

Influence of application of energy on the effectiveness of chemical additives in suspension preparation

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Introduction

Nanoparticles are increasingly used in many fields of the ceramic industry. For this reason the nanoparticle production becomes more and more important. In many cases, a minor demand for product cleanliness enables the often less expensive production via milling of a submicron powder, i.e. the top-down process, instead of the bottom-up synthesis. The possible reduction ratio of the particle size during grinding strongly depends on the stabilisation of the particles in the slip. To obtain a nanopowder by milling, it is necessary to prepare a highly concentrated, stable suspension with a low viscosity and good flow behavior. Hence, in many cases, dispersing agents are added. It has to be considered that the interactions between powder surface, fluid and additives and the stabilizing effect of the dispersing agents can significantly change during the milling process in comparison with interactions within the slip before the powder processing. Therefore detailed information about the interactions before and during milling has to be obtained whereby it is special important to know the influencing variables of possible changes.

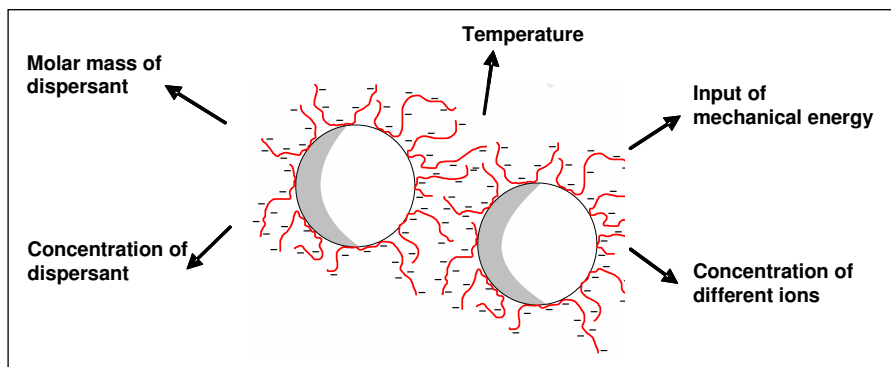


Fig. 1: Possible influencing variables of changing interactions between powder surface and dispersing agents

Experimental

The electrosteric stabilization of the commercially available boehmite powder NBAOH 400 from Nabaltec AG (see Fig. 2) in water is investigated to reduce the particle size to the nanoscale range via milling in a laboratory ball mill (AHM 90, Hosokawa Alpine AG). After sonication in water the suspended particles have an average particle size x_{DLS} of 240 nm. The specific surface area (BET) of the powder is 44.8 m²/g. The effect of sodium polyacrylate dispersants with different molar masses (2100, 8000, 15000 g/mol) on the particle properties in aqueous slips before and during milling is assessed by electroacoustic measurements, i.e. the detection of the electrokinetic sonic amplitude (ESA), in comparison with rheological tests. The amount of polyelectrolytes adsorbed on the particle surface is investigated through measurement of the chemical oxygen demand (COD) in the background solution. Preliminary investigations of the milling behavior of the powder and the slip respectively are performed in a planetary ball mill (Pulverisette 5, Fritsch GmbH).

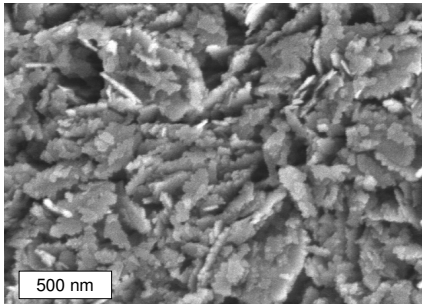


Fig. 2: SEM picture of NBOH 400 (boehmite)

Results and Discussion

The ESA signal of the boehmite particles as a function of polyacrylate dispersant concentration in alkaline pH region is shown in Fig. 3. All additives are qualified for stabilizing the boehmite particles in water. The higher the added amount the higher are the negative surface charges, whereas after an addition of 0.2 wt% only small changes in the ESA values occur. Fig. 3 clearly illustrates a higher negative ESA signal after addition of polyacrylates with higher molar masses. Charge measurements of the additives yielded no charge differences of the pure polymers based on its mass. Different adsorption properties of the polymers could be the reason for the unequal ESA signals of the boehmite particles.

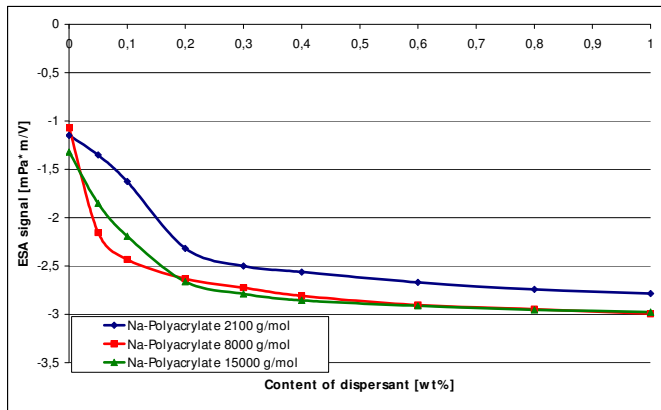


Fig. 3: Surface charge of boehmite in a 10 wt% suspension as a function of dispersant concentration (additive content refers to solid content)

Adsorption measurements are made to prove this theory. Fig. 4 (dashed lines) illustrates the amount of adsorbed polymer as a function of content in the suspension. The additives with higher molecular weights show a better adsorption on the boehmite surface, i.e. more acrylate monomers are adsorbed. Hence, the higher negative ESA signals are detectable. The adsorption curves do not have a saturation point. The higher the amount of the dispersing agents added, the higher the amount of them adsorbed. It is assumed that the transfer from monolayer to multilayer adsorption is not well defined and therefore difficult to detect.

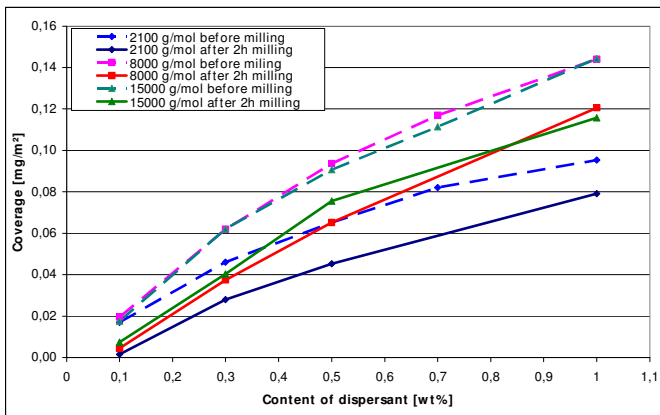


Fig. 4: Adsorption of polyacrylate dispersants on the boehmite surface in a 10 wt% suspension (additive content refers to solid content)

However, viscosity measurements show no differences in flow behaviour with addition of the dispersants (Fig. 5). All polyacrylates exhibit the same decrease in viscosity independent of their molar mass. After an addition of 0.4 wt% dispersant the viscosity has the same low value.

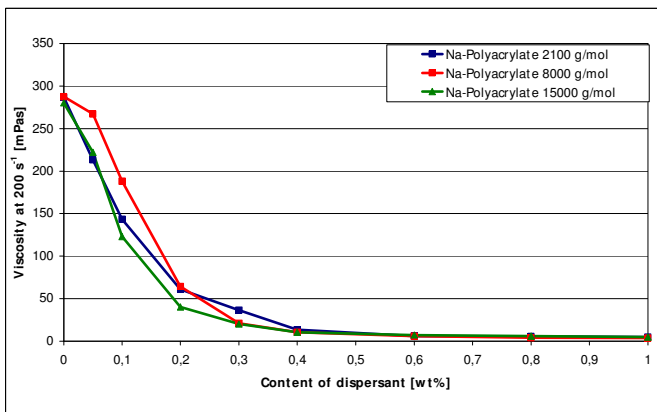


Fig. 5: Dependence of the viscosity of a 10 wt% boehmite suspension on the content of polyacrylate dispersants with different molar masses (additive content refers to solid content)

Due to the high adsorption and the resulting high ESA signals and low suspension viscosity the sodium polyacrylate with a molecular weight of 15000 g/mol were elected for milling experiments in a laboratory ball mill. For this purpose, a 25 wt% boehmite suspension with 0.5 wt% additive was used. The milling test resulted in a quite considerable loss of the stabilizing effect with an increase in yielded energy. The viscosity in the slip increased rapidly. For the purpose of determining whether the decrease in stability was caused by the formation of surface due to the deagglomeration of the particles by the milling process, a new milling test with a high excess of dispersant (2 wt%) was carried out. The same results in stability loss and increase of viscosity were detected (Fig. 6). Therefore, an insufficient amount of dispersing agent can not be the reason for the instability. Particle size measurements showed only a small change in the particle size during the milling process. The reaction of the sodium polyacrylate with the particle surface, i.e. the adsorption on the surface, seems to be not strong enough to resist the application of mechanical energy. Electroacoustic measurements of a boehmite suspension after milling show significant changes in the particles surface charge and indicate an alteration in additive adsorption. Fig. 4 (continuous line) illustrates the adsorbed

amount of polyacrylates after 2h milling in a planetary ball mill. All dispersing agents are desorbed in the same proportion from the surface, independently of their molar mass. ATR-FTIR measurements show only a weak adsorption of the polyacrylates via outer-sphere complexation by electrostatic or hydrogen bonds, which can be broken by the input of energy [1]. Due to this case, all polyacrylates are not qualified to stabilize the boehmite particles in aqueous suspensions during milling, independently of their molecular weight.

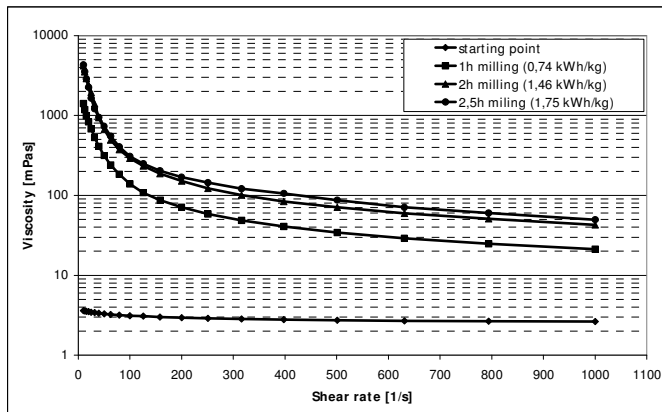


Fig. 6: Viscosity curves for a 25 wt% boehmite suspension with 2 wt% sodium polyacrylate (15000 g/mol) as a function of milling time and applied energy (denoted in brackets)

Conclusion

Stabilization investigations on a commercially available boehmite powder in water for subsequent milling in a laboratory ball mill demonstrated the feasibility of the production of highly concentrated suspensions with good flow behavior due to the addition of polyacrylate dispersing agents. Milling experiments showed a significant desorption of all additives from the boehmite surface in the same proportion, independently of their amount in the slip or their molar mass. ATR-FTIR measurements approved the weak adsorption on the boehmite surface via an outer-sphere complexation by electrostatic or hydrogen bonds. All investigated sodium polyacrylate dispersants (2100, 8000, 15000 g/mol) are not suitable to stabilize the boehmite particles in aqueous suspensions during milling.

Acknowledgment

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Literature

[1] Meyer, A., Nebelung, M., Lenzner, K.; Müller, M.; Ouyang, W., Potthoff, A.: Impact of milling conditions on the effectiveness of chemical additives in suspension preparation *cfi/Ber. DKG*. 86(2009), 13-20.