at a critical additive dosage of 0.012 wt percent for SPA and 0.03 percent for XFS 4272. Because there must be adsorption before these effects can take place, there are solution (pH, ionic strength, contaminant ions) and mineral-specific (adsorption sites, surface charge) effects. Polymers which stabilize suspensions adsorb directly onto the particle surface and must be sufficiently charged that they induce electro-static repulsion between interacting particles. The polymer molecules must be large enough to prevent the particles from coming close enough together for the attractive forces to operate (steric stabilization) and must be highly charged to give rise to strong electrical repulsion.

The three polymers studied by Velamakanni and Fuerstenau (32) have different effects on the behavior of mineral suspensions. PAA had no effect on the viscosity of dolomite and hematite suspensions. This appears to be the result of pH (6.5 with PAA and 9.2 with SPA). At pH 9.2 the zeta potentials of the polymer-coated dolomite and hematite particles are sufficiently high that strong electrostatic repulsion between particles contributes to viscosity reduction. SPA and PAA do not adsorb on clean quartz, but over the pH range of 4 to 6 the viscosity of the suspension of quartz that had been ground in a steel mill is markedly reduced because of the strong PAA adsorption induced by Fe(III) activation.

Those polymers used in rheological studies on suspensions of dolomite, hematite and quartz were also tested for their efficacy as additives in grinding these same minerals. The polymer dosage required to enhance grinding was taken as the critical polymer concentration obtained from the rheological studies on suspensions. To ensure free-flowing slurries during grinding, a slight excess over the critical polymer concentration must be present. **Table 4** summarizes the final pH, the slurry viscosity, and the amount of fines produced after wet grinding the minerals with and without polymers. These results clearly show the relationship between the effect of the polymer and pH on the rheology of the mineral suspension and its effect on grinding kinetics.

Klimpel (33) has also demonstrated that polymeric additives can affect breakage kinetics. In ball milling 20×30 mesh coal at low solids concentrations (57.0 wt percent solids), the breakage rate follows first-order behavior in both the presence and absence of the grinding aid (**Figure 8**). When the solids concentration is increased to 72.3 wt percent, the grinding rates deviate from first-order behavior as grinding proceeds (**Figure 8b**) and the slurry becomes viscous. By adding the carboxylate polymer, the rate again becomes first order. The absolute rate of breakage with and without polymer at 57 wt percent solids was 125 grams per minute. At 72.3 wt percent solids, it was initially 120 grams per minute, dropping to 54 grams per minute as the slope of the breakage rate function decreased (**Figure 8b**). By adding the polymer under these conditions, the absolute breakage rate was increased to 134 grams per minute. Under these conditions, the development of a yield stress and high slurry viscosity causes the grinding kinetics to deviate from first order. The addition of the grinding aid eliminates the yield stress and reduces the viscosity. Klimpel (34) has also experimentally demonstrated that slurry viscosity affects the sharpness of classification in cyclones. Thus, reduction of

Table 4 The effect of polymeric additives on the viscosity of mineral slurries and on the production of minus 37 μm particles after wet ball milling (Ref 32).

Additive	DOLOMITE			HEMATITE			QUARTZ		
	pH	Slurry Condition	Prodn. <37 μm (%)	pH	Slurry Condition	Prodn. <37 μm (%)	pH	Slurry Condition	Prodn. <37 μm (%)
None	9.2	viscous	46	8.5	viscous	35	6.4	viscous	35
XFS 4272	9.5	free-flow	54	9.2	free-flow	50	9.2	viscous	22
SPA	9.5	free-flow	54	9.2	free-flow	50	9.2	viscous	21
PAA	6.5	viscous	31	4.8	viscous	33	4.3	free-flow	53

Fig. 7 The effect of polymer dosage on the apparent (Brookfield) viscosity of 82 wt % (61vol. %) dolomite suspensions. Dolomite is a minus 65 mesh ground product (after Ref. 32).

Fig. 9 Net production of minus 325-mesh taconite vs. the net energy expended for grinding (data taken from Katzer et al., Ref. 30).

Fig. 8 Rate of feed size disappearance in the wet grinding of 20 x 30 mesh coal at (a) 57.0% solids and (b) 72.3% solids, with and without XFS 4272 grinding aid (Ref. 28).

slurry viscosity may have the added effect in wet comminution systems of improving the separation efficiency of the classification system.

Fuerstenau et al. (35) analyzed the results from Katzer et al. (Figure 6) in terms of the energy expended per unit mass of material being ground, that

is in terms of specific energy. A plot of the mass fraction of minus 325-mesh material produced per kWh of energy expended results in a single straight line, the slope of which gives the tonnes of minus 325-mesh material produced per kilowatt-hour of energy expended (Figure 9). This convincingly suggests that

in terms of specific energy, there is little improvement in grinding in the presence of the grinding additive in this system.

To delineate what must be happening, Fuerstenau et al. (35) conducted 70-minute batch grinding tests in which the instantaneous mill torque was recorded continuously. In separate experiments, the viscosity of the pulp obtained after grinding was measured for different grind times. **Figure 10** presents a plot of the instantaneous torque drawn by the mill versus grinding time for the 82% dolomite slurry, with and without 0.03 wt percent grinding additive. As can be seen by the results given in **Figure 10**, the torque drawn by the mill is essentially the same up to about 25 minutes of grinding, irrespective of the presence or absence of the grinding additive. The important observation from the plots in **Figure 10** is that without the grinding aid, the torque drawn by the mill decreases rather sharply with grind time between 30 and 55 minutes. Further, during the time when the torque is decreasing, it fluctuates widely about the instantaneous mean value. Beyond about fifty minutes, again the torque remained constant (but at a significantly lower value) and the instantaneous fluctuations also dampened. In the presence of the additive, the trend is reversed, though it is not as dramatic as that in the absence of the additive.

Fuerstenau et al. (35) quantitatively explained how modifying the pulp viscosity by an additive alters the dynamics of grinding media inside the mill. In wet grinding, there is a critical pulp viscosity above which the grinding media “centrifuge” because the

balls cannot be detached from the mill wall during the time of rotation. An estimate of this critical viscosity can be made by analyzing the forces acting on the grinding media (**Figure 10**). When the media “centrifuge” in a pulp with viscosity greater than the critical value, fewer balls cataract/cascade. The mill power decreases, and a correspondingly smaller amount of fines is generated. Certain additives are able to reduce pulp viscosity to a value less than the critical viscosity (about 4000-5000 centipoise) and provide conditions where the grinding balls do not centrifuge so that the mill draws more power and more fines are generated. Additives are ineffective at lower pulp densities because pulp viscosity is already less than the critical value.

In summary, for wet grinding at high solids concentrations, when improved grinding results from the presence of an additive, it is always accompanied by increased energy consumption. The results from Fuerstenau et al. (35) suggest that the main beneficial effect of a polymeric additive for grinding minerals is to permit full utilization of grinding media inside the mill through pulp viscosity reduction. When grinding results are analyzed in terms of specific energy expended for comminution, no beneficial effect is observed for the systems discussed.

Subsequently, Fuerstenau et al. (36) showed how slurry rheology can affect grinding behavior by causing changes in the split of the charge between the cascading and cataracting zones in the mill. In the absence of a dispersant, as the pulp thickens, there occurs an increasingly disproportionate split of the

Fig. 10 Mill torque versus grind time for the wet grinding of minus 10-mesh dolomite feed slurry at 82% solids in the presence and absence of grinding aid XFS-4272. Also indicated are the instantaneous torque fluctuations. The attachment of a grinding ball to the mill shell by a viscous slurry is also shown schematically (after Ref. 35).

grinding charge between cascading and cataracting/centrifuging masses, resulting in a complex relationship between the instantaneous viscosity and mill torque. In the presence of dispersants, the partitioning of charge in a relatively fluid suspension occurs to a much lesser extent. A multi-torque mill model has been derived which tracks the overall mill torque as a function of changing viscosity of the pulp, permits estimation of the charge split between cascading and cataracting-centrifuging regimes, and explains the occurrence of a peak torque value at some intermediate stage. As a consequence, the grinding rate should be at its maximum when the torque peaks that is, when the slurry has acquired some pseudo-plastic character, in line with the observations by Klimpel. The model also explains the shape of the curves given in **Figure 10**.

Kapur et al. (37) extended these concepts to a cascade-ataracting model for the power draft of tumbling mills and tested the model against published data. **Figure 11** shows both the experimental and model results for dolomite ground wet in a heavily loaded slurry (61 vol % solids) in a 254-mm diameter ball mill, with and without the addition of a grinding aid. Without additives, initially when particles are coarse and a viscous homogeneous pulp is yet to be formed, the mill charge moves at the mill speed in a cascading pattern. The amount of cataracting increases with grinding time as the solids become finer and the pulp thickens, while at the same time the torque goes through a maximum. The lower portion of **Figure 11** gives the results for the same

milling system but with the addition of sodium polyacrylate as a dispersant, which prevents the pulp from becoming excessively viscous. With the grinding aid, the fraction of material cataracting remains low and the torque high.

In Australia, Kapur et al. (38) investigated the use of polymeric dispersants in a continuous, closed-circuit, stirred ball mill grinding system to produce a target product of minus 10 μm from zinc sulfide flotation middlings. The dispersant used was Displex at a dosage of 0.5 % by weight. With slurries at 50 % solids content, the performance with and without dispersant was the same. At 65 % solids, it was impossible to grind the material in the stirred ball mill without dispersant but with dispersant the system performs well. Since the power draw was found to be the same in both cases, adding the dispersant increased the production of fines by nearly 50%

Summary and Conclusions

In order to improve the efficiency of comminution systems, there has been a wide interest in the use of grinding aids. Dry grinding additives for cement have found extensive industrial application whereas wet grinding additives for rheology control are just now becoming important. The mechanism for their action appears to be quite well understood in some instances and unclear in others. Many of the observed results are clouded because surface areas were measured by air permeametry and the lack of energy measurements. In dry grinding, crack propagation appears to be too rapid for strength reduction by adsorption to occur. However, practical cement grinding aids appear to function by adsorbing on the external particle surface and thereby preventing reagglomeration. The influence of the liquid, particularly polar water, enhances grinding. Perhaps the most fully understood system involves more recent work on the use of polymers for rheology control in wet grinding mills. Rheology affects grinding kinetics and slurry transport.

The size distributions of the ground product are a function of the cumulative energy input only in normal grinding systems, even when the power drawn by the mill varies appreciably with milling conditions and/or grinding time. The implication is that the grinding rates are proportional to the mill torque and the latter can be used directly to monitor and analyze mill performance and the role of grinding aids, notwithstanding the fact that the slurry may undergo major changes in its rheological character. In plants

Fig. 11 Mill torque and fraction of charge load cataracting as a function of time when dolomite slurry is ground in a ball mill without an added dispersant [upper figure] and with sodium polyacrylate added as dispersant [lower figure] (after Ref. 37).

being operated at high slurry densities for maximum throughput, control of rheology is necessary so that the viscosity does not exceed the critical value. It is for this purpose that polymer grinding aids have their utility.

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