ULTRA FINE GRINDING OF YTTRIA STABILIZED ZIRCONIA IN POLYACRYLIC ACID SOLUTIONS

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ABSTRACT

Two different groups of mechanisms have been considered in the past to explain the effects of chemical additives on grinding. While one group of explanations is based upon alterations of surface and mechanical properties of the individual particles, the other group depends mainly on the arrangement of particles and their flow in suspensions. In this paper some of the past work on grinding aids is reviewed and attrition grinding of a commercially important ceramic material, zirconia (stabilized with yttria) with polyacrylic acid as grinding aid, is studied in order to determine the effect of the aid on the ground product itself. It was observed that even though polyacrylic acid did cause a drastic decrease in the viscosity of the pulp, it did not have any major effect on the grinding of zirconia at least up to 2000 ppm and only minor detrimental effect above it. Importantly, complexation by the polymer was found to cause extraction of yttrium into solution with possibly significant changes in the surface chemical composition of the product.

INTRODUCTION

Grinding has been reported, in general, to be enhanced by the addition of moderate amounts of appropriate surfactants or electrolytes (Somasundaran and Lin 1972; Malati et al, 1968/1969; Ghosh et al, 1960; Frangiskos and Smith, 1957). Further increase in the concentration of additives, however, causes poor grinding. It is known that the zeta potential of mineral particles will decrease with adsorption of oppositely charged surfactants and this can lead to flocculation (Somasundaran et al, 1986). Also, under these conditions, the pulp can sometimes stick to mill walls and balls and this can be expected to reduce the grinding performance drastically (Somasundaran and Atli, 1986). Hence, it is not clear whether the lower grinding efficiencies reported are due to experimental artifacts introduced by flocculation and adhesion of fine particles during milling and the size analysis or the result of changes in other interfacial properties brought about by the surfactant during grinding. The influence of electrolytes on the dispersion of particles in the pulp could be the primary reason for the reported effects of these additives on the grinding efficiencies. The importance of proper dispersion of the ground products has been substantiated by El-Shall and Somasundaran (1984a). With microscopic examination of selected size fractions, the authors found that even sodium silicate was not sufficiently effective as a dispersant for the wet sieving of quartz ground in 10^{-4} mol/dm^{3} amine solution. The grinding results in this case initially suggested the use of amine to be detrimental. However, after proper dispersion of the ground products using alcohol/acetone washes to remove the amine before sizing, amine in the mill was observed to have acted as a grinding aid.
In order to elucidate the mechanisms by which grinding additives act, it is necessary to establish correlations between the grinding results and relevant pulp properties. Towards this purpose, El-Shall and Somasundaran (1984b) determined the effect of the addition of dodecylamine hydrochloride on ball milling of quartz, and correlated it with basic properties of the system such as pulp viscosity, flocculation and dispersion, and primary breakage. Simple impact tests to determine the effect of amine on the primary breakage of quartz were also done with a falling mass on a layer of 10 x 20 mesh quartz particles wetted by the desired solution. In an investigation by Narayanan et al (1983), dispersion of hematite pulp (the suspension examined under microscope) was correlated with its ball milling. In both studies, no attention was paid to the effects of the solid to liquid ratio and to the size fraction used. Ideally, adsorption density of the chemical additive, and therefore dispersion properties, should not depend on the amount of solid present. However, numerous studies have shown that adsorption density usually decreases with increasing adsorbent concentration as well as fineness (Sato, 1971; Morgan et al, 1987; Hollander et al, 1981). In addition, grinding often leads to the release of dissolved species which may precipitate the adsorbate on the surface of the solid and increase the depletion of the surfactant (Ananthapadmanabhan and Somasundaran, 1985). Evidently, the amount of additive adsorbed and the resulting properties of the grinding pulp may be very different from what would be observed with a suspension prepared with a size fraction of the initial material.

This work was aimed towards improving the mechanistic understanding of the effect of grinding aids and based on a study of the relationship between powder characteristics after grinding and properties of suspensions containing polymers as grinding additives. Specifically, the effect of polyacrylic acids of different molecular weights on the attrition milling of zirconia is investigated. Particular attention was paid to polymer adsorption and solid dissolution during grinding.

EXPERIMENTAL

Materials

Polycrylic Acid

Low molecular weight polyelectrolytes can produce both an electrostatic and a steric barrier to aggregation provided that the material to be ground has sufficient adsorption sites for its species and that its adsorption affect slurry dispersion. Furthermore, the polymer should provide constant dispersion characteristics throughout the grinding process during which the amount of impurities, the shear rate and the dispersant concentration can vary continuously. Also chemicals used as additives should not adversely affect downstream processes such as flotation, pelletization and slip casting. Polycrylic acid fulfills these conditions and was therefore selected for the study. Adsorption of polymers on mineral particles and the effectiveness of the adsorbed polymer in promoting stabilization or flocculation are known to be dependent to a large extent on its molecular weight. The polycrylic acid sample used was purchased from Polysciences Inc. It was received as concentrated aqueous solutions (50 wt% for PAA 5,000 and 25 wt% for PAA 150,000) and was used without further purification. Information given by the manufacturer indicates the presence of residual isopropanol (0.5%), acrylic acid (0.1%), and propanoic acid (0.1%) for PAA 5,000, but such impurities were not reported for PAA 150,000. Both polymers had a polydispersity of Mw/Mn equal to 4.

Zirconia

Yttria stabilized zirconia with nearly 100% tetragonal structure is drawing attention as a ceramic material with superior strength and toughness. Because of its extremely high melting point of about 2,700°C (Ichinose, 1987), its original application was as a refractory material. But its use is limited because of the peculiar transformations from monoclinic to tetragonal to cubic which are accompanied by substantial volume changes leading to the formation of cracks. The addition of Y₂O₃ into the crystal lattice maintains the tetragonal structure even at room temperature (Gupta, 1977). Such "stabilized" zirconia can undergo stress-induced phase transformations from tetragonal to monoclinic ZrO₂ (Ichinose, 1987; Gupta et al, 1977; Porter and Heuer, 1977; McMeeking and Evans, 1982). The metastable tetragonal to monoclinic transformation occurs also during ball milling of zirconia (Murase and Kato, 1979; Itoh, 1986; Bailey et al, 1972), but as pointed out by Murase and Kato (1979), only in the presence of water vapor. The tetragonal to monoclinic phase transformation is believed to cause also a reduction in fracture toughness and fracture strength of sintered yttria stabilized zirconia when aged at low temperatures (70 to 400°C) in the presence of water vapor. Lange et al (1986) showed that water vapor reacts with yttrium to produce clusters of small crystallites of Y(OH)₃. They hypothesized that depletion of yttria produces monoclinic nuclei which grow spontaneously when greater than a critical
size. Lu and Chen (1987) reported that zirconia, below a critical grain size of 0.5 μm, retains its tetragonal symmetry and thus degradation is avoided. It is clear that zirconia is a very complex material and the presence of yttrium is critical.

Zirconia stabilized in the tetragonal phase by the addition of 3 mole% of yttria obtained from Rhone-Poulenc was used in this study. The specific surface area obtained by nitrogen BET adsorption was 4.1 m²/g. The density of the zirconia powder was measured with an air pycnometer (Beckman) to be 6.02 g/cm³. The Scanning electron microscopic analysis of the material showed the zirconia powder to consist of an hierarchy of aggregates of primary particles of an average of 0.12 μm size, compact micro-aggregates of approximately 1.5 to 2.5 μm size and macro-aggregates of 10 to 20 μm size.

Variables and Methods

pH

As the amount of polymer adsorbed is known to have a significant effect on the stability of dispersed particles (Somasundaran, 1980), pH, on which it is dependent, is a major parameter in this investigation. However, a precise control of the pulp pH at selected levels is difficult, especially in batch experiments since the pH always drifts towards a given value during the grinding test. The equilibrium pH attained after a few minutes of grinding is usually the point of zero charge of the oxide. Since no pH drift is expected at the point of zero charge, all grinding tests were done at the point of zero charge of zirconia.

Additive Concentration

Mechanisms used in the literature to explain the influence of the physico-chemical environment on wet milling are based on the grinding aid adsorption. For polyacrylic acid, the shape of the adsorption isotherm is usually of a high affinity type: a steep rise of the adsorption density in the low equilibrium concentration region, followed by a plateau level at higher concentrations (Gebhardt and Fuerstenau, 1983). Studies on the stabilization of colloids by PAA adsorption (Foissy et al, 1982) have shown that flocculation or dispersion can be obtained depending on the amount of polymer adsorbed. In addition to the extent of adsorption, configuration and charge of the polymer also determine whether flocculation or stabilization is obtained. In the past investigations on grinding additives, the range of reagent concentration was selected either for compatibility with the step following wet grinding, usually flotation (Ryncarz and Laskowski, 1977; Malati et al, 1968/1969), or for economic reasons. In this study, polymer concentrations were selected based on the adsorption isotherm of the polyacrylic acid on zirconia.

The amount of polymer adsorbed was estimated from the difference between the initial concentration of the solute and the supernatant concentration after removal of the solids by centrifugation. A Dohrmann Carbon Analyzer was used to determine the residual polymer concentration.

Dissolved Elements Concentration

Several reports in the literature suggest dissolution of minerals during wet grinding. For example, Lin and Somasundaran (1972) observed that the small size fractions of quartz particles obtained by grinding in air had a lower density than the particles ground in water. This was attributed to amorphization of the surface of the particles during both dry and wet grinding, but dissolution of the amorphous material during wet grinding. Analysis of zirconium and yttrium concentrations was hence carried out using a Perkin-Elmer ICP/6500 Inductively Coupled Plasma System.

Surface area of the ground samples was measured with nitrogen using a Quantasorb apparatus. Pen Kem Lazer Zee 501 was used to determine the zeta potential of the particles. Viscosity of the pulp was determined using a Brookfield LVTD digital viscometer implemented with a SC4 sample adapter.

Procedure

To estimate the point of zero charge of zirconia and solid dissolution, suspensions were prepared at 10 and 0 wt% concentrations and 0 and 10⁻² mol/dm³ added NaCl concentration for 10 wt% of slurry. The solutions were first adjusted to the initial pH values and the necessary amount of solid was then added. The suspensions were agitated for 24 hours at room temperature and then centrifuged in a laboratory centrifuge for 10 minutes. Final pH values of the clear supernatant were then measured.
Adsorption isotherms were obtained at the grinding pulp solid concentration (60 wt%). For each test, dry powder was added to one of two polymer solution samples and after 3 minutes of manual shaking to disperse the particles, the suspension was subjected to wrist action shaking for 24 hours at room temperature. The second sample served as blank. The suspensions were then centrifuged in a small lab centrifuge for 10 minutes and then twice in a high speed centrifuge at 10,000 rpm for 15 minutes. Residual PAA concentrations of the test samples and the initial concentrations of the blanks were measured using the Total Carbon Analyzer and yttrium and zirconium concentrations by the ICP.

Grinding experiments were done at a pulp concentration of 60 wt% (about 20 volume%) and a volume of 1 liter. Ball to pulp volume ratio was two. For the grinding test, the suspension was poured into the grinding chamber after 24 hours of shaking, 1 kg of 1.2 mm zircon balls were added to the pulp and then stirred for 100 minutes at 545 rpm. The stirring speed was calibrated with a tachometer and maintained during the grinding test irrespective of variations in pulp viscosity during the grinding test. The grinding chamber was water-jacked to keep the pulp temperature at 25°C.

At the end of the grinding test, the viscosity of the pulp was measured with the Brookfield viscometer. The pulp was then centrifuged and the supernatants analyzed for adsorption. Ground powder samples for specific surface area measurements were obtained by freeze-drying the centrifuge cake.

Most of the slurry was first washed away with regular tap water, the grinding media being stirred manually at the same time. When the water was no longer turbid, the balls were washed five times stirring for 5 minutes at 545 rpm. The attrition which occurs in the bowl between the grinding balls detaches the fine particles remaining on the grinding media.

RESULTS AND DISCUSSIONS

Adsorption of Polyacrylic Acid on Zirconia

The point of zero charge of zirconia obtained from the ΔpH versus initial pH plot is 7.4 (see Figure 1). As a result, all of the solutions used for this study were adjusted to this particular pH. Adsorption densities of PAA 5,000 and 150,000 on zirconia are plotted in Figure 2 as a function of the residual polymer concentration. Both isotherms show a steep rise in the low concentration region followed by a plateau with further increase in the residual concentration. These are high affinity type adsorption isotherms with the adsorbed quantities at the isotherm plateau consistent with literature data for this pH range (Gebhardt and Fuerstenau, 1983; Foissy et al., 1983). Polyacrylic acid adsorption is expected to take place preferentially on the positive sites of the oxide particles. In the present case, adsorption is carried out at pH 7.4, the point of zero charge of the powder. At this particular pH, it can be assumed that yttrium oxide sites are positively charged since pzc of yttria is 9.0 whereas the pzc of zirconia is 6.7 (Parks, 1965). As a result, the polymer is expected to interact preferentially with the yttrium sites.

It is to be noted that in contrast to the reported molecular weight dependence of polymers, adsorption capacity of zirconia for PAA 5,000 is three times higher than that for PAA 150,000. In other words, the amount of adsorbed polymer decreases with molecular weight increase on the assumption that equilibrium conditions have been achieved. This was tested by studying the adsorption kinetics of polyacrylic acid. It is clear from Figure 3 that the adsorption of polymers does take place extremely rapidly and is essentially completed in the few minutes necessary to separate the supernatant from the solid. Although the surface is apparently not saturated, because a slight increase in adsorption is detected for both polymers after several hours of conditioning, such differences cannot account for the observed dependence on the molecular weight.

Release of Yttrium

Yttrium concentration in the supernatant is plotted in Figure 4 as a function of equilibrium polymer concentration. For both molecular weights, the yttrium concentration in the supernatant gradually increases with the residual polymer concentration and then reaches a plateau. It is to be noted that no dissolved yttrium was detected in the supernatant in the absence of polyacrylic acid. While the concentration of yttrium at the plateau corresponds to 2.2 x 10¹⁴ potentially extractable atoms, assuming a parking area of 20 Å² for the yttrium site, 3 mole% of yttrium on the surface corresponds to 1.5 x 10¹⁷, suggesting that all of the surface yttrium is in solution under the plateau conditions. No correlation is observed between adsorption density of the polymer and the release of yttrium into solution. According to Figures 2 and 4, both molecular weights pull out the same quantity of yttrium whereas the polymer absorbed is three times higher.
for PAA 5,000. Furthermore, it is seen that the release of yttrium continues for several hours after the polymer adsorption is complete (see Figure 5).

FIGURE 1. Determination of the point of zero charge of zirconia by the powder addition method.

FIGURE 2. Adsorption isotherms of polyacrylic acid of molecular weight of 5,000 and polyacrylic acid of molecular weight of 150,000 on zirconia.
FIGURE 3. Adsorption kinetics of polyacrylic acid of molecular weight of 5,000 and polyacrylic acid of molecular weight of 150,000 on zirconia.

FIGURE 4. Amount of yttrium released from zirconia vs the equilibrium concentration of polyacrylic acid.

It can be concluded that corrosion of the surface by the polymer during grinding takes place independent of its
adsorption. It is suggested that a complex is formed between the carboxylic group of the polyelectrolyte and yttrium, but the residence time of the complex on the surface is too short to affect the adsorption density. The rate of yttrium extraction in such a case is a function of the diffusion coefficient of the polymer; this suggestion is in agreement with the larger removal of yttrium observed for PAA 5,000 in the kinetic study (see Figure 5). Such interactions between polyelectrolyte and multi-valent ions are not unusual and have been reported in the literature (Foissy et al, 1983; Burlamacchi et al, 1983). A slight increase in the supernatant pH (0.3 to 0.4) was observed during the adsorption test and this is consistent with the expected release of hydroxyl ions upon the formation of the ion-polymer complex.

If the above hypothesis is correct, since some positive sites will remain even at one pH unit above the pzc, adsorption of polyacrylic acid can be assumed to take place on these zirconium sites. In addition, Lee and Somasundaran (1989) have shown for polyacrylamide that its adsorption may take place on the neutral hydroxyl sites. The surface of the material can then be pictured as a few positive zirconium sites scattered on the surface with mainly negative and neutral sites. Cade and Robb (1982) have shown using E.P.R. spectroscopy that in the absence of the electrolyte, polyacrylic acid has a flat configuration with more than 90% of the segments in contact with the surface. At the pH considered, polyacrylic acid is almost completely ionized. The high molecular weight polymer can be considered to be more effectively repelled by the surface than the smaller one which may be able to approach the positive sites on the surface more easily. This dependence of adsorption on the molecular weight could be attributed to the above reason.

![Figure 5](image-url)

**FIGURE 5.** Kinetics of yttrium extraction from the oxide surface.

Stability

The sediment volume at the end of settling of a suspension is normally a function of the nature of its dispersion. Smaller the final sediment volume, higher is the degree of dispersion. Sediment volume coupled with zeta potential was used in this study to estimate the degree of dispersion of the pulp before grinding.

As can be seen from Figure 6, sediment volumes decrease sharply in the low residual concentration region and then decrease slowly and become almost similar with increase in concentration for both molecular weights. Zeta potential versus residual concentration follows a similar pattern with respect to concentration for PAA 5,000 (Figure 7). In the
case of PAA 150,000, however, a minimum in zeta potential (maximum negative potential) is observed around 500 ppm. The release of yttrium from the surface cannot explain the shift towards a less negative zeta potential at high residual concentrations since the quantity of yttrium extracted by the smaller polymer is similar. The difference between the amounts adsorbed of the polymers does not account for the change observed either, since both zeta potential curves coincide below 500 ppm. Large molecules adsorbed on particles can shift the shear plane away from its original location (Somassundaran, 1980). The observed decrease in the magnitude of the zeta potential obtained above 1000 ppm for PAA 150,000 could be attributed to its dangling negatively charged loops and tails repelled by the negative solid surface. Thus, even though the zirconia zeta potential curves for the two polymers were different, the degree of dispersion of the suspensions as assessed by the sediment volume was similar for both polymers.

![Figure 6. Sediment volumes of zirconia slurries vs residual polymer concentration.](image)

**FIGURE 6.** Sediment volumes of zirconia slurries vs residual polymer concentration.

**Effect of Polyacrylic Acid on the Grinding of Zirconia**

First tests were done to determine the grinding time at which some difference between grinding with and without the additive could be observed. Figure 8 shows that the specific surface area of the material ground without additive as a function of grinding time is almost linear. The drastic increase in pulp viscosity observed with grinding time did not affect the particle size reduction in this case. A long grinding time of 100 minutes was hence selected so that enough supernatant could be recovered for subsequent experiments. The pH of the grinding supernatant measured was close to the point of zero charge of zirconia which suggested that the kinetics of hydration of both zirconium and yttrium sites is similar during particle size reduction. Analysis of the supernatants showed neither yttrium nor zirconium ions in the grinding supernatants.

Results obtained for the specific surface area of the ground product are given in Figure 9 as a function of the initial polymer concentration. Neither the additive concentration nor the molecular weight of the polymer had any effect on the production of surface by grinding upto 2000 ppm. The decrease in the specific surface area observed at high initial concentration was first thought to be due to the influence of the absorbed polymer on nitrogen adsorption in the B.E.T. measurements. This possibility was checked with dried samples from the adsorption experiments. The results obtained showed the B.E.T. surface areas to be systematically below the surface areas of the initial powder for both molecular weights. However, the decrease did not exceed 10% and was independent of the initial concentration of the polymer. These variations were probably due to segregation of the particles during the centrifugation step. Turbid supernatants were obtained at the end of the first centrifugation in the presence of the polymer. The increase in dispersion of the
suspension due to polymer addition would therefore account for the observed decrease in the surface area.

Micrographs of the material ground in water and in PAA 5,000 solutions (0.3 wt% on the basis of dry powder) further confirmed the absence of any effect of the additives on grinding. Both ground products show similar features. Interestingly, particle size reduction in this case is found to consist almost exclusively of breakdown of aggregates.

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**FIGURE 7.** Zeta potential of zirconia particles as a function of residual polymer concentration.

**FIGURE 8.** Specific surface area of the product ground without additives as a function of grinding time.
Surprisingly, a drastic change in the pulp viscosity was observed in the presence of the additive at the end of the
grinding test. Exact values of viscosity could not be established: at low polymer concentrations, shear-thickening behavior of the pulp led to unstable viscometer readings, whereas at high polymer concentrations calculations gave a viscosity of the order of that of water. Qualitatively, a sharp decrease in pulp viscosity was observed with the addition of the polymer. This result is in contradiction with the higher grinding efficiency with increase in pulp fluidity reported in the literature. In the present case, the excess mill energy input would make the pulp insensitive to any change in viscosity, and would thus cancel any effect due to the additive.

Adsorption and Ion Release during Grinding

Adsorption densities of PAA 5,000 and PAA 150,000 measured after grinding are plotted as a function of the residual polymer concentration in Figures 10 and 11. For both molecular weights, it can be seen that the amount of polymer adsorbed is much higher than the one indicated by the adsorption isotherm. Since adsorption density of polymers can be affected by agitation, the stirring of the pulp can be considered to be the cause for the observed increase in adsorption during grinding.

Interestingly, the adsorption of PAA 5,000 and PAA 150,000 determined after grinding are similar. This phenomenon can be due to polymer degradation into monomeric units during grinding; as shown in Figure 12, such a possibility is not indicated by the fact that yttrium extraction during grinding does depend on the molecular weight. Adsorption of polyelectrolytes is known to be independent of molecular weight for adsorption with a flat configuration. Evidently, attrition of zirconia produces a very reactive surface toward the medium and the polymer adheres strongly on these new surfaces.

Fig. 12 shows the dissolved ion concentrations as a function of the residual polymer concentration. For both molecular weights, a linear increase of yttrium concentration in the grinding supernatant is observed. As suggested earlier, this phenomenon can be considered to be due to a continuous linear extraction of yttrium from the surface of zirconia by the polymer.

Zirconium ions are also present in the grinding supernatant. As can be seen from Figure 12, this extraction also depends on the molecular weight of the polymer. However, the dissolved zirconium concentration is not as easily related to the residual polymer concentration and the mechanism of extraction is considered to be different from the one
COMMINUTION

proposed for yttrium.

![Figure 12. Dissolved ion concentrations in the grinding supernatant vs the residual polymer concentration.](image)

SUMMARY

1. Effect of polyacrylic acids of 5,000 and 150,000 molecular weights on the attrition grinding of yttria stabilized zirconia was investigated by determining with the same samples the product surface area along with polymer adsorption, zirconium and yttrium dissolution and flocculation.

2. In contrast to the reported dependence of molecular weight of the polymers on their adsorption, the low molecular weight polyacrylic acid was found to adsorb three times more than the high molecular weight one. Adsorption, done at the point of zero charge of the sample (7.4), is considered to take place mostly on yttrium sites since the point of zero charge of yttria is 9.0 while that of zirconia is 6.7.

3. While sediment volumes decrease sharply at low polymer dosages and then slowly at higher dosages similarly for both polymers, zeta potential changes are significantly different for the two polymers possibly due to the conformational differences of the two polymers at the interface.

4. Polyacrylic acids did not have any measurable effect on the surface area of the ground product at least up to 2000 ppm and only minor detrimental effect above it.

5. Interestingly, yttrium was released from the oxide in amounts corresponding to that on the particle surface, but only in the presence of the polymer. Zirconium also was detected in the grinding supernatant. The yttrium release is considered to be the result of its complexation with polyacrylic acid charged sites. Implications of changes in surface chemical composition due to such release on the ground product performance are to be noted.
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