

## MINERAL PROCESSING APPLIED TO ADVANCED MATERIALS TECHNOLOGY

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### ABSTRACT

The ever increasing need for treating fine complex mineral bodies has led to the evolution and rapid development of advanced processing techniques for fine grinding, classification and mineral separation and purification. With the introduction of these new technologies and understanding of underlying fundamental principles, mineral processing is now being applied to materials ranging from ceramics and composites to superconductors. In this review, current and potential applications of mineral engineering techniques to advanced materials processing are discussed. Particularly, material processing involving ultrafine grinding, dispersion and flocculation and thin film formation is examined. Novel techniques of solid/liquid separation involving manipulation of interfaces and use of high intensity high gradient superconductor magnetic equipment for solid/solid separation are discussed.

### INTRODUCTION

The recent discovery of high temperature superconducting ceramics and high performance structural ceramics has drawn the attention of researchers worldwide towards the emerging field of advanced ceramics and has increased the awareness towards the need for improving current ceramic processing methods. While the production of advanced ceramics involves sophisticated chemical processing and is closely dependent on the quality and purity of the compounds used, the basic raw materials - the oxides and silicates - are among the most abundant in the earth's crust. The only drawback faced is that the ores mined are complex and finely disseminated. This would not only require finer grinding for liberation, but also development of novel processing techniques for upgrading such ores. The future of ceramics lies in efficient and economic extraction of the raw materials and the development of new processing methods designed to eliminate the flaws inherent to traditional ceramic processing methods. Most of these defects are generated during powder processing prior to firing, hence advances in the field of ceramic processing will depend upon a better control of the powders processed and of the subsequent suspension stability since most ceramics are fabricated, at least in part, using solid/liquid mixtures (Bleier, 1984). Ultrapure minerals are also being used for the fabrication

of electronic components, optical fibers and even biomaterials. Production of such materials, maintaining the quality in terms of such properties as size, surface area, shape and purity consistently requires new and modified processing techniques often with use combined use of many mechanical, chemical, electrochemical and pyrometallurgical subprocesses.

Research in the field of mineral processing has long since been aimed at solving these problems. Judicious use of interfacial phenomena has led to the evolution and development of processes aimed at treating low grade and fine grained ores. Grinding being a key unit operation has received much attention in the field of mineral processing, particularly the mechanisms of grinding and the kinetics involved. In this paper the applications of mineral processing techniques to advance materials technology are discussed.

### GRINDING

Grinding of coarse-grain material to produce fine powders is of concern in many areas of ceramics, health sciences, agriculture, etc. The science of fine grinding in ceramics has lagged considerably behind other technological advances. Fines and ultrafines present unusual difficulties during their processing. It has been suggested in the past that reductions in mass and increase in surface energy and surface area are mainly responsible for it (Somasundaran, 1976). However, morphology and surface mineralogical and chemical heterogeneity also play a major role in determining the interfacial behavior of fines which is very critical in downstream processes and these properties can be controlled to a large extent by using appropriate grinding methods (Somasundaran and Roussev, 1985).

Major differences occur between the morphologies of particles prepared using different mechanisms. For example, a sample of - 400 mesh quartz particles prepared by impact show surface characteristics unlike those prepared by abrasion using a mortar and pestle. The ones prepared by abrasion undergo significant erosion in comparison to those from the impact tester. Grooves resulting from such erosion can have a profound effect on the wetting characteristics of the particles (Somasundaran, 1984). Prolonged grinding often used in the preparation of

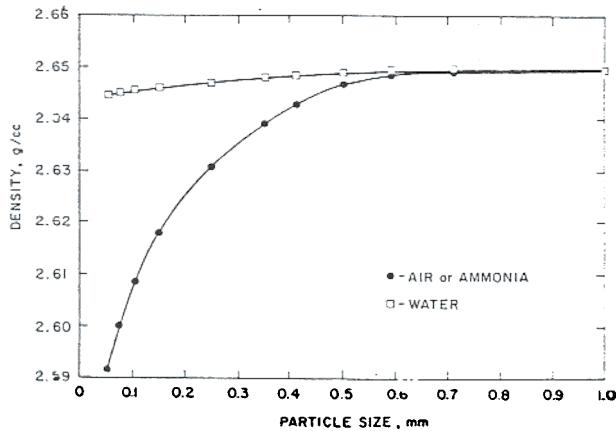


Fig. 1 Comparison of density of quartz of different size produced by grinding in water and air and ammonia.

fine and ultrafine particles produces major differences in, in addition to morphology, surface crystal structure and even chemical composition (Lin and Somasundaran, 1972). This has been confirmed during prolonged grinding of quartz, calcite and massicot-sulfur mixture. Gravimetric, thermogravimetric and X-ray diffraction analyses of the ground particles showed measurable changes in properties in all cases. Thus, the density of quartz particles was found to decrease as a function of grinding time apparently due to the creation of deep amorphous layers on the particles (Fig. 1). In the case of massicot and calcite, polymorphic transitions were found to alter their structures to litharge and aragonite respectively. On the other hand, in the case of grinding of massicot or litharge with sulfur, solid state reactions took place causing total chemical conversion of the samples to the sulfides (Fig. 2).

Metals and metal sulfides have been reported to undergo rapid surface oxidation on grinding. Such surfaces can acquire higher hydrophilic properties and can adsorb large quantities of water vapor. Increased reactivity of samples due to grinding is well-known. Increase in cation exchange capacity of such minerals as alumina, silica and mica during grinding (Gregg, 1968) has also been observed in the past.

Thus it is clear that particles can show differences in morphology depending on how they are produced. Such differences can have a major effect on the wettability of particles and hence, on their aggregation. For example, in the study of contact angle of teflon and nitrocellulose subjected to various mechanical treatments it was found that the receding contact angle decreased and the advancing angle increased as the surface was made rougher (Oliver, *et al*, 1980).

A major problem in the production of fines is the poor efficiency of the process of grinding. It has been stated that the grinding efficiency is of the order of 1%. In this regard an understanding of the effects of changes in the physico-chemical environment on comminution is essential since such changes have been clearly shown to produce beneficial or detrimental effects. Use of grinding aids is a reported practice in the cement industry. Grinding in water is usually more effective than dry grinding. This effect of water has been ascribed to a reversible reaction between unsatisfied surface bonds and water molecules (Lin and

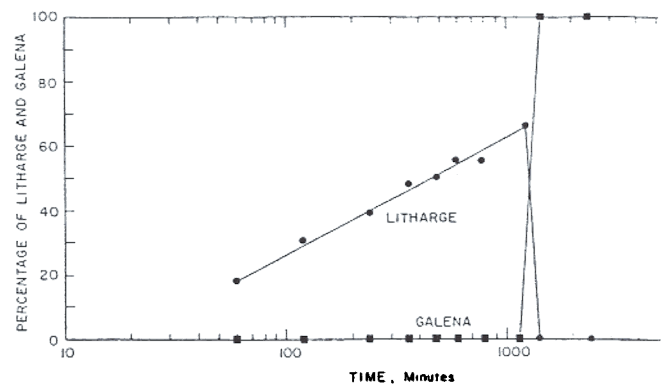


Fig. 2 Conversion of massicot to litharge and sulfur to galena during dry grinding in a ball mill.

Mitzmager, 1968). However 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 in dry grinding, since the fine particles tend to remain suspended in the water in the former case. It has also been reported that grinding in organic liquids is more efficient than in water (Somasundaran, 1978).

Surfactants have been widely reported as effective grinding aids (Somasundaran and Lin, 1972). The effect of adding a flotation agent called Flotigam P on wet ball-milling of quartz and limestone is shown in Fig. 3 as an example. In some cases, however, the presence of surfactants has led to a decrease in the grinding efficiency. Hydrophobization of the 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. 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 (El-Shall and Somasundaran, 1982). Effect of  $AlCl_3$  and  $CaCl_2$  on wet grinding of quartz is shown in Figure 4. The effect of the reagents on grinding has been shown to be their cumulative effect on subprocesses involved such as crack initiation and propagation, flocculation of ground product, pulp flow, adhesion of ground product to mill walls and grinding medium.

Future technological developments in the electronic industry are aimed at designing devices of the order of micrometers. For this miniaturization of electronic devices, fine fabrication of other surrounding devices is necessary. Attainable dimensions of the devices depend on the size of the ceramic particles: the smaller the particles, the more miniature the solid device can become (Ichinose, 1987). Therefore, manufacturing particles with sizes that suit the desired ceramics is a prerequisite. Grinding is an useful tool for achieving such results. Work done in mineral processing to elucidate the mechanisms and means to improve the efficiency of this operation stands to prove beneficial in the manufacture of high performance electronic devices.

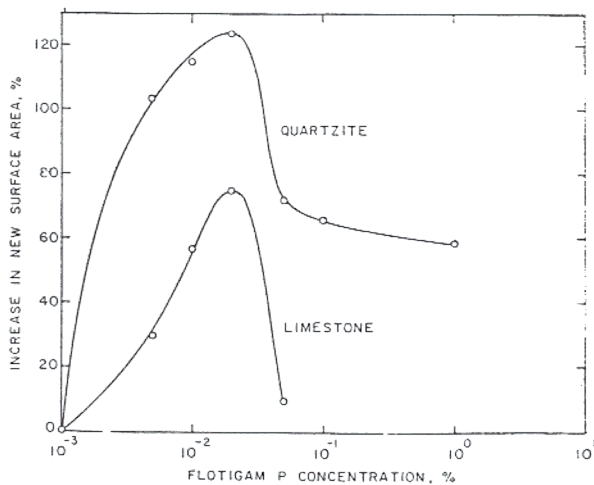


Fig.3 Effect of Flotigam P on grinding of quartzite and limestone in a rod mill.

## DISPERSION TECHNOLOGY

Most ceramic greenware is fabricated using solid/liquid suspensions. The elements of ceramic processing that rely, to various degree, on suspension stability are powder formation, powder dispersion and powder packing. The traditional medium for the processing of ceramic powders has been water but in recent developments, organic media have sometimes been preferred (Reed, 1988). For instance, some ceramics of current interest such as nitrides or carbides, tend to develop oxide surfaces when processed in water and hence non-aqueous media are preferred when working with these materials. But whatever be the dispersing media, for successful processing it is of paramount importance to have a stable dispersion of the solid particles in the liquid. Unagglomerated powders with a narrow size distribution have enormous potential in advancing the science of ceramics processing.

Phenomenologically, suspension stability may be characterized by the dispersion state of the individual particles: without stabilizing additives, naked, uncharged particles usually undergo very rapid aggregation. Colloidal particles have indeed a natural tendency to collide with each other, being subject to Brownian motion. These collisions happen to be aggregative due to the action of London-Van der Waals attractive forces between the colloids. The resulting aggregates are morphologically compact and tightly bound. Potentially, these aggregates represent a major source of defects in structural ceramics and in magnetic media. Colloid stabilization is aimed at preventing this type of aggregation.

In order to stabilize a dispersion, it is necessary to provide strong repulsive forces between the particles. Two basic mechanisms are generally accepted as being able to provide such stabilization (Sato and Ruch, 1980): 1. **Electrostatic stabilization** and, 2. **Steric stabilization**.

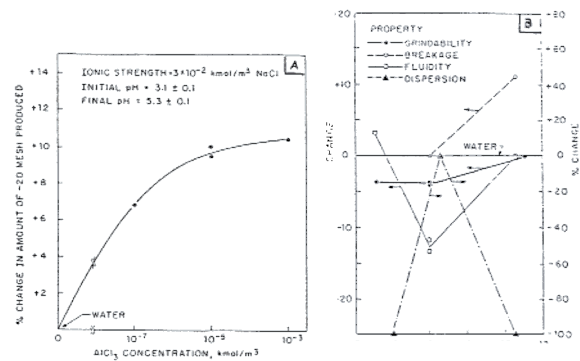
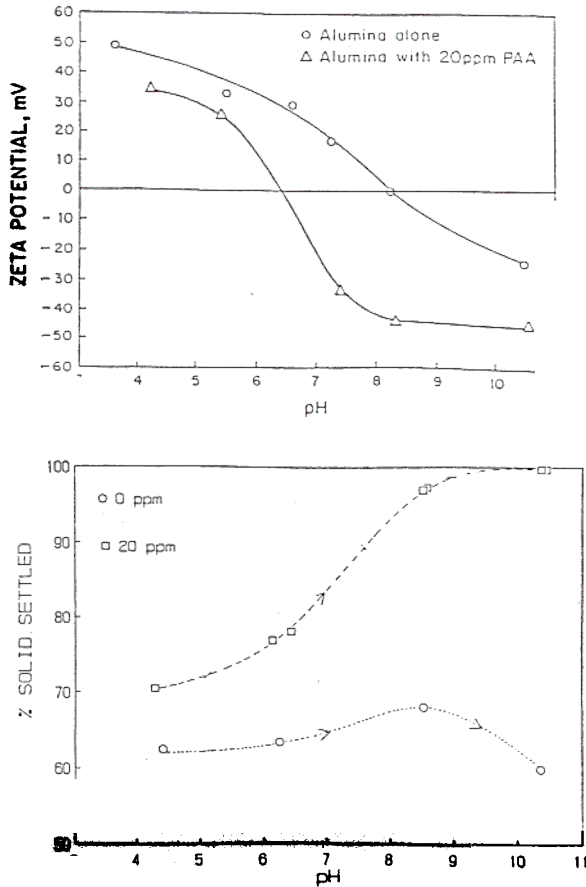


Fig.4 [A] Effect of addition of  $\text{AlCl}_3$  on wet ball milling of quartz in acidic solutions.

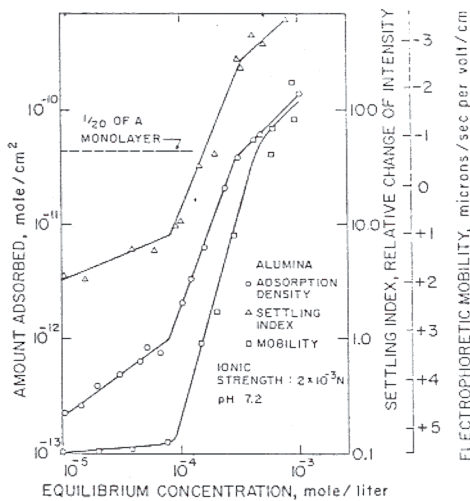
[B] Change in different properties of quartz suspensions due to  $10^{-5} \text{ kmol/m}^3 \text{ CaCl}_2$  addition.

**ELECTROSTATIC STABILIZATION:** the existence of a charge on the particle surface (or its creation by adsorption of a charge control agent on the colloid) induces a net charge of opposite sign in the dispersion medium by principle of electroneutrality. These so-called counter ions, which neutralize the particle charge, surround the particle, giving rise to the electrical double layer. It is the mutual repulsion of these double layers that prevents aggregation of particles when colloidal stabilization is electrostatically controlled.

Most particles in liquids are electrically charged, the nature and magnitude of which are dependent on the mechanisms responsible for the charge generation on their surfaces and the properties of the solids and solution comprising the system. The point of zero charge of a solid defines the solution condition at which the particles possess zero net charge and is an important experimentally accessible property of the system since its location with respect to solution conditions will essentially determine the repulsion or lack of it between particles and consequently the stability of a suspension of these particles. The charge at the solid-liquid interface can be modified by controlled adsorption of ionized chemical species or polymers. This is possible since it is not the surface potential that is directly controlling the interactions between the particles, but an interfacial potential at some distance away from the surface that the particle will have to work against as they approach each other. Control of this potential, which can be assumed for convenience to be the potential at the shear plane, known as the zeta potential, is possible usually by adjusting the ionic composition and pH of the medium. Figure 5 shows the zeta potential of alumina as a function of pH and its effect on the settling rate of the suspensions (Somasundaran, 1975). Stability is minimum near zero zeta potential conditions, as indicated by the maximum in percent solid settled. The effect of added polymer (polyacrylic acid) is also indicated in the figure. The presence of polymer leads to higher settling rates and the conformation of the polymer is instrumental in determining the solids settled in addition to the zeta potential (Huang, *et al*, 1988). It is estimated that aggregation can usually be obtained in the absence of steric forces if the zeta potential is less than 15 to 20 mV or if the particles are oppositely charged (Somasundaran, 1980).



Comparison of stability of alumina suspensions with zeta potential of the particles at various pH values in the presence and absence of polymer.



Settling index, adsorption density and electrophoretic mobility of alumina - sodium dedecyl sulfonate system as a function of sulfonate concentration.

**STERIC STABILIZATION:** When two particles with a layer of macromolecules adsorbed on their surface approach one another, the overlap of the adsorbed layer creates an osmotic pressure which keeps the particles apart. This mechanism known as steric stabilization can also be achieved by attaching short chains to particle surfaces through reactive end groups, giving rise to "hairy" particles which cannot approach one another closer than the combined thickness of the two adsorbed layers.

Recently there has been an increasing awareness of the value in applying dispersion science to ceramics processing. A particularly important example is colloidal stabilization using macromolecular (polymeric) additives. In the presence of polymers, a colloidal dispersion can undergo charge stabilization, steric stabilization or flocculation. These phenomena are always attributed to the extent and nature of the polymer adsorption on the substrate, type and magnitude of the surface charge on the particles, and the conformation of the adsorbed polymer at the solid-liquid interface.

Long chain ionic surfactants can also adsorb on mineral particles and cause destabilization of suspensions to a extent greater than inorganic ions can. In Fig. 6, stability ratio of an alumina-sodium dodecyl sulfonate system is shown along with sulfonate adsorption density and the zeta potential (Somasundaran and Fuerstenau, 1966). It should be noted that the ionic strength of the system is maintained at a constant level of  $2 \times 10^{-3} M$  under all conditions and therefore the observed changes in electrokinetic and stability isotherms are not due to the double layer compression one gets with the addition of a salt. The sudden increase in the rate of adsorption of the surfactant at about  $10^{-4} M$  has been attributed to lateral association between adjacent hydrocarbon chains of the adsorbed surfactant ions and this process has been termed hemimicellization since the aggregates formed are analogous to two-dimensional micelles. Recently they have been called solloids (colloids on solids) to include other types of adsorbed aggregates.

It is generally accepted that, in non-polar media, charge formation by ionic surfactants is due to their adsorption on the colloid surface followed by dissociation of a few of the adsorbed ions (Novotny, 1981). This weak dissociation leads to sufficient surface charge to induce electrostatic stabilization. An important aspect to be noted is that in non-polar media, dispersions can be drastically affected by minute amounts of impurities, especially those that influence the surface charge. Presence of water, therefore, is very critical because of its ionizing properties. In Figure 7, the effect of water on a stable dispersion of alumina in cyclohexane is illustrated (Malbrel and Somasundaran, 1989). Aerosol OT as surfactant was added in this case to disperse the particles in concentration such that a monolayer of surfactant was present on the alumina particles. Figure 7a shows the settling rate of the alumina-supernatant interface as a function of residual water concentration at two different surfactant concentrations ( $8.5$  and  $26 \times 10^{-3} M$ ). Figure 7b shows the corresponding water adsorption isotherms. As the water concentration in the system is increased, the suspension exhibits a succession



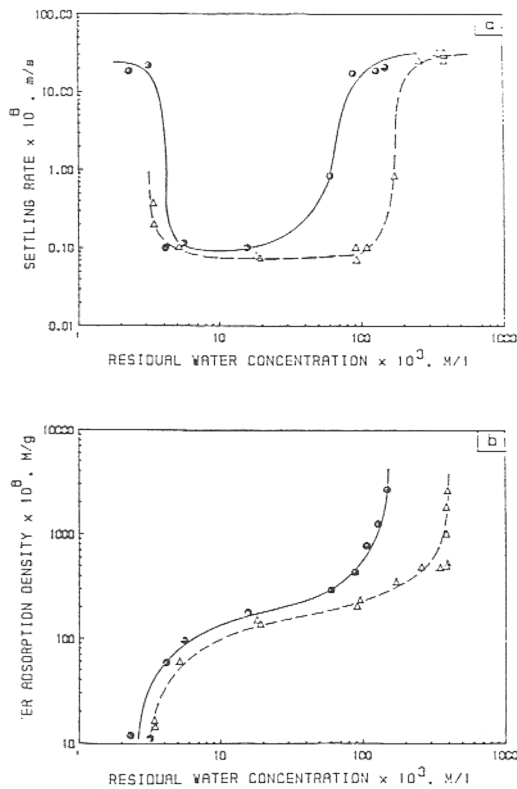


Fig.7 (a) Effect of water on the alumina in cyclohexane suspension settling rate.  
(b) Adsorption of water on alumina from Aerosol OT/cyclohexane solution.

of flocculated and dispersed states. At low water concentrations, the settling occurs rapidly. The onset of stabilization corresponds to a sharp increase in the amount of water adsorbed on alumina, showing that the adsorption of water indeed plays a critical role in the stabilization phenomenon. Even though a monolayer of surfactant is adsorbed on alumina throughout the entire range of water concentration studied, stabilization takes place only when traces of water are added to the system. Since the stabilization by Aerosol OT is considered to be due to a partial dissociation of the surfactant at the interface, it is reasonable to conclude that water is required for the dissociation of ions to take place in non polar media. At higher water concentrations, a sharp increase in the suspension settling rate at both surfactant concentrations studied is seen. However, as the surfactant concentration is increased, the water concentration at which flocculation takes place is also found to increase.

To achieve reliability and reproducibility in ceramics processing, uniformly packed green microstructures must be obtained. Uniform particle packing, the consequence of a stable dispersion of uniform-size powder, not only influences sinterability, but also results in uniform, controlled shrinkages with minimum flaws and microcracks. Optimum control over the dispersion stability is a prerequisite for achieving the desired results. Factors influencing dispersion stability, agglomeration and settling are outlined in the above discussions. Advances in the field of interfacial technology will prove beneficial in the design of better processing techniques.

## ADVANCED SEPARATION TECHNIQUES

The basic raw materials necessary for the production of advanced materials are present in the earth's crust but occur in the form of finely disseminated ores together with unwanted impurities. Conventional separation techniques using such processes as flotation and flocculation fail in the colloidal and micron ranges. In the mineral industry, magnetic separation has been successfully employed but limited to a few systems primarily because relatively few minerals exhibit magnetic responses of practical use with the feeble magnetic forces offered by available magnets. The emergence of powerful magnets with higher gradients has enabled wider application of magnetic separation at least on a laboratory scale recently in the mineral industry. Superconducting magnets can produce extremely intense and uniform magnetic fields with lower power consumption. By incorporating these superconducting magnets into separators it is possible to have large working volumes to accommodate finer as well as coarser particles at high capacities. Commercial application of high gradient magnetic separation has been limited so far, to our knowledge, to the beneficiation of kaolin. Use of extraneous reagents to pretreat the ore to generate areas of higher magnetic susceptibility might possibly extend the application of the magnetic separation.

Combining the principles of mineral processing and the discovery of superconducting magnets it should be possible to design advanced separation techniques using super intensity high gradient magnetic equipment to achieve separation of colloidal and ultrafine particulates. Herein possibly lies a potential application of mineral processing which if properly harnessed could lead to the elimination of several current limitations in the separation industry.

## CONCLUSIONS

Ultrastructure processing of crystalline ceramics begins with the controlled formation of powders, and continues through controlled particle packing to densification. In this paper, the application of mineral processing techniques to these features have been considered. Parameters critical to fine grinding, grinding efficiency and dispersion stability have been discussed. Finally the potential of magnetic separation when superconducting magnets are incorporated is also outlined.

## ACKNOWLEDGMENT

Financial support from the National Science Foundation (MSM-86-17183) and the New York Mining and Mineral Resources Research Institute (NY MMRR) is gratefully acknowledged.

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