

The Influence of Lignosulphonate on the Properties of Single and Mixed Si_3N_4 and ZrO_2 Suspensions

Hedvig Byman-Fagerholm,^{a*} Pasi Mikkola,^a Jarl B. Rosenholm,^a Eva Lidén^b and Roger Carlsson^b

^aDepartment of Physical Chemistry, Åbo Akademi University, FIN-20500 Åbo, Turku, Finland

^bSwedish Ceramic Institute, Box 5403, S-40229 Göteborg, Sweden

(Received 20 November 1997; accepted 26 May 1998)

Abstract

Lignosulphonate (LS), was evaluated as a dispersing agent for single and mixed powder slips, containing Si_3N_4 and ZrO_2 powders, respectively. The surface charge was investigated by measuring the electrophoretic mobility in dilute powder dispersions. The slip stability was determined by visual observations of the settling of the powder and the fluidity of the slip was monitored by measuring the viscosity. It was evident that the different powder dispersions were most successfully stabilized by a high charge induced at high pH-values. However, in order to produce a sufficient fluidity of the slip, a dispersing agent had to be introduced. The optimal concentration range of LS at pH = 10 was found to be 0.2 wt%. The stabilizing mechanism in alkaline dispersions seems to be electrostatic depletion stabilization. The flow properties were finally tested by recording the viscosity for a mixed (composite) powder containing 68.4 wt% Si_3N_4 and 31.6 wt% ZrO_2 at a total solids content of 29–37 vol%. © 1998 Elsevier Science Limited. All rights reserved

Keywords: Si_3N_4 , ZrO_2 , suspensions, lignosulphonate, slip casting

1 Introduction

Colloidal ceramic powders (i.e. with a grain size smaller than a micrometer, 10^{-6} m) may be mixed to dispersions of high solids content but still maintaining an adjustable stability and fluidity. In order to reach these goals it is necessary to carefully characterize the powders and to use this

information when defining the optimal processing conditions. A homogenous slip is a prerequisite for the manufacture of a defect free microstructure in the green body and in the final ceramic material. In multicomponent systems the surface properties of each powder has to be examined separately in order to assess the optimal process conditions for the composite slip.

In previous investigations we have analyzed the surface properties of both Si_3N_4 ^{1–3} and ZrO_2 ^{1,4,5} powders in stable aqueous dispersions with high solids content. We have also succeeded to cast these slips to green bodies with a homogenous microstructure and to further sinter them to ceramic bodies of nearly 100% densities and high mechanical strength.^{5,6} It was found that each set of as-received powders should be characterized separately utilizing at least some critical process parameters before using them in powder mixtures. This precaution is called upon due to the highly variable surface properties found depending on the manufacturing process of the powders and the conditioning of the dispersion.⁴

Although the particle size distribution, the deformation of the powder particles (grains), and the leaching of ions may influence the electrophoretic mobility measured in dilute dispersions it has been found that the zeta potential derived successfully represents the electrostatic interaction between the particles in the dispersion.^{7–9} Moreover the electrostatic interaction seems to be the predominating feature for the stability of particle dispersions.^{10,11} The electrolyte may produce close packing transitions well below the theoretical space filled close packing limit.^{5,12} Additionally at a high ionic strength and volume fraction of particles all interaction of electrolyte added or dissolved from the particles becomes specific.^{5,13} This hydration interaction is very dependent on both the mutual

*To whom correspondence should be addressed

interaction of the cation and anion in solution and the affinity of the cation to the surface, respectively.^{5,13,14}

A pure electrostatic stabilization may be easily achieved for both Si_3N_4 and ZrO_2 dispersions by simply adjusting the pH, e.g. to the highly alkaline range where the particles have a strong negative surface charge.^{2,4,5} However, due to the expanded effective radius of the particles the slips have a much greater apparent solids volume fraction and may thus show a too high viscosity or yield stress for slip casting purposes.³⁻⁵ In order to overcome this obstacle a wide range of dispersants (polyelectrolytes) have been successfully used.¹⁵ Alternatively indifferent ions may be used to adjust the viscosity of the slips.⁵ Less attention has, on the other hand, been paid to the mechanism by which the dispersants enhance the fluidity of the slip.

In previous papers we have investigated the influence of pH³⁻⁵ and lignosulphonate³ on the flow properties of single and mixed powder systems. However, the influence of the pH dependent leaching of the ions from the surface of the powder on the properties of the suspensions as a function of pH remained unclear. It was thus felt of importance to characterize the surface reactivity and to investigate whether the dispersant, lignosulphonate (LS) used to stabilize and fluidize single and mixed (composite) ceramic powder slips is affected by the dissolution from the surface. The standard electrophoretic mobility was engaged to probe the interactions between the particles on one hand, and between the dispersant and the particles on the other hand. The stability was related visually to the observed sediment volume and the fluidity was investigated by recording the viscosity of the slips. In concomitant investigations the influence of inorganic sintering aids, such as Y_2O_3 ¹⁻³ and Al_2O_3 ^{1,6} as well as true potential determining ions, such as Zr in ZrO_2 ^{1,5} have been reported.

2 Experimental Procedure

2.1 Raw materials

The silicon nitride powder (SN-E10) was supplied by UBE Industries, Japan and the zirconium oxide powder stabilized with 5 wt% yttrium oxide (TZ-3YS) was supplied by Tosoh Corporation, Japan.

The particle sizes were determined by X-ray sedimentation technique (Sedigraph 5000 ET, Micro-metrics Inc., USA). The average diameters d_{50} found were $0.41 \mu\text{m}$ ($d_{90} < 1.4 \mu\text{m}$) for Si_3N_4 and $0.38 \mu\text{m}$ ($d_{90} < 3.6 \mu\text{m}$) for ZrO_2 . For silicon nitride this value agrees reasonably well with the value reported by the manufacturer ($0.4 \mu\text{m}$) and found by using alternative methods ($0.48\text{--}0.5 \mu\text{m}$).^{1,2} For

zirconia the value reported by the manufacturer was considerably larger ($0.5 \mu\text{m}$). The value found with independent measurements ($0.42 \mu\text{m}$)^{1,4,5} is an intermediate between these results. Since the light scattering gave a further slightly diverging value of $0.3 \mu\text{m}$,^{4,5} the divergencies may, at least in part be explained by the alternative experimental techniques used to determine the particle size from powders of considerable polydispersity.

The specific surface areas were determined by a single point BET method (Flowsorb II 2300, Micro-metrics Inc., USA) to be $10.2 \text{ m}^2 \text{ g}^{-1}$ for the silicon nitride powder and $6.2 \text{ m}^2 \text{ g}^{-1}$ for the zirconium oxide powder. The corresponding values found in previous measurements were 10.2 and $9.7 \text{ m}^2 \text{ g}^{-1}$ ⁵ and 8.0 and $6.1\text{--}6.6 \text{ m}^2 \text{ g}^{-1}$ respectively.¹⁻³

The chemical surface composition was analyzed using ESCA (XPS) analysis.² The powders were dispersed in water and dried on molybdenum plates before analysis. The as-received Si_3N_4 powder was found to consist of Si (32.5%), N (37.3%), O (19.7%), and C (10.4%). The washed powder showed at pH = 7 the following atomic composition Si (33.9%), N (40.0%), O (20.4%), and C (5.7%).² From the peak positions it was deduced that the Si was in the form SiO_2 and SiN_x , respectively. The latter species could not, due to unresolvable peaks, be distinguished from, e.g. $\text{Si}_2\text{N}_2\text{O}$ peaks.^{7,8} According to recent FTIR studies, however, the surface has been found to consist of silanol groups and basic primary (SiNH_2), secondary (Si_2NH) and tertiary (Si_3N) amine groups.^{7,8} The ZrO_2 powder surface consisted of Zr (22.8%), O (61.3%), Y (2.3%), and C (13.6%). The carbon peak is of typical magnitude and originates from impurities of the type CO_x . All the values are given in corrected atomic percent values.

The lignosulphonate (Wanin OS) was supplied by Lignotech, Sweden. The molecular weight was (84%) in the range of less than $20\,000 \text{ g mol}^{-1}$. Assuming a $\langle M_w \rangle = 10\,000 \text{ g mol}^{-1}$ and a density of 1 g cm^{-3} the diameter of the roughly spherical polymer particle is 3 nm.

The water used in the electrophoretic measurements was distilled and purified with a Milli Q system to obtain a minimum resistivity of $8 \text{ M}\Omega \text{ cm}^{-1}$. In all experiments the water was double distilled.

The HCl and NaOH (Titrisol) and NaCl (pro analysi) were all supplied by Merck AG, Germany, and used as received.

2.2 Surface reactivity

The buffer capacity of the powder was investigated by recording the change of the pH of a dispersion consisting of 5 vol% powder in deionized water. After the initial adjustment of the pH of the

dispersion with HCl and NaOH the final reading was taken after four weeks of standing.

The solubility of ions was investigated from a 20 wt% dispersion after conditioning at a constant pH (HCl–NaOH) for 1 day and 1 week, respectively. The supernatant was investigated with a Spectra Span IIIB Plasma Emission Spectrometer while the powder was investigated with a Perkin–Elmer PHI 5400 ESCA (XPS) spectrometer. In the latter experiment, the washed powder was dried on molybdenum plates before analysis. All the ESCA values are given in corrected atomic percent values.^{2,4}

2.3 Electrophoretic mobility

The electrophoretic mobility (EM) measurements were measured at 25°C as a function of pH and the concentration of the dispersant. The solids content was kept low (ca 0.03 wt%) to comply with the instrumental constraints. The instrument used was the Zetasizer IIc of Malvern Instruments, UK. The pH was adjusted with HCl and NaOH. The ionic strength was kept constant at 0.001 mol dm³ NaCl. The powder suspensions were conditioned over a 2 and 18 h period, respectively. The LS addition was made to the suspension conditioned for 18 h.

Due to the extensive leaching found from all powders, the only appropriate value is the electrophoretic mobility. Thence the electrophoretic mobility was not recalculated to zeta potentials.

2.4 Stability experiments

The stability was determined by visual inspection of the sediment volume at 25°C for 5 vol% powders mixed in 25 ml of deionised water. The suspensions were ultrasonicated for 15 min and conditioned to initial pHs while stirring for at least 30 min. After pH adjustment the suspensions were poured into graded tubes. The initial sediment volume defined as the turbid part of the 25 ml sample was determined after 30 min and several readings were recorded during 4 weeks.

2.5 Viscosity measurements

The viscosity was measured on the high solid contents slips at 20°C after ultrasonication and ball milling for at least 18 h. For single powder slips the viscosity was measured as a function of the concentration of the dispersant. From these measurements the optimal dosage was evaluated and kept constant when measuring the viscosity for a mixed (composite) powder slip consisting of 68.4 wt% Si_3N_4 and 31.6 wt% ZrO_2 as a function of the solids content. The viscosity was measured with a small gap rotary viscometer (Rheomat 30 Contraves, Switzerland) at different shear rates.

3 Results and Discussion

3.1 Surface reactivity

The silicon nitride has been found to change in composition from the theoretical value in the bulk solid to a silica and silicium nitroxide enriched surface.^{7–9} At the outermost layer the composition changes to hydrolyzed silica (silanol) and primary-, secondary-, and tertiary amine groups.^{8,9} The hydrolysis of the surface increases the number of silanol groups and makes the surface acidic. In alkaline solutions (pH = 8–10) and partly upon ageing of neutral suspensions, ammonia and soluble silicates are expected to be leached out from the surface making the surface more basic due to additional exposure of silicon nitride groups.^{7–9} The highly variable surface composition of formally the same powder supplied by different manufacturers⁴ is exemplified for Si_3N_4 in Table 1. The pH dependent solubility observed is consistent with previous studies^{2,3} indicating that the OH[−] ion catalyses at room temperature the hydrolysis. These features are exposed in Fig. 1 as an increasing atomic ratio of Si over O and N over O both in the acidic and in the basic range. However, since the Si/N ratio remains roughly constant over the entire pH range it may be concluded that the hydrolysed groups are, indeed, remained unchanged in the neutral range. The slightly enhanced scatter of the measured values around the electroneutrality point is reduced upon ageing with a minimum developing around pH = 7.

The dissolution of silica is, indeed, confirmed for alkaline solutions (Fig. 2). As may be expected for pure hydrolyzed silica a considerable amount is leached out when the pH of the solution exceeds pH = 8–9. The slightly reduced Si/N ratio (Fig. 1) indicates that slightly less amine groups are leached out giving rise to an increased surface basicity. However, only a slight dissolution of silica is found in the acidic solutions where there is a low amount of OH[−] ions to catalyze the dissolution. There is thus a clear distinction between the conditions for hydrolysis and dissolution.

Table 1. The electrophoretic mobility (EM) in ($\mu\text{m s}^{-1}$)/(V cm^{-1}) and the native pH for a range of commercial Si_3N_4 powders in 0.001 mol dm^{−3} KCl solutions at 25°C

Powder	EM	Native pH	Particle size d_p/nm^{-1}
Si_3N_4 (SN-E10)	−3.2	8.2	410
Si_3N_4 (TS-7) ^a	−0.09	6.49	1266
Si_3N_4 (LC-12) ^b	1.95	5.44	364
Si_3N_4 (SN-A1) ^c	2.53	5.58	514

^a90% α -phase, Tosoh Corp.

^b>90% α -phase, ~3% β -phase, HCST Ampersint.

^c92% α -phase, Dynamit Nobel.

As previously presented^{4,5} the surface properties of yttria stabilized zirconia is to most parts determined by the dissolution of yttria in the acidic range, while some zirconia is leached out in alkaline solutions upon ageing. All the aquo, hydroxo and oxo ions formed with the free ion in solution or at the particle surface have thus pH dependent

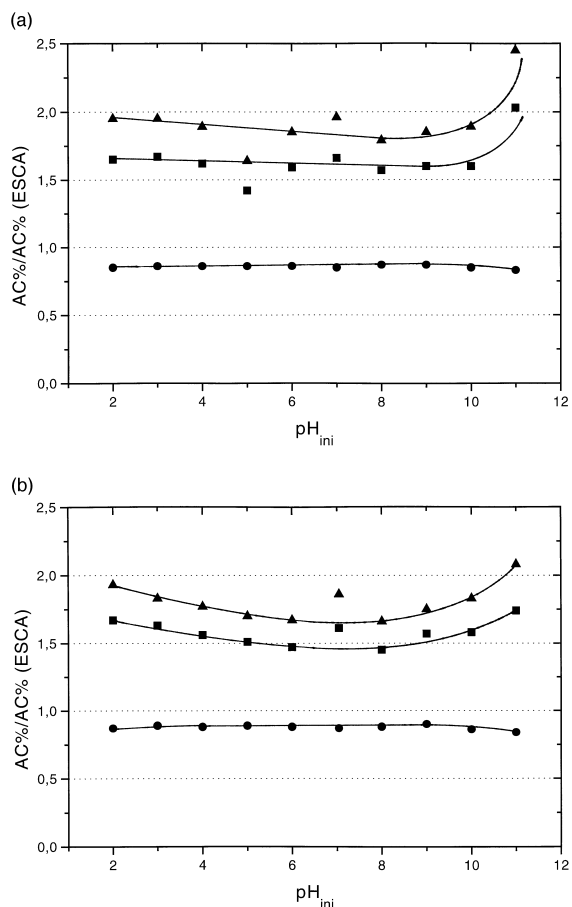


Fig. 1. The amount of constituent ions extracted from the particle surface expressed as the relative atomic ratio of Si/N (●), Si/O (■) and N/O (▲), respectively, measured with ESCA spectrometry after a 1 day (a) and 1 week (b) conditioning time at different pH.

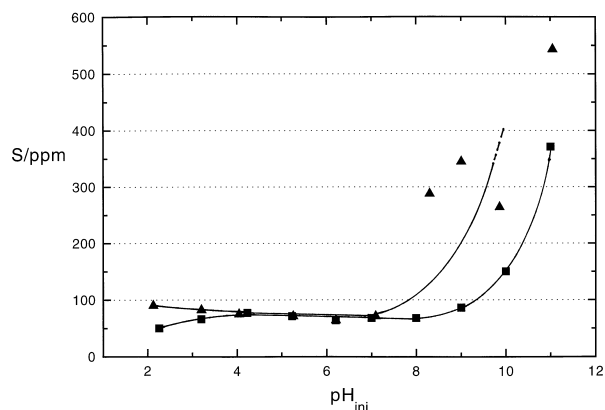


Fig. 2. The solubility of Si-ions leached into the aqueous phase measured with Plasma Emission Spectrometry after a 1 day (■) and 1 week (▲) conditioning time at different pH.

mutual affinity. The metal ion complexes formed may thence be redeposited on the particle surfaces.⁶ This provides an additional complexity when interpreting the results.

The surface reactions and the ions leached produce considerable time dependent buffering of the dispersions (Fig. 3). After 4 weeks the silicon nitride dispersions show a maximal upward shift of three pH-units at an initial pH of 4. In alkaline solutions of pH = 10 the initial pH is reduced by 1.5 pH-units. The neutrality point is found at pH \approx 8.0.

The largest buffering for zirconia dispersions is found at pH \approx 11 where a two unit reduction of the initial pH is observed. In acidic solutions the maximal increase of the final pH by 1.5 units is found at pH \approx 4. The neutrality point is found at pH \approx 6.8.

When comparing the values reported for zirconia dispersion with the previously published results measured after only two days of conditioning⁴ it is found that the neutrality point is shifted to higher pH-values. The same applies to the maximum buffer point found in alkaline dispersions, while the total buffer capacity is reduced by one pH unit. The pH of maximum buffering capacity remains

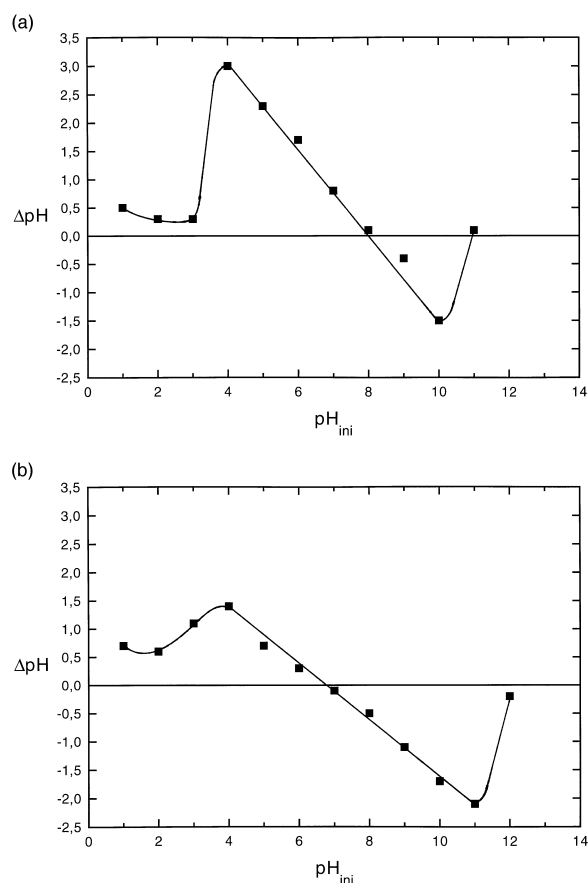


Fig. 3. The pH change of Si₃N₄ (a) and ZrO₂ (b), respectively, found after the initial pH adjustment during a 4 week period plotted against the initial pH recorded after the conditioning time.

roughly unaltered at low pH, while an enhanced residual buffer capacity is found for strongly acidic dispersions. Obviously the surface properties are time dependent due to the continuous hydrolysis and leaching of constituent metal ions (Zr and Y).

In concomitant experiments with HNO_3 and NH_3 used to adjust the pH it was found that the buffering capacity is also dependent on the acid and base pair.⁵ The strength and number of the acidic and basic sites giving rise to the pH-dependency of the surface have previously been reported by Pettersson *et al.* in cyclohexane where no ion dissociation is expected to occur.¹ The value where the strongest acid or basic groups are equal to or lower than the pK_a of the probe (indicator) molecules in cyclohexane, $H_{0,\text{max}}$ (Hammett Function) respectively, has been found to be 2 for silicon nitride and 5.5 for zirconium oxide. As shown the pH_{iep} of both the Si_3N_4 and ZrO_2 particles used become in aqueous solutions more basic upon ageing due to the dissolution of constituent ions and impurities. It is, however, obvious that the surface of the Si_3N_4 particles are predominantly covered by silanol groups⁹ and that the very acidic hydrolyzed Zr-ion species contribute decisively to the surface properties of the ZrO_2 particles.⁵ Similar results have been obtained when adsorbing aromatic probe molecules covering a large scale of Lewis acidity/basicity from cyclohexane or benzene onto Si_3N_4 particles.¹⁶

3.2 Suspension stability

The stability of the suspensions at various times was deduced from the change of the height of the sediment from 25 ml as a function of pH and the time. As shown for Si_3N_4 in Fig. 4(a) there is a considerable shift of the pH where an optimum stability is achieved. However, already in a few hours the final features for the silicon nitride dispersions evolve. Up to $\text{pH} = 3$ the dispersion is practically stable with only a small sediment. From $\text{pH} = 3$ on, in the range of maximum buffer effect [Fig. 3(a)], an increased sedimentation is induced being at maximum after ageing in the $\text{pH} = 6\text{--}8$ range. At $\text{pH} \approx 9$ the stability of the Si_3N_4 -dispersion seems to be restored this is in accordance with the particle size measurements where the aggregation was found to be very large at $\text{pH} = 7$, but the original particle aggregates rather break up at $\text{pH} = 10\text{--}2$

For zirconia dispersions [Fig. 4(b)] the stability remains over the entire acidic range to the neutrality point of $\text{pH} = 6\text{--}8$. For strongly acidic suspensions, however, some instability is found for initially mixed dispersions. The slightly enhanced stability found upon ageing in alkaline dispersions is in accordance with previous observations^{4,5} of

restored stability in the $\text{pH} = 9\text{--}11.5$ range. The variable stability is probably related to the shift in maximum buffering behaviour discussed above. Again, the range of maximum sediment volume coincides with the pH region of maximum particle growth.^{4,5}

The use of the settling volume as a measure for the dispersion stability is, however, somewhat dubious. No detailed analysis was performed in order to establish the relative contributions of flocculated and coagulated sediments, respectively. Since these sediment fractions are expected to have considerable different densities the mass or dry volume of particles sedimented (consolidation) cannot be established. However, as shown in Fig. 4(a) and 4(b) the relative values seem to agree with the change in the other physical properties reported.

3.3 Influence of dispersant

The pH_{iep} found for Si_3N_4 particles [Fig. 5(a)] at ca 4.9 is much lower than the theoretical value of 9.3 (ref.⁹) indicating that only a small fraction of the silanol group is covering initially the surface ($H_{0,\text{max}} \approx 2$) have dissolved from the surface (Figs 1 and 2). The addition of lgnosulphonate to acidic

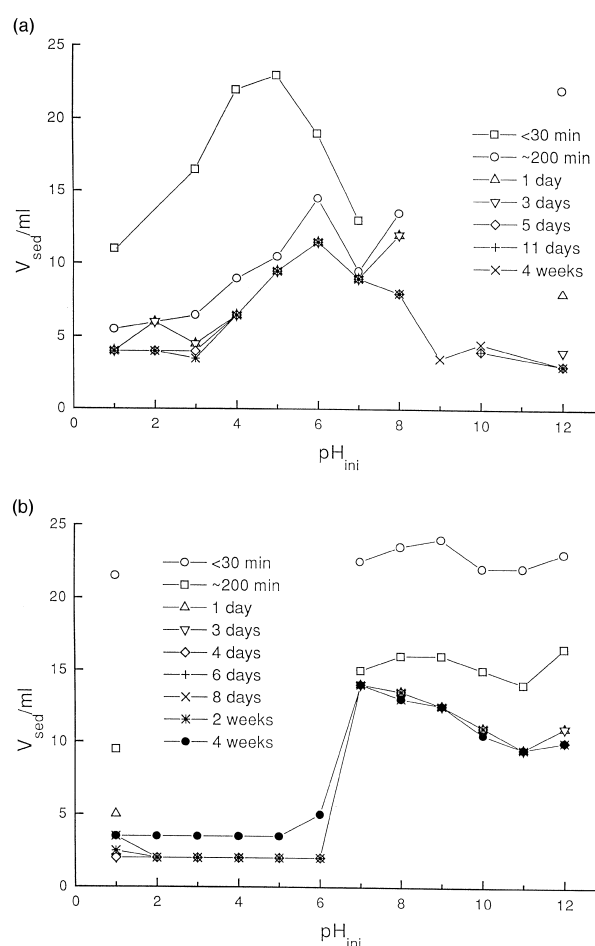


Fig. 4. The sediment volume of the silicon nitride (a) and zirconia (b) dispersions at the different initial pH.

suspensions induces, as expected, a charge neutralization and subsequent charge reversal of positively charged silicon nitride particles [Fig. 5(a)] and (b). It may be assumed that the cationic particles are characterized by their capability to attract opposite charges but also to specifically adsorb multivalent cations. The latter feature makes the excess adsorption of the LS-dispersant possible. The extensive adsorption gets less pronounced towards the neutral pH-range and is almost insignificant in the alkaline solutions. This trend is in line with the recharging of the silanol and amine groups to predominantly anionic sites^{6,7} producing a charge repulsion both between the particles and the dispersant molecules. It has been suggested that the lignosulphonate molecules remain free in the neutral-alkaline solution range.^{2,3,17} The electro-neutralization - reversal of charge due to adsorption is thus replaced with depletion stabilization (repulsion) of free and highly charged LS-particles of a ca 3 nm (= 10 000 g mol⁻¹) size.

The $\text{pH}_{\text{iep}} \approx 6.5$ indicates that the conditioning of the ZrO_2 powder has removed a considerable amount of the adsorbed ions and impurities shifting the pH_{iep} (from $\text{H}_{0,\text{max}}$ 5.5) close to the pristine

value of 7.6. Lignosulphonate is observed to adsorb strongly on the zirconia particles over the entire pH range (Fig. 6). This is expected since the surface groups are predominantly cationic in acidic and neutral dispersions. Similarly as found for the Si_3N_4 powder the LS seem to be both electrostatically attracted and specifically adsorbed onto the ZrO_2 particles. When the pH_{iep} is exceeded the charge effect is reduced. In alkaline dispersion where both the zirconia and the LS are strongly negatively charged, the LS addition has no significant influence on the electrophoretic mobility. Again it may be concluded that the highly charged LS acts as an unadsorbed ionic colloidal stabilizer. This is in line with the observations of Le Bell¹⁷ who described the stabilizing effect of well characterized LS in alkaline solutions by the (electrostatic) depletion stabilization mechanism.

Visual inspection of the settled volume was also chosen to estimate the optimal dispersant concentration for stability of the (5 vol%) dispersions. At the chosen pH of 10 where both the particles and the dispersant is highly charged, the stability values were read at different time intervals, ranging from minutes to two months. Since the reference

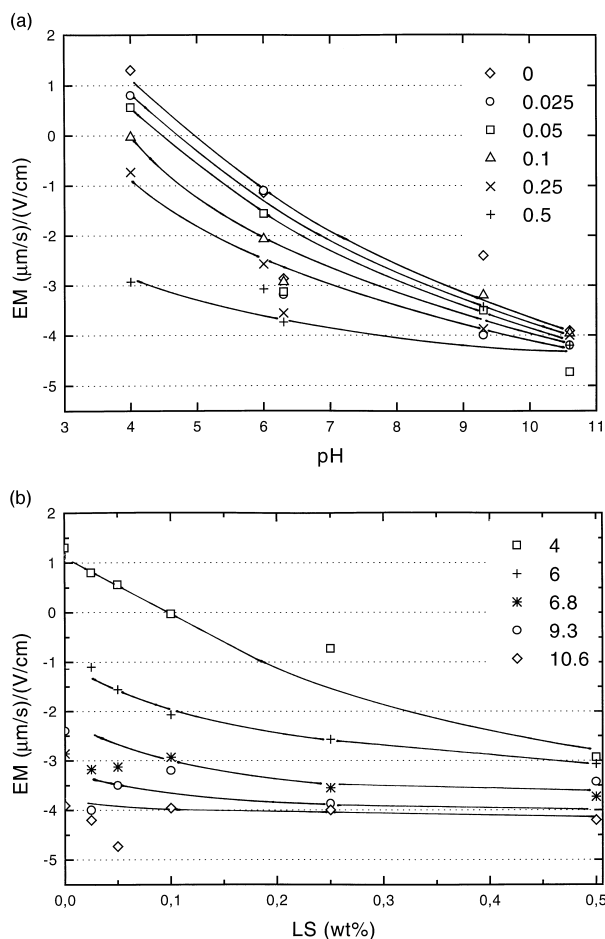


Fig. 5. Electrophoretic mobility of silicon nitride powder conditioned for 18 h in $0.001 \text{ mol dm}^{-3}$ NaCl. The different pH and increasing amount of lignosulphonate is indicated.

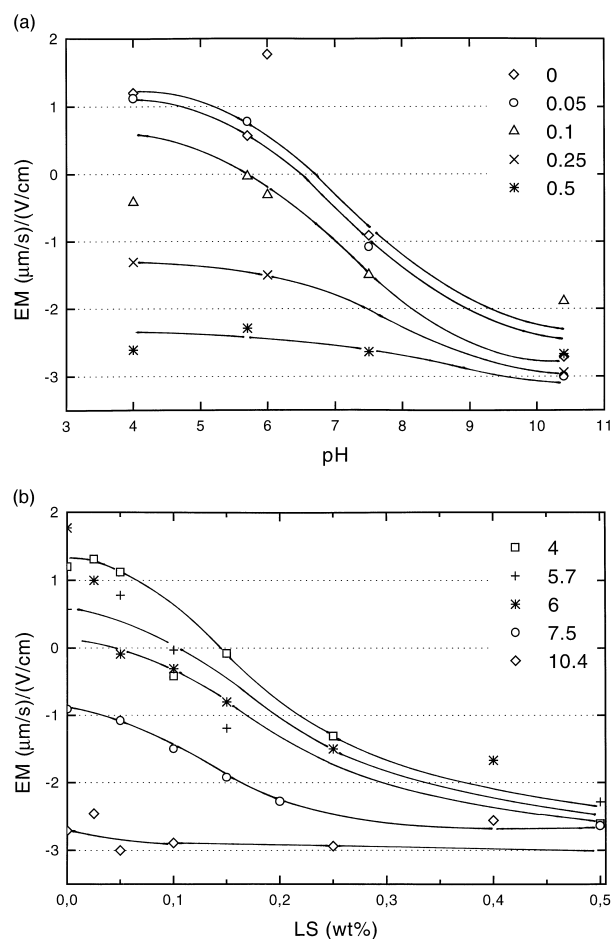


Fig. 6. Electrophoretic mobility of zirconium dioxide powder conditioned for 18 h in $0.001 \text{ mol dm}^{-3}$ NaCl. The different pH and increasing amount of lignosulphonate is indicated.

samples without dispersants were found to be relatively stable the addition of lignosulphonate did not influence the sedimentation volume extensively. Adding up to 1 wt% LS to the dispersions enhanced the stability of the Si_3N_4 powder by a negligible amount while a 30% reduced sediment

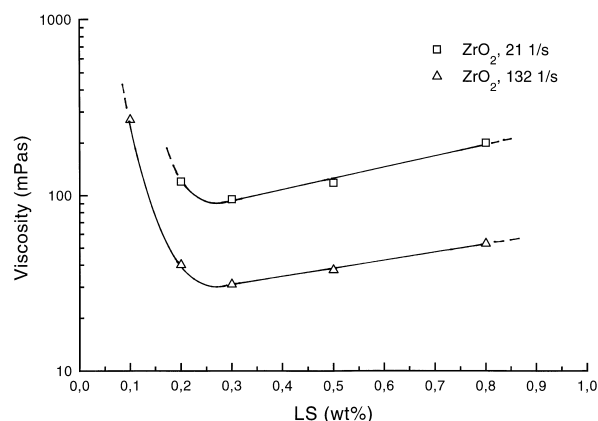


Fig. 7. Viscosity of 73.3 wt% (31.3 vol%) zirconia slip read at two shear rates of 21 and 132 s^{-1} as a function of the lignosulphonate concentration.

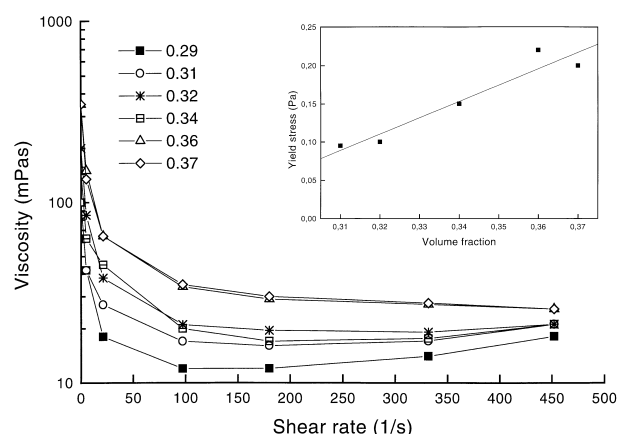


Fig. 8. Viscosity and yield stress values (insert) of 68.4 wt% silicon nitride-31.6 wt% zirconia slips of various total solids content (in vol%) but constant amount (0.2 wt%) lignosulphonate as a function of the shear rate.

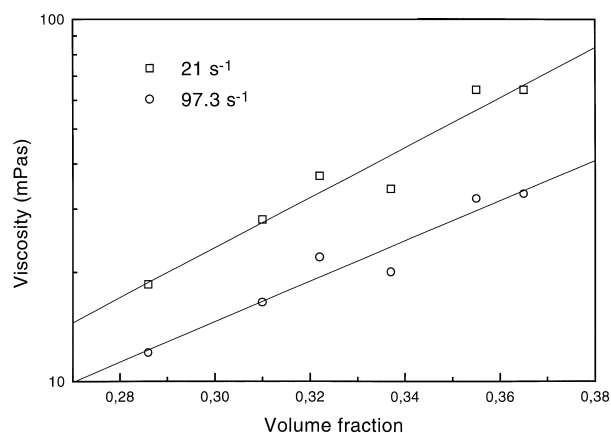


Fig. 9. Viscosity of a mixed powder containing 68.4 wt% silicon nitride and 31.6 wt% zirconia stabilized by 0.2 wt% lignosulphonate at $\text{pH} = 10$ read at two shear rates of 21 and 97.3 s^{-1} as a function of the solids content in vol%

volume was found for the ZrO_2 dispersions.¹⁸ As indicated by the measured surface charges the stability relies mainly on the interparticular repulsion with less contribution provided by the much smaller LS. Some enhanced interaction may, however, be discerned for the zirconia suspension at higher LS concentrations.

The viscosity measurements showed that in order to obtain slips with sufficient fluidity, at the desired solids content, an addition of a dispersing agent was necessary. In all cases the viscosity was too high to be measured in the absence of the dispersing agents. However, upon addition of a sufficient amount of LS the viscosity of both the silicon nitride³ and the zirconia (Fig. 7) slips were reduced to very acceptable levels. The presence of the dispersant is thus shown to be crucial when the slip is under flow. The dispersant does, however, not disturb the drainage as indicated by the sediment volume which is independent of the concentration of the dispersant.¹⁸ Since LS is strongly crosslinked its shape remains spherical under shear being an ideal lubricating compound in the flowing concentrated particles matrix. The minimum viscosity was reached when ca 0.3 wt% of LS is added to the ZrO_2 dispersion (Fig. 7). For silicon nitride a minimum viscosity was obtained for ca 0.2–0.5 wt% LS.^{3,19} The amount required increases with the increasing surface area of the powder^{3,20} but is relatively independent of the solids content.³ The optimum LS concentration is self evidently dependent on the charge of the particles, which determines their effective radius.⁵

The 0.2 wt% dosage of LS was chosen to stabilize mixed (composite) dispersions of a constant relative composition of 68.6 wt% of Si_3N_4 and 31.4 wt% of ZrO_2 , but with an increasing solids content of the mixed powder. As shown in Fig. 8 the powder dispersions were plastic and showed a typical shear thinning when the shear rate was increased. The yield stress shown in the insert to the Fig. 8 increases linearly with the solids content. Similarly the viscosity read at two relatively low shear rates are linearly increasing with the solids content (Fig. 9). The total observed viscosity seems to be the sum of the approximative relative vol% contributions of each powder. This is probably due to the coinciding optimal conditions found for both powders in the alkaline range.

4 Conclusions

1. Surface properties of ceramic powders are strongly dependent on the manufacturing of the powders and on the crystalline state of the granules. Prolonged conditioning (washing) of

the powders removes some of the differences found.

2. The surface charge provides a favourable tool to choose optimal conditions for colloidal slip casting. Together with the neutrality point and the acid/base properties determined for the powder it may also give an insight into the mechanism of the dispersant action at optimal processing conditions.
3. Settling experiments can be used to investigate the stability (sediment volume of the dispersions). It also gives an indication of the storability of the dispersion prior to slip casting.
4. Viscosity and the yield stress value are important parameters in order to define a successful slip for casting of complex ceramic bodies. The yield stress provides information on the suitability of the dispersion for pressureless (gravitational) slip casting.
5. The final assessment of the optimal properties of the slip must, however, be made after the use of the slip to produce fractureless complex ceramic bodies that after consolidation exhibit superior strength and toughness properties.

Acknowledgements

The work has been supported by the Neste Ltd. Foundation and the Academy of Finland (MATRA).

References

1. Pettersson, A. B. A., Byman-Fagerholm, H. and Rosenholm, J. B., Surface acid-base and electrokinetic properties of Si_3N_4 , ZrO_2 , Al_2O_3 , Y_2O_3 and TiO_2 Powders, In *Proceedings of the fourth Int. Ceramic Materials & Components for Engines*. ed. R. Carlsson, T. Johansson, and L. Kahlman. Elsevier Appl. Publ., Essex, UK, 1992, pp. 260–268.
2. Fagerholm, H., Johansson, L.-S. and Rosenholm, J. B., A surface study on adsorption of lignosulphonate on mixed Si_3N_4 - Y_2O_3 powder dispersions. *J. Eur. Cer. Soc.*, 1994, **14**, 403–409.
3. Fagerholm, H. M., Johansson, L.-S., Graeffe, M. and Rosenholm, J. B., A surface study on adsorption of lignosulphonate on mixed Si_3N_4 - Y_2O_3 powder dispersions, Part 2. *J. Eur. Cer. Soc.*, 1996, **16**, 671–678.
4. Rosenholm, J. B., Manelius, F., Fagerholm, H., Grönroos L. and Byman-Fagerholm, H., Surface and bulk properties of yttrium stabilized ZrO_2 powders in dispersions. *Progr. Colloid & Polymer Sci.*, 1994, **97**, 51–58.
5. Rosenholm, J. B., Manelius, F., Strandén, J., Kosmulski, M., Fagerholm, H. M., Byman-Fagerholm, H. and Pettersson, A. B. A., *Colloidal processing related to the properties of the ceramic particles and the sintered ceramic body*. The Institute of Materials Press (UK), in press.
6. Byman-Fagerholm, H., Lidén, E., Carlsson, R. and Rosenholm, J. B., Slip casting and pressureless sintering of Si_3N_4 - ZrO_2 composites. In *Euro-Ceramics II*, Vol. 2. *Structural Ceramics and Composites*, Deutsche Keramische Gesellschaft e.V., Köln, Germany, 1993, pp. 1511–1515
7. Bergström, L. and Pugh, R. J., Interfacial characterization of silicon nitride powders. *J. Am. Cer. Soc.*, 1989, **72**, 103–109.
8. Bergström, L. and Bostedt, E., Surface chemistry of silicon nitride powders: electrokinetic behaviour and ESCA studies. *Colloids and Surfaces*, 1990, **49**, 183–197.
9. Nitzche, R., Friedrich, H., Boden, G. and Herel, W., Electrokinetic surface investigations — an important technique for ceramic powder processing. In *Advances in Measurement and Control of Colloidal Processes*. ed. R. A. Williams, and N. C. de Jaeger, Butterworth-Heinemann Ltd, Oxford, 1991, pp. 280–921.
10. Larson I., Drummond, C. J., Chan, D. Y. and Grieser, F., Direct force measurements between TiO_2 surfaces. *J. Am. Chem. Soc.*, 1993, **115**, 11885–11890.
11. Horn, R. G., Surface forces and their action in ceramic materials. *J. Am. Ceram. Soc.*, 1990, **73**, 1117–1135.
12. Kobayashi, Y., and Hachisu, S. Kirkwood–Alder transition in monodisperse latexes, II. Aqueous latexes of high electrolyte concentration. *J. Colloid Interface Sci.*, 1974, **46**, 470–476.
13. Kosmulski, M. and Rosenholm J. B., Electroacoustic study of adsorption of ions on anatase and zirconia from very concentrated electrolytes. *J. Am. Cer. Soc.*, 1996, **100**, 11681–11687.
14. Fuesternau, D. W., Manmohan, D. and Raghavan, S., The adsorption of alkaline earth metal ions at the rutile/aqueous solution interphase. In *Adsorption from Aqueous Solutions*, Vol. II, ed. P. H. Tewari. Plenum Press, New York, 1981, p. 93.
15. Persson, M., Slip casting and pressing of ceramics based on colloidal processing techniques. PhD thesis, Chalmers Tekniska Högskola, Göteborg, Sweden, 1989.
16. Bergström, L., Surface chemistry of silicon nitride powders; adsorption from non-aqueous solutions. *Colloids and Surfaces*, 1994, **69**, 53–64.
17. Le Bell, J. C., The influence of lignosulphonate on the colloidal stability of particulate dispersions. PhD thesis, Åbo Akademi University, Åbo (Turku), Finland, 1983.
18. Byman-Fagerholm, H., Chemical modification of the surface properties of ceramic powders. The properties of ceramic slips and ceramic materials. Lic. Tech. Thesis, Åbo Akademi University, Åbo (Turku) Finland, 1996.
19. Rabinovich, E. M., Leitner, Sh. and Goldenberg, A., Slip casting of silicon nitride for pressureless sintering. *J. Mater. Sci.*, 1982, **17**, 323–328.
20. Hartman, W. J. A. M., van Dijien, F. K., Metselaar, R. and Siskens C. A. M., Slip casting parameters for commercial Si_3N_4 powders. *Science of Ceramics*, 1986, **13**, C1–7893.