Short-range repulsive potential developed by the addition of Mg(II) ions to aqueous alumina slurries

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Abstract

The effect of magnesium acetate additions on the interparticle potential of diluted well-dispersed aqueous alumina suspensions, prepared with the Dolapix CE64 dispersant at inherent pH, and the rheological properties of these suspensions, have been studied. In order to destabilise these suspensions a 0.5 M aqueous magnesium acetate solution was added and the pH and viscosity changes were monitored. The neutralisation of the surface charge on the particles occurs because of the formation of coordinative bonds between magnesium ions and carboxylic groups of the dispersant molecules, which is reflected in the destabilisation of the suspension. A thin and rigid neutral layer on the surface of the particles is formed which prevents the close contact between particles. As a consequence, weak flocculation of the suspension takes place and the resulting short-range repulsive potential was confirmed with force measurements. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Colloidal processing is a relatively new method for wet processing of ceramic powders which offers the potential to reliably produce advanced ceramic parts with improved mechanical properties. To efficiently exploit the benefits of colloidal processing, accurate control of the interparticle potential and the rheological properties of the suspension is required. In the first step, a well-dispersed dilute suspension is needed for the successful removal of heterogenieties such as agglomerates and large particles by filtering or decanting from the powder prior to shaping the green parts. These heterogenieties are the cause of strength-limiting flaws in the sintered specimen.[1] However, the problem with using such suspensions is their inadequate viscosity for forming green parts, as mass segregation tends to occur during solidification.[2,3] To avoid this problem the viscosity must be increased by destabilising the suspension.[4] This can be done by changing the pH of the suspension to the isoelectric point where no net charge is present on the particles and as a result of the attractive van der Waals forces, particles form flocs i.e. the suspension flocculates.[5] An alternative route, known as colloidal processing of a weakly flocculated suspension,[6] involves the formation of a thin neutral layer on the surface of each particle to prevent the close contact driven by the van der Waals forces. When such particles are forced together, short-range repulsive forces begin to act and the particles can slide over one another resulting in the formation of a close-packed structure[7] with a minimum of defects in the green compact.

Literature reports suggest that a thin layer on the surface of the particles can be obtained in two different ways. Lange et al. introduced the method of hydration layer,[8–12] while the second method is known as steric hindrance. Steric hindrance can be achieved in aqueous,[13,14] as well as in nonpolar, suspensions.[15,16] With all these methods, in order to fully exploit the benefits of colloidal processing, weak flocculation is achieved by the addition of ions which later act as impurities and can affect the properties of the sintered product.

In our previous work[22] we have reported that a weakly flocculated aqueous alumina suspension can be achieved without introducing undesired impurities to the sintered ceramics. This can be done by the addition

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of an appropriate amount of magnesium acetate to a well-dispersed aqueous alumina suspension at an inherent pH with the addition of the anionic dispersant Dolapix CE64. The structure of Dolapix CE64 enables the formation of a thin rigid layer on the surface of the particles. This is in contrast to polyacrilyc acids, which are commonly used as dispersants for the preparation of aqueous alumina suspensions, because their structure prevents the formation of a thin surface layer when magnesium acetate is added due to bridging flocculation of the particles in the suspension. With the addition of magnesium acetate to a suspension containing Dolapix CE64 the surface charge of the particles is neutralized, which is reflected in the destabilisation of the slurry, and because of the formation of coordinative bonds between the Mg ion and two dissociated carboxylic groups of the dispersant, a thin neutral layer is formed on the surface of the particles, establishing a nontouching particle network.

In the present paper we present additional experimental evidence to support the existence of a short-range repulsive potential between the particles. In order to better understand the mechanism of the destabilization, an aqueous alumina suspension with a surplus of dispersant has been prepared and characterized in terms of rheological properties[17] and the short-range repulsive forces were determined using atomic force microscopy (AFM).

2. Experimental work

Aqueous alumina suspensions were prepared by ball milling A16SG alumina powder (Alcoa Co. Pittsburgh, USA), the dispersant Dolapix CE64 (Zschimmer & Schwarz, Germany) and distilled water. Milling was carried out for 2 h in a planetary mill. The prepared suspensions contained 15 vol.% of alumina powder to which either 0.25 or 0.4 wt.% of the dispersant Dolapix CE64 was added. Dolapix CE64 is a carboxylic acid, free from alkalis, delivered as a 70 wt.% aqueous solution with a pH of 7. Our characterization of the dispersant indicates that the average molecular mass of Dolapix CE64 is 320 g mol^{-1} and that it is an ethanolaminic salt of citric acid. Subsequent destabilisation of the suspensions was achieved by the addition of magnesium acetate solution (0.5 M) or concentrated hydrochloric acid, with a further homogenisation with impeller mixer for 30 min.

The viscosity of the suspensions was measured with a HAAKE VT500 rotational viscometer using a MV-1 measuring system. Additional measurements were performed with a HAAKE RS 150 viscometer and the DC 60/4 measuring system.

For the adsorption measurements, 0–0.7 wt.% of Dolapix CE64 was added to a suspension containing 15 vol.% alumina at its inherent pH. The residual concentration of the dispersant in the supernatant was measured using potentiometric titration based on a stoichiometric reaction between a cation and a polyanion.[18] The standard cationic electrolyte solution 0.05 M hexadecyltrimethylammonium bromide-CTAB (Aldrich, Germany) was used as a titrant. A streaming current detector provides a measure of the charge neutralisation.[19] A PCD02 (Mütek, Germany) particle charge detector and titrator (DL21, Mettler, Switzerland) were used to determine the residual concentration of Dolapix CE64 in the supernatant.

Potentiometric titration was also used to determine the influence of magnesium ions on the number of dissociated carboxylic groups of the dispersant in the pH range from pH 6 to 10. For these measurements aqueous solutions of the Dolapix CE64 dispersant ($c = 1$ g l^{-1}) were prepared to which the magnesium acetate and magnesium nitrate (0.01 M) were added. The pH of the solutions was adjusted with the addition of dilute HCl and NH$_4$OH.

The same procedure was also used to determine the influence of magnesium acetate on the number of dissociated carboxylic groups of the dispersant at a pH of 9.7. In this case an aqueous solution of the Dolapix CE64 dispersant ($c = 5$ g l^{-1}) was prepared to which the magnesium acetate (0–0.08 M) was added. The total number of dissociated carboxylic groups of the dispersant was calculated from the titrant consumption when no magnesium acetate was added. The number of Mg atoms was calculated from the concentration of the magnesium acetate addition. The Mg/COO$^-$ ratio was obtained by dividing the number of Mg atoms by the total number of dissociated carboxylic groups.

The electrophoretic mobility of the alumina particles was used to determine their zeta potential in distilled water and in the supernatant of the suspensions with added Dolapix CE64 and magnesium acetate (Zeta-sizer MK II, Malvern Instruments, UK). The supernatants were prepared by centrifugation of the prepared suspensions at 5000 rpm for 10 min. The zeta potential results represent an average of ten measurements under constant conditions.

The forces between an A 16SG alumina particle and a flat, polished, alumina surface were measured in solution using a Nanoscope III Atomic Force Microscope-AFM (Digital Instruments, CA) equipped with a liquid cell. A spherical alumina particle (≈ 15 μm in diameter) was attached to a standard V-shaped AFM cantilever[17] with a spring constant of 0.1 N m^{-1}, as shown in Fig. 1. The surface topography of the alumina surfaces was investigated with AFM, this revealed a smooth surface in a 5×5 μm scan area with a root-mean-square (RMS) roughness of 6 nm for the sintered colloid probe and 3 nm for the sintered flat surface. The radius of the spherical alumina particles, which is used for calculating the normalizing force, was determined by imaging the surface of particles glued to the cleaved-mica surface by contact-mode AFM. The alumina particles are composed of
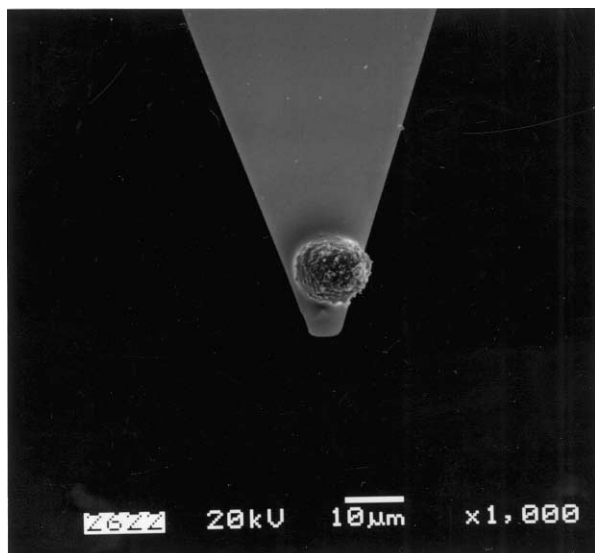
Fig. 1. SEM image showing a colloid probe. A 10 μm A16 alumina sphere is mounted on triangular AFM cantilever.

smaller spherical grains with a typical radius of curvature of 700 nm. As we are concerned with forces in the region of 20 nm from the surface, only the nearest grain is important for the interaction.

The AFM measurements are presented as force divided by the radius of curvature of interacting surface, as a function of separation. The point of zero separation is determined from the force plots in such a way that there is hard contact between the two surfaces. This is clear from the force versus separation plots, where all the data points collapse onto a straight vertical line at zero separation. The AFM was operated in the force-plot mode, as has been described elsewhere.[17]

3. Results and discussion

The Dolapix CE64 dispersant was used in the preparation of A 16SG aqueous alumina suspensions at inherent pH. After the addition of alumina particles to the distilled water, the equilibrium pH is reached due to adsorption or desorption of protons at the surface of the particles. The equilibrium pH depends on the amount of added powder, and for the alumina used in this study, the pH becomes constant when more than 10 vol.% of alumina powder is added. This constant pH is called the inherent pH, and for A 16SG alumina it has a pH value of 9.9.

The adsorption isotherm, which shows the extent to which the Dolapix CE64 adsorbs onto the surface of the A16SG alumina particles, is shown in Fig. 2. The graph indicates that the maximum amount of dispersant which can be adsorbed onto the surface of the alumina particles at inherent pH is 0.25 wt.% (on a dry-weight basis), corresponding to 0.21 mg m^{-2} of adsorbed dispersant
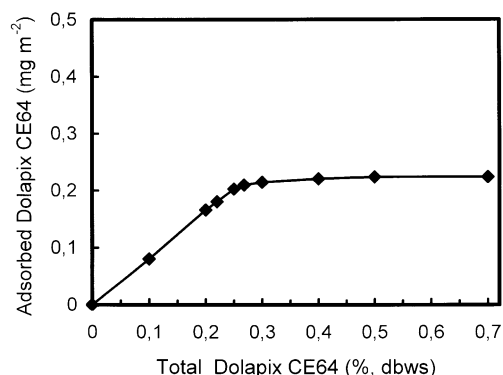

Fig. 2. Adsorption isotherm for Dolapix CE64 on A 16SG alumina powder at inherent pH (pH = 9.7) as a function of dispersant concentration.

per unit surface area. As reported previously,[20] the addition of Dolapix CE64 is effective in reducing the viscosity of concentrated A16SG suspensions by establishing a highly negative surface charge on the A16SG alumina particles at inherent pH, and by shifting the isoelectric point (IEP) of the alumina particles from a pH value of 8.7 to 6.3.

Alumina suspensions with 15 vol.% of alumina powder were prepared, making it easier to observe changes in the suspension viscosity, which can change rapidly when the suspension is destabilised. The changes in viscosity and pH value with the addition of a 0.5 M solution of magnesium acetate to a dispersed alumina suspension prepared at inherent pH with the addition of 0.25 and 0.4 wt.% Dolapix CE64 were observed. As shown in Fig. 3, the addition of magnesium acetate to the suspension resulted in the destabilisation of the alumina suspensions. The drop in pH value following the addition of magnesium acetate can be explained by the formation of the magnesium hydroxy species in the solution.[21,22] The
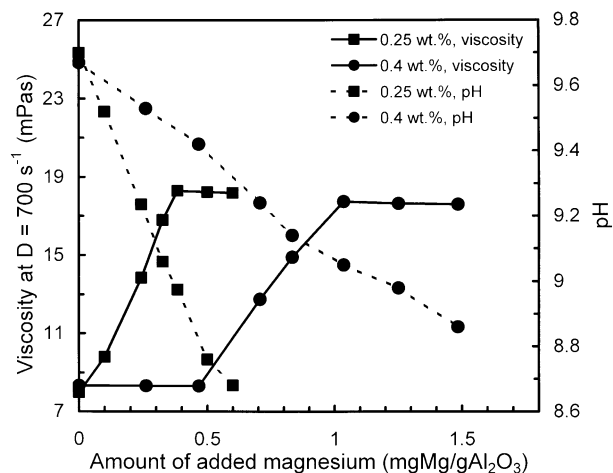

Fig. 3. Change of viscosity (η) and pH value with the addition of magnesium acetate to the alumina suspension prepared at inherent pH with 0.25 and 0.4 wt.% of the dispersant Dolapix CE64. Suspensions contain 15 vol.% of the alumina powder.

viscosity of the suspension with the addition of the magnesium acetate solution increases because of the change in the pH of the suspension from 9.9 to 9.0.

As reported previously,[22] the addition of magnesium acetate to the suspension containing 0.25 wt.% of Dolapix CE64, which is the minimum amount of Dolapix CE64 needed for the preparation of a well-dispersed A16SG alumina suspension, caused an immediate increase in the suspension viscosity (Fig. 3). The addition of magnesium acetate to the slurry containing an excess of the dispersant (0.4 wt.%) resulted in an immediate decrease in the pH, whereas the viscosity remained unaffected until an amount of magnesium acetate corresponding to approximately 0.46 mg Mg/g Al_2O_3 was added. With further magnesium acetate addition the viscosity starts to increase steadily and reaches its maximum value at approximately 1.06 mg Mg/g Al_2O_3.

These results tend to indicate that the magnesium cationic species did not replace the dispersant on the surface of the particles. Had they done so, the viscosity's dependence on the addition of magnesium acetate would not be affected by the excess of added dispersant. Since it was strongly affected, magnesium ions must have reacted with the dissociated carboxylic groups of the dispersant, and preferentially with those of the excess dispersant. This can also explain the observation that with additions of magnesium acetate up to 0.46 mg Mg/g Al_2O_3 the viscosity of the slurry containing excess of dispersant did not increase.

In order to check whether magnesium ions react with the dissociated carboxylic groups of the dispersant, the titrant consumption for a potentiometric titration of Dolapix CE64 solution in distilled water with and without the addition of two different magnesium salt solutions in the pH range from pH 6 to 10 was determined.

As shown in Fig. 4, in the presence of magnesium acetate or magnesium nitrate a significant shift to a lower consumption of titrant was observed. Since the type of anion clearly has no influence on the dissociation of the dispersant's carboxylic groups, the reduced number of dissociated carboxylic groups on the dispersant indicates that the magnesium cationic species did react with the dissociated carboxylic groups of the Dolapix CE64 dispersant. This particular dispersant is an aqueous solution of an ethanolaminic salt of citric acid,[22] and is expected to form chelates in the presence of magnesium ions. Citric acid is commonly used as a chelating agent for different metal ions including magnesium ions[23,24] and the structure of these chelates has been extensively studied. As such, the reaction leading to the formation of magnesium citrate necessitates the formation of coordinative bonds between the Mg(II) ion and the two monovalent dissociated carboxylic groups of the citric acid.[25]

To determine the number of dissociated carboxylic groups associated with the dispersant, which can be
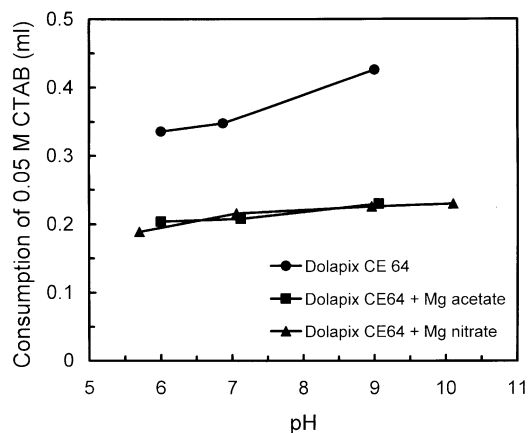
Fig. 4. Titrant consumption for polyelectrolitic titration with various pH values of Dolapix CE64 solutions ($c = 1$ g l^{-1}) in distilled water with and without the addition of magnesium acetate (0.01 M) or magnesium nitrate (0.01 M).

neutralised by magnesium acetate addition, the titrant consumption versus Mg(II) ion concentration was monitored. As shown in Fig. 5, Mg(II) ions are able to neutralize most ($>95\%$) of the dissociated carboxylic groups in the solution, provided that a surplus of magnesium acetate (1.7 Mg/COO$^-$) with respect to the stoichiometric ($=0.5$ Mg/COO$^-$) ratio, is added.

Fig. 6 shows an alternative way of presenting the viscosity data first shown in Fig. 3, the values relating to the abscissa are converted from amount of added magnesium' to the 'Mg/COO$^-$ ratio'. From this re-plotted data it is clear that the rate of viscosity increase is almost the same for the two levels of dispersant addition. Assuming the same reactivity between the magnesium acetate and the adsorbed dispersant on the surface of the particles, the fraction of neutralized carboxylic groups on the surface of the particles in the slurry can be estimated from Fig. 5. The amount of magnesium acetate addition (0.384 mg Mg/g Al_2O_3) needed to reach the peak viscosity of the slurry containing 0.25 wt.% of
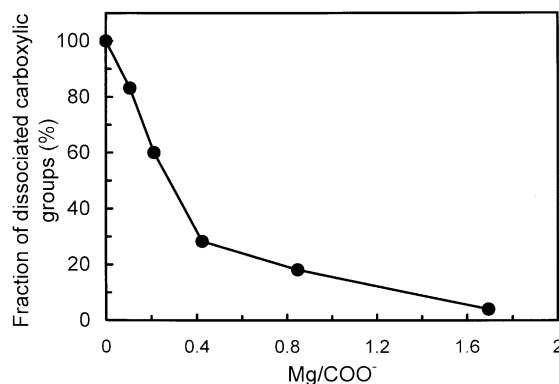
Fig. 5. Fraction of dissociated carboxylic groups as a function added magnesium acetate calculated as the ratio of magnesium atoms per total number of dissociated carboxylic groups (Mg/COO$^-$) for Dolapix CE64 aqueous solution at a pH of 9.7.
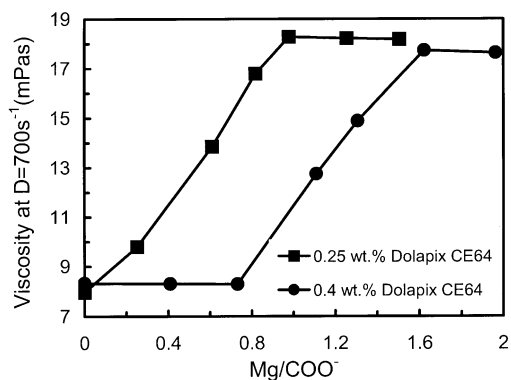
Fig. 6. Viscosity dependence of the aqueous alumina suspensions prepared with 0.25 and 0.4 wt.% of the Dolapix CE64 as a function of the ratio of magnesium atoms per total number of dissociated carboxylic groups (Mg/COO⁻).

Fig. 7. Fraction of dissociated carboxylic groups as a function added magnesium acetate calculated as the ratio of magnesium atoms per total number of dissociated carboxylic groups (Mg/COO⁻) for the supernatant prepared from the aqueous alumina suspensions at a pH of 9.7 with added 0.4 wt.% of the Dolapix CE64.

the Dolapix CE64 (Fig. 5) corresponds to an Mg/COO⁻ ratio of 0.978. By referring to Fig. 5 it appears that about 85% of the dissociated carboxylic groups can be neutralized at this Mg/COO⁻ ratio. In the case where the slurry was prepared with 0.4 wt.% of dispersant, the viscosity of the suspension did not change until the Mg/COO⁻ ratio was 0.73 Mg/COO⁻. Assuming that up to this Mg/COO⁻ ratio magnesium ions react only with the excess dispersant molecules, the calculation of Mg(II) per carboxylic group of the 0.15 wt.% excess dispersant gives a ratio of 1.91 Mg/COO⁻. According to Fig. 5, at this Mg/COO⁻ ratio the number of dissociated carboxylic groups of unadsorbed free dispersant is negligible. This result clearly shows that the Mg(II) ions must first react with the dissociated carboxylic groups of the excess dispersant, which has no effect on the viscosity of the diluted suspension. When the majority of the dissociated carboxylic groups of the excess dispersant are neutralised, Mg(II) ions begin to react with the carboxylic groups of the adsorbed dispersant on the surface of the particles.

The assumption was experimentally confirmed with the potentiometric titration of supernatants of slurries prepared from 0.4 wt.% of dispersant with added magnesium acetate. As shown in Fig. 7, the number of dissociated carboxylic groups in the supernatant decreases quickly and at a 0.94 Mg/COO⁻ ratio, it becomes almost negligible. If Mg(II) ions reacted equally with the free and adsorbed dispersant molecules, for the 0.94 Mg/COO⁻ ratio the number of free dissociated carboxylic groups should be 20%, according to Fig. 5. However, when the magnesium ions started to react with dispersant molecules adsorbed on the surface of the particles, the number of dissociated carboxylic groups is decreased and a reduced electrostatic charge on the particles and a lower stability of the suspension resulted. When the surface charge on particles is low enough, the van der Waals attractive forces between particles become significant, which results in the formation of an
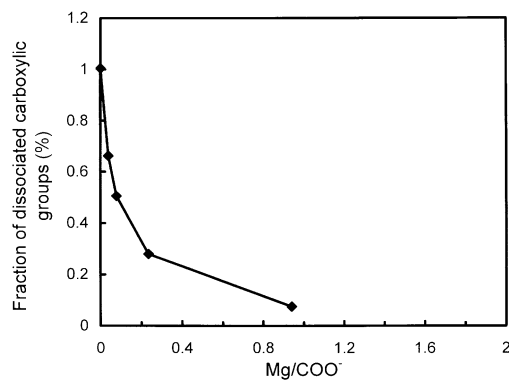
attractive network in the suspension, similar to that in a flocculated suspension, causing a rise in the suspension viscosity.

Fig. 8 is a schematic representation of the magnesium acetate's effect on the zeta-potential of alumina particles in a dilute aqueous suspension, prepared with the Dolapix CE64 dispersant. Point A in Fig. 8 represents the zeta-potential of alumina particles in the suspension prepared with added 0.25 wt.% of Dolapix CE64 at inherent pH. The zeta-potential measurements of alumina particles dispersed in a supernatant, obtained by centrifuging a 0.25 wt.% dispersant-containing slurry at maximum viscosity, yielded values close to zero (Fig. 8, point B). This indicates that most dissociated carboxylic groups have been neutralized by the addition of magnesium acetate. In contrast, when the zeta-potential of alumina particles was measured in a supernatant obtained by centrifuging a suspension prepared with a surplus of the dispersant (0.4 wt.%) and magnesium acetate corresponding to a Mg/COO⁻ ratio of 0.7 (i.e. before viscosity started rising, see Fig. 6), the measured value of
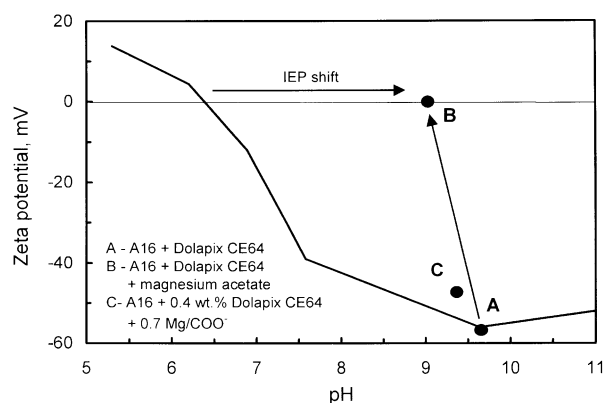

Fig. 8. Schematic presentation of the effect of magnesium acetate addition on the zeta potential of alumina particles with adsorbed dispersant Dolapix CE64 in zeta potential–pH diagram.

the zeta-potential was still −47 mV (Fig. 8 point C). This result additionaly supports the assumption that Mg(II) ions preferentially reacted with the excess dispersant. A slight decrease in the zeta-potential from −57 mV (point A) to −47 mV (point C) was not detected by the viscosity measurements because of the low powder loading of the suspension.

According to the literature,[25] coordinative bonds can be formed between a magnesium cation and two dissociated carboxylic groups on the same dispersant molecule or between different dispersant molecules. This enables the formation of a thin neutral layer on the surface of the particles, which is the condition for the occurrence of short-range repulsive forces.[26] A rigid surface layer on the particles prevents them from coming into close contact as a result of the attractive van der Waals forces, which in turn should be reflected in an altered rheological behaviour of the slurry.

Viscosity measurements were performed on two alumina suspensions, which were destabilised in two different ways. The first suspension was flocculated with a HCl addition to change the pH of the suspension to pH = 6.3, which is the IEP of alumina with added Dolapix CE64. The second suspension was destabilised with the addition of magnesium acetate. The differences between the flow curves of these two suspensions are shown in Fig. 9. The suspension with added magnesium acetate exhibited a lower viscosity, an important difference between the two suspensions.

For a more detailed look at the differences between these two suspensions, the viscosity vs. shear stress measurements are shown in Fig. 10. Significant differences between the two suspensions are observed. The flocculated suspension shows normal behaviour, i.e. after the yield stress is reached, the internal structure of the suspension is formed and the suspension becomes rigid. This happened almost instantaneously at 20 Pa, which can be considered as the yield stress. In comparison with the flocculated suspension, the suspension to which magnesium acetate was added shows a rather different dependence of viscosity. When the stress was lowered the viscosity increased sharply until a critical value of the viscosity was reached. A plateau between the upper and lower regions where the viscosity is almost constant for stresses between 5 and 12 Pa is clearly seen in Fig. 10. This plateau could be explained in terms of a wall slip, a phenomenon commonly observed in weakly flocculated suspensions, as reported by Buscall et al.[27] In both cases the suspensions were destabilised and attractive forces play the dominant role in determining the rheological behaviour of the suspension. The differences between the suspensions appear because of a thicker rigid layer of dispersant molecules on the surface of the particles when magnesium acetate was added, causing greater distances between the particles and so close contact between the particles is prevented.

For an experimental confirmation of the existence of the thin neutral layer on the surface of the particles, AFM force measurements were performed on the same two supernatants of the destabilized suspensions used for the rheological measurements. The AFM measurements are presented as force divided by the radius of

Fig. 10. Viscosity as a function of shear stress for flocculated suspension and suspension destabilised with magnesium acetate (0.25 wt.% of Dolapix CE64, 25 vol.% of alumina powder).
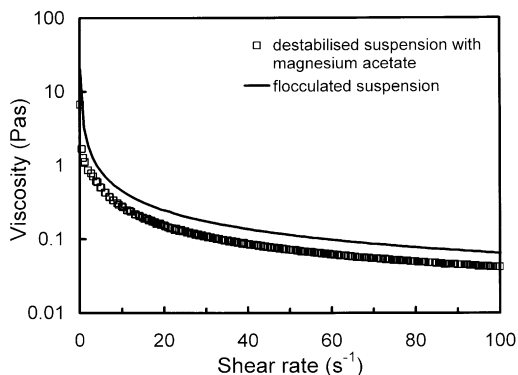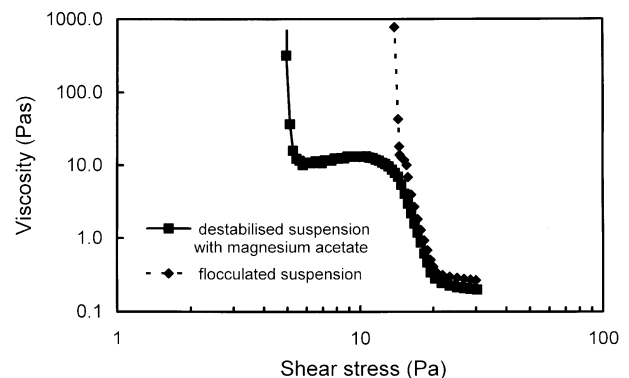

Fig. 9. Flow curve of 25 vol.% aqueous alumina suspensions prepared with 0.25 wt.% of the Dolapix CE64 dispersant destabilised with the addition of hydrochloric acid to pH value of 6.3 (IEP) and with the addition of magnesium acetate.
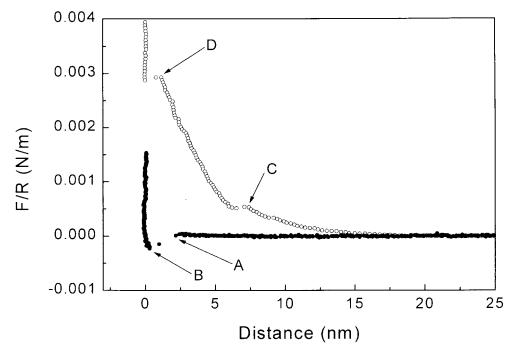

Fig. 11. Normalized forces measured in an AFM between an alumina particle and a flat alumina surface in the supernatant of a flocculated suspension with (solid circles) and without (empty squares) dispersant.

curvature of the interacting surface as a function of separation, Fig. 11. The point of zero separation is determined from the force plots, in such a way that there is a hard contact between the two surfaces. This is visible in the force versus separation plot, where all the data points fall on a straight vertical line at zero separation. In the presence of the supernatant obtained from the flocculated suspension (solid circles), the van der Waals attraction results in a sudden jump of the cantilever from a distance of 2.5 nm (point A) into close contact with the surface (point B). In contrast, for the weakly attractive particle network (empty circles), the interaction is always repulsive and a weak force minimum is observed at a separation of 6 nm. By further decreasing the separation, the surface layer deforms (point C to D), until it quenches irreversibly at a separation of 1 nm (point D). This is conclusive evidence for the existence of a thin neutral layer on the surface of the particles and also proof that magnesium acetate does not replace the dispersant on the surface of the particles when it is added to the suspension. This neutral layer displays some interesting characteristics. When the applied stress is large enough, particles can slide over each other so that they can re-arrange into a close-packed layer of particles and voids, and inhomogenieties are avoided during green-body formation. Also, fully formed, saturated green specimens can exhibit plastic behaviour during additional shaping. But if the applied stress is greater than the strength of this neutral layer on the surface of the particles, the particles are brought into close contact and plastic is converted to elastic behaviour.

4. Summary

The results of the present study can be summarized as follows.

(1) The maximum amount of Dolapix CE64 dispersant, which can be adsorbed onto the surface of A16SG alumina particles at inherent pH, is 0.25 wt.%.

(2) The addition of magnesium acetate to a well-dispersed dilute aqueous alumina suspension at inherent pH prepared with either 0.25 or 0.4 wt.% of the Dolapix CE64 dispersant resulted in an immediate decrease in pH. This is due to the formation of magnesium hydroxy species and an increase of the suspension viscosity. With excess dispersant, the viscosity starts to increase at a magnesium acetate addition of 0.46 mg Mg/g Al_2O_3 and not immediately after the first addition as in the case when the suspension was prepared with 0.25 wt.% dispersant. This result indicates that Mg ions react first with the excess dispersant.

(3) The particle surface charge was neutralized with the addition of a sufficient amount of magnesium acetate to the slurry, this was reflected in the destabilization of the slurry. The surface charge is neutralized due to the formation of coordinative bonds between two dissociated carboxylic groups and a Mg(II) ion, this is reflected in the neutralization of the charge on the dispersant molecules.

(4) Mg(II) ions are able to neutralize most ($>95\%$) of the dissociated carboxylic groups of the Dolapix CE64 anionic dispersant in the solution. Assuming the same reactivity between magnesium acetate and adsorbed dispersant, for the Mg/COO^- ratio at which the maximum viscosity was reached, up to 85% of the dissociated carboxylic groups of the dispersant on the surface of the particles could be neutralized.

(5) A thin neutral layer of the dispersant was formed on the surface of the particles which results in a weakly flocculated suspension. This was confirmed with the rheological measurements. Force measurements with AFM revealed a short-range repulsive potential acting between particles due to the formation of a thin neutral layer of the dispersant on the surface of the particles, preventing the attractive van der Waals forces from bringing them into close contact.

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