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Theories of Grinding

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The previous chapters have dealt with agglomerates and the breakdown of hard agglomerates by grinding. The grinding of coarse-grain material to produce fine powders is also of concern in many areas of ceramics. The science of fine grinding in ceramics appears to have lagged considerably behind the technological advances. Considering the large energy consumption and capital equipment costs in grinding, and the importance of the size and size distribution of the ground powder, it would be helpful to understand more about the mechanisms of grinding and the kinetics involved. These factors have received much attention in the field of mineral processing. This chapter reviews concepts in grinding and discusses the theoretical progress in fine grinding and effects of grinding aids.

STRENGTH OF INDIVIDUAL PARTICLES

The fracture of a particle involves the propagation of cracks that are present or initiated in the particle. The stress σ required for fracture is given by the Griffith relationship[1]

$$\sigma = \sqrt{\frac{2E\gamma}{L}}$$

where E = Young's modulus
γ = fracture energy
L = crack length

For brittle materials, γ is between 10^3 and 10^4 erg/cm^2. With plastic deformation, γ is much greater than 10^4 erg/cm^2.

When a particle is repeatedly fractured, each new particle (fragment) tends to be stronger. The larger cracks existing in the original particle propagate first, leaving the finer cracks in the new particles. The probability of finding a flaw of a given minimum fracture stress decreases. As fragmentation continues, eventually the fracture stress required may increase to the extent that some plastic deformation is possible. With plastic deformation occurring, the particle cannot be ground further; consequently, a limit of fineness in grinding exists. This limit is reported to be 1 μm for quartz and 3 to 5 μm for limestone.

The possibility that new flaws are created during the fragmentation process has not been considered by past investigators. However, it can expected that movement and merger of dislocations and other defects can produce additional flaws and can retard the tendency of increasing fracture strength with decreasing particle size. Another overlooked factor is that the amount of elastic energy that must be stored to propagate a crack is limited to the volume of the particle, and very small particles may not have sufficient stored energy.

The effect of rate of stress application is reported to be a gradual increase in the fracture stress initially when the rate is increased from that of slow compression tests to that of fast compression tests. Fracture stress further increases with low-velocity impact but then decreases when the velocity of the impact is further increased.[2] The initial increase is attributed to larger plastic deformation before failure when a higher rate of compression is used.

Increase in temperature of the fracture environment can be expected to cause an increase in plastic deformation. In this regard it is interesting to note that even under low-temperature conditions, the temperature near a propagating crack-tip can be very high owing to release of large quantities of energy in the form of heat. The magnitude of this energy is 10 to 10^5 times that of the surface energy requirement for fracture.[3] The temperature at the crack tip under such conditions can even be above the melting point.[3] After the propagation of the fracture, such a region, probably of the order of 100 A to 1 μ, cools down rapidly, freezing amorphous or other high-energy structures at the fracture surface.

Newly forming, high-energy surfaces can react with the surrounding environment if the possible rate of penetration of the environment is equal to or larger than the speed of crack propagation. Figure 11.1 shows the effect of water vapor on the specific crack-extension energy of glass to be significant, but only when the crack velocity is less than about 0.1 to 10^{-4} cm/second. Below such crack velocity, cracking is assisted by water penetration

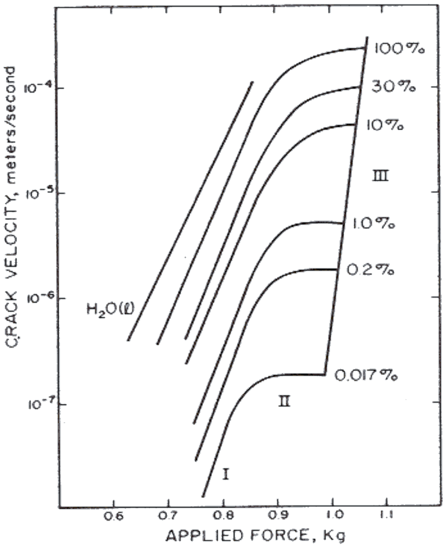

Figure 11.1. Crack velocity v in soda-lime glass as a function of the applied force, with relative humidity shown for each line. [S. M. Wiederhorn, *J. Amer. Ceram. Soc.* **50**, 407 (1967).).]

followed by "hydrolytic stress corrosion," whereas above this velocity water penetration is apparently not fast enough for it to be in contact with the advancing crack tip.

GRINDING MECHANISMS

During grinding several particles are simultaneosly and repeatedly subjected to stress application in the grinding zone. With each stress application, several fractures may occur in each particle. Theories of crack initiation and propagation discussed above are therefore compounded by the interaction of flaws in a particle, secondary breakage, interaction of particles with each other and with the surface of the container, secondary interactions between particles and the grinding media, and physical and chemical interactions between particles and the grinding environment. In addition, the type of transport of the material through the grinding zone and size classification of it, if any, in the mill will also affect the nature of the product obtained. The present understanding of the above interactions is limited and in several cases is intuitive or speculative.

The distribution of cracks and the interaction among them during propagation will essentially determine the size distribution of the particles obtained during fracture of a single particle. Interaction of a propagating crack with a dormant crack can accelerate, decelerate, or terminate the propagation and can possibly activate the dormant one during the process, depending possibly on the relative orientation between them. Shock waves generated in the specimen as a result of stress application or crack propagation can also activate dormant cracks. Shock waves that diverge from a peripheric point of contact in a sphere or disc can be focused at a point a distance of one-third the diameter from that point on the symmetrical axis to cause tensile fracture.[5]

Fracture fragments possessing sufficient kinetic energy can undergo further fragmentation by impacting on the walls of the container. Slow compression tests on single spheres have shown that the particles, when allowed to undergo secondary breakage, produced 3.6 times as much surface area for a given specific energy input than those subjected to single fracture when they were embedded in gelatin.[6] Primary fragments rich with flaws have been found to degrade much more readily than a new sphere comparatively free of surface flaws.[7,8] During grinding a significant amount of secondary breaking can occur as a result of the impact of primary fragments with the grinding media and container wall, as well as with other particles.

Interaction among particles can be significant, depending on the grinding mechanism, relative hardness and size of particles, and the extent of size classification during grinding. A number of interaction phenomena can take place. Particles can nip each other and thereby remove chips, releasing a certain amount of elastic stress. They can also reduce their rugosity and even change their shape by abrasion, which in turn will alter the effects of subsequent comminution events. Most importantly, the presence of fines in the mill can reduce the grinding efficiency considerably because of the cushioning effect produced by a bed of fine particles.[8] Energy is wasted in deformation and flow of the bed of fines. The above effect is more prominent under dry-grinding conditions than under wet-grinding conditions and all the more so for ball milling. In a rod mill coarse particles are considered to be preferentially ground, and the fines are protected by the wedging of the rods by the coarse particles.[8]

In addition to these physical interactions, chemical reactions have also been shown to occur, as in the case of prolonged grinding of a mixture of massicott and sulfur.[9]

While impact-type comminution will produce fragments with a more normal size distribution, nipping by the grinding media or the other particles will produce a distribution with more coarse particles. Also, abrasion will produce a distribution with more ultrafine particles. Intense point loading produces fine fragments of the intensely stressed region and much larger fragments of the remaining material.[2] The combination of the above types of fragmentation yields a product characteristic of the ground material and the grinding media,[10] as each type is active to a different extent with different machines and materials.

SIZE DISTRIBUTION

The size distribution of powders is most conveniently represented by comparing y versus x, where x is the size of the particle and y is the cumulative weight percent of all particles finer than size x.

A plot of log y verus log x often yields a straight line for the range $10 < y < 40$. However, for y values below 10 and above around 40, the linearity in the plot no longer applies. To describe the distribution over a broader range mathematically, several equations have been proposed.[11-21] Some are largely empirical fits to data, while others are based on models involving distribution of Griffith flaws,[12-16] probability of survival under constant stress,[11] and statistical consideration of random division of particles.[18-20] Most equations are of the form

$$y = 1 - f(x/a)$$

where $f(x/a)$ is a function that involves exponents or power relationships and constants that determine the average size and breadth of the distribution. The various equations fit specific situations and no universal equation has yet been widely accepted.

RATE OF GRINDING

The size reduction as a function of time has been considered mainly in terms of the energy consumption. If the rate of energy consumption is constant with time, then the time and total energy consumption are directly proportional to each other. Major relationships between particle size and time or energy have been recently discussed by Agar and Somasundaran.[22] Attempts have been made to relate energy consumption to surface area,[23,24] volume, or weight of the particles,[25] size and size distribution parameters,[3,26] and fracture stresses.[27] The more recent treatments satisfy specific experimental observations that were considered by the investigator, but none appear widely acceptable for all conditions.

Other approaches have involved the monitoring of the rate of disappearance of material coarser than a certain size[28,29] or the rate of production of fine material from a narrowly sized feed.[30,31] In some cases the forms of the equations can be shown to be equivalent to certain size versus time relationships mentioned previously.

Changes in the entire size distribution of ground material with time have been studied[32-48] extensively. One of the simpler equations presented is one obtained by curve fitting a three-parameter equation[49]:

$$y(x, t) = 1 - \left[1 - \left(\frac{x}{x_0}\right)^s\right]\frac{(t)p}{t_0}$$

where t is time and s, p, and t_0 are constants. This equation fits several sets of data in the literature, particularly those for ball milling.

ULTRAFINE GRINDING

As grinding proceeds into an ultrafine region, it becomes more and more difficult to obtain further reduction in size because a grind limit is approached. A practical grind limit exists for most systems. This is most importantly determined by the tendency of the product particles to re-aggregate and establish a physical equlibrium between aggregation and fragmentation. In addition, the probability of a particle becoming involved in a comminution event, as well as that of its fracture when it is involved in an event, decreases with decreasing particle size. Depletion of flaws during the grinding as well as a decrease in volumetric capacity to store elastic stress energy, increases the required stress for initiating fracture. Difficulty in obtaining particles below a limiting size has also been attributed to "excessive clearance between impacting surfaces," diminished utilization of energy due to transmission of forces "through a long chain of particles few of which suffer sufficient strain to shatter," semifluid nature of the final product, and protection of smaller particles by the larger ones.[50]

Additional flaws can probably be generated in the fine particles by applying thermal shocks. It is of interest to note that laser techniques, even though still uneconomical, have been studied for reducing the drilling strength of rocks.[51]

Aggregation can be retarded using a number of techniques. It can be minimized by removing the finest particles continuously using closed-circuit grinding. It is also considered advisable to successively reduce the size of the grinding medium (balls, pebbles, etc.) as the grinding proceeds into fine and ultrafine regions, since the ratio of the size of the grinding medium to the size of the particles should be kept within certain limits for maximum grinding efficiency. Cooling the machines by improving the ventilation or by external or internal watersprays minimizes agglomeration due to rising temperature.[52] Addition of dispersive chemical agents is found to be beneficial for ultrafine grinding.[53] Both grinding aids and grinding liquids have significant influence on ultrafine grinding.[54] Inorganic salts with multivalent ions or complex anions were found to be the most effective grinding aids. Adsorption of multivalent ions on the particles to increase the electrical repulsion between them is possibly the major reason for their influence. Formation of brittle or corrosive surface films has also been considered as a reason for their effect.

An "attritor ball mill" in which balls are rotated with a stirring arm was found to be significantly more efficient than use of a standard ball mill for fine grinding.[54] Milling time was 5 to 10 times less with the attritor ball mill for the same output. This grinding method is stated to be good also for alloy powders and refractory compounds. Vibration grinding,[55-57] centrifugal grinding,[58] and fluid energy milling[59] have been considered recently for efficient fine grinding. Grinding time with a two-chamber (1.5 in. wide diameter) experimental vibratory ball mill was found to be less than 3 hours for producing graphite fines with a specific surface area of 400 m^2/g.[55] This is to be compared with 26 hours of grinding with a 15 in. ball mill for the same surface-area development. Theories of rate of vibrational milling have been presented along with experimental analysis of the theories.[60]

Relations described earlier become usually inapplicable in the fine-size region. The following equation, which takes into account the possible existence of a grind limit, was proposed[61]:

$$S = S_m [1 - \exp(-KE)] \tag{20}$$

where F is again the energy input, S is the specific surface area reaching a limiting value S_m, and K is a constant. Harris[62] has a more general equation in which E is raised to a constant. The data fit however, is, better with another relation of Harris', developed on the basis of a logistic growth function model for fine grinding:

$$\frac{\Phi_m}{\Phi} = 1 + \left(\frac{h}{t}\right) h'$$

t is grinding time and h and h' are two constants. Φ is a measure of fineness reaching a maximum value of Φ_m. It is assumed to be proportional to specific surface area or to the inverse of size modulus. None of these relations, however, represent cases where the Φ_m exists at $0 < t < \infty$.

It is important to note that surface area and related surface activity are the parameters of importance in a system using very fine particles. It is therefore most meaningful to represent the fine-grinding system by surface area versus time or even cumulative surface area versus size models instead of weight versus time or cumulative weight versus size models.

MECHANOCHEMICAL EFFECTS

Both physical and chemical characteristics have been found to undergo significant changes during powder preparation by prolonged grinding.[9] There is sufficient evidence in the literature[53,63] that, in addition to desired and expected changes in physical properties such as specific surface area, changes occur also in shape, sintering activity, chemical reactivity, and so forth. The exact nature of alterations is dependent on, among other things, the conditions of grinding and the method of grinding used. Using gravimetric, thermogravimetric X-ray diffraction and electron microprobe analyses, the change in various properties of samples of quartz, calcite, and massicot ground in a pebble mill for several hundred hours was studied.[9] It was found that the density of the particles decreased in the case of quartz as a function of grinding time (or particle size) apparently owing to the creation of deep amorphous layers on the particles. This effect however, was, absent when the grinding was done in water, possibly because of continuous dissolution of amorphous material in water. More than half of the quartz particles with diameters of 200 μ was converted to amorphous quartz during prolonged ball milling. Such effects have been also reported in several other cases.[64-66] During grinding of hematite, a distinct change in color was observed owing to the production of ferrous oxide at the surface.[65] Work with clay minerals has provided additional evidence for the effects of prolonged grinding. Bloch,[67] for example, found that prolonged grinding of montmorillonite caused disruption of its crystalline structure and release of some alumina and magnesia. Reactivity of materials is in general found to be enhanced by comminution, as in the case of kaolinite and molybdenum sulfide, the latter becoming particularly reactive towards oxygen when ball milled in air. Researchers on catalytic activity of metallic oxides, ionic crystals, metal sheets, and wires have observed a favorable increase in such activity due to grinding. Ceramic powders activated by prolonged grinding are reported to sinter more readily. Snow and Luckie[63] and Naeser and Fielder[68] have recently reviewed these effects. Increase in catalytic and sintering activities has been proposed to occur as a result of an increase in the dislocation density of the materials. Even though no simultaneous work on both reactivity and dislocation density has been carried out by any of the above workers, it is not unreasonable to expect a change in sample reactivity owing to an increase in dislocation density that naturally occurs during most mechanical treatments.

Polymorphic transitions have been reported to occur during grinding[9,69-73] possibly owing to temperature and pressure changes that take place locally as a result of the grinding process. Thus, during grinding or massicot and calcite, such transitions altered the structure of these materials to those of litharge and aragonite, respectively.[9]

In addition to the above physical and structural changes, even solid-state reactions have been reported to occur during grinding. Figure 11.2 shows the changes in the massicot–sulfur system when it is ground for several hours.[9] Massicot converts itself slowly to litharge up to about 20 hours; a chemical reaction then follows in which the oxide in both forms and sulfur are converted to galena. Such solid-state reactions have been reported to be most prominent during the grinding of carbonates. For example, zinc carbonate[65] and cadmium carbonate[74] with relatively low decomposition temperatures give carbon dioxide by mere grinding at room temperature. In the case of carbonates such as magnesium with higher decomposition temperatures, prolonged dry grinding lowered their decomposition temperatures significantly. Another important example of chemical decomposition during grinding is that of $Na_5P_3O_{10} \cdot 6H_2O$ to form ortho- and pyrophosphates.[75] Several hydrated salts, such as $FeSO_4 \cdot 7H_2O$ and $BaCl_2 \cdot 2H_2O$, have been found to decompose during grinding.[76] These reactions are most prominent when the mill atmosphere is dry. An interesting complete chemical reaction that has been discovered to occur as a result of grinding is that between black lead sulfide and white cadmium sulfate to form white lead sulfate and yellow cadmium sulfide, the progress of the reaction being indicated by the gradual change in color.

A point to note is that contamination of the samples with the grinding medium can also occur during prolonged grinding. Mullite contamination

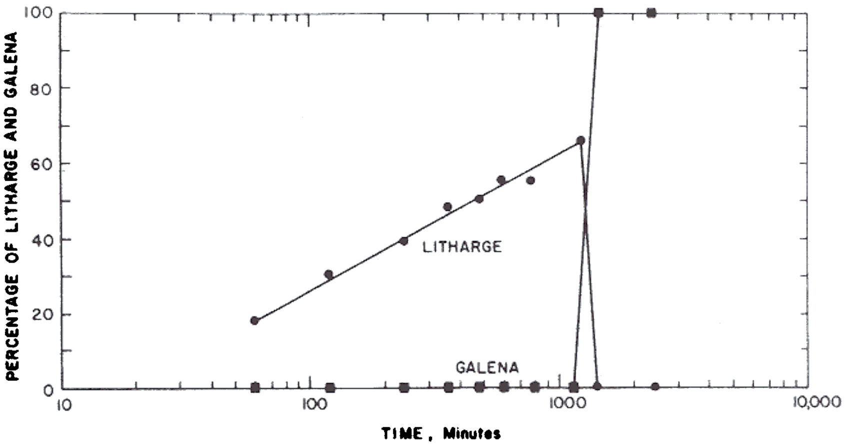

Figure 11.2. Amount of litharge and galena formed during grinding in a massicot–sulfur system.[9]

was found in a sample ground with a mortar and pestle.[77] The implications of these effects on powder preparation for various purposes, including sample preparation by grinding for chemical analysis, must be recognized.

GRINDING AIDS

Use of grinding aids and the mechamisms by which they act are discussed in a recent review by Somasundaran and Lin.[53] Grinding aids in vapor form, such as ethylene glycol, proplylene glycol, butylene glycol, are used commercially in Germany and Yugoslavia for improving the efficiency of cement grinding.[78-80] Amine acetates and diethylene glycol are used in Japan as grinding aids in plant-size mills.[81,82] Any such attempt to improve the grinding efficiency is highly desirable, since the current grinding operations are notorious for their efficiencies, which are of the order of 1%. Parts of our review[53] relevant to grinding aids are given below.

WATER (MOISTURE)

Grinding in water in usually more efficient than dry grinding.[83-86] This effect of water has been ascribed by Lin and Mitzmager[86] to a reversible reaction between unsatisfied surface bonds and water molecules. Water in the form of vapor also should be expected to produce such hydrolytic corrosive effects. Even though there is no grinding work in the literature reported as a function of humidity, some evidence exists that this factor does affect the process. For example, the grinding rate of soda lime glass is higher in humid air than in a vacuum.[87] It must be noted that the increased efficiency of wet grinding can also be due to physical reasons. Cushioning effects due to the presence of a bed of fines will be less during wet grinding than during dry grinding, since the fine particles tend to remain suspended in the water in the former case. This would of course cause an increase in the efficiency of the grinding. In addition, effects of viscosity and specific gravity of the medium can also be significant.[88,89]

Organic Liquids

Grinding in organic liquids is reported to be more efficient than in water. A 12-fold higher production of surface area for grinding in organic liquids, such as isoamyl alcohol, than for that in water was shown.[90] Higher grinding rates were obtained in carbon tetrachloride and methylcyclohexane than in nitrogen.[86] An interesting observation was that the grinding efficiency was lower in the two organic liquids than in water but became the same when small amounts of water were present in the organic liquids in dissolved form.

Surface Active Agents

Surfactants have been widely reported as effective grinding aids. The effect of adding a flotation agent called Flotigam P on wet-ball milling of quartzite and limestone[91] is shown in Figure 11.3 as an example. It can be seen that as much as 100% increase in specific surface area was obtained by additions of up to 0.3%. Additions in amounts higher than 0.03% caused a decrease in specific surface area. Sodium oleate in large concentrations has also been reported to produce a net decrease in specific surface area. The effect of Armac T on the grinding of quartz in a ball mill[92] is shown in Figure 11.4. The effect is detrimental under all concentrations studied. It is not yet known whether these detrimental effects are due to experimental artifacts introduced by the aggregation of fines or are the result of change in interfacial properties due to adsorption of surfactant adsorption on particles. Flocs in the mill during grinding could consume some of the impact energy for deflocculation. In addition, hydrophobization of particles by the adsorbed surfactants can result in the attachment of air bubbles to them and consequent levitation. The grinding efficiency can be expected to be lower if the particles remain levitated. The beneficial effect of these grinding aids has been considered to be due to the reduction in surface energy upon

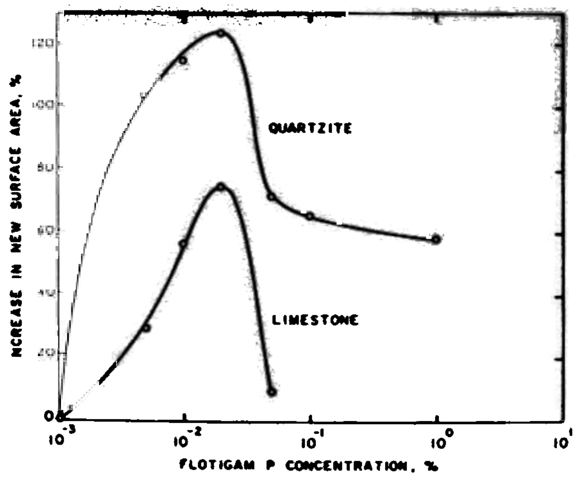

Figure 11.3. Effect of Flotigam P on grinding of quartzite and limestone in a rod mill.[91]

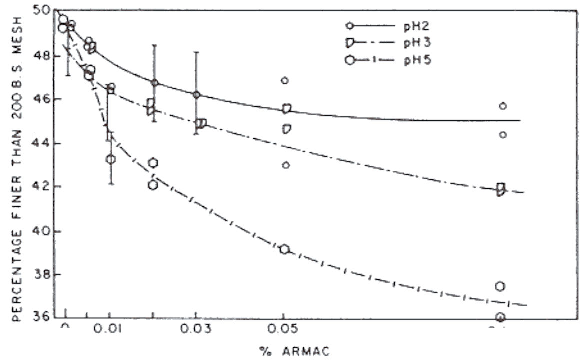

Figure 11.4. Effect of Armac T on the comminution of quartz in a ball mill at different pH values.[92]

their adsorption, making it easier to produce new surfaces under such conditions. This reasoning is in line with the explanation offered by Rehbinder and coworkers for the observed increase in drilling rate on the addition of these agents. On the other hand, it is also possible that it is an indirect result of several other phenomena that could occur in the system, such as the interaction of the surfactant molecules adsorbed on the surface and the resultant effects on various interfacial properties. In some cases it could also be the result of the ability of the reagents to enhance the dispersion of the particles and thus indirectly to facilitate fragmentation.

Examples of grinding aids used in the past include polysiloxane in the grinding of ultraporcelain and talc; silicones in the drop-weight crushing of limestone and quartz; glycols, amines, organosilicones, organic acetates, carbon blacks, and wool grease in the grinding of cement; silicones in the ball milling of quartz; acetones in nitromethane benzene, carbon tetrachloride and hexane in vibratory milling of ground glass, marble and quartz; and wool grease in the milling of gypsum, limestone, and quartz. Some of these reagents are reported to act by preventing ball coating but not aggregation of particles.[93] This effect of additives is very beneficial, since it is known that ball coating impairs the grinding efficiency.

Inorganic Electrolytes

Use of inorganic electrolytes during drilling was noted in the forties by Rehbinder et al.[94] to increase the efficiency significantly. A number of workers have attempted to establish corresponding effects during grinding.[95-100] Even though all the reported results are not in agreement, grinding is in general found to be more efficient in the presence of inorganic electrolytes. In the ceramic industry, grinding of metallic and refractory-type materials is found to be more efficient when multivalent electrolytes are used as additives.[101-109] Effect of $AlCl_3$ and $CuSO_4$ on wet grinding is shown in Figure 11.5. Both reagents aid the grinding, the extent of the effect being determined both by the valency of the active ion of the salt and the manner of grinding. In some cases use of salts above certain levels is reported to cause poor grinding.[96,99] In addition to any effect that these electrolytes might have on the hardness of the materials, the influence on the flocculation or dispersion of particles is also possibly a major reason for their overall observed effect.[53] This reasoning is supported by work that showed that the addition of dispersing agents always improved the comminution of solids.[95]

Physical Nature of the Environment

Properties such as viscosity and density of the grinding environment can be expected to have an effect on the hydrodynamic behavior of particles, as well as of the grinding medium, and therefore on the grinding performance. Grinding is normally dependent on the viscosity of the medium up to about 20,000 mill revolutions and is then independent.[110] Similar results were found for the viscosity of the environment.[89] The effect of density of the suspending fluid by grinding quartz and pyrite in air, water, and tetrabromoethane has been studied.[88] Grinding in water was more efficient than in air. The results obtained in tetrabromoethane however, were, inferior,

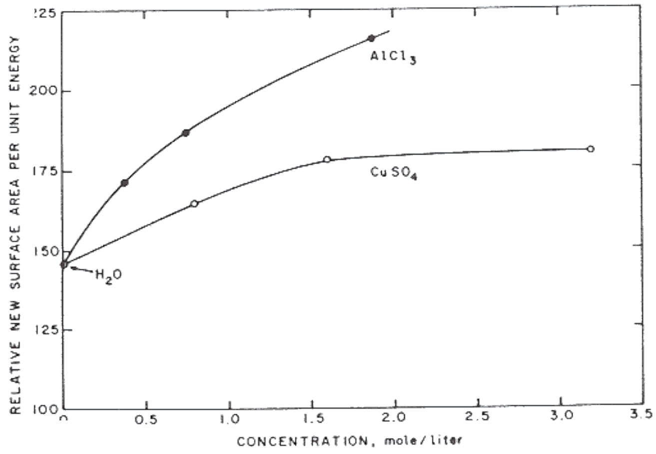

Figure 11.5. New surface area produced per unit energy applied during mill grinding in aqueous solutions as a function of $CuSO_4$ and $AlCl_3$ concentrations.[53]

possibly because quartz particles, which are lighter than tetrabromoethane, remained partially afloat and thus out of the path of the impacting grinding media.

Mechanisms

The main two mechanisms proposed to explain the effects of comminution aids are Rehbinder's[111] mechanism based on adsorption-induced surface energy changes and Westwood's[112,113] mechanisms based on adsorption-induced mobility of near-surface dislocations. Rehbinder's mechanism is based on the concept that a fruitful comminution event involves the production of new surfaces and that to accomplish this an amount of energy proportional to the free energy of the surface should be spent. Addition of chemical agents to reduce the effective surface energy of the solid particles should, on the basis of the above concept, enhance the grinding process. According to Westwood, the Rehbinder effect is more likely due to changes in the electronic states near the surface and point and line defects caused by the adsorption of the additives on the solid. Such changes are known to influence the specific interactions between dislocations and point defects that control the dislocation mobility and hence the hardness. Hardness of materials has been recently proposed by Westwood et al. to be controlled by the zeta potential of the material in solutions.[113] Since addition of surface active agents does affect the zeta potential significantly, it can be then expected to affect the grinding performance.

On the basis of the results obtained during abrasion and grinding tests on cement clinker in the presence of organic liquid vapor, it was found that the effectiveness of the vapor grinding aids in industrial ball milling is due to reduction of adhesive forces leading to prevention of aggregation of powder and of coating of balls and liners.[78] Influence of adsorption of vapors on plastic deformation itself is considered to be significant only for cases where stresses are applied for long intervals and for grinding where stresses are applied rapidly.

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