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Characterisation of aqueous suspensions of fumed aluminium oxide in presence of two Dolapix dispersants

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Abstract The stability of a fumed aluminium oxide nano powder suspended in water has been assessed through measurement of zeta potential and streaming current, using the fact that the particles exhibit maximum repulsion at high magnitude of charge. Two commercial dispersants belonging to a Dolapix series have been tested. Dolapix CE 64 has shown a better deflocculating action than Dolapix A 88. The iso electric point of the powder suspension has been found close to pH 9. A notable shift in the pH of iso electric point when Dolapix CE 64 was present, indicating that the interaction between particles and dispersant has involved chemical sorption. It has been found out, that at the relative low solids loading studied and within the limits of the pH measurement accuracy, a dispersant supplied in dose levels from 12 to 24 mg/g, has confined the pH of iso electric point to a relatively narrow range. A capillary suction time technique has been tried for evaluation of suspension fluidity as function of dispersant concentration and pH. For the dispersant stabilised suspensions, a correlation between their capillary suction time and pH of iso electric point has been documented.

Introduction

Flame synthesized nano-scaled oxides find wide use in many innovative applications. The aluminium oxide, among them, is mainly designed for improving the flowability of powder products (e.g. powdered lacquers), for thickening of liquids, for rheology maintaining and as antiblocking agent in PET films production. As a rule, most of the commercial products formulated on fumed oxides basis are used as aqueous dispersions, therefore their characterisation in terms of surface and interfacial properties, parallel to size, shape and morphology is mandatory. This is because any change in powders composition and characteristics directly influences their processing (rheology, dust generation, mixing, segregation etc.), and product performance. These challenges have motivated a large number of investigations devoted to structure–effect correlation, for enabling sound control over important product properties relevant to their engineering applications [1]. For a particular application, given properties of the powder in aqueous medium might be beneficial, while for other niches, the same properties might be undesirable and detrimental. For instance, the generic principle of gel casting, which is one of the emerging direct consolidation methods for colloidal processing of ceramics, is to ensure well-dispersed powder suspension and to prevent agglomeration before slurry casting in moulds. After slurries casting, they are transformed into rigid bodies without removal of water. Mainly two approaches have been followed here: in the first category, the generic principle is to encourage polymers (or monomer reacted to form polymers) to create a 3-D gel network keeping the particle suspension stable, while in the second category, particle coagulation is encouraged via colloidal based consolidation (i.e. by changing external conditions such as pH, ionicity, temperature etc.).

The aluminium oxide presented here, was characterised by high specific area, nano size and γ phase presence [2, 3], which determines its unique characteristics. The aim of the

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present study was, by involvement of an established approach for dispersant optimisation in colloidal processing of ceramics, to compare two common dispersants towards stabilisation of aqueous powder suspension and to discuss its behaviour in terms of fluidity.

Experimental

Materials

An aluminium oxide powder of high purity obtained from Degussa AG, Germany, has been used. Its main characteristics, as reported by the product specification sheet, are summarised in Table 1.

The two dispersants used, have been Dolapix A 88 (2-amino 2-methyl propanol) and Dolapix CE 64 (carbonic acid based polyelectrolyte), supplied by Zschimmer & Schwarz, Germany. According to product information data, the A 88 is a pseudo cationic in nature and its deflocculating effect on the ceramic particles surface is expressed by generation of charges of same polarity, which cause the particles to repel each other. The CE 64 possesses bivalent functional groups and is characterised by adsorption on the particle surfaces and complete dissociation at pH above 8.5 [4]. De-ionised water from ''Modulab'' purification system with conductivity in the range 0.1–0.2 μS/cm has been used. NaOH and HCl from Merck (1 M) have been chosen for pH adjustment. Unless otherwise stated, suspensions with solids fraction of 4.76% w/v have been tested through all the studies.

Particle size distribution, zeta potential and streaming current measurement

A DT 1200 spectrometer from Dispersion Technology, USA has been used in acoustic attenuation mode to measure particle size distribution and in electro acoustic mode for zeta potential, calculated on the basis of colloidal vibration current. The instrument precision in obtaining particle size distribution is determined by the error in the attenuation spectra, the later normally being very low for suspensions with good density contrast. The zeta potential probe has been calibrated against a standard Silica–Ludox suspension. For the titration tests, 5 g of the powder have been added to 100 ml water, containing a predetermined amount of dispersant, calculated on solid mass. The suspensions have been agitated for 2 min with magnetic stirrer, followed by 20 s with an ultrasonic disintegrator model UP 400 S, Dr. Hilscher, Germany. Immediately after, they have been transferred into the spectrometer measurement chamber, where were kept in circulation by the built-in magnetic stirrer. Their natural pH denotes the starting pH before titration. In case of volumetric titration, one of the integrated micro burettes has been filled with dispersant solution, which exact amounts dispensing inside suspension volume has been enabled by software control. Streaming current has been measured by means of a particle charge detector, PCD-03-pH from Mütek, Germany. It consists of cylindrical cell fitted with a displacement piston, which moves back and forth at constant frequency forcing a relative motion between the liquid and particles, thus inducing development of a streaming potential of either positive or negative sign. The powder–liquid mixing has been realised directly inside the 10 ml cell for 2 min, a duration which has been considered sufficient, as indicated by establishment of a stable steaming current. A small pH electrode has been fitted to the cell, enabling on-line pH monitoring. Upon requirement, the exact magnitude of the charge could be estimated by titration with oppositely charged standard polyelectrolyte until neutralization of the streaming potential to zero value.

Table 1 Main characteristics of the Aeroxide Alu–C powder

Average primary particle size (nm)	Specific surface area (BET) (m^2/g)	Density (g/cm^3)	pH as 4% w/v suspension
13	100	2.9	4.5–5.5

Capillary suction time measurement

In order to evaluate fluidity of the powder suspensions, capillary suction time experiments have been envisaged. They have been realised with a ''CST 100/A'' device from HeGo Biotech Germany, equipped with a hollow cylinder capable of handling 5 ml suspension, standing on a filter paper similar to a Whatman 17 type. Two successive measurements have been carried out and their mean value taken. The suspensions for the CST tests have been prepared under the same mixing procedure like the samples measured by the DT 1200 system.

Determination of optimum dispersant dosages

The optimum dose level of polyelectrolyte required for obtaining maximum powder dispersion in water has been estimated by two means: by the zeta potential obtained by the DT 1200 spectrometer and from the streaming current readings of the particle charge detector. The inflection point in the plots between the dispersant dose level vs. zeta potential and streaming current should indicate the optimum dispersant dosage, leading to a maximum dispersion [5, 6]. Settling tests, linking sediment height with dispersant dosage, are also commonly used as a tool for selection of dispersant type and its optimal concentration. For the case of the studied powder however, such tests were found not suitable, since the suspensions did not settle even after long time.

Results and discussion

Powder characterisation

A microphotograph of the powder taken by a raster electronic microscope (model Zeiss DSM 962) is shown at Fig. 1. Large clusters consisting of particles with irregular shape could be seen. It was impossible to visualise single particles, since they agglomerate possibly due to the high surface area pertinent to this nano powder. It should be noted, that previous studies of fumed silica powder, have also reported that isolated primary particles did not exist [2, 7].

A typical particle size distribution of the powder suspension, as measured by the acoustic spectrometer, is shown at Fig. 2. The mean and median particle size was determined respectively as 50 and 39 nm with standard deviation of 0.27 and at 2.6% fitting error. Since the producer specifies an average particle size for the dry powder about 13 nm—Table 1, it could be presumed that the powder agglomerates when suspended in water.

Dispersant selection and dose level optimisation

The dispersants efficiency towards keeping the particles in suspension has been evaluated by zeta potential and streaming current characteristics of suspension. The results obtained in this direction are shown at the Fig. 3 in form of a volumetric titration curves performed by progressive supply of the tested dispersants in dose levels up to 27 mg/g.

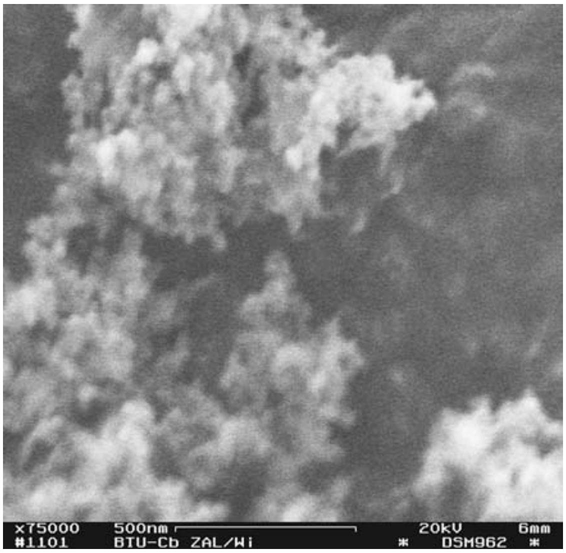

Fig. 1 REM image of an agglomerated Alu–C powder

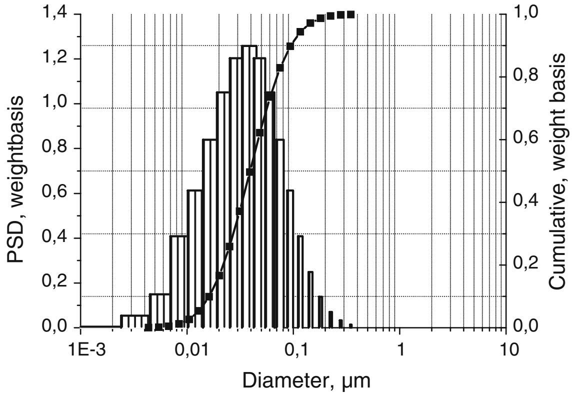

Fig. 2 Particle size distribution of powder suspension at natural pH

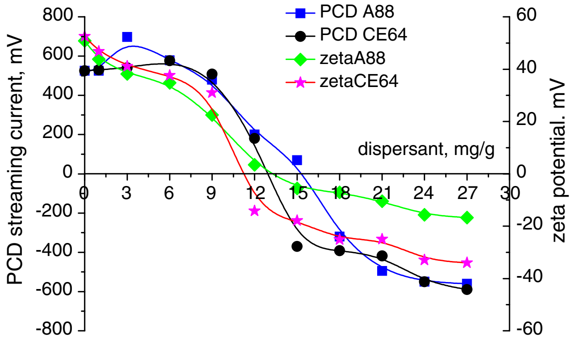

Fig. 3 Effect of dispersant concentration on zeta potential and streaming current

As could be seen from the figure, all curves are characterised by a similar trend, decreasing monotonically parallel to dispersant addition. While the streaming current curves for the both dispersants nearly overlap, the zeta potential curves differ at higher dosages of dispersants. Both dispersants have completely neutralised the initial positive charge, but the Dolapix CE 64 has provided higher charge loading compared to Dolapix A 88. It is worth to note the slight deviation in the dose levels leading to exact zero charge, gained independently from the zeta potential and from the streaming current curves for a same dispersant. The both methods are viewed as identical regarding determination of $pH_{(iep)}$ by potentiometric titration [8]. In case of the volumetric titration however, the observed shift could be attributed to the different mode of dispersant addition adapted for the DT 1200 spectrometer and for the particle charge detector. In case of the DT 1200 system, the plotted curve originates from measurement of one and a same sample of suspension, treated with step-addition of dispersant, the amount of which has been exactly calculated for each point. Each zeta potential value has been taken after 2 min elapsing required for mixing/equilibration. It should be noted, that owing to the minute amounts of supplied dispersant, any dilution effects were viewed negligible regarding the measured zeta potential. In case of the particle charge detector however, each streaming current value relates to a single sample, prepared and measured separately. Therefore, mixing effects could be responsible for the observed deviation, considering also the high specific area of the powder and the fact that the measurement accuracy has been found within the acceptable limits.

It is evident, that without addition of dispersant, the suspension system acquires high positive charge, as result of surface hydroxyl groups, which dissociate in water or act as proton acceptors. Thus, the natural stabilisation without dispersant, could be due to electrostatic repulsion forces, which are known as weak and short ranged ones, and as such could lead to less stable powder suspensions. Additionally, hydration forces could be suspected to exist. Their origin is debatable and for SiO_2 sols could be linked to hydration effects due to presence of silanol groups [9].

With the addition of dispersants, both the zeta potential and the streaming current are reduced. At 15 mg/g, the suspension could be still partially stabilised by electrostatic and steric forces. At 18 and 21 mg/g dose levels, the zeta potential has almost approached –30 mV, a level considered as a minimum for full steric stabilisation. It has appeared from the CE 64 curve (star symbols), that an inflection point is poor for description. Nevertheless, after 24 mg/g, a curve flattening could be distinguished, the potentials remaining almost constant thereafter. Based on this, a dose level of 24 mg/g has been viewed as an optimal one for maximum powder dispersion. As a rule, any amount of dispersant supplied above that optimum, will remain unbounded in suspension and lead to unwanted high viscosity.

In order to evaluate any pH effects resulting from dispersant dissociation, it was important to follow the pH variation after dispersant addition, since any significant shift in suspension pH resulting from dispersant addition above the optimal dosage, could lead to higher ionic strength in the suspension and subsequently affect its colloidal stability. This relationship is plotted at Fig. 4, where it could be noted that the both dispersants when supplied above 12 mg/g, have shifted the pH towards alkaline region. However, above this dose level and further passing through the optimal one, the CE 64 maintains a steady milder level of pH compared to that of A 88, an added argument for choosing the former dispersant for more detailed study further.

Shift in $pH_{(iep)}$ resulting from dispersants addition

The pH of iso electric point is an important characteristic when considering the stabilisation/destabilisation phenomena in colloidal systems. According to the DLVO theory, rendering the pH to the respective iso electric point, should lead to repulsive forces weakening and to fast agglomeration. Therefore, for evaluating the shift in the $pH_{(iep)}$ and the effect of dispersant addition on the same, a potentiometric titration has been carried out. Since during the volumetric titration, CE 64 has shown better performance in comparison to A88, its effect upon the shift in $pH_{(iep)}$ has been studied within a broader dose level range, i.e. from 12 to 24 mg/g. This range has been intentionally chosen, since after 12 mg/g, a reversal in the zeta potential sign has been documented—Fig. 3. The titration results for CE64 are depicted at Fig. 5 and the respective shift in $pH_{(iep)}$ are summarised at Fig. 6.

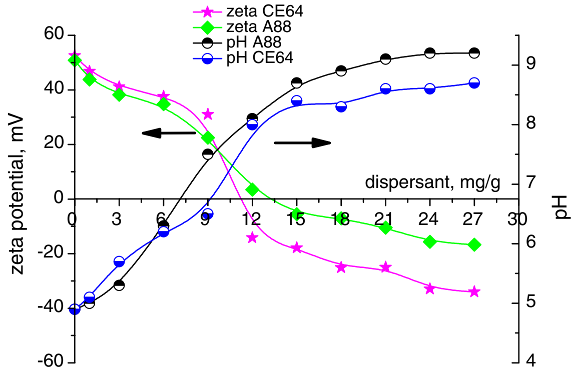

Fig. 4 Zeta potential and pH of suspension as function of dispersant concentration

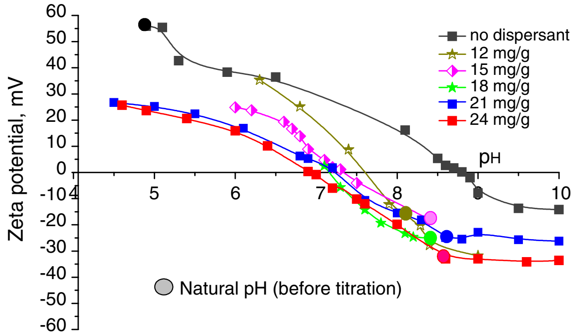

Fig. 5 Determination of zeta potential as function of suspension pH, with and without addition of Dolapix CE64

Figure 5 indicates, that without dispersant, the $pH_{(iep)}$ of the suspension is around 8.9. This value is lower than the one of 9.9 reported for a similar powder [2]. Upon addition of dispersant in concentration from 12 to 24 mg/g, the $pH_{(iep)}$ is shifted towards neutral region. From other side, the natural pH of the suspension is shifted from an acidic range of pH 4.9, towards an alkaline pH region of 8–8.5 where the dispersant should be nearly 100 % dissociated [4], according to the reaction:

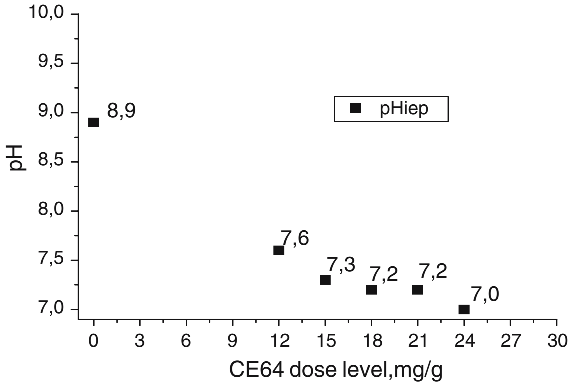

Fig. 6 Effect of CE 64 dose level on $pH_{(iep)}$ shift

$$RCOONH_4 = RCOO^- + NH_4^+ \qquad (1)$$

The $pH_{(iep)}$ shift resulting from dispersant addition (Fig. 6), could be an indication that the dispersant is well fixed on the powder by formation of H-bond between its dissociated $RCOO^-$ group and the OH^- group on the alumina surface. It should be noted also, that the natural pH of the suspension after addition of dispersant found in the range of 8–8.5, is relatively apart from the range of the respective $pH_{(iep)}$ being between 7 and 7.5.

Potentiometric titrations of suspensions treated with A88 supplied at 15 and 18 mg/g have been done in a similar manner as well. It has been found out, that in contrast to the CE64 case, the addition of A88 did not shift markedly the $pH_{(iep)}$. The iso electric points for both 15 and 18 mg/g dose levels have been found at pH 8.7, which is a negligible shift from the value of pH 8.9 established for the non-treated dispersion. This nearly coincidence in the $pH_{(iep)}$, with and without dispersant, clearly indicates that the interaction between the powder and the A88 is a physical in nature, which additionally favours CE64 as a better dispersant.

Evaluation of suspension fluidity by CST

The rheological properties and fluidity of suspensions are affected by the surface structures of the particles, which often are determined by the powder manufacturing history. For the case of the studied fumed oxide powder, it was important to find out, if a correlation between the suspension fluidity and the optimal level of dispersant determined by the volumetric titration exists. At this point, only CE 64 dispersant has been considered. Figure 7 displays the CST evolution for the suspension treated with increasing concentration of dispersant. The respective pH values are plotted as well.

A perusal of the relationship shown at Fig. 7 indicates a pronounced maximum for 15 mg/g dispersant dose, after which point, the CST has dropped. At the optimum level of 24 mg/g suggested by the volumetric titration, the suspension is characterised by low CST and at the same time has been visually appearing quite fluid.

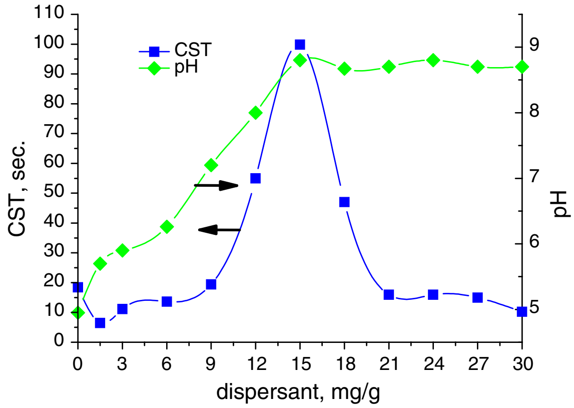

Fig. 7 CST and pH of suspension as function of dispersant concentration

In a separate group of experiments, the CST variation with pH has been evaluated, for suspensions without dispersant and for such treated with 12, 15, 18 and 24 mg/g. The relationships shown at Fig. 8 indicate, that without addition of dispersant, the suspension CST rises continuously with pH increase. This trend is not affected, even when the suspension has been adjusted to the respective $pH_{(iep)}$ of 8.9. A maximum CST value is observed at pH above 10. From other side, the CST curves for the dispersant treated suspensions always have passed through a peak. It is interesting to note, that for 12, 18 and 21 mg/g, the maximum CST lies within the region of $pH_{(iep)}$ found for the respective dose level, i.e. between 7 and 7.5. Effectively, the more the pH of suspensions has been buffered towards $pH_{(iep)}$, the more they have been structured to gel. For 15 mg/g however, the maximum CST has been found at pH 8.5, coinciding with the natural pH of the suspension and being higher than the $pH_{(iep)}$ for this dose level.

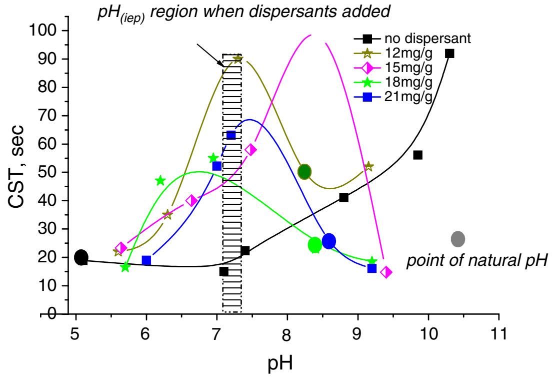

Fig. 8 CST as function of pH at different dispersant dose level

The above observations are quite intriguing and a possible explanation could be found in the CST measuring principle. Whilst the exact pore size of the CST filter paper is not known, it is for sure much larger than the primary particle size of the suspended powder. An assumption could be launched, that when the suspension has been treated with optimal dispersant dose and when its pH has been maintained away from the IEP, the suspended particles will go through the pores and the suspension will flow like water giving short suction time. On the other hand, at pH close to IEP, particles agglomerate and tend to block the pores, thus yielding high CST values—Fig. 8. For the non-treated suspensions, the lack of pronounced peak around the IEP could be due to a continuous particles agglomeration, which is irreversible and is unaffected by driving the pH towards alkaline region. Therefore, the CST value, which normally characterise sludge water holding capacities, in case of the studied powder suspension, could not be directly related to its structure and rheology, rather to its fluidity.

Conclusions

Experimental data about zeta potential and streaming current of water suspension containing aluminium oxide nano powder are reported. Being from an initial study phase, the presented results do not lead to fundamental conclusions. They are believed to have implication on revealing some properties of the powder in water dispersion (stability, durability) and the role, which common deflocculants could play in maintaining the characteristics of the suspension. The results could be relevant to other fumed oxides as well. Due to the pyrogenic method of synthesis they possess some common properties.

The studied nano powder has its main application as filler, rheology maintainer etc., but one could find its use in quite diverse fields also. For example, the same gama aluminium oxide has been used among others as a model colloidal system, for investigation of aggregate structures relevant to flocculation and dewatering processes [10]. Whichever the application niche is, it is conceivable that its dispersion stability is of primary importance.

The anionic deflocculant CE64 has shown better effect in terms of electrosteric stability and suspension pH, than the cationic A88. The electroacoustic method used for measuring particle size distribution and zeta potential of the nano powder has shown good results at the moderate solid concentrations. The zeta potential and streaming current techniques have provided comparable data for determination of pH of iso electric point for the studied gamma alumina nano powder, likewise it has been established for alpha alumina powders [11]. The CST method has an advantage being simple and rapid, but in our case, it has yielded limited information about suspension structure and rheology. The studied nano powder belongs to the fumed oxides family and undoubtedly possesses indigenous characteristics and a liquid media such as water and its composition, could markedly change its state and accordingly the particle–particle interactions and the properties of the entire suspension. For further elucidation of the presented findings, more studies, encompassing rheology as well should be pursuit.

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