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Mechanisms of Grinding Modification by Chemical Additives: Organic Reagents

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SUMMARY

The effect of dodecylammonium chloride on properties of quartz slurries that are relevant to grinding, such as pulp fluidity, flocculation and dispersion, and primary breakage, have been investigated in this study. These tests were conducted under chemical conditions (pH, ionic strength, additive concentration, etc.) similar to those used in wet ball milling tests. The data obtained were correlated with the grinding results. Amine was found to improve grinding, pulp fluidity, and primary breakage of quartz suspensions, especially in the alkaline pH range. These beneficial effects are attributed to the formation of highly surface-active amineaminium complexes in this pH range. In contrast to the above, amine decreased the grinding rate in the acidic pH range owing to increased flocculation of quartz fines in the presence of amine in this pH range. These results show that grinding of quartz can be improved by amine if other conditions such as pH are controlled. Also, the results indicate that the effect of chemical additives on grinding cannot be attributed to a single mechanism, but that the cumulative effect on different pulp properties has to be taken into consideration. Examination of the effect of all properties has led to a better understanding of the mechanisms responsible for the observed grinding aid effects in the present study.

INTRODUCTION

Past investigators have considered two major mechanisms to be mainly responsible for the observed effects of chemical additives on grinding: the first based on the reduction of surface-free energy of solids induced by the adsorption of surface active agents [1], the second related to changes in surface hardness due to the influence of the adsorbing species on the mobility of near-surface dislocations [2]. Based on the results of a research program studying the effect of fluidity modifiers on the performance of batch and industrial grinding mills, other workers [3 - 13] have adopted a third mechanism. The proposed mechanism has emerged from correlation of the grinding results with the rheological behavior of slurries of similar solid content. Such correlations indicate that certain water-soluble chemicals can improve the fluidity of highly concentrated solid suspensions, leading to higher throughputs or finer products at constant feed rates.

The above discussion suggests that the effect of chemical additives on the grinding process has been attributed to individual mechanisms. However, grinding is an integral process involving several simultaneous subprocesses such as transport of particles to and from the grinding zone, where they are subjected to different kinds of stresses. Evidently, such subprocesses depend on pulp properties such as fluidity, state of flocculation or dispersion, and mechanical properties of particles. Therefore, the individual as well as the cumulative environmental effects on the pulp properties should be considered when formulating mechanisms controlling the influence of chemical additives on grinding.

In this study, the results of adding dodecylammonium chloride during quartz wet ball milling are correlated with its effects on basic properties of the system such as pulp fluidity,

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flocculation and dispersion, and crack initiation and propagation (primary breakage).

EXPERIMENTAL

Material and chemicals

A highly crystalline quartz sample of 99.9% purity (Hot Springs, Arkansas variety) purchased from Ward's Natural Science Establishment was used in this study.

The amine was dodecylammonium chloride (DDACl) of practical grade purchased from Eastman Kodak. pH adjustments were made using reagent grade NaOH or HCl. Reagent grade NaCl was used to adjust the ionic strength. $Fe(NO_3)_3$ or $FeCl_3$ crystals purchased from Fisher Scientific Company were used in the basic studies to simulate the dissolved iron introduced into the mill during grinding. Triple-distilled water was used for the preparation of all solutions.

Equipment and methods

In this study, the following experiments were conducted:

1. Tests to determine the effect of amine on the primary breakage of quartz (single impact tests)

These tests were conducted in a drop-weight mill of a similar design to the one used by other workers [14, 15]. The impact was applied by means of a falling mass on a spread layer of (10 × 20 mesh) quartz particles wetted by the desired solution. The size distribution of the broken products was determined, and the percentage change in amount passing a 20 mesh screen calculated.

2. Turbidity tests

Flocculation characteristics of quartz slimes were studied by determining turbidity under different chemical conditions. These tests were conducted by measuring the percentage of transmitted light through a suspension. The instrument used was a Spectronic 20 spectrophotometer. For this purpose, 0.3 g samples of −400 mesh quartz were prepared in an agate morter, then mixed with 50 cm^3 of 10^{-4} mol/l of ferric nitrate adjusted to the desired pH, ionic strength, and additive concentration to simulate the grinding environment. Ferric nitrate was added to account for the iron that is released from the mill during grinding. After tumbling the suspension for 10 min, a 6 ml sample was poured into the instrument holding tube to measure the percentage light transmitted. All the measurements were made at a wavelength of 620 nm. In each case, the instrument was calibrated with water for a reading of 100% transmission.

3. Rheological studies (torque measurements)

These experiments were performed under selected conditions to identify the effect of the above additives on the flow behavior of pulps at high solid concentrations. The equipment and experimental conditions for the measurements are summarized below.

Driver and control: Master servodyne (Cole–Palmer, Chicago); constant speed and torque control unit model 4424; digital millivoltmeter (Weston 1240); motor (EC Motamatic Model E600-013)

Impeller: 6-blade MixCo turbine, 4 in diameter, 0.8 in above tank, speed 200 ± 2 rpm

Tank shape: Octahedral; 4.8 in largest dimension

Solid: 420.0 g of quartz, density = 2.65 g/cm^3

Pulp density: 1.6 g/cm^3 (67.8% solids by weight)

Pulp volume: 0.2 litre

RESULTS AND DISCUSSION

Grinding results

Earlier work [16] has suggested that amine can influence wet ball milling of quartz both beneficially and deterimentally, depending on pH and additive concentration. These results are reproduced in Fig. 1. It can be seen that the amine addition to the ball mill is beneficial, except under acidic conditions, where detrimental effects are obtained at all amine levels. Also, in the neutral pH range, addition of amine at levels lower than 10^{-3}mol/l is found to lead to reduced grinding.

Single impact tests

The effect of pH on the size distribution of quartz broken by single impact in 10^{-5} mol/l dodecylammonium chloride and 10^{-4} mol/l $FeCl_3$, at three different pH values, is shown

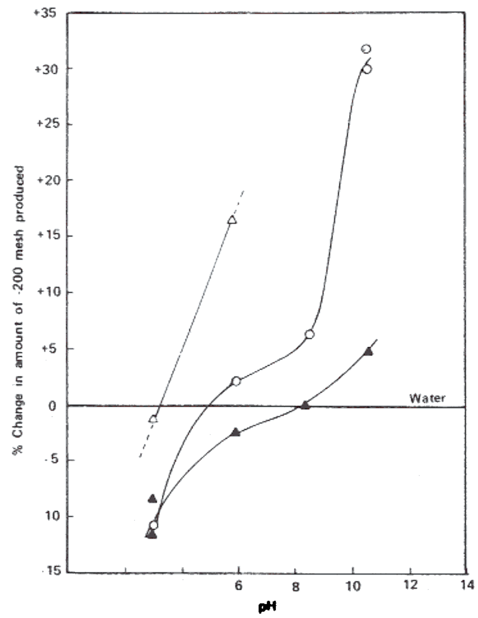

Fig. 1. Effect of amine on amount of —200 mesh produced by wet ball milling of quartz. DDACl concentration: ▲, 10^{-5} mol/l; ○, 10^{-3} mol/l; △, 10^{-1} mol/l. Ionic strength 3×10^{-2} mol/l (KNO_3).

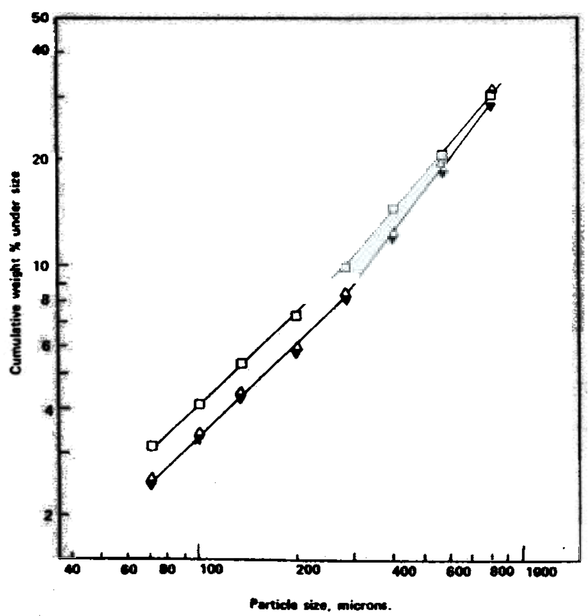

Fig. 2. Gaudin–Schuhmann size distribution of quartz crushed in (10^{-5} mol/l DDACl + 10^{-4} mol/l $FeCl_3$) solution at different pH values, by a single impact in a drop-weight mill. pH: □, 10.5; △, 5.9; ▼, 3.0. Ionic strength: 3×10^{-2} mol/l (NaCl).

in Fig. 2. The data show that quartz can be broken more easily at this amine level at pH 10.5 than at neutral (pH 5.9) or acidic pH values (pH 3.0). It is interesting to compare these results with the maximum flotation recoveries that are usually obtained for quartz using amine under similar pH conditions. The observed maximum has been attributed in the past [17 - 19] to the adsorption of the neutral amine molecules along with the ions. Recently, the increase of flotation recoveries at pH 10.5 has been attributed to the formation of ionomolecular complexes which has significantly higher surface activity than that of the complexing species [20, 21]. Similarly, the observed increase in primary breakage of quartz at pH 10.5 could be related to the presence of such ionomolecular amine complexes in the alkaline pH range.

Torque measurements

The effect of two levels of dodecylammonium chloride on the torque exerted on an impeller in quartz suspension, in 10^{-4} mol/l ferric chloride solution, at three different pH values is investigated. The results indicate a decrease in torque in the amine solution, compared with that in ferric chloride solution alone, at all pH values. The data obtained at pH 10.5 are given in Fig. 3. It should be mentioned that the reduction in torque, due to amine addition, is more pronounced at pH 10.5 than at pH 3.0 or at pH 5.9. As discussed earlier, this might again be related to the formation of highly surface-active ionomolecular amine complexes in the alkaline pH range.

Flocculation studies

Results obtained for the transmission of light through quartz suspensions in water containing 10^{-4} mol/l $Fe(NO_3)_3$ and in amine solutions of different concentrations are given in Fig. 4. The data suggest a strong possibility of quartz flocculation in the presence of amine even at lower levels of additions. In the 10^{-3} mol/l amine solution, quartz particles are found to exhibit less flocculation than in 10^{-5} mol/l solution. This is in accordance with the expected flocculation behavior on the basis of a higher zeta potential of quartz particles in 10^{-3} mol/l than in 10^{-5} mol/l solution [22]. This is further confirmed by the theoretical estimates of the stability ratio W from the reported zeta potential values (see Fig. 5). Notice that as W decreases, rapid coagulation occurs. The values of stability ratios are calculated using the following formula [23]:

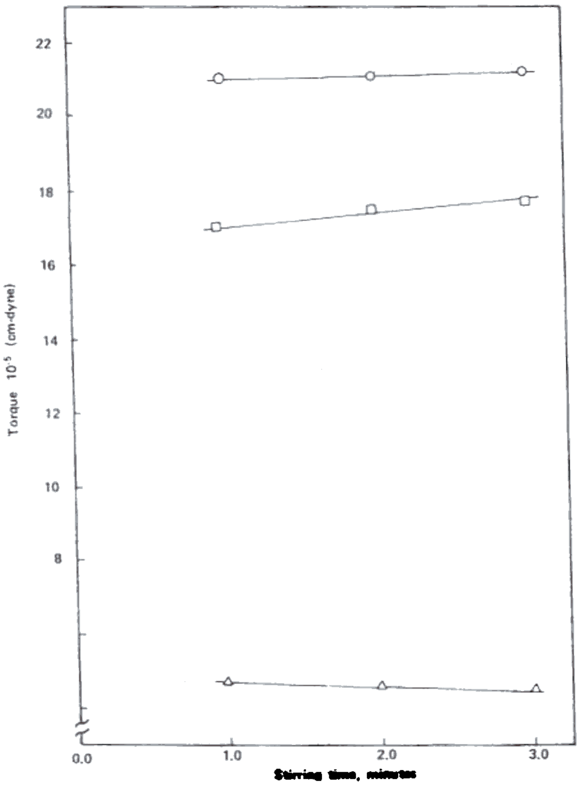

Fig. 3. Effect of amine on the torque exerted on an impeller stirring quartz suspension in 10^{-4} mol/l $FeCl_3$ solution. Amine concentration: ○, 0.0 mol/l; □, 10^{-5} mol/l; △, 10^{-3} mol/l. Initial pH, 10.5 ± 0.1; final pH, 9.9 ± 0.1. Ionic strength: 3 x 10^{-2} mol/l (NaCl).

$$\ln W = \frac{A}{24KT}\left(\frac{D^2\psi_\delta{}^2 - D\psi_\delta}{1+a}\right)$$

$$\frac{3\ \ln(D\psi_\delta)^2}{4} + B$$

where

$$12(2\kappa a + 1)\epsilon a$$

$$B = \ln^2\sqrt{\pi} - \frac{1}{2}\ \ln\ \frac{A}{\text{----}} + \frac{A}{24KT}$$

where A is the Hammaker constant = 10^{-12} erg for the present system, κ is the Debye–Huckel reciprocal length, ϵ is the dielectric constant, K is the Boltzman constant, T is the absolute temperature, a is the particle radius, and ψ_δ is the stern potential. In our calculations, we have used the zeta potential values for ψ_δ.

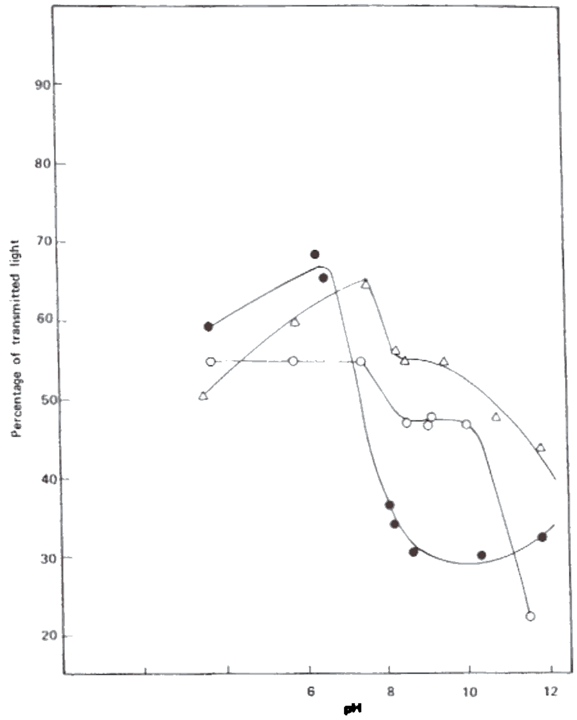

Fig. 4. Effect of dodecylammonium chloride on the turbidity of quartz suspension in 10^{-4} mol/l $Fe(NO_3)_3$ solutions. Quartz in 10^{-4} mol/l $Fe(NO_3)_3$ and: ●, distilled water; △, 10^{-5} mol/l DDACl; ○, 10^{-3} mol/l DDACl. Ionic strength 3 x 10^{-2} mol/l (KNO_3).

Correlations

For breakage to be achieved, particles should be captured in the grinding zone and subjected to a fruitful grinding event of either impact or abrasion. In other words, the rate of grinding will depend on the probability of breakage, P (breakage), which can be visualized as a function of probability of capture, P (capture), and probability of breakage upon capture, P (breakage/capture), as suggested by Hartley *et al.* [24]. P (breakage/capture) can be expected to depend on the strength properties of the solid while P (capture) can be expected to depend, among other factors, on pulp fluidity and flocculation.

To foster correlations for the dodecylammonium chloride/quartz system, the data obtained under different conditions in the presence of amine will be compared with those obtained in its absence in the three pH regions, *i.e.* acidic (pH 3.0), neutral (pH 5.9) and alkaline pH range (pH 10.5). The changes in different properties of quartz suspensions

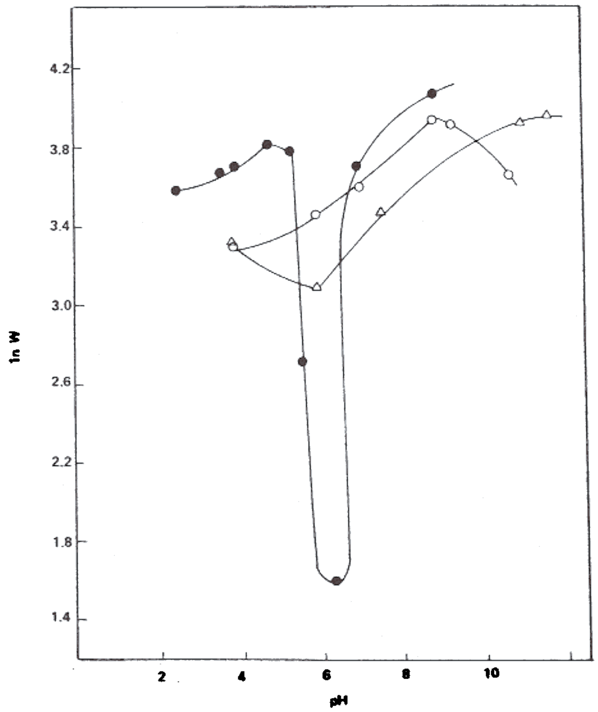

Fig. 5. Effects of dodecylammonium chloride on the stability ratio W of quartz suspensions in 10^{-4} mol/l $Fe(NO_3)_3$ solutions. Quartz in 10^{-4} mol/l $Fe(NO_3)_3$ and: ●, water; △, 10^{-5} mol/l DDACl; ○, 10^{-3} mol/l DDACl. Ionic strength: 3×10^{-2} mol/l (KNO_3).

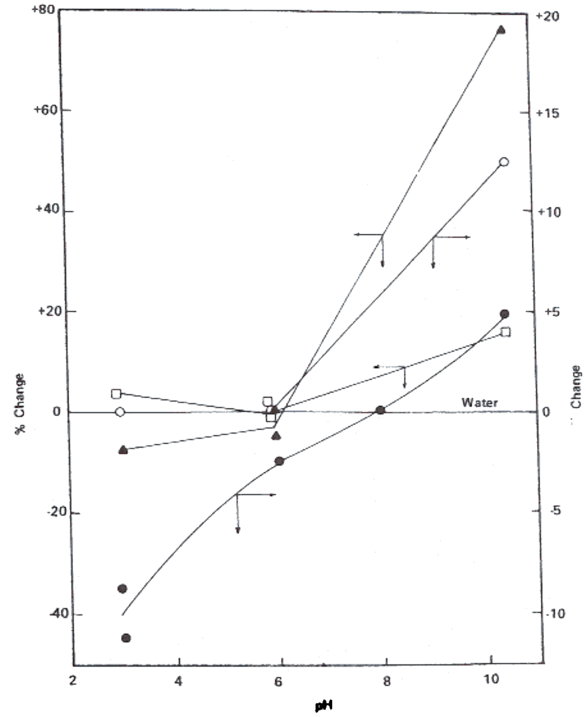

Fig. 6. Change in different properties of quartz suspension due to 10^{-5} mol/l amine addition as a function of pH. ●, grindability; ○, breakage; □, fluidity; ▲, flocculation.

due to amine addition are shown in Figs. 6 and 7.

A. Acidic solutions (pH 3.0)

a) The results show a decrease in grinding rate in the presence of amine at all levels of amine addition.

b) Amine addition does not affect the primary breakage of quartz particles in this pH range.

3) Addition of 10^{-3} mol/l amine does cause an improvement in the flow properties of the quartz suspension. Lower levels of amine addition (10^{-5} mol/l) show only a small effect on fluidity at this pH.

d) At both levels, amine does not appreciably affect the flocculation state of quartz suspension. However, it is possible that the flocs formed in the presence of amine are stronger than those formed in its absence, as a result of interactions between the hydrophobic amine chains.

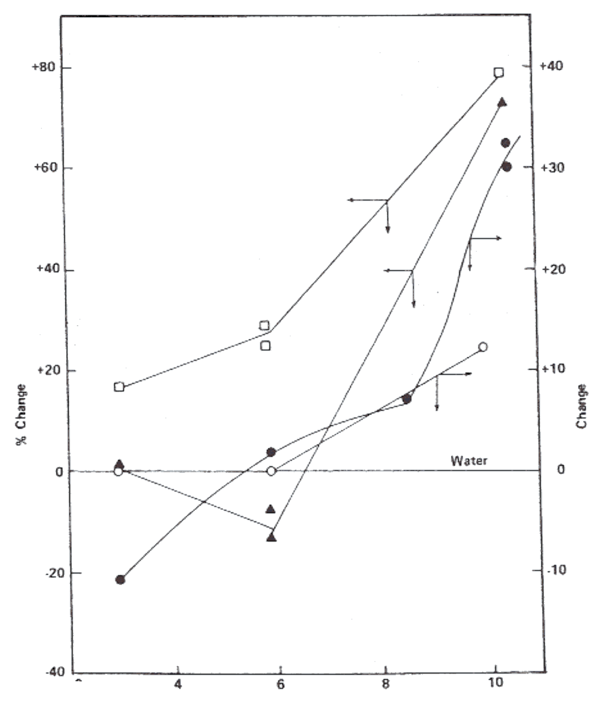

Fig. 7. Change in different properties of quartz suspensions due to 10^{-3} mol/l amine addition as a function of pH. ●, grindability; ○, breakage; □, fluidity; ▲, flocculation.

Possible mechanisms

From the above discussion, it appears that the decrease in grinding rate is due to the strength of the flocs when amine is used. Formation of strong flocs could affect grinding owing to:

a) decrease in energy utilization due to disintegration of flocs and dislodging of the fines leading to: 1) a decrease in the probability of coarse particles breakage, *P* (breakage upon capture), and 2) decrease in the probability of nipping of coarse particles due to the increase in diameter of particles, *P* (capture) will, in such a case, be less in the presence of amine.

B. Neutral solutions (pH 5.9)

a) The grinding data suggest a slight decrease in the grinding rate in 10^{-5} mol/l amine solution at this pH. Increased addition (10^{-3} mol/l) enhanced the grinding rate only slightly.

b) Primary breakage characteristics remain unaltered by the addition of amine.

c) Amine does not change the pulp fluidity at 10^{-5} mol/l. However, increased pulp fluidity was observed in 10^{-3} mol/l amine solutions.

d) As in acidic solutions, there is no effect of amine on the extent of flocculation of the pulp. However, the flocs themselves can be stronger in the presence of amine due to interactions between the hydrophobic chains of the amine species.

Possible mechanisms

The above analysis suggests that the increase in the strength of the flocs in the presence of amine is possibly the reason for the detrimental effect on grinding at this pH when 10^{-5} mol/l amine is added. This, along with the slight flocculation effects, could have also masked some of the beneficial behavior expected at higher levels (10^{-3} mol/l) of amine due to the improvement in pulp fluidity at such levels.

C. Alkaline solutions (pH 10.5)

a) The data at pH 10.5 indicate an increase in the grinding rate.

b) Primary breakage is increased by the addition of amine in this pH range.

c) The pulp fluidity is better in the presence of amine.

d) Quartz particles are flocculated in amine solutions.

Possible mechanism

From the above observations, it can be concluded that the beneficial effect of amine on grinding at pH 10.5 is due to the summation of positive effects on primary breakage and the pulp fluidity. Negative contribution from the flocculation is apparently unable to dominate over the beneficial effects.

CONCLUSIONS

Correlation of the grinding results in amine solutions with the results of basic studies conducted under simulated chemical conditions has led to the following conclusions:

1. The decrease in grinding rate due to amine additions (10^{-5} mol/l and 10^{-3} mol/l) at pH 3.0 and pH 5.9 is attributed to the formation of stronger flocs when amine is used (owing to chain–chain interactions).
2. Formation of such flocs could affect grinding owing to: a) decrease in energy utilization owing to use of it for disintegration of the flocs also; b) cushioning of the coarser particles.
3. Improved grinding is obtained at pH 5.9 on adding amine at a dosage of 10^{-3} mol/l. This is attributed to the improvement obtained in pulp fluidity due to such amine addition. The small magnitude of this beneficial effect is due to the retarding negative contribution from pulp flocculation.
4. Marked beneficial effects were obtained at both levels of amine (10^{-5} mol/l and 10^{-3} mol/l) at pH 10.5. These effects resulted from the cumulative effect of improved primary breakage and the flow properties of the pulp. Negative contribution from flocculation at pH 10.5 was not sufficiently large to mask the beneficial effects.
5. It is suggested that at pH 10.5 amine affects various interfactial properties significantly and, consequently, the grinding, owing to the formation of highly surface-active iono–molecular complexes in this pH range.

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REFERENCES

1 P. A. Rehbinder, *Physik, V. 72* (1931) 191.
2 A. R. C. Westwood and D. L. Goldheim, *J. Appl. Physics, 39* (1968) 3401.
3 H. E. Rose and R. M. E. Sullivan, *Ball, Tube and Rod Mills*, Chem. Pub. Co., New York, 1958, p. 30.
4 K. I. Savage, L. G. Austin and S. C. Sun, *Trans. AIME, V. 225* (1974) 89.
5 R. Klimpel and W. Manfroy, *Development of Chemical Grinding Aids and their Effect on Selection-for-Breakage and Breakage Distribution Parameters in the Wet Grinding of Ores*, paper presented at XIIth Int. Min. Proc. Cong. Sao Paulo, Brazil, 1977.
6 K. M. Hanna and A. E. Gamal, *Powder Technol., 17* (1977) 29.
7 R. R. Klimpel and W. Manfroy, in S. Ramani (Ed.), *14th Int. Sym. on Applications of Computers in the Mineral Industry*, AIME, New York, 1977, pp. 197 - 206.
8 R. R. Klimpel and W. Manfroy, *Ind. Eng. Chem. Process Des. Dev., 17* (1978) 518.
9 R. R. Klimpel and R. Samuels, *Proc. Annual Meeting of Canadian Mineral Processors, Ottawa, 1979.*
10 R. R. Klimpel, in P. Somasundaran (Ed.), *Proc. Symposium on Fine Particles Processing, Las Vegas, 1979*, AIME, New York, 1980, p. 1129.
11 M. Katzer, R. Klimpel and J. Sewel, *Mining Engineering, 33* (1981) 1471.
12 R. R. Klimpel and L. G. Austin, *Powder Technol., 31* (1982) 239.
13 R. R. Klimpel, *Powder Technol., 32* (1982) 267.
14 H. E. Rose, *10th Int. Minl. Proc. Congress, London, 1973*, pp. 143 - 170.
15 A. Z. Frangiskos and H. G. Smith, *Trans. Minl. Dressing Congress, Stockholm, Sweden, 1957*, 67.
16 H. El-Shall, S. Vidange and P. Somasundaran, *Int. J. Min. Proc., 6* (1979) 105.
17 F. Aplan and D. W. Fuerstenau, in D. W. Fuerstenau (Ed.), *Froth Flotation*, 50th Anniversary Volume, AIME, 1962, p. 196.
18 R. W. Smith, *Trans. AIME* (1963) 226.
19 H. Schubert, *Freiberg, Forsch., A 355* (1965) 51.
20 P. Somasundaran, *Int. J. Min. Proc., 3* (1976) 35.
21 K. Ananthapadmanabhan, P. Somasundaran and T. W. Healy, *The Chemistry of Oleate and Amine Solutions in Relation to Flotation*, paper presented at 107th Annual AIME Meeting, Denver, 78-B-68 (1978).
22 H. El-Shall, A. Gorken and P. Somasundaran, *Effect of Chemical Additives on Wet Grinding of Iron Ore Minerals*, paper presented at the XIII International Mineral Processing Congress, Warsaw (June 1979).
23 P. Somasundaran, T. W. Healy and D. W. Fuerstenau, *J. Colloid and Interface Sci., 22* (1966) 599.
24 J. N. Hartley, K. A. Prosbrey and O. J. Wick, *Energy Reduction in Ore Grinding*, paper presented at the 83rd Annual Convention of the Northwest Mining Association, Spokane, Washington (Dec. 1977).