Physico-Chemical Aspects of Grinding: a Review of Use of Additives

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SUMMARY

The efficiency of energy utilization in tumbling mills is discussed in terms of component processes taking place inside the mill. The past reports on the effect of physicochemical parameters of the environment on mechanical properties and grindability of materials are reviewed. Reported mechanisms explaining such effects are analyzed and possible ways to improve the grinding efficiency, through the use of chemical additives, are also discussed.

EFFICIENCY AND ENERGY CONSUMPTION IN ORE GRINDING

Grinding is an important industrial operation that is used for the size reduction of materials, production of large surface area and/or liberation of valuable minerals from their matrices. In addition to mineral processing, it is widely used in the manufacture of cement, pigments and paints, ceramics, pharmaceuticals, and cereals. However, the efficiency of this operation is very low [1].

In mineral beneficiation, grinding is also the most energy-consuming process. Energy consumed in ore grinding in various mills as compiled by Hartley *et al.* [2] is shown in Table 1. It is to be noted that the energy consumed in grinding alone represents up to 70% of the energy for the whole beneficiation process (see Table 2 reproduced from a 1934 article [3]). Corresponding figures for the present operations can be expected to be much higher. The decrease in ore grade and concomitant increase in the degree of fineness of values in the ore increase also the need for

fine and ultrafine grinding. Consequently, the energy consumption is now higher, and the grinding cost represents a relatively higher portion of the total beneficiation cost. Therefore, it becomes an important task to improve the energy utilization inside the grinding mill.

A scheme for the flow of energy and its utilization in tumbling mills is shown in Fig. 1 [4 - 6]. It can be seen that grinding energy is expended for 1) elastic deformation, 2) plastic deformation, 3) lattice rearrangements and mechano-chemical reactions, and 4) new surface energy. External to the particles, energy can be expended for 1) friction between the particles and the grinding media as well as between particles and particles, 2) sound energy, 3) kinetic energy of the products, and 4) deformation and wear of the grinding media. The scheme shown in Fig. 1, and the data given in Tables 3 and 4 suggest that the actual energy needed for fracture (*i.e.* to produce new surface area) is only a small fraction (less than 1%) of the total energy input to the grinding mill. A great proportion of the energy input (more than 75%) is lost as heat, probably due to friction, non-productive collisions, elastic and plastic deformation, etc. However, as considered by Piret [8], the energy expended in elastic and plastic deformations might be necessary activation energy for subsequent fracture process. If this deformation energy is included, grinding efficiency can be considered to be 20 - 50% [6].

The above discussion suggests that energy utilization can be improved by using suitable means for minimizing the crushing media and the interparticle and pulp losses. Evidently, a clear understanding of the grinding component processes and their dependence on the

TABLE 1

Energy consumed in grinding at various mills [2]

Concentrate produced	Plant	Energy (kWh/t)
Cu	Calumet & Hecla, Michigan	8.5
Cu	Anaconda Co., Montana	7.5
Cu	P. D. Lavendar Pit, Arizona	7.0
Cu	Mulfulira, N. Rhodesia	8.2
Cu	Silver Bell	9.1
Cu	Galena (Idaho)	11.2
Cu	Copper Cities	7.0
Cu–Fe	Cyprus Mines, Cyprus	10.9
Cu–Fe	Keretti, Finland	10.7
Cu–Fe	Boliden, Sweden	13.3
Cu–Fe	San Manuel, Arizona	11.2
Cu–Ni	Kotalahti, Finland	10.5
Cu–Ni	Inco-Copper Cliff, Ontario	7.0
Cu–Ni	Inco-Creighton, Ontario	17.2
Pb–Zn, Cu–Zn, Zn	Tennessee Copper	6.2
Pb–Zn, Cu–Zn, Zn	St. Joseph Indian Creek	8.8
Pb–Zn, Cu–Zn, Zn	A.S. & R Buchans	15.8
Pb–Zn, Cu–Zn, Zn	A.S. & R Page	20.8
Pb–Zn, Cu–Zn, Zn	Idarado	9.8
Pb–Zn, Cu–Zn, Zn	Gilman	5.9
Pb, Zn	St. Joseph Lead, Montana	7.5
Pb, Zn	Broken Hill, Australia	4.1
Pb, Zn	New Broken Hill, Australia	6.3
Pb, Zn	North Broken Hill, Australia	7.0
Pb, Zn	Broken Hill South, Australia	7.3
Pb, Zn	Soc. Algerienne, Morocco	7.9
Pb, Zn	Bunker Hill, Idaho	14.7
Mo	Climax Colorado	4.9
Au	Carlin Gold Mining Company	7
Au	Benguet Consolidated	10.18
Au	Cortez Gold Mines	7
Au	Homestake Mining Company	9.5
Au	Rosacio Dominicana, Dominican Rep.	4.5
Au	Hogon–Suyoc Mines, Incorporated	19.5

environment in the mill is needed in order to identify possibly ways for improving the grinding efficiency.

GRINDING COMPONENT PROCESSES

Two major simultaneous component processes, namely pulp flow and stress application, are involved in grinding operations. Specifically, these processes include transport of material to the grinding zone, and subjecting the material to the grinding actions, leading possibly to propagation and/or initiation of cracks, followed by the transport of the products to the discharge end of the mill. Any parameter affecting any or all of these processes will affect the grinding efficiency.

Breakage of a particle can be achieved if the particle is captured in the grinding zone and subjected to a fruitful breaking action. Probability of breakage, P (overall breakage), is thus the product of probabilities for the above two basic processes [2]:

P (overall breakage)

$= P$ (capture) $\times P$ (breakage upon capture)

The probability of capture, P (capture), is the probability that a particle will be captured in a grinding zone and is expected to depend,

TABLE 2

Energy consumed in grinding in different plants compared with the total energy needed for the whole beneficiation [3]

Plant	Power consumed in grinding (% plant total)
A Copper ores	
Hayden	30
Harmony	50
United Verde	60
Copper Queen	35
Old Dominion	56
Arther and Magna	45
Engelo	57
Walker	59
Britannia	59
B Lead and zinc ores	
Chief consolidated	38
Tybo	65
Hughesville	36
Morning	46
C Gold ores	
Spring Hill	56
Porcupine	44
Kirkland Lake	70

TABLE 3

Experimental measurements of crushing and surface energies [6]

Material	Crushing energy (erg/cm^2)	Surface energy (erg/cm^2)
Quartz (SiO$_2$)	117000	920
Glass (SiO$_2$)	82000	1210
Calcite (CaCO$_3$)	32400	1100
Halite (NaCl)	26100	276
Barite (BaSO$_4$)	71600	1250

TABLE 4

Distribution of energy in a ball mill [7]. Reproduced by permission from G. C. Lowrison, Crushing and Grinding, Butterworths, London, 1979.

Energy distribution	Energy consumptio (%)
Bolt friction	4.3
Gear losses	8.0
Heat losses from drum	6.4
Heat absorbed by air circulation	31.0
Theoretical energy for size reduction	0.6
	97.6

among other things, on the fluidity and the particle transport in the mill and the flocculation of particles. The probability of breakage, provided that capture has occurred, P (breakage upon capture), is related to the particle strength. Additives can affect grinding rates
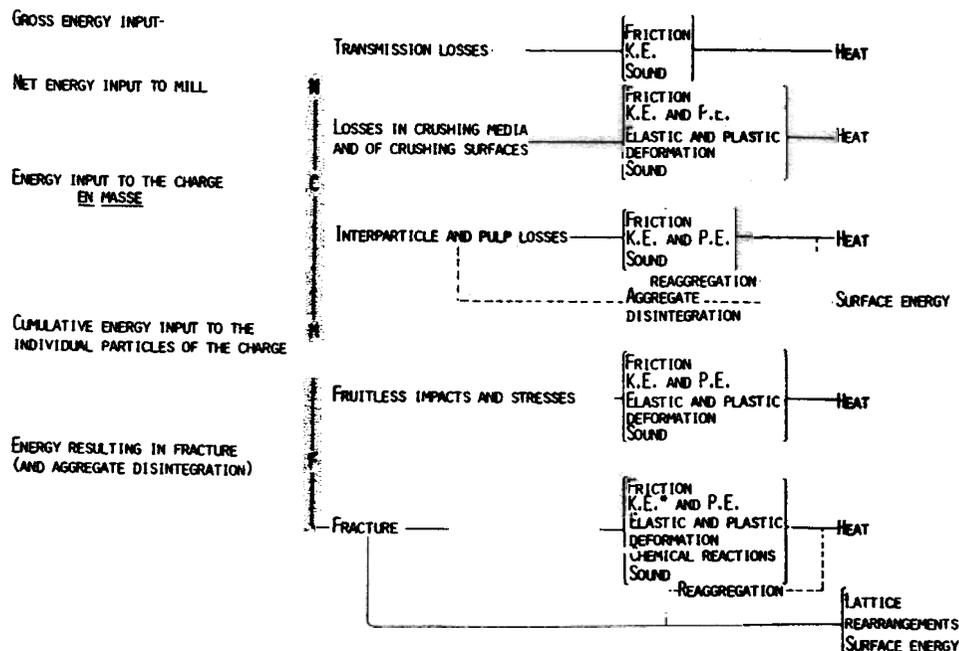
Fig. 1. Energy utilization in model tumbling mill: gross energy >N > C > H > F [4]. (*Residual kinetic energy after possible secondary fracture has occurred.)

through viscosity, flocculation and agglomeration (*i.e.*, affecting *P* (capture)).

Pulp flow process

The transport of material inside a mill depends primarily on the pulp fluidity, which is influenced, among other things, by the state of aggregation or dispersion of the fine particles inside the mill, determined essentially by the nature of interactions between the particles and the grinding media and those between particles themselves.

Modification of the flow of pulp in the grinding mill has been considered to have special potential for increasing the efficiency of the grinding process. This is possibly because the fluidity of the pulp can determine how well particles are transported to regions where grinding action is most severe [2]. In this regard, the effect of the grinding environment on the pulp fluidity and consequently on the grinding efficiency cannot be ignored.

Stress application process

Breaking of solids in grinding operations results essentially from subjecting the particles to stresses in the grinding zone, causing possibly several fractures in each particle.

For fracture to occur, cracks must be present or initiated and propagated. All natural materials have defects as cracks, flaws, or dislocations. These defects will act as stress modifiers leading to strength values lower than the theoretically expected strengths.

Application of a stress on a body activates the propagation of cracks creating surface. Griffith [9] has considered the theoretical energy balance for this process by equating the energy loss from the elastic strain field to the gain in surface energy. The minimum stress required for fracture, according to Griffith's law, is given by

$$\sigma = \sqrt{\frac{4E\gamma}{L}}$$

where *E* is Young's modulus, γ is the free energy of the created surface, and *L* is the crack length.

In actuality, energy will also be consumed for plastic deformation of the material in the surface and sub-surface regions. Griffith's formula must, therefore, contain a surface stress term that includes, in addition to the surface energy, the energy consumed for plastic deformation in the vicinity of the crack [10, 11]. Another important parameter that might affect the strength of materials is the radius of the crack tip. The sharper the crack tip, the higher the localized stress concentration and, consequently, the lower the strength of the material. It is important to note here that the surrounding environment may react with the crack surfaces, leading probably to changes in the length and/or the radius of the crack and, as a result, in the strength of the particles.

Clearly, grinding efficiency depends primarily on factors that affect these component processes. Unfortunately, the present understanding of such processes and their interactions with the mill environment is limited and mostly intuitive or speculative [12]. Reported effects of the physico-chemical environment on mechanical properties and grindability of materials and mechanisms considered as responsible for the observed efforts are disucced next.

EFFECT OF THE PHYSICO-CHEMICAL ENVIRONMENT ON MECHANICAL PROPERTIES AND GRINDABILITY OF MATERIALS

Rehbinder and co-workers [13] were probably the first to conduct a systematic investigation on the effect of liquids with and without additives on the failure of solids. They claimed that liquids, in particular water, played an active part in the process of failure and that this effect could be amplified by adding surface active agents. Since then, various researchers have tested the effect of different additives on mechanical properties of solids and on various comminution processes, *i.e.* drilling, grinding, etc.

Effect of environment on mechanical properties of materials

The effect of surface active agents on the deformation behavior of a rock under various triaxial compression loads has been studied, among others, by Boozer *et al.* [14]. Their results indicated a decrease in the ultimate strength of sandstone when the pores were saturated by oleic acid or oleylamine. This effect was attributed by the authors to the adsorption of surfactant molecules on the rock grains even though no adsorption test
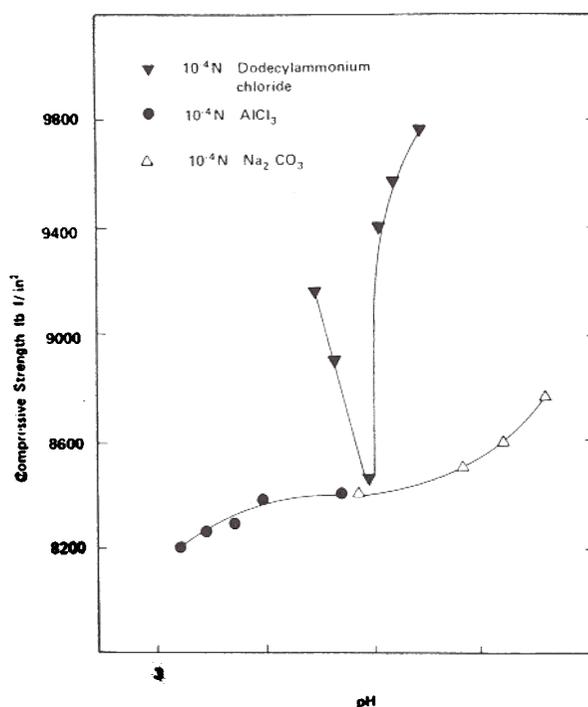
Fig. 2. Effect of organic and inorganic additives on the compressive strength of sandstone (ref. 15). ▼, 10^{-4} N dodecylammonium chloride; ●, 10^{-4} N AlCl$_3$; △, 10^{-4} N Na$_2$CO$_3$.

itself was performed. It should be noted that there was also no control or monitoring of critical parameters such as pH and ionic strength in this work.

In a similar work, Wang [15] examined the effect of organic (dodecylammonium chloride) and inorganic (AlCl$_3$ and Na$_2$CO$_3$) electrolytes on the compressive strength of sandstone. Their results showed that the effect of the additives was pH dependent, as shown in Fig. 2. The investigators attributed this to reduction in surface energy upon the

adsorption of such additives on the solid surface.

Other reports [16] have shown a decrease in the compressive strength of some rocks due to the presence of water (see Table 5). However, no explanation was offered for these observations.

Vutukuri [17] reported the tensile strength of quartzite immersed in 0.06% aluminum chloride solution to be 11.1% lower than that in water. However, the data (given in Table 6) have a statistical variance of 30%, which makes the conclusion questionable. In another investigation, Tweeton and co-workers [18] were, however, unable to find any effect of aluminum chloride when used as an additive at a concentration of 0.05 ppm on the tensile strength of fused-quartz thread.

There have been many other investigations of the influence of environment on mechanical properties of materials [19 - 29]. In all of these investigations, the decrease in the fracture strength of glass-like materials due to different environments has been found to range from a few per cent to 300%. Hammond and Ravitz [29], for example, in their study of the effect of saturated vapors of water, n-propyl alcohol, acetone and benzene, on the brittle fracture of silica, observed water vapor to cause a 40 - 50% decrease in the fracture strength from its value in vacuum. In general, their data indicated the environments with polar molecules to cause maximum effects.

These authors attributed the observed effects to stress corrosion cracking [30, 31]. This mechanism is related to that of fracture of metals when simultaneously stressed and exposed to certain chemical environments.

TABLE 5

Effect of water on the compressive strength of rocks [16]

Type of rock	Compressive strength (lbf/in^2)		Saturated/dry (%)
	Dry	Saturated	
Basalt	24438	12297	50.3
Basalt with sandstone	9386	4118	44.0
Diabase	19994	25106	125.6
Dolomite	16614	13774	83.0
Granite	22862	15478	67.7
Gniess	22550	25333	112.3
Limestone	12354	6958	56.3
Quartzite	37204	29820	80.2

TABLE 6

Effect of $AlCl_3$ solutions on the tensile strength of quartzite [17]

Concentration (%)	Number of experiments	Mean tensile strength (lbf/in^2)	Standard deviation (%)	Percentage change compared with water
0 (*i.e.* water)	20	2006	32	—
0.02	30	2008	30	—0.1
0.04	30	2027	37	—1.1
0.06	30	1783	30	11.1
0.10	30	1788	34	10.9

TABLE 7

Specific environments known to cause stress-corrosion cracking [31

Metal	Aqueous environment	Comments
Carbon steels		
Mild steel	NO_3^-, OH^-	Also (1) anhydrous liquid NH_3, (2) $SbCl_3$, HCl, $AlCl_3$ in hydrocarbon
Medium strength	HCN	
Ultra-high strength	H_2O, H_2	
Stainless steels:		
Austenitic	Cl^-, Br^-, OH^-	Immune above 50% Ni.
Ferritic		Susceptible to hydrogen cracking or blistering. Immune to Cl^-, OH^-, NO_3^-.
Martensitic		Susceptible to hydrogen cracking. Also, when heat treated to high hardness, to H_2O and various aqueous solutions.
α-brass	Cupric ammonium complex. NH_3 or amine atmosphere in presence of H_2O and O_2	Nitrates may reduce to NH_4^+ causing scc. SO_2 is reported to cause scc, but probably causes intergranular corrosion instead.
β, β + γ brass	H_2O	
Aluminum alloys:		
4 - 20% Zn—Al	H_2O	
Commercial, containing Cu or Mg	NaCl solutions, various aqueous solutions	
Magnesium alloys	H_2O	
Titanium alloys:		
8% Al, 1% Mo, 1% V, Balance Ti	Cl^-, Br^-, I^-	Also H_2O, CH_3OH, CCl_4, methylene chloride, trichlorethylene at room temperature; NaCl at >250 °C.
6% Al, 4% V, Balance Ti		N_2O_4.
Gold alloys:		
Cu—Au	$FeCl_3$,	Immune above 40% Au.
Ag—Au	*Aqua Regia*, NH_4OH, HNO_3	

Uhlig [31] observed cracking of this kind to be present only when the metal was under tensile stress in a damaging environment. Table 7 lists specific environments observed by Uhlig to cause stress-corrosion cracking of metals.

In addition to strength properties, material hardness has been known to be affected by the surrounding environment [13, 32 - 38]. In this regard, Rehbinder [13] classified hardness reducers into two groups. The first group contained inorganic salts such as NaCl, NaOH, Na_2CO_3, $MgCl_2$, $CaCl_2$ and $AlCl_3$, and the second group contained organic chemicals with polar molecules. The effect of the additives in the first group has been found to

increase rapidly with the level of addition, reaching a maximum at a given level for each reagent. For example, concentrations of 0.01% to 0.05% $AlCl_3$ were reported by Rehbinder [13] to produce maximum effect on quartzite rocks. The influence of organic chemicals are, on the other hand, found to depend mainly on the molecular weight. For example, in a homologous series of organic acids, hardness reduction has been found to increase with increase in molecular weight. Subsequent work by Montrove [34] on the effect of xylene and benzene on the hardness of muscovite showed this mineral to be harder in such environments than in air.

Interestingly, even water and moist air have been reported by Westbrook and Jorgensen [35, 36] to decrease hardness of different materials such as oxides, silicates, sulfides, fluorides, carbides, and carbonates.

Westwood and co-workers have done a comprehensive study on the effect of different environments on the hardness of MgO [37] and CaF_2 [38]. They found the hardness of these two minerals to increase or decrease, depending on the surrounding environment. The authors ascribed the observed effects to adsorption-induced changes in the flow properties of the near-surface region as controlled by the movement of surface dislocations.

In other investigations [39, 40], the same researchers correlated the observed effects with the surface charge properties of the materials in different environments. They found MgO and quartz to be harder (i.e. less dislocation mobility) at their corresponding isoelectric points. In contrast, Engelmann et al. [41] used the oscillating pendulum technique to measure the hardness of granite sample in $AlCl_3$ and oleylammonium acetate solutions, and found that granite was easily penetrated at the isoelectric point.

In a recent investigation, Shchukin and Yushchenko [42] studied environment-sensitive mechanical behavior of materials on an atomic scale using a molecular dynamic (MD) simulation of strain and failure of a crystal. They have undertaken a series of experiments to reveal the environment-induced qualitative changes in the atomic picture of strain and failure. The results indicated that adsorption-active atoms often caused brittle cracking. This was attributed to

a sharp decrease in the surface energy of the solid in contact with the environment. Besides interacting with the crack walls, the environment atoms create a force compatible with the interatomic bond strength, which promotes crack propagation.

In addition to mechanical properties, environment has been found to affect size reduction of materials. The following paragraphs summarize the published reports, in this regard.

Effect of the environment on grinding

Size reduction of solids in grinding processes is achieved by subjecting particles to different stresses, leading ultimately to the fracture of particles.

Fracture may proceed within the particle itself (intragranular fracture) or along the grain boundaries (intergranular fracture). While intragranular fracture is sufficient for size reduction processes, it is intergranular fracture that is required for liberation. Generally, fracture process involves rupturing of chemical bonds to create new surfaces. Any phenomenon that can help in breaking of the chemical bonds and retard rejoining of the ruptured surfaces can be expected to help the grinding process [1].

Grinding has, in the past, usually been considered as a physical process controlled only by the mechanical conditions of the grinding system. Researchers in the field did not pay as much attention to the effects of the physico-chemical parameters of the grinding environment on the grinding efficiency. Only after Rehbinder [13] had reported his findings on the effect of chemicals in enhancing the mechanical failure of materials, did researchers began to study comminution processes in the presence of chemical additives.

Lowrison [7] has compiled a list of additives used in grinding investigations together with the changes claimed (see Table 8). The data suggest that as much as a 20-fold increase in grinding rate can be obtained by using chemical additives. It is the purpose of the following discussion to review reported effects of environment on grinding processes and mechanisms that are responsible for these effects.

TABLE 8

Additives used in comminution [7]. Reproduced by permission from G. C. Lowrison, *Crushing and Grinding*, Butterworths, London, 1979.

Additive	% added	Material ground	Wet or dry	Grinding rate factor*
Water	0.06	Ceramic enamels	D	—
	0.06	Marble	D	1.6
	0.04	Cement clinker	D	1.3
Alcohols and phenols				
Methanol	▪	Quartz		—
Isopentanol	▪	Quartz		1.29
		Iron powder		20.0
sec-Octanol	—	Quartz		1.4
Series normal alcohols	—	Soda lime glass	D	20.0
Glycerol	—	Iron powder		0.5
Phenols and polyphenois	0.01	Cement		
	0.25			
		Gypsum		
Ketones				
Acetone	0.2	Cement clinker	D	
Amines				
Triethanolamine	—	—		
Flotigan (C_{12}-C_{14} amine ex coconut oil)	0.02	Quartzite		2.2
	0.02	Limestone		1.7
Sulphonic acids				
Arylalkyl sulphonic acid (RDA)	0.06	Graphite		
		Cement		1.3
Fatty acids				
Oleic acid	0.003	Limestone		1.1
		Zinc blende		
Butyric acid		Quartz		1.27
Stearic acid	1.0	Pumice		
	—	Limestone		
Sodium oleate	0.1	Quartz		2.0
	0.1	Limestone		2.0
Vinsol resin (calcium stearate)	0.05	Limestone		
	0.10			
Sodium stearate	—	Dolomite		
	0.15	Cement clinker		1.2
Aluminium stearate	—	Cement		
Caprilic acid	0.5	Chrome ore–magnesite	D	1.2
Marine oil	0.5	Chrome ore–magnesite	D	1.1
Beef tallow	—			
Wool grease	5.0	Limestone		
		Gypsum		
Other carboxylic acids				
Napthenic acid	0.1	Cement clinker	D	1.33
Sodium napthenate	1.0	Quartzite	W	1.40
Sodium sulphonapthenate	1.0	Quartzite	W	1.80
Hydrocarbons				
n-alkanes, various		Soda lime glass	D	
Esters				
Amylacetate		Quartz		1.23
Others				
Carbon black	0.08	Cement		1.3
	0.32	Cement		

(continued)

TABLE 8 *(continued)*

Additive	% added	Material ground	Wet or dry	Grinding rate factor*
Sodium silicate	1.16	Clay slip		—
Sodium hydroxide	—	Magnesite		—
	0.008	Limestone		1.5
Sodium carbonate	0.02	Limestone		2.0
Sodium chloride	0.08	Quartzite		1.2
Carbon dioxide	—	Magnesite		—
	—	Dolomite		—
	0.03	Quartzite	W	1.55
Aluminum chloride		Carbon black		—
		Graphite		
		Talc		—
Ammonium carbonate		Mica		—
		Vermicullite		—
Hardwood pitch	—	Pumice		—
Sodium polymetaphosphate (Calgon)	0.01·	Lead-zinc ore		1.3
	0.04			
Kaolin	10.0	Sulphur	D	—
Thalium chloride	0.02	Quartzite	W	1.65

*Grinding rate factor = new surface produced with additive/new surface produced without additive.

Grinding in water

Wet grinding is generally more efficient than dry grinding [43 - 46]. This has been attributed mainly to chemical reactions between broken surface bonds and water molecules [46]. On the basis of this consideration, water vapor should also be expected to cause similar effects since it can easily penetrate to the crack tip. Ziegler [47] has found that water vapor can increase the efficiency of cement dry grinding in a small vibratory mill, but he also observed organic vapor to produce such effects. Additional evidence has been provided by Locher et al. [48], who have reported that the grinding rate of soda lime glass was higher in humid air than in vacuum. In contrast to the chemical effects discussed above, investigators have also considered physical factors such as reduced cushioning in water of coarse particles and the grinding media by the fines as well as effects of viscosity and specific gravity [1, 12, 49 - 76].

Grinding in organic liquids

There have been several reports indicating the grinding in organic liquids to be more efficient than in water [46, 51 - 57]. For example, Kiesskalt [51] has obtained a 12-fold increase in surface area for grinding in organic liquids, such as isoamyl alcohol,

from that in water. In a similar investigation, Engelhardt [53, 54] studied the effect of alcohol on quartz grinding. His results indicated that in the case of alcohol, less energy was needed to produce the same surface area than that required in water.

In 1956, Ziegler [47] reported a 40% increase in the capacity of cement grinding mills by the use of organic liquids such as ethylene glycol, propylene glycol, butylene glycol and triethanol amine. Since then, organic liquids have been reportedly used in grinding of cement commercially [52]. It was suggested [52, 55] that the vapors of the organic liquids reduced the forces of adhesion between the particles and that led to reduced agglomeration and enhanced material flow and, in turn, to improved grinding.

In another investigation, Lin and Metzmager [46] ground quartz in different environments. Their data showed as much as a 25% increase in grinding rate in carbon tetrachloride and methyl cyclohexane than in nitrogen. Grinding in water was more efficient than in any of the other environments tested. Interestingly, when water was added to the organic liquids, the efficiency of grinding was restored to its value in water alone.

Other organic liquids have been used by Savage et al. [57] to grind silicon carbide in a

TABLE 9

Effect of surface active agents on grinding of quartzite and limestone [59]

Feed	Additive	Additive concentration (%)	Percentage increase in new surface
Quartzite	Flotigam P	0	0
		0.005	+103.2
		0.01	+114.7
		0.03	+123.4
		0.05	+71.4
		0.1	+65.8
		1.0	+58.3
Limestone	Oleic acid	0	0
		0.008	0
		0.0017	+7.3
		0.003	+10.6
		0.006	−17.2
		0.06	−61.3
		1.33	−99.9
Limestone	Sodium oleate	0	0
		0.04	−35.7
		0.08	−1.8
		0.5	−84.5
		1.0	−92.4
Limestone	Flotigam P	0	0
		0.005	+29.2
		0.01	+56.4
		0.02	+74.6
		0.05	+9.6

laboratory vibratory mill. They obtained a 100% increase in the grinding rate in benzene in comparison with that in water alone, while the effect of ethanol was considerably less.

Effect of surfactant addition to grinding environments

There have been several reports in the past that grinding efficiency can be influenced by the addition of surface active agents into the grinding mill. For example, Flotigam P ($(C_{12}-C_{14})$ amine from coconut oil) was found by von Szantho [58] to produce as much as a 100% increase in the surface area of quartz and 75% increase in the surface of limestone when the reagent concentrations were in the range of 0.005 to 0.02% (see Table 9). However, above the concentration of 0.02% of the additive, the effect was noticed to be reduced. Similar results were obtained with an oleic acid/limestone system except that in this case detrimental effects were observed above a concentration of 0.003% oleic acid. On the other hand, sodium oleate decreased the grinding rate of limestone at all levels of

addition (Table 9). It should be mentioned here that the method used for measuring the surface area of the ground product was not described in the paper. In addition, it appears that there was no proper control of important variables such as pH and ionic strength in this work. The observed decrease in surface area above a certain concentration of the additives could be due to experimental artifacts introduced by possible aggregation of the ground products. There is no discussion in the paper on the state of dispersion of the ground products or on any microscopic examination of the products.

In a similar investigation, Gilbert and Hughes [59] studied the effect of additions of Armac T (a mixture of saturated and unsaturated C_{16} and C_{18} amine acetate) on the ball milling of quartz. In this case, the additive was found to produce, at a concentration of 0.01%, a 4 to 12% decrease in the amount of minus 200 mesh produced in the pH range of 2 to 5. An increase in the surfactant concentration from 0.01% to 0.1% decreased the grinding efficiency further at all pH

(a)
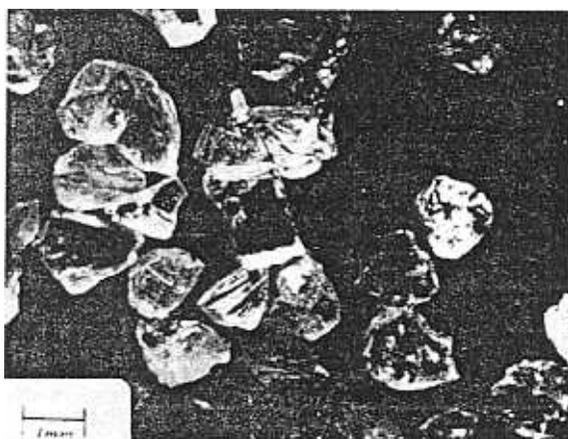
(b)

Fig. 3. Photomicrographs of (−14 +20 mesh) size fraction of quartz ground in 10^{-1} mol/l amine in a stainless steel mill [60]; (a), dispersed using 8 g/l sodium silicate solution; (b), dispersed using 8 g/l sodium silicate solution and then washed with alcohol and acetone.

values. For example, the level of addition of 0.1% at pH 5.0 produced as much as a 36% decrease in the amount of 200 mesh produced as compared with that produced in water alone. The authors have not offered any explanation for the observed effects. Somasundaran and Lin [1] have examined these data and suggested that physical adsorption of Armac T (cationic surfactant) on the quartz surface (negative above pH 2.0) could have decreased the charge on the particles and thereby caused an increase in their flocculation. According to them, it is not clear whether the reported low grinding efficiency was due to any experimental artifact introduced by such aggregation of the ground products, or the direct result of a change in interfacial properties brought about by the

surfactant. The importance of proper dispersion of the ground products has been verified recently by El-Shall *et al.* [60]. Using microscopic examination of selected size fractions, the authors have found that sodium silicate was not a sufficiently effective dispersant for the product ground in 10^{-1} mol/l amine solution (see Fig. 3(a)). The grinding results in this case suggested initially the use of amine to be detrimental (see Fig. 4). However, after proper dispersion of the ground products using alcohol/acetone washes (see Fig. 3(b)), amine was observed to have acted as a grinding aid.

Other reports of the effect of surfactant addition include that of Kukolev *et al.* [61, 62], who obtained improved grinding efficiency of alumina on using organo-silicone at a concentration of 0.005%. Malati and his co-workers [63] and El-Shall *et al.* [64] have independently produced finer products by adding oleic acid to the wet milling of hematite.

The influence of dodecylammonium chloride on grinding of quartz in a porcelain ball
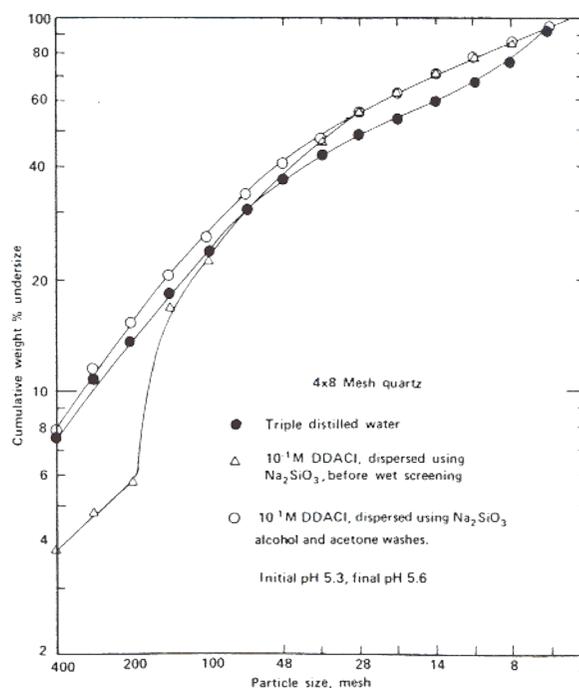
Fig. 4. Effect of 10^{-1} mol/l DDACl on size distribution of 4 × 8 mesh quartz products ground in a stainless steel ball mill at natural pH [60]. ●, triple-distilled water; △, 10^{-1} mol/l DDACl, dispersed using Na_2SiO_3 before wet screening; ○, 10^{-1} mol/l DDACl, dispersed using Na_2SiO_3, alcohol and acetone washes. Initial pH, 5.3; final pH, 5.6.

mill has been investigated by Ryncarz and Laskowski [65]. The effect of the additive was found, in this case, to depend on its concentration and the pH of the solution. The authors correlated their grinding results with the zeta potential of quartz in amine solutions. They concluded that grindability was minimum under conditions of zero zeta potential. It should be noted that the investigators have not taken into account the possibility of surface contamination by aluminum species from the porcelain mill and consequent effects on the interfacial properties of the ground material. Aluminum species at concentrations as low as 10^{-5} mol/l have been found to reverse the zeta potential of quartz fines [66]. Adsorption of cationic collectors (e.g. amine) can indeed be prevented under such conditions. In this regard, Ryncarz and Laskowski [65] have pointed out that grinding was extremely sensitive to the concentration of iron species present in their grinding system. Although the authors have concluded that wet grinding of a given mineral could be improved by the proper choice of additives, they have also warned that it would appear to be almost impossible to predict any effects accurately in the case of

ore grinding, due to the possibility of the presence of extraneous ionic species.

Recently, El-Shall et al. [64] have obtained finer products in the neutral and alkaline pH range, on adding dodecylammonium chloride during quartz grinding in a stainless steel ball mill. Detrimental effects were obtained in the acidic solutions, as shown in Fig. 5. The authors correlated their results with the effect of amine on interfacial properties of quartz (zeta potential and flocculation characteristics) under simulated chemical conditions. Ferric salts were added in this case to simulate the iron released from the balls and the mill during grinding. This is very important since ferric ions can even reverse the charge on quartz particles and consequently affect the flocculation properties, as shown in Figs. 6 and 7.

Effect of addition of inorganic electrolytes to grinding environments

The effect of inorganic electrolytes on grinding of minerals has been investigated by several workers [58, 77, 78]. Although results reported in the literature are often contradictory to each other, grinding has in general been found to be more efficient in the presence of inorganic electrolytes [19].

In 1948, Kukolev and Melnishenko [79] studied the effect of caustic soda and soap on the ball milling of magnesite ($MgCO_3$) and dolomite ($MgCO_3 \cdot CaCO_3$). They found caustic soda to be beneficial to the grinding of magnesite, with no effect on the grinding of dolomite. Soap, on the other hand, was found to help the grinding of dolomite, with no effect on magnesite. The authors attributed the observed effects to the difference in adsorption of sodium hydroxide on the two minerals. Somasundaran and Lin [1] have noted that there is no reason for sodium hydroxide not to have the same adsorption capacity on both minerals. They supported their argument with the help of the reported beneficial effects of the above reagents on the grinding of limestone, which is chemically similar to dolomite [80, 81].

In another work, Frangiskos and Smith [80] investigated the influence of sodium hydroxide and sodium carbonate on the grinding of limestone using a laboratory drop-weight mill. These workers obtained improved grinding efficiency in the presence of the
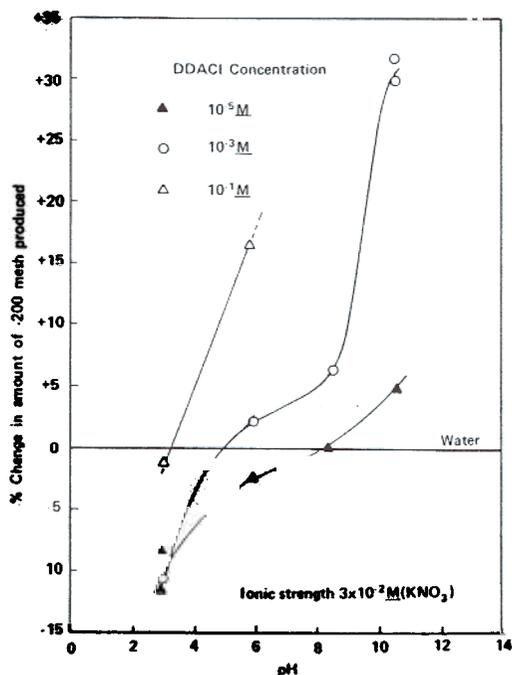
Fig. 5. Effect of amine on the amount of −200 mesh produced by wet ball milling of quartz [64]. DDACl concentration: △, 10^{-5} mol/l; ○, 10^{-3} mol/l; ▼, 10^{-1} mol/l. Ionic strength: 3×10^{-2} mol/l (KNO_3).
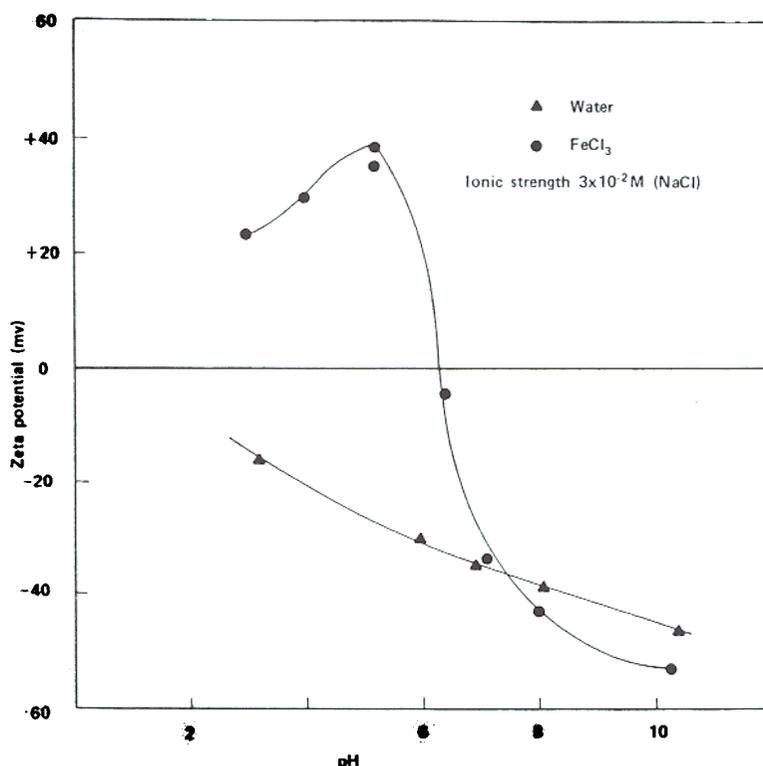
Fig. 6. Effect of 10^{-4} mol/l $FeCl_3$ on zeta potential of quartz as a function of pH [67]. ▲, water; ●, $FeCl_3$. Ionic strength: 3 x 10^{-2} mol/l (NaCl).

above additives. Ghosh and co-workers [81] have subsequently repeated some of Frangiskos and Smith's experiments. Their data also indicated increased beneficial effects but with a maximum at an additive concentration of 0.02%. Increase of the concentration to 0.04% produced less beneficial effects. The authors failed to give any explanation for the observed maximum. The presence of such maximum has also been reported by other workers [58], who obtained poor grinding on increasing additive concentration above certain levels. Additional evidence is provided by Halasyamani and co-workers [82, 83] in their investigation of the influence of pH on the grinding rate of quartz and calcite in a steel ball mill using HCl and NaOH. Maximum grinding rate of quartz was obtained around pH 7.0. In this case, the authors explained the observed results as due to increased flocculation of quartz in the neutral pH range compared with the acidic or the alkaline pH range. They claimed that the flocculated material in the mill was in a better position to receive impacts, leading to improved grinding. It should be noted that these investigators did not verify whether the quartz was flocculated.

Actually, it is not clear why quartz should flocculate at any pH other than close to its point of zero charge, i.e. pH ~2.0 [84]. In another work, Mallikarjunan et al. [83] reported an increase in surface area of calcite with decreasing pH in the pH range of 8 to 4, whereas the surface area of quartz was found to decrease with pH in the same pH range. This observation could, however, have been due to better dispersion of the particles since the direction of pH change for surface area increase was away from the point of zero charge for both quartz and calcite (2.0 and 10.5, respectively) [84, 85].

Savage et al. [57] studied the effect of sodium chloride and various salts of multivalent ions on the grinding of silicon carbide, using water or ethanol as the grinding fluid. They classified the salts into flocculants ($MgCl_2$, $CaCl_2$, and $FeCl_2$, and $FeCl_3$) and dispersants (NaCl and $Na_4P_2O_7$). The authors concluded that in both water and ethanol, dispersants significantly improved the grinding rate.

It has been reported by various workers that multivalent ions do affect the grinding efficiency of minerals. For example, Fran-
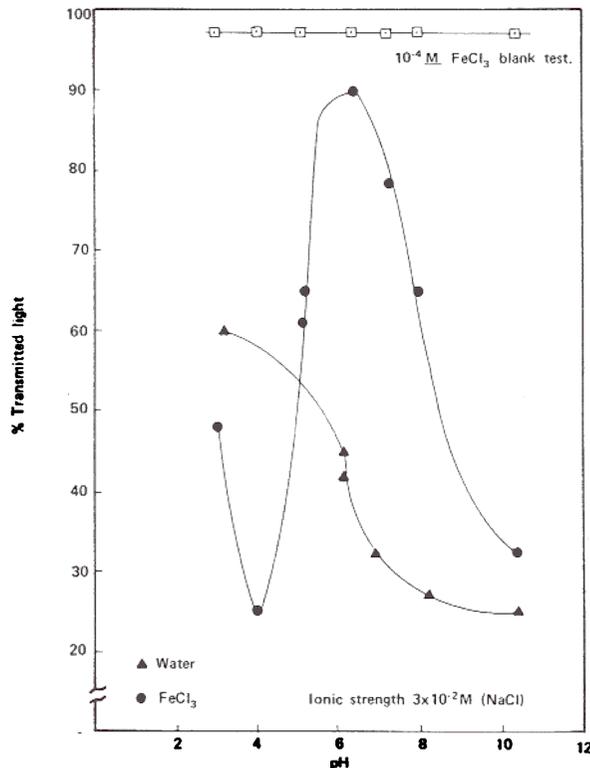
Fig. 7. Effect of 10^{-4} mol/l $FeCl_3$ on the turbidity of quartz slimes as a function of pH [67]. □, 10^{-4} mol/l $FeCl_3$ blank test; ▲, water; ●, $FeCl_3$. Ionic strength 3×10^{-2} mol/l (NaCl).

giskos and Smith [80] have reported an increase of as much as 50% and 15% in surface area of ground quartz due to addition of 2.0 mol/l $AlCl_3$ and $CuSO_4$, respectively. Furthermore, they found iron-stained quartz crystals to grind faster than the clear ones. On this basis, they have suggested that ferric ions might have affected the fracture of quartz during grinding. It should be noted that there was no indication as to whether these investigators have controlled the pH or the ionic strength of the grinding solution. Thus, no conclusion can actually be drawn about the mechanisms involved in such systems.

Recently, Hartley et al. [2] have studied the effect of sodium hydroxide on wet ball milling of taconite ore. They obtained an increase in surface area when the feed was of narrow size range; however, when they used a feed of complete size distribution, no effect was obtained. They assumed the ineffectiveness of the additives in the latter case to be the result of changes in viscosity due to the presence of fines in the feed.

In addition to the works discussed above, higher efficiency of grinding has been reported in mineral processing plants using sea water to make up the pulp instead of the ordinary tap water [86 - 88].

Effect of the physical properties of the grinding environment

As mentioned earlier, transport of the material through the grinding mill is one of the important component processes in the grinding operation. The material transport in the mill depends primarily on physical properties of the pulp, such as pulp fluidity, state of dispersion or flocculation of the pulp, density of the solids and density of the medium. In other words, these properties determine how well particles are transported to the grinding zone itself. In addition, such properties can be expected to have an effect on the hydrodynamic behavior of particles as well as on the grinding media such as balls or rods, and consequently, on the grinding performance [1].

It has been reported [57, 89 - 92] that pulp viscosity can influence the grinding of ores. Schweyer [89] found grinding in pebble mills to be dependent on the viscosity of the medium up to a certain grinding time, and then to be independent of it. In a similar work, Hockings et al. [90] studied the effect of pulp viscosity (using corn syrup to control the viscosity) on the rate of production of quartzite fines in a rod mill and found the increase in the pulp viscosity from 1 to 1000 cP to cause as much as a 50% decrease in the grinding rate when the grinding was conducted for 1 min. The observed effect was of a smaller magnitude for 2, 3, and 4 min grinding (see Fig. 8). Additional results in this area have been reported by Savage et al. [57], who ground silicon carbide in liquids of different viscosities and the results indicated faster grinding rates in liquids of lower viscosities.

Fluidity modifiers and dispersants have been reported to produce both an increase and a decrease in grinding efficiency [2, 67, 68 - 75, 92]. For example Hartley, et al. [2] have obtained a marked decrease in grinding efficiency of molybdenum ore when they added sodium tripolyphosphate to their grinding circuit. On the other hand, Hanna and Gamal [92] found that sodium silicate enhanced grinding of limestone.
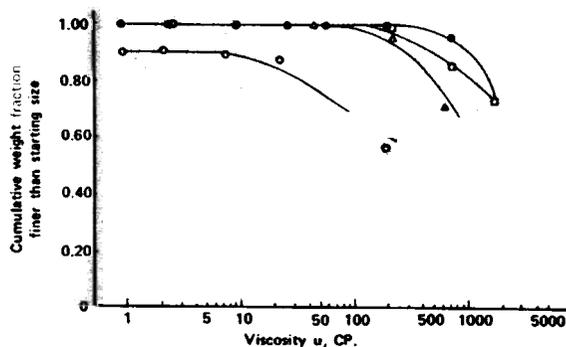
Fig. 8. Cumulative percentage finer than the starting size *vs.* viscosity for rod mill grinding of 10 X 14 mesh quartzite in corn syrup–water mixtures for various grinding times; after Hockings *et al.* [90]. ●, 240 s; □, 180 s; △, 120 s; ○, 60 s.

Fig. 9. Back-calculated S curves for taconite ore slurries ground in 8 in batch ball mill showing effect of grinding additives [72]. All slurry densities at 84 wt.%. +, experimental (one-size fraction method); ─, computer back-calculation.

Fig. 10. Typical response curve for industrial-scale mill [72].

In 1970, Klimpel and co-workers [68 - 75] have initiated a research program aiming at identifying possible grinding aid chemicals. They have conducted several laboratory and industrial scale tests using fluidity modifiers. Examples of the results obtained in these tests are shown in Figs. 9 and 10. The data given in Fig. 9 suggest an increase in the specific rate of breakage due to the grinding aid addition. Similarly, the industrial data shown in Fig. 10 indicate that a finer product could be obtained with approximately constant feed rate whenever the aid is added. Also, a constant grinding size is achieved with higher feed rates, due to addition of the grinding aid.

The behavior of these reagents has been characterized by measuring their effects on the rheology (viscosity) of the ground products. Correlation of rheological data and laboratory grinding results [74, 75] has made it possible for the investigators to identify slurry conditions when chemical additives would increase rates of breakage. In this regard, they have concluded that chemicals that can work as grinding aids should maintain pseudoplastic behavior in the slurry without yield stress, or reduce the yield stress in a dense pseudoplastic slurry.

On the basis of the above discussions, one can conclude that comminution processes can, in general, be enhanced by the use of inorganic and organic additives under selected conditions. Indeed, in order to fully develop and utilize such effects, it is necessary to establish the mechanisms involved in such effects.

Unfortunately, most of the past work is not of much practical use due to lack of proper control of relevant variables such as solution, pH, ionic strength, etc., and possibly owing to experimental artifacts that can arise out of agglomeration of products that were not properly dispersed before size analysis after contacting with surfactants.

An additional experimental problem can be the frothing of the pulp in the presence of surfactants during grinding and the consequent change in the hydrodynamic characteristics of the grinding environment, as well as possible entrapment of the mineral particles in the froth (see Fig. 11) [60]. The entrapped particles can remain levitated and escape the grinding actions, with resultant reduction in grinding efficiency. This possibility has not been taken into consideration by the past workers.

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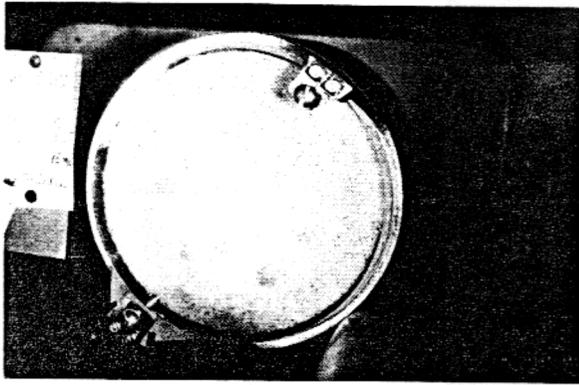
Fig. 11. Photograph showing frothing during milling in 10^{-1} mol/l amine at 78% critical speed, elapsed time of grinding = 5 s [60].

Unless precautions are taken to avoid or to account for such experimental artifacts and problems, observations, even though real, can be misleading. In addition, without a full understanding of all the interfacial properties of the systems under study, comminution results are likely to be attributed directly to the effect of additives on fracture.

The above review of the past results clearly shows that most of the past works have not taken into account the above-mentioned problems, and therefore no definite mechanisms could be derived on the basis of such results.

Reported mechanisms

Most of the past results of the effect of chemical additives on comminution of materials have been interpreted in terms of two major mechanisms. The first is called 'Rehbinder's effect' [93]. It is based on the reduction of surface free energy of solids induced by the adsorption of surface active agents. Since fracture of materials in comminution processes involves creation of new surfaces, the amount of energy required should be proportional to the surface free energy of the created surfaces. If the surface free energy could somehow be reduced, then the energy consumption in creating the same surface area could be expected to be less. On this basis, adsorption of surface active agents during grinding should be expected to improve the grinding efficiency. However, as discussed earlier, the actual amount of energy needed to create new surface represents only about 1% of the energy input to the comminution system. In addition, the effect of

chemical additives on other important parameters and properties of the system such as plastic deformation, crack initiation and/or propagation, flocculation and dispersion, etc., are neglected in this mechanism.

Primarily, presence or initiation of cracks is the prerequisite factor for fracture to occur. Additionally, parameters such as crack length, crack tip radius, plastic flow at the crack tip, propagation of the cracks, etc., will determine the strength of materials. The effect of chemical additives on such parameters, in addition to their effect on the surface free energy, should therefore be noted.

The second mechanism, based on adsorption-induced mobility of near surface dislocations, was proposed by Westwood *et al.* [37 - 40], who studied the effect of various additives on the hardness of different crystalline and non-crystalline materials. They correlated their hardness measurements and drilling rates with near-surface dislocation mobility and interpreted 'Rehbinder's effect' as a result of changes in the electronic states near the surface, and point and line defects caused by the adsorption of the additive on the surface of the solid. Such changes can influence specific interactions between dislocations and point defects which control the dislocation mobility and hence the hardness. However, this mechanism cannot be used exclusively to explain the effect of the environment on grinding, because important properties such as pulp fluidity, flocculation, and dispersion, etc., are not considered.

Chemisorption or formation of activated complexes between the additive molecules and the crack surface has been considered by several workers, including Somasundaran and Lin [1], to be important to the fracture process.

Other investigators [31] have considered enhanced corrosion due to stress application (stress-corrosion cracking) as a mechanism responsible especially for the fracture of metals. The mechanism responsible for stress-corrosion cracking is not, however, clear at present, particularly because of the inconsistencies in reported results.

Another mechanism considered by some investigators [44, 57, 67, 68 - 75, 92] is based mainly on the role of reagents in dispersion and, hence, the flow of particles in the mill during comminution processes.

As discussed earlier, grinding is an integral process composed of several simultaneous sub-processes, and chemical additives can affect these sub-processes due to one or all of the previously discussed mechanisms. Identification of the role of each mechanism is possible only if the relevant properties of the solid and of the solution in contact with the solid during its fracture are simultaneously determined. The experimentally accessible properties, in this regard, include zeta potential, surface tension, pH, ionic strength, temperature, chemical composition of the solution, and frothing and flocculation characteristics of the system. Also, it is necessary to control and monitor pretreatment of the material to be ground and its physical as well as structural and surface properties. Finally, the machine characteristics such as speed, size, and mechanisms of stress application and other related parameters like loading, material filling, etc., must be taken into account.

It is clear from the above review that chemical additives can influence grinding for a number of reasons:

a) modification of the flow of pulp in the grinding mill;

b) influence on reagglomeration of the freshly produced fines;

c) modification of frothing characteristics of the pulp during grinding;

d) influence of interactions between mineral particles and balls and mill wall and among particles themselves (due to changes in frictional characteristics);

e) influence on the strength of the material due to: 1) effect on crack initiation and crack extension energy, and 2) retardation of rejoining or sealing of the freshly created cracks.

Elucidation of the mechanisms governing the effect of environment on grinding depends essentially on identification of the effects on all the above factors and interactions between them.

ACKNOWLEDGEMENT

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