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Effect of impurities on dispersion properties of alpha-alumina powder

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Abstract

Ceramic powders frequently have traces of different ions remaining from powder manufacturing. To understand how much the impurities will change the dispersion behaviour the powders were characterised very carefully. This study was focused on the surface composition and the dispersion behaviour of two α-Al_2O_3 powders from different manufacturing processes in aqueous suspensions at various pH. Several techniques have been used to determine the degree of dispersion (dispersion stability). More attention has been paid to moderate particle concentrations where the dissolved impurities play a decisive role. The variation in surface composition between the powders led to differences in initial dispersion pH and in the magnitude and sign of the initial mobility (zeta potential) of the dispersion. Both observations show the importance of examining ceramic powder dispersions near the concentrations that are used to process the material, e.g., slip casting or dip-coating.

Keywords: A. Suspensions; B. Impurities; B. Surfaces; D. Al_2O_3

1. Introduction

In the colloidal processing of high performance ceramic oxides, knowledge of the interfacial properties is of crucial importance. Most commercial oxides contain traces of water-soluble impurities that may shift the isoelectric point (iep). Moreover, the surface composition changes upon ageing. In the dilute suspensions analysed with classical electrophoresis most ionic species dissolve in water and at moderate pH only a fraction of these ions re-adsorb. The ion extraction thus causes only a small shift of the iep. In the concentrated suspensions analysed with electroacoustic methods (solid to liquid weight ratio extends typically up to 0.4) most impurities are adsorbed on the oxide surface causing a substantial shift of the iep [1].

Generally, a much more pronounced shift of the iep due to impurities is expected in concentrated systems than in dilute systems. Adsorbed impurities interfere with surface-charging and influence the wetting and therefore their presence has an indirect effect on electrostatic and capillary forces [2]. These forces are governing factors for slip behaviour and layer build-up while processing concentrated colloidal suspensions [3,4]. The impurities may also cause harm during sintering. They may affect the sintering mechanisms by changing the diffusion coefficient of the liquid phase formed on grain boundaries. Local concentrations of cations, like Si or Ca, may form a glassy phase in grain boundaries and enhance the grain growth and densification during pressureless sintering [5]. Glassy phases influence electrical, mechanical and corrosion properties of the final ceramic body.

The powder surfaces were investigated with ESCA (electron spectroscopy for chemical analysis) and compared to the bulk composition obtained with XRFS (X-ray fluorescence spectroscopy). Particle size measurements and acoustophoretic (dynamic) mobility measurements were made to estimate dispersion stability of moderately concentrated dispersions. Potentiometric titration was used to determine the surface charge of the particles. Usually potentiometric titrations of oxide powders have been made on cleaned surfaces, i.e., the

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surface impurities are washed before their aqueous interactions are studied. This approach inherently alters the surface characteristics of the powder being examined. In this investigation the aim was to determine to what extent the as-received powder surface chemistry affects the properties of aqueous dispersions.

Long-term colloidal stability is desired to achieve castable slips less sensitive to ageing. The colloidal stability investigated in this paper is defined as the stability against sedimentation. Moreover, the slips should be castable at neutral pH to avoid corrosion problems.

2. Experimental procedure

2.1. Materials

The ceramics used in this study were of sub-micron size α-Al_2O_3 powder. Baikowski Chimie, France, supplied Baikalox CR6. According to the manufacturer the specific surface area is 5–7 m^2/g and the ultimate particle size is 0.25 μm (mean agglomerate size 0.55 μm). Aluminium Chemicals, USA, supplied ALCOA A-16SG. According to the manufacturer the specific surface area is 8–10 m^2/g and the particle size is 0.4–0.5 μm. Both powders were used without further purification.

The water used was doubly distilled and purified with a Milli-Q system to obtain a minimum resistivity of 18 MΩ/cm. The pH was adjusted with standardised analytical-grade HCl and NaOH solutions (0.1 and 1.0 mol/dm^3) (Titrisol, Merck). Analytical-grade NaCl and KCl by Merck were used to adjust the ionic strength.

2.2. Sample preparation

The powder was mixed with the chosen solution and ultrasonicated for 2 min to break the agglomerates. The pH was controlled and adjusted during conditioning by frequent additions of acid or base until the pH was stable. Prior to the measurements the pH was readjusted to the respective correct pH value. The concentration of the slurry was 5 vol% in most of the experiments. In potentiometric titrations and AFM experiments more dilute concentrations, 1 vol.% and 4 wt.%, respectively, were used. The slurry was allowed to equilibrate for 24 h before the measurements under stirring.

2.3. Methods

2.3.1. Surface and bulk analysis

A Perkin-Elmer Small Spot PHI 5400 ESCA system with unmonochromatized MgK_α radiation was used in all measurements. The sample area analysed was a spot of ~1 mm in diameter. The base pressure in the spectrometer was typically 1.7×10^{-7} Pa and the pressure during the measurement was typically 7×10^{-7} Pa.

A survey spectrum of 1–1100 eV was recorded for each sample, using 0.5 eV step and 89.5 eV analyser energy together with a utility resolution spectrum (0.1 eV step and 37.5 eV analyser energy) for O1s, Al2p, Na1s, Si2p, Mg2p and C1s regions. The surface atomic composition was measured from as-received powders, and after sputtering with Ar-ions for 2 min. Sputtering was performed in order to leach the impurities adsorbed from the air.

The bulk composition of the two powders was analysed by a Philips PW 1400 XRFS (X-ray fluorescence spectrometer).

2.3.2. Particle size and shape

Transmission Electron Microscope (TEM, Jeol 2010, Japan) and Atomic Force Microscopy (AFM, Nanoscope III, Digital Instruments, USA) were used to evaluate particle size and shape of dry powder. Samples for TEM studies were prepared by placing alumina powder on carbon coated grid and analysed with 200 kV. For AFM imaging 4 wt.% slurries were dispersed and stabilised by pH adjustment. Powder was dried on a mica plate and scanned in tapping mode.

2.3.3. Potentiometric titration

Matec ESA-8000 device was used for potentiometric titrations. The volume fraction was 1 vol.%. Samples were prepared by adding 250 ml of three different concentrations (10^{-3}, 10^{-2} and 10^{-1} mol dm^{-3}, respectively) of NaCl-electrolyte to a pre-weighed amount of powder. This addition resulted in a suspension containing about 60 m^2 powder. The suspensions were dispersed with an ultrasonic device for 2 min and then allowed to equilibrate for 1 h in a sealed container in normal atmosphere under stirring. Pure electrolyte solutions were used as blanks. The pH of dispersion was raised to 10 with 1.0 mol dm^{-3} NaOH and titrated down to 3 with 1.0 mol dm^{-3} HCl. The relative surface charge density was calculated from the consumption of acid and base recorded for dispersions and blank solutions, respectively.

The surface charge as a function of pH was determined from the net adsorption densities Γ_i/mol cm^{-2}) by

$$\begin{aligned}\sigma_0 &= F(\Gamma_{H+} - \Gamma_{OH-}) \\ &= F/S\left[(n_{H+} - n_{OH-}) - \left(n^b_{H+} - n^b_{OH-}\right)\right]\end{aligned}$$

where n_{H+} and n_{OH-} are the total number of moles H^+ and OH^- added to the suspension, n^b_{H+} and n^b_{OH-} are the number of moles added to the blank to give the same pH, S is the surface area and F is the Faraday constant.

2.3.4. Zetapotential and particle size

More concentrated slurries were measured by the AcoustoSizer (Matec Applied Sciences, USA), which allowed us to measure the particle size and charge simultaneously up to moderate particle loadings (20 wt.% ~ 5 vol.%). The net charge of the dispersion is given as Smoluchowski zetapotential. For this work the instrument was calibrated using a monodisperse silica suspension of 0.3 μm diameter particles (PST3, Nissan Chemical Industries, Japan). Background correction of the electroacoustic signal was tested and the corrected zetapotential values differed only by a fraction of 1 mV for the electrolyte concentrations used. More extensive calibration procedure [6,7] was not required for the relatively low conductivities used in this study. The acoustophoretic titrations were started from an initial pH close to isoelectric points of the dispersions. This leads to hysteresis in particle size measurements and a more reliable behaviour is reached when the dispersion is first titrated to a pH where an electrostatic stabilisation is expected to occur. Acid and base titrations gave essentially the same zetapotential values without hysteresis.

2.3.5. Sedimentation volume and ΔpH

The degree of dispersion stability in the ceramic slurries was determined by visual inspection of sedimentation volume. If the particles are well dispersed in the solution (highly stable), they settle separately, forming a dense, low-volume compact. If the particles are not well dispersed (low stability), they settle in clusters leading to lower packing density and a larger sedimentation volume [8].

The sedimentation behaviour was followed visually at 25 °C for 5 vol.% powders mixed in deionized water with various pH. The suspensions were processed in an ultrasonic bath for 15 minutes to break hard agglomerates. Under magnetic stirring (30 min) the initial pH was adjusted. After pH adjustment, 25 ml of each suspension were poured into graded cylinders and the particles were allowed to settle. The sediment volumes were recorded after 4 weeks. The influence of leached ions on pH was checked with parallel samples. The buffer capacity of the powder was investigated by recording the change of the pH of dispersion consisting of 5 vol.% powder in deionized water.

3. Results and discussion

3.1. ESCA results on surface composition

ESCA results of as-received and sputtered powders are summarised in Table 1. For comparison the bulk results from XRFS are included. The impurities are clearly emphasised in ESCA, where the data are collected within the first few nanometers from the surface.

Table 1
Properties of α-alumina powders

	CR6		A-16SG	
	Water slurry	Sputtered	Water slurry	Sputtered
ESCA results in AC%				
Al 2p	32.6	35.98	29.1	32.59
O1s	55.73	60.70	53.8	60.23
Na1s	0.75	0.40	5.46	2.17
Si 2p	0.85	0.74	1.99	1.01
C1s	9.71	2.17	7.89	0.71
Mg 2p	0.36	–	0.92	0.29
XRFS results in %				
Al_2O_3	99.84	99.57		
Na_2O	0.022	0.082		
SiO_2	0.000	0.122		
Fe	0.007	0.017		
CaO	0.003	0.023		
MgO	0.000	0.000		
Cl	0.027	0.009		
K_2O	0.005	0.003		
Ti	–	0.001		

The differences between as-received and sputtered samples indicate that there is a considerable amount of impurities that may leach from the powder surfaces. Sputtering may not quite correspond with the amount leaching in aqueous solutions but gives an idea of the possible ions that can cause ion exchange on the powder surface in aqueous dispersion. However, out of the components found it seems that only Al and to a lesser degree Si and Na may contribute to the surface phenomena observed. The amount of Mg on the surface is negligible.

3.2. Particle size and morphology

A TEM micrograph (Fig. 1a) of CR6 powder seems to consist of agglomerates of finer primary particles, while A-16SG powder (Fig. 1b) consists of both small and large particles. The shape of CR6 particles is smoother than that of A-16SG where particles are irregular in shape with sharp corners as a result of grinding during the manufacturing step. The same can be noticed from AFM images (Fig. 2a and b). The dispersions for AFM imaging were stabilised electrostatically, i.e., by pH control but he samples had to be dried before the measurement. Drying will thence cause aggregation of the particles. According to acoustophoretic sizing the CR6 powder seems to have a slightly broader particle size distribution than that of A-16SG. The present software calculates only the average particle size assuming a unimodal lognormal distribution and the real particle size distribution can not be obtained. Moreover, the acoustophoretic measurements give only floc size and

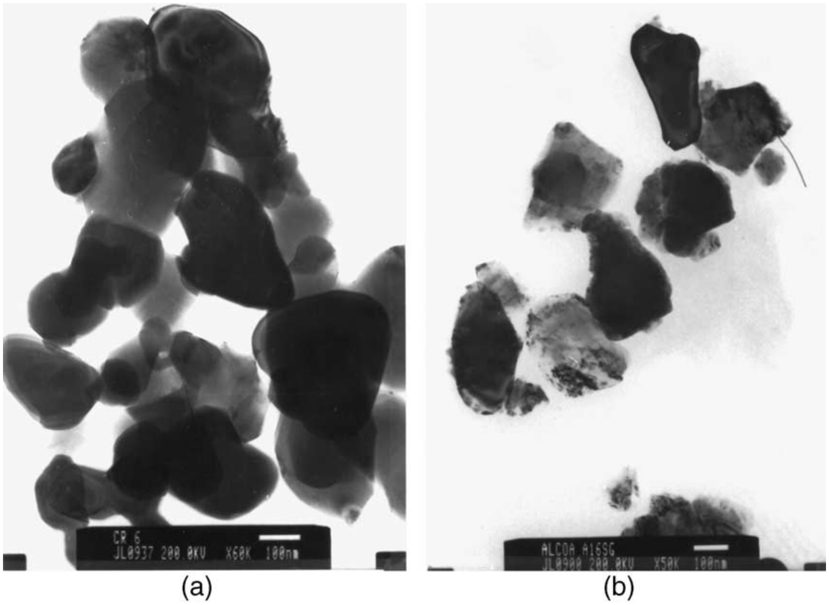

Fig. 1. TEM micrographs of as-received powders. CR6 (a), A-16SG (b).

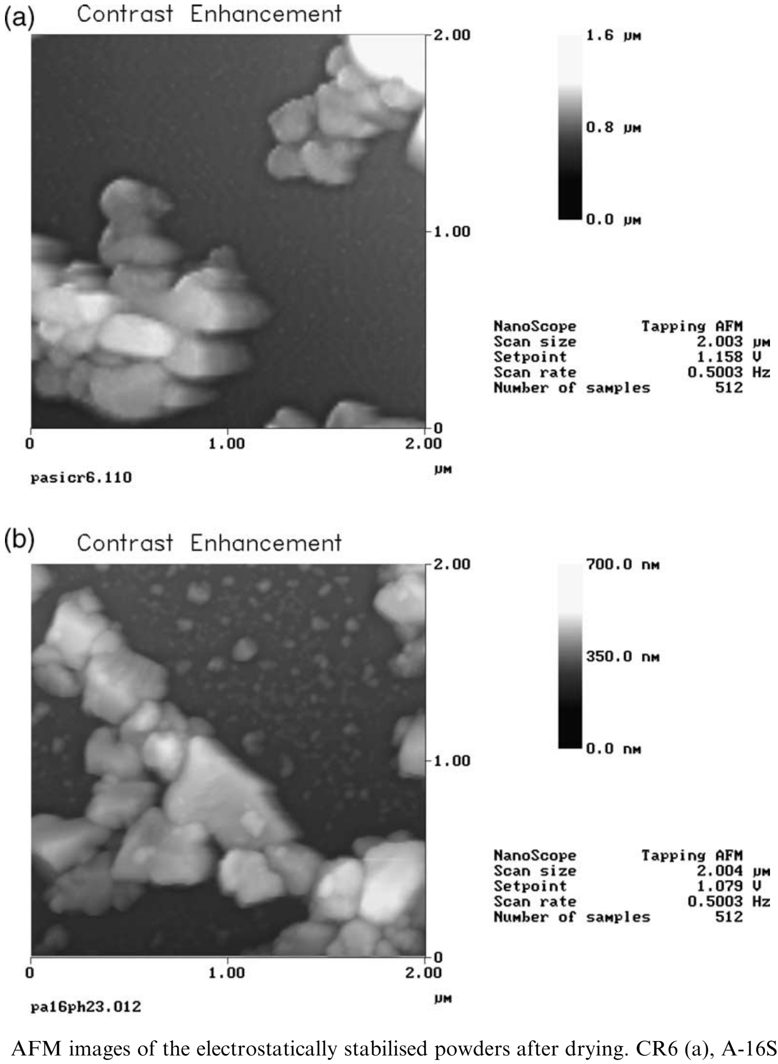

Fig. 2. AFM images of the electrostatically stabilised powders after drying. CR6 (a), A-16SG (b).

can not distinguish between agglomerates and separate particles.

3.3. Potentiometric titration

An oxide particle obtains negative, positive, and neutral surface sites by hydroxyl reactions. In aqueous solutions the potential determining ions are H^+ and OH^- and the amount of positive and negative sites depend on the pH of the solution [9]. At pH well below the iep of alumina, the aqueous solution permits charge and proton transfer at the solid–liquid interface, resulting in an electrically positive surface on alumina, e.g., formation of $AlOH_2^+$. This is the reason why alumina particles in weakly acidic water solution exhibit a positive surface potential [10]. However, the impurities present may drastically change the formation of positive ion species. Such impurities are Na_2O and other ionizable oxides. Na_2O on the surface can release Na^+ and form a negative NaO^- to compensate $AlOH_2^+$.

The studied powders are manufactured in a different manner and influence of residual ionic species was measured with potentiometric titrations. Relative surface charges for α-aluminas in NaCl electrolyte solutions are given in Fig. 3. Differences between the two alumina powders are due to impurities or redeposited dissolved species at the surface. Within pH-range 5–8 the pH of A-16SG dispersion is buffered most and the

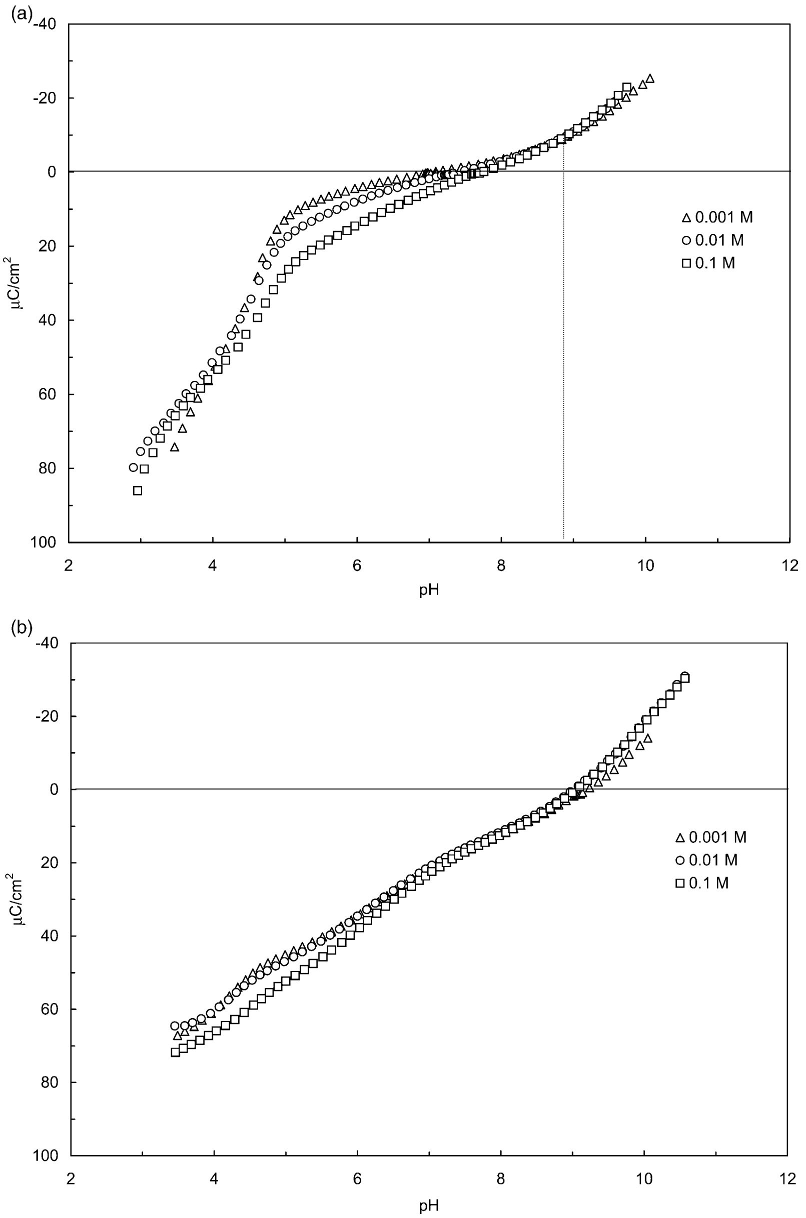

Fig. 3. Titrimetric data for CR6 (a) and A-16SG powders (b) in NaCl solutions.

consumption of acid is increased. The same buffering effect can be noticed also in ΔpH determinations. The acid-base titration will also affect the ionic strength of the dispersion. At higher electrolyte concentrations the ionic strength is clearly increased. However, the change of ionic strength is subtracted by measuring the blank solutions and considered to be negligible in the titrated 1 vol.% dispersions.

With specifically adsorbing ions, common intersection point (cip) can be observed, but this does not always correspond to the point of zero charge (pzc) [11]. The cip is a property of uncontaminated surface and it is justified to identify this point as the pzc only in the absence of specific adsorption. The physically adsorbed ions do not affect the pzc (or iep) but can change the sign of zetapotential. A chemisorbed ion shifts the pzc and the iep in opposite directions and can remain adsorbed even when the underlying surface has the same sign as the ion itself [12]. The difference between iep and pzc corresponds to the contribution of extraneous ions to charging process. Over the entire pH range, ions different than H^+ and OH^- such as solvated Al (and Si) complexes must be responsible for the additional positive or negative surface charge, respectively. However, it is unlikely that the adsorption of such ions would change with pH, pointing to irreversible adsorption of these contaminants [13].

The pzc and the iep of CR6 powder was found to be 8.8±0.1 (Figs. 3a and 4a) for both electrolytes, NaCl and NH_4Cl, respectively, indicating that the powder was rather pure. The dotted line in Fig. 3a points out the pzc value if the relative surface charge is converted to absolute values.

A clear intersection point (pzc) of the three different electrolyte concentrations could not be found for A-16SG powder (Fig. 3b). This indicates that the impurity ions must be chemically adsorbed onto surface. When the electrolyte was changed from NaCl to NH_4Cl the phenomenon was the same verifying the indifferent nature of the cations. It is unlike that these so-called indifferent electrolytes correspond to surface charging at the concentrations used. Even though the clear intersection point can not be found one may assume that the pzc is close to pH ~8 and iep round pH 8.3 (Figs. 3b and 4b).

In our experiments only pure electrolyte solutions were used as blanks and the relative surface charge density values are high. Using supernatant as blank would decrease these values but this should not affect the pzc value [14]. High values can be explained by a large number of titrable species leached from the powder surface. The odd behaviour at pH lower than 5 can be explained by Al-ions leaching from the particle surface. Extraneous ions will have a pronounced effect on ionic strength for dispersions with lower electrolyte concentration. This phenomenon is not corrected by titration of blank solutions.

3.4. Dispersion stability

The iep of aluminas can vary with the sources of alumina and the varieties of measurement techniques. Since the Bayer process alumina, A-16SG, contains a considerable amount of Na^+ and Si^{2+} species on the particle surface the iep is found to shift to somewhat lower value than the more pure CR6 powder. On the other hand, the ESCA results indicate the presence of Si^{2+} on CR6 powder, which may also shift iep. According to literature the iep of alumina is generally between 8 and 9 [15–22]. Most of these results are obtained with microelectrophoresis or streaming potential, which may be more sensitive to surface impurities, unless impurities are not completely removed. In concentrated dispersions the trace impurities are distributed over a much larger area and the effect is decreased. On the other hand, electrokinetic measurements give a net charge of the particles and despite the existence of many ionic species one may still get an iep that is close to literature values.

With electroacoustics it is possible to characterise slurries with high solid loading, corresponding to the slip or spray casting slurries used in manufacturing of microfiltration membranes. In Fig. 4 the particle sizes of two different alumina powders are correlated with zeta potential values. Due to the instrument facilities it is impossible to know whether the size distribution is mono- or bimodal or not but it will give an idea how the median particle size changes as a function of pH. However, the particle size distribution of CR6 dispersion seems to be rather stable over the whole pH-range and an increase can be seen only close to iep (pH~8±1). Unstable particle size region of A-16SG dispersion can be noticed at pH ~5. It is the same pH-region that was found to have the most effective buffering tendency.

Solid content also influences the suspension stability. At high solids content the particle repulsive forces will decrease due to double layer overlap and compression when the particle separation distance in the suspension approaches the particle double layer thickness [1,23].

The broader particle size distribution and the presence of hard agglomerates (CR6) may cause differences in the sedimentation behaviour. Thus, the governing factor of these two powders is the degree of purity. A-16SG powder contains more silica on the surface, which causes the iep to shift to lower pH value. On the other hand, A-16SG contains also Mg^{2+} ions that are found to shift the iep up to 10 [15]. A-16SG powder seems to be less stable at pH under iep due to Si^{2+}, and moreover, the Mg^{2+} ions increase the sedimentation volume at pH above the iep (Fig. 5). The solid symbols and lines in Fig. 5 indicate the sedimentation volumes of initial pH values, whereas open symbols and dotted lines indicate the real pH-values after 4 weeks conditioning. The profile of sedimentation volume remains basically the same but for A-16SG one can notice a clear shift towards higher pH values.

3.4.1. ΔpH

The main difference of the two powders can be noticed in the initial pH. The initial pH-values of the two powders give acoustophoretic mobilities of opposite sign. The initial mobility of CR6 (pH ~ 7.9) in water was negative while that of A-16SG (pH ~ 9.6) was positive. The difference in initial pH between the dispersions is most likely due to an ion exchange reaction on the surface of the alumina between sodium and hydrogen ions in the aqueous solutions (more sodium on the surface of A-16SG than on the surface of CR6).

The surface reactions and the leached ions produce a considerable time dependent shift in pH. After 4 weeks conditioning the CR6 dispersion showed a maximal upward shift of two pH-units at an initial pH 2. At slightly acidic, neutral and alkaline pH the shift is relatively small, but again, in the alkaline pH range the pH starts to decrease and is reduced at its most by 1.5 pH-units. The pH of A-16SG powder is increased more in the acidic and neutral pH-range and stays rather constant at pH 9-12. The largest shift of A-16SG dispersion was found at pH 5 where a 2.5 units increase was recorded (Fig. 6).

Some change is expected to happen at pH around 4–5 according to thermodynamic calculations [15]. The hydrated alumina surface becomes highly positively charged due to the positive ionic species that become dominating species at this pH-region. These ionic species will also change pH when leached from the surface.

The buffering effect does not quite correspond to an extended modelling of equilibrium pH at high oxide

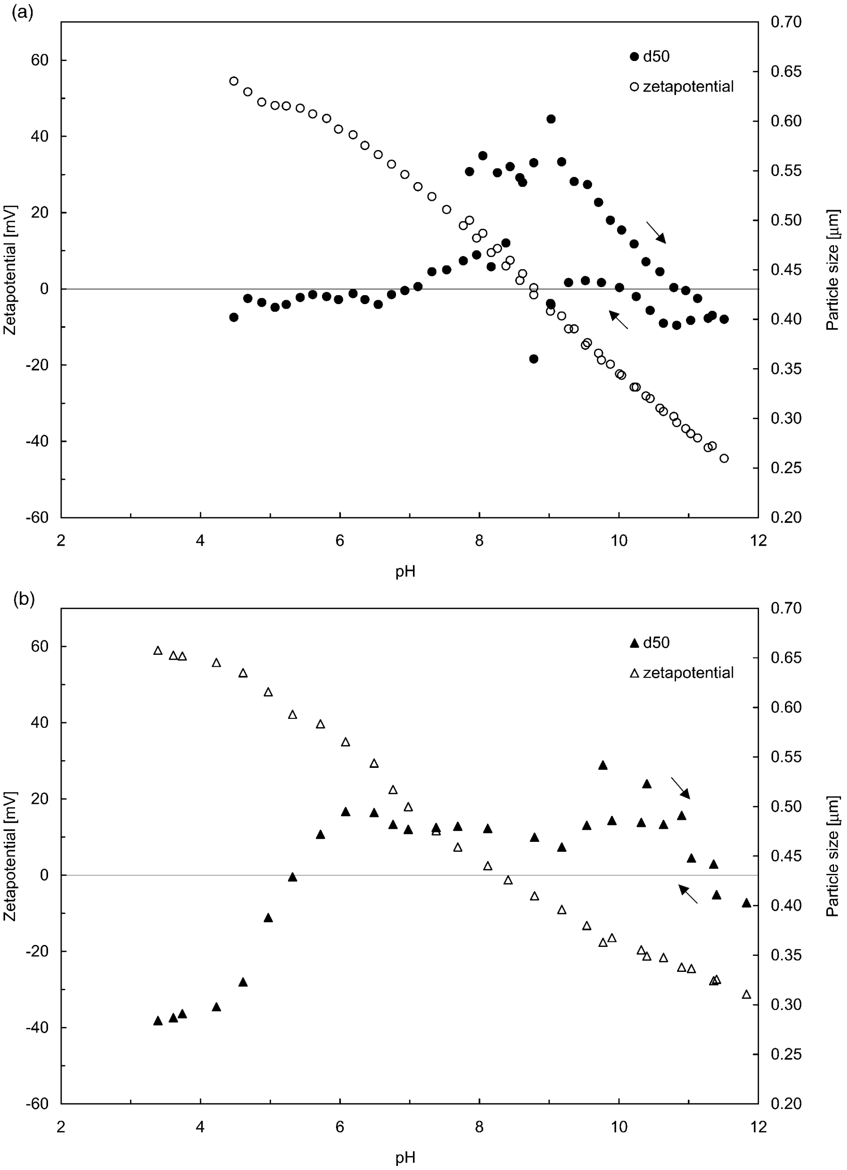

Fig. 4. Zeta potential and particle size of 20 wt.% CR6 powder (a) and A-16SG powder (b) in 10^{-3} M NaCl.

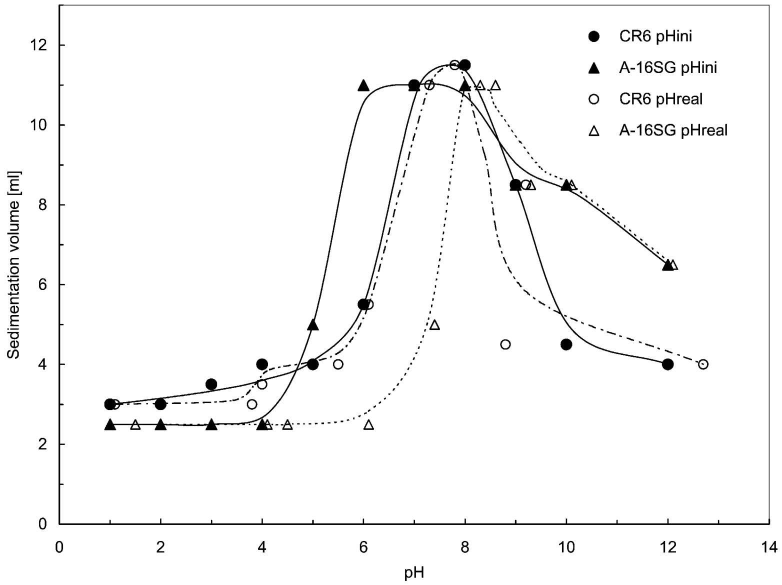

Fig. 5. Sedimentation volumes after 4 weeks ageing for the two powders as a function of initial and real pH-values.

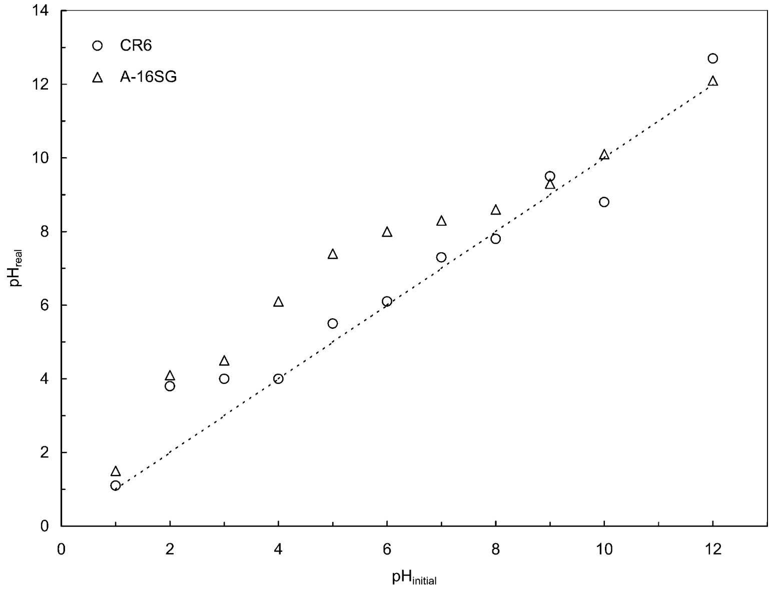

Fig. 6. ΔpH after 4 weeks conditioning.

loading [24]. One explanation is that in this study the pH of dispersion was forced to initial pH by frequent pH-adjustments. If the powders are dispersed well below iep without further pH control one will get an equilibrium pH of 7,9 and 9.6 for CR6 and A-16SG, respectively. The same kind of buffering is reported elsewhere [8,10].

4. Conclusions

The surface chemistry differences between the powders lead to differences in initial dispersion pH and in the magnitude and sign of initial acoustophoretic mobility (zetapotential) of the dispersions. The differences in initial characteristics and the reasons for different degrees of stability could be detected by combining different techniques. Powder containing more impurities is more difficult to stabilize electrostatically due to extensive buffering tendency. Also the unstable pH-region is broadened due to impurities.

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