Influence of Polyvinyl Alcohol/Zirconium Polycation Interactions on the Properties of Aqueous Alumina Suspensions

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Abstract

This paper presents and describes the interactions occurring in polyvinyl-alcohol-containing alumina suspensions containing different multivalent cations. The influence of Mg (+II), Ca (+II), Al (+III) and Zr (+IV) cations was studied systematically by means of surface potential, viscosity, sedimentation and adsorption measurement techniques. The results were compared with the results obtained for a monovalent reference (K (+I)). Whereas for Mg (+II), Ca (+II) and Al (+III) the interactions can be explained by compression of the electric double layer or formation of hydroxides, Zr (+IV) shows a unique affinity for polyvinyl alcohol. This interaction yields a significant improvement in suspension flowability and sedimentation stability. Moreover this specific interaction is independent of the solid surface. Thus the stabilizing effect of polyvinyl alcohol/Zr (+IV) can be combined with the effect of a polyacrylate dispersant.

Keywords: Processing, suspension, alumina, polyvinyl alcohol, zirconium cations

I. Introduction

Organic additives are widely used in ceramic powder processing to adjust the suspension properties and interparticle forces within the suspension as well as in spray-dried granules or finally in the precast green body. They are utilized as dispersants to prevent agglomeration of the primary particles and to lower the viscosity of the suspension, as binders to increase the strength and toughness of the green body and as lubricants to optimize the compaction behaviour during dry pressing. Combinations of multiple organic additives are generally used for achieving the desired suspension and powder properties required for each processing step [1].

Several studies investigating the interactions between organic additives and powder surfaces have been conducted recently. It could be shown that carboxyl-bearing molecules and polymers acting as dispersants have a high affinity to alumina surfaces and are associated with good particle stabilization as well as low suspension viscosity at high solid contents [2–11]. In contrast, polyethylene glycol (PEG) and polyvinyl alcohol (PVA) acting as binders and lubricants only show minor affinity to alumina surfaces and do not change suspension properties owing to a change in interparticle forces. The more complex interactions that can occur when multiple organic species are combined have received little attention in the literature, but it has been shown that the effect of the dispersant, e.g. decreased viscosity and increased surface potential, is not influenced by the presence of PEG or PVA additives. Hence the strong interactions between carboxylates and the particle surface govern the suspension properties [12–15].

Besides the intermolecular interactions of different additives, the influence of multivalent cations is an important factor in ceramic formulations. Contamination of aqueous solvents with multivalent cations can occur in several ways, the main ones being i. ionic strength of or electrolyte content in the process water [16–22], ii. impurities in technical-grade powders [23–25], iii. usage of sintering aids [26, 27], iv. dissolution of particles under the given environmental conditions [28, 29] and v. abrasion from grinding media during milling [30, 31].

According to the theory of Derjaguin, Landau, Verwey and Overbeek (DLVO), the presence of multivalent cations, e.g. Mg (+II), Ca (+II) and Al (+III), causes particle destabilization through greater compression of the electric double layer in comparison with monovalent alkali cations at a comparable ionic concentration [32–34]. Accordingly, the stability of the suspension against agglomeration and sedimentation decreases with increasing cationic charge. Moreover, multivalent cations show high affinity for complex formation with carboxyl-bearing molecules. This affinity in turn leads to a competitive reaction and therefore a reduction in the stabilizing effect of the dispersant can occur [16, 20, 35, 36]. The literature contains no information about interactions of multivalent electrolytes with other organic additives, e.g. binders or lubricants also used in ceramic wet processing.

In this context the influence of multivalent Mg (+II), Ca (+II), Al (+III) and Zr (+IV) cations and K (+I) as a monovalent reference on the interactions of the widely used binder polyvinyl alcohol (PVA) are presented and

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discussed in this paper. The systematic determination of polymer interactions as a function of cationic charge and cationic concentration was performed using surface potential, adsorption, viscosity and sedimentation measurement techniques for the purposes of gaining a global understanding of the impact of multivalent cations in PVA binder-containing aqueous alumina suspensions. Finally, the effect of the polyacrylate dispersant in the presence of Zr (+IV) cations and PVA as a binder was determined.

II. Materials and Methods

(1) Powder and chemicals

A commercial alumina powder (α-Al_2O_3, 99.99 % purity, Baikalox CR1, Baikowski, France) with a median particle size of 1.6 μm (Mastersizer 2000, Malvern Instruments, England) was used as the raw material without further treatment. The powder exhibited a specific surface area of 3.4 m^2/g (ASAP 2010, Micromeritics, USA) and a density of 4 g/cm^3 (Pentapycnometer, Quantachrome Instr., USA). The organic additives sodium polyacrylate (NaPA, 8000 g/mol, Sigma-Aldrich, Germany) and polyvinyl alcohol (PVA, 27000 g/mol, 98 mol% hydrolyzed, TER HELL, Germany) were used as the dispersant and the binder respectively. Unless otherwise indicated, the concentration of the organic additives is given in weight percent (wt%) with respect to the solid content. All reagents used to adjust the pH value (NaOH) and the different electrolytes (KNO_3, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Al(NO_3)_3$: Merck KGaA, Germany; $ZrO(NO_3)_2$: Sigma-Aldrich, Germany) were of analytical grade.

(2) Sample preparation

Aqueous suspensions (40 wt%) were prepared by addition of alumina powder to a 10^{-3} mol sodium nitrate solution ($NaNO_3$: Merck KGaA, Germany, analytical grade) under constant stirring using a laboratory dissolver stirrer (Ultra Turrax T50, IKA, Germany). In the first part of the experiments a fixed amount of 3 wt% PVA was mixed into the alumina suspension. Owing to its extreme tendency to foam, the binder was added after homogenization and the suspension was mixed for another 30 minutes by means of a magnetic stirrer. After the suspensions were prepared, different aliquots of 1 mol electrolyte stock solutions were added. In the second part of the experimental procedure an alumina suspension with a NaPA/PVA mixture was generated and the influence of different Zr (+IV) concentrations was analyzed. For this purpose up to 1 wt% NaPA was titrated into the suspension. The pH was kept constant at 9.5 using NaOH in all cases.

(3) Electroacoustic measurements

The changes in the electrophoretic mobility of the alumina particles due to the addition of different electrolytes and polymeric additives were determined using the Zetaprobe measurement system (Colloidal Dynamics, USA). Electrophoretic values were automatically converted to zeta potential values by the analyzer. Measurement conditions were kept constant at 25 °C by application of external thermostatization and continuous stirring of the undiluted suspensions [37–39].

(4) Rheological measurements

Changes in flow behaviour were monitored using the rotational and oscillating rheometer MCR 101 (Anton Paar GmbH, Austria). The flow characteristics were analyzed at 25 °C using rotational measurements with a double gap measuring system at shear rates ranging from 10 s^{-1} to 1000 s^{-1}. Before measurement was started, pre-shearing was performed in order to transmit the same rheological history to all the samples being tested. For comparison purposes the viscosity values at a shear rate of 100 s^{-1} were used.

(5) Analytical centrifugation

The analytical centrifuge LUMiSizer (LUM GmbH, Germany) was used to study the sedimentation properties. This characterization instrument allows the measurement of the intensity of transmitted light as a function of time and position over the entire sample length. The shape and progression of the transmission profiles yield information about the kinetics of the separation process and allow the evaluation of particle-particle interactions [40, 41]. To analyze the sedimentation velocity or the sediment height, the time-dependent movement of the phase boundary during the segregation process is visualized by a position-time plot at a defined transmission intensity. In our experiments the transmission intensity was fixed at 15 %.

In the first part of the experimental section the sedimentation experiments were conducted to determine the sedimentation velocity of particles as a function of concentration and type of electrolyte within a PVA-containing alumina suspension. The slope of the phase separation and the sedimentation height as a function of suspension composition were analyzed in the second part of the study. All measurements were executed at 25 °C and a relative centrifugal force of 109 g.

(6) Adsorption measurements

For the purposes of analysis of the amount of PVA adsorbed on the alumina surface as a function of cationic concentration, the chemical oxygen demand (COD) of the continuous phase before and after contact with the alumina powder was measured. Equilibrium of PVA adsorption was ensured by mixing of the suspensions for 24 h in an overhead shaker (REAX 2, Heidolph, Germany). Before the COD measurements were conducted, the suspensions were centrifuged (Sigma 4K15, Sigma Laborzentrifugen GmbH, Germany) and the supernatant was removed and transferred to a precast COD cuvette (Hach Lange GmbH, Germany). After a 15-minute heating period the amount of organic additive could be calculated via photometric measurements.

Adsorption data at a PVA concentration of 20 g/l (3 wt%) were difficult to establish because of the small difference between two increasingly large numbers (i.e. the initial and equilibrium PVA concentrations). Therefore the adsorption data were measured at a reduced PVA concentration of 3.3 g/l (0.5 wt%).

(7) Particle size measurements

To study the interactions between PVA and cations, aqueous solutions with 7.4 mol/l PVA (equal to 3 wt% PVA in a 40 wt% alumina suspension) and K (+I), Ca (+II), Mg (+II) and Al (+III) at 6.8 mol/l as well as Zr (+IV) at 1.7, 3.4 and 6.8 mol/l were prepared. After equilibration for 1 h in an overhead shaker, impurities were removed from the samples by means of filtration using an Acrodisc 25-mm syringe filter with a 0.1-μm Supor membrane (Pall GmbH Life Sciences, Germany). Measurements were conducted using a Zetasizer Nano ZS (Malvern Instruments, UK) with a measurement principle based on dynamic light scattering. Both analyses of particle and polymer size distributions are possible with this characterization technique. For each concentration two independent samples were measured in a 10-mm polystyrene square cuvette (Sarstedt, Germany). Each sample was measured six times, yielding 12 results from which the mean was determined for each concentration.

III. Results

In Fig. 1 the zeta potentials of binder-containing (3 wt% PVA) alumina suspensions are plotted against the concentration of added electrolytes. The initial surface potential of around -24 mV was comparable to the surface potential of the pure alumina suspension at the given pH value of 9.5. Already at low ionic concentrations, clear differences in the effect of added cations could be recognized. With increasing electrolyte concentration a positive trend in zeta potential progression was measured in all cases. The divalent alkaline earth metal ions yielded the strongest effect. In the presence of Ca (+II) even a change from a negative to a positive surface potential was observed. However, the addition of K (+I) and Al (+III) only caused a shift of 6 mV and 9 mV respectively in zeta potential. Obviously these cations had the least influence on the electrokinetic properties within the examined concentration range.
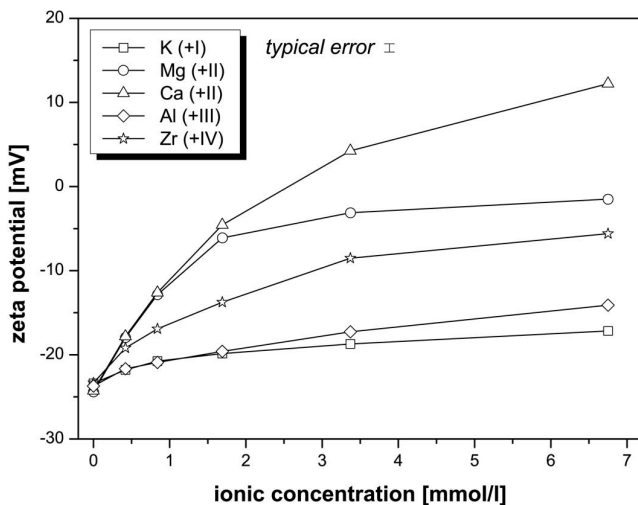

Fig. 1: Zeta potential of alumina particles as a function of concentration and type of cations.

The flow behaviour of alumina suspensions expressed by viscosity as a function of electrolyte concentration is shown in Fig. 2. Starting at an initial viscosity of around 78 mPa·s, three main tendencies were observed. In the

presence of the divalent Mg (+II) and Ca (+II) cations, the viscosity rose until a maximum was reached at an electrolyte concentration of approximately 1.7 mmol/l. Further additions resulted in a decrease in viscosity. In the case of K (+I) cations only a slight change with respect to the initial value could be seen. Thus far the flow behaviours are consistent with the data obtained from surface potential measurements. A decrease in the absolute value of zeta potential yields an increase in the suspension viscosity owing to a decrease in the interparticle repulsive forces. Hence small changes in zeta potential cause small changes in viscosity, as can be seen in Fig. 2. Ultimately the addition of Al (III) and most notably Zr (+IV) cations induced a clear decrease in suspension viscosity. Based on the decrease in absolute value of zeta potential in the presence of these cations this flow behaviour does not correlate with the electrokinetic properties. Usually a reduction in absolute value of zeta potential is connected with an increase in viscosity owing to formation of particle agglomerates. Therefore the experimental data does not match with the expected behaviour.

The results of analytical centrifugation are presented in Fig. 3. In contrast to the findings above, the sedimentation velocities showed little sensitivity to additions of K (+I), Mg (+II) and Ca (+II) cations. In the presence of Al (III) the sedimentation velocity increased until a value of around 40 μm/s was reached; an increasing Zr (IV) concentration interestingly led to a significant decrease in the sedimentation velocity. Furthermore the suspensions showed different types of sedimentation behaviour. The particles in the Zr (+IV)-containing suspension exhibited free settling, whereas all other cations caused zone settling (results are not shown) [42–44].
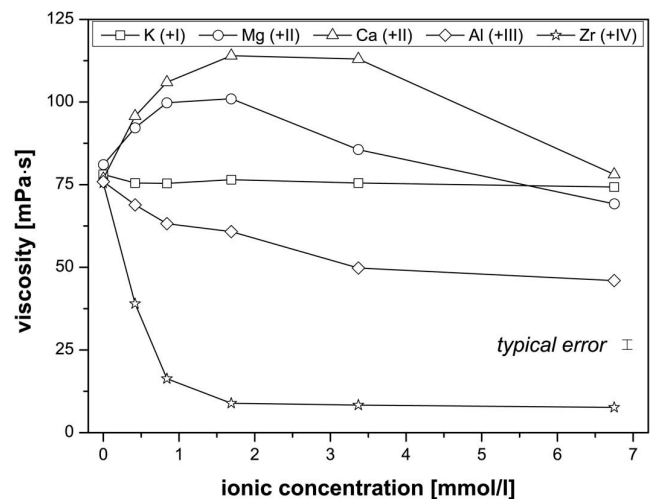

Fig. 2: Viscosity as a function of cation concentration and type for different alumina suspensions.

In the case of K (+I), the sedimentation velocity was constant at about 37 μm/s over the entire concentration range. According to Stokes' law the sedimentation velocity of comparable particles has to decrease with increasing viscosity [45]. However, despite an increase in viscosity for Mg (+II) and Ca (+II), the sedimentation velocity varied only in a small range. Hence the sedimentation velocity of K (+I)-containing suspension represents a lower limit for

zone settling governed by attractive particle forces. Otherwise the differences with respect to Al (III)-containing suspensions can be explained by a decrease in viscosity.

In this context Zr (+IV) cations not only yielded another sedimentation type. Together with the results of viscosity measurements it can be concluded that a combination of PVA binder and Zr (+IV) cations results in a decrease in suspension viscosity as well as a decrease in sedimentation velocity. Thus the interactions between cationic species and the organic additive have the same macroscopic effect as a dispersant [46].
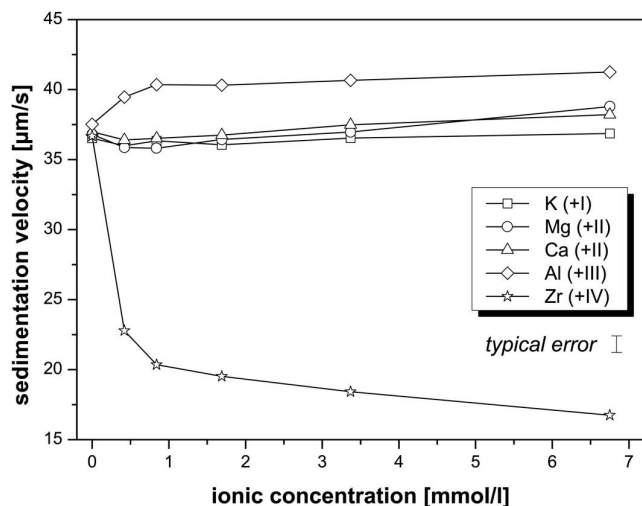

Fig. 3: Sedimentation velocities of alumina particles for different cation concentrations and types.
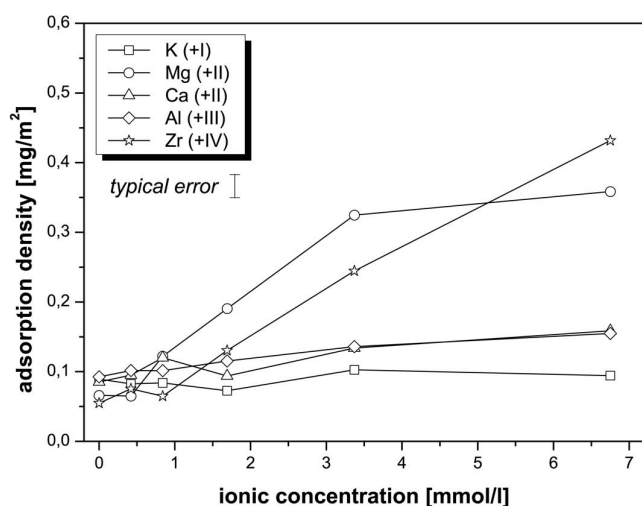

Fig. 4: Adsorption density of PVA on alumina as a function of cation concentration and type.

In Fig. 4 the adsorption density of PVA is depicted as a function of electrolyte concentration. Obviously the adsorption density on alumina is influenced by the type and concentration of multivalent cations. The presence of Mg (+II) and Zr (+IV) was found to result in the highest adsorption densities (around 0.4 mg/m²), whereas the adsorption density remained nearly constant when K (+I) cations were added. Certainly with values of around 0.1 mg/m² the adsorption density of PVA remained low, in agreement with the adsorption data reported by Hidber *et*

al. (0.08 mg/m²; PVA: 22000 g/mol, 98 % hydrolyzed) [12] and Santhiya *et al.* (0.12 mg/m²; PVA: 25000 g/mol, 88 % hydrolyzed) [13] on alumina (α-Al$_2$O$_3$) in comparable conditions. For Zr (+IV) the adsorption density rose to 0.42 mg/m² and the alteration of the macroscopic suspension properties could be explained by disproportionately high PVA adsorption. However, the adsorption density also increased in the presence of Mg (+II) to 0.37 mg/m². The results of viscosity and sedimentation measurements were accordingly influenced by interactions between PVA and Zr (+IV) suspected to occur in the continuous phase.

The influence of PVA/Zr (+IV) interactions on a stabilized suspension was investigated based on analysis of a polyacrylate dispersant (NaPA)-containing suspension using surface potential and sedimentation measurement techniques. In Fig. 5 the zeta potentials of alumina suspensions with various compositions are plotted against the amount of added NaPA. The addition of the dispersant had a significant effect on the surface charge properties (– ■ –) which demonstrated an attractive interaction between the polyacrylate molecules and the alumina surface. Even in the presence of PVA, 0.3 wt% NaPA was enough to generate a strong negative surface potential, which indicates good electrostatic stability. Hence the surface potential properties were found to be mainly governed by the polyacrylate dispersant, in agreement with the literature [12–15] However, with increasing Zr (+IV) concentration, the effect of the dispersant clearly decreased until it disappeared completely above a Zr (+IV) concentration of 3.4 mmol/l. Hence the suspension became unstable from the point of view of electrokinetics.
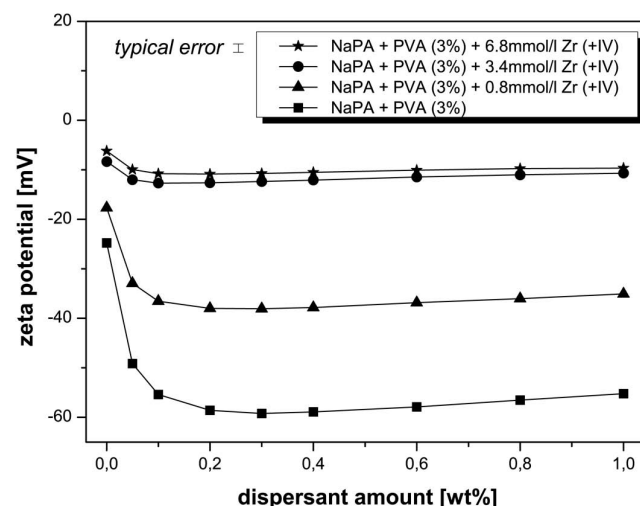

Fig. 5: Zeta potential of alumina particles as a function of dispersant amount and concentration of Zr (+IV) cations.

The sedimentation profiles are presented in Fig. 6. In general the time-dependent phase separation contains two pieces of information. For one thing it is possible to determine and compare the sedimentation velocities represented by the linear slopes of the initial parts of the curves. After completion of sedimentation, a plateau is formed because the phase boundary position remains constant over time. Therefore, based on the plateau level it is possible to obtain information about the state of particle-particle interactions and thus form conclusions about the state of

particle agglomeration. According to the literature, low-density sediments of larger volume are related to unstable suspensions containing particle agglomerates, whereas high-density sediments of lower volume indicate stable suspensions with fully deagglomerated particles [2, 6, 23].
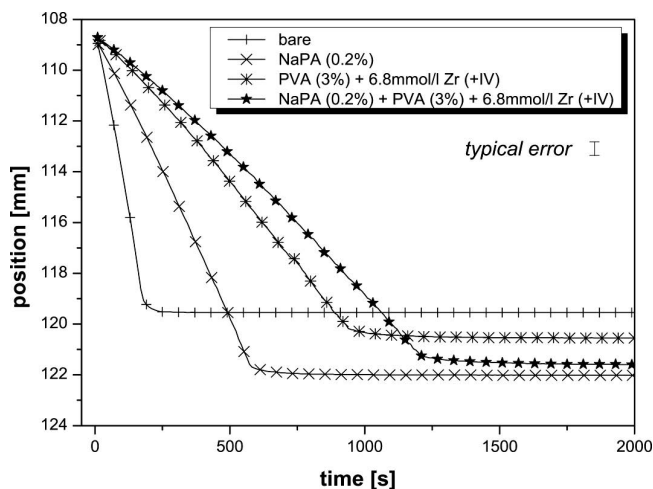

Fig. 6: Influence of suspension composition on the sedimentation properties of alumina suspensions.

In contrast to the electrokinetic stability (Fig. 5), the sedimentation stability was found to increase when the suspension contained PVA and Zr (+IV) cations, as shown in Fig. 6. For a pure suspension with no organic additives or Zr (+IV) cations the segregation was characterized by a sharp decline in slope and a high sediment level, as expected for an unstabilized suspension. With addition of dispersant the suspension became more stable, as expressed by a longer time to complete phase separation. Moreover the time for phase separation nearly doubled in the presence of the PVA binder and Zr (+IV) cations indicating a specific interaction between the organic additive and the multivalent electrolyte. Finally the combination of all three ingredients exhibited the highest suspension stability. Both dispersant/alumina and PVA/Zr (+IV) interactions resulted in an increase in the sedimentation stability of the alumina suspensions. Unlike in the case of the surface potential measurements, here the stabilizing effects did not cancel each other out. In fact the observed stabilization mechanisms acted side by side and there was no evidence of a competitive reaction between NaPA and PVA/Zr (+IV) at the particle surface.

IV. Discussion

To interpret the presented results, it is necessary to discuss cation chemistry in aqueous solutions in more detail. The first important factor is the solubility of the corresponding hydroxides at the given pH value. The solubility products are listed in Table 1. Additionally the maximum cation concentration for formation of hydroxides that can be calculated with the known solubility product and the given pH value of 9.5 is specified [47, 48]. Apart from potassium (KOH, solubility 20.14 mol/l), all cations used formed hydroxides of low solubility. However, within the examined concentration range, Ca (+II) cations did not form hydroxide precipitates. The maximum Mg (+II) concentration for hydroxide formation was 1.5 mmol/l, thus ly-

ing within the examined concentration range. The different solubilities of alkaline earth metal hydroxides can be elucidated from the curves given in Fig. 1. Whereas the zeta potential showed a steady upward trend with increasing Ca (+II) concentration, the surface potential for Mg (+II) remained constant above a concentration of 1.7 mmol/l. This behaviour indicates a deactivation of the cations by precipitation of magnesium hydroxide in the higher concentration range.

Table 1: Solubility products of hydroxide compounds and the corresponding cation concentration that is necessary for hydroxide formation.

Solid phase	Solubility products (K_s)	Max. cation concentration at pH 9.5 [mmol/l]
$Ca(OH)_2$ [47]	3.9×10^{-6}	3.9×10^{6}
$Mg(OH)_2$ [47]	1.5×10^{-12}	1.5
$Al(OH)_3$ [47]	1.9×10^{-33}	6×10^{-17}
am. $ZrO_2 \cdot xH_2O$ [48]	3.2×10^{-26}	3.2×10^{-14}

Based on this chemical background the results for alkaline earth metal cations containing suspensions are consistent. Up to a concentration of 1.7 mmol/l, the addition of Mg (+II) and Ca (+II) cations led to a reduction in surface potential and thus to a decrease in interparticle repulsive forces which directly caused an increase in viscosity. Further addition led to precipitation of $Mg(OH)_2$ on the one hand and a change from a negative to a positive surface potential in the presence of Ca (+II) on the other hand. Both effects induced a reduction in viscosity. The sedimentation velocities were obviously unaffected by variations in surface potential within the examined particle concentration range because zone settling is mainly influenced by attractive interparticle forces.

According to Table 1, Al (+III) and Zr (+IV) cations form insoluble hydroxides at the lowest concentrations for the given pH. However, in contrast to alkaline earth metal ions, these hydroxides had a completely different behaviour in aqueous solutions. In dependence on the given pH value and the cation concentration Al (+III) formed different aqua, aquahydroxo and hydroxo complexes which were soluble at these pH levels. They were also able to polymerize to multinuclear hydroxoaluminates under moderate pH conditions (pH of 6 – 8). At the given pH and cation concentration $[Al(OH)_4]^-$ was a dominant species [47]. This alumina species was inert in terms of reaction with the negatively charged alumina surface because it was negatively charged itself. Hence little change in surface potential was measurable after the addition of Al (+III) cations.

Similarly to Al (+III), the Zr (+IV) cations could also form aqua and hydroxoaqua complexes, but even in highly acidic condition polymerization reactions appeared [50]. Starting from mononuclear precursors the complexes formed polycations [47, 49 – 52]. By the release of water, the formation of hydroxyl bridges (olation) was preferred and thus multinuclear clusters or rings were formed (Fig. 7).

The olation reaction was favoured by increasing the metal ion concentration and, more particularly, by increasing the alkali concentration or pH value.
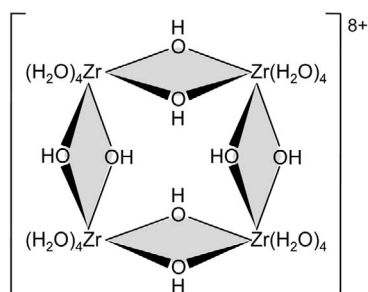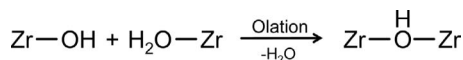
$$Zr-OH + H_2O-Zr \xrightarrow[-H_2O]{Olation} Zr-\overset{\displaystyle H}{\underset{\displaystyle}{O}}-Zr$$

Fig. 7: Olation reaction and schematic drawing of zirconium tetramer which is stable in aqueous solutions (following Wiberg [39]).

However, the formation of positively charged polynuclear complexes alone is not enough to cause the unexpectedly low viscosity and the clear increase in sedimentation stability. In Fig. 8 the surface potentials are given as a function of cationic concentration in the absence of PVA. The shift of initial surface potential in comparison with Fig. 1 is related to the absence of the binder and is already described in the literature [53, 54]. The general trends for K (+I), Mg (+II), Ca (+II) and Al (+III) were comparable with those observable in Fig. 1, but the presence of Zr (+IV) cations did not change the surface potential over the entire concentration range and showed a similar progression to K (+I). Accordingly Zr (+IV) did not affect the electrokinetic properties or macroscopic suspension properties in the absence of PVA. Obviously the specific interactions between PVA and cationic zirconium species represent the main reason for the changes in macroscopic suspension properties.
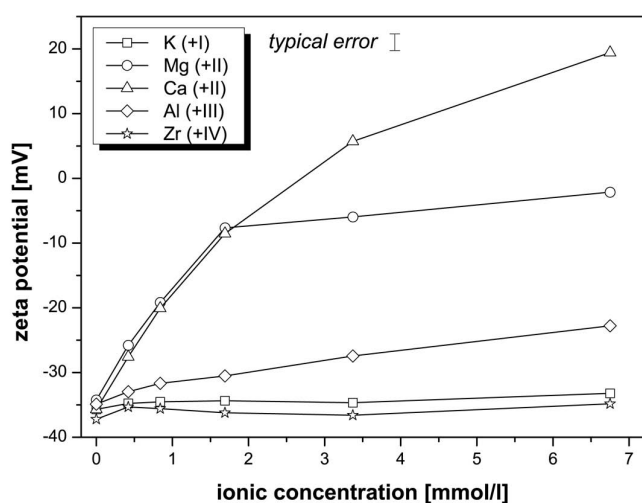
Fig. 8: Zeta potentials of different alumina suspensions with different concentrations and types of cations (suspensions contain no PVA).

Owing to its high coordination number and small radius, Zr (+IV) showed a very high affinity to alkoxide groups as found in the PVA molecules [55]. An infrared spectroscopic analysis of these interactions could not be conducted by the authors because the ratio of PVA (concentration in continuous phase of 7.4 mmol/l) and the highest Zr (+IV) cation concentration (6.8 mmol/l) was approximately 1:1. In the case of $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ (Fig. 7), this ratio was 4:1. Based on the degree of polymerization, around 600, the number of coordinated alkoxyl groups within a PVA molecule compared with uncoordinated ones was too small to generate a separate evaluable signal in the infrared spectra.
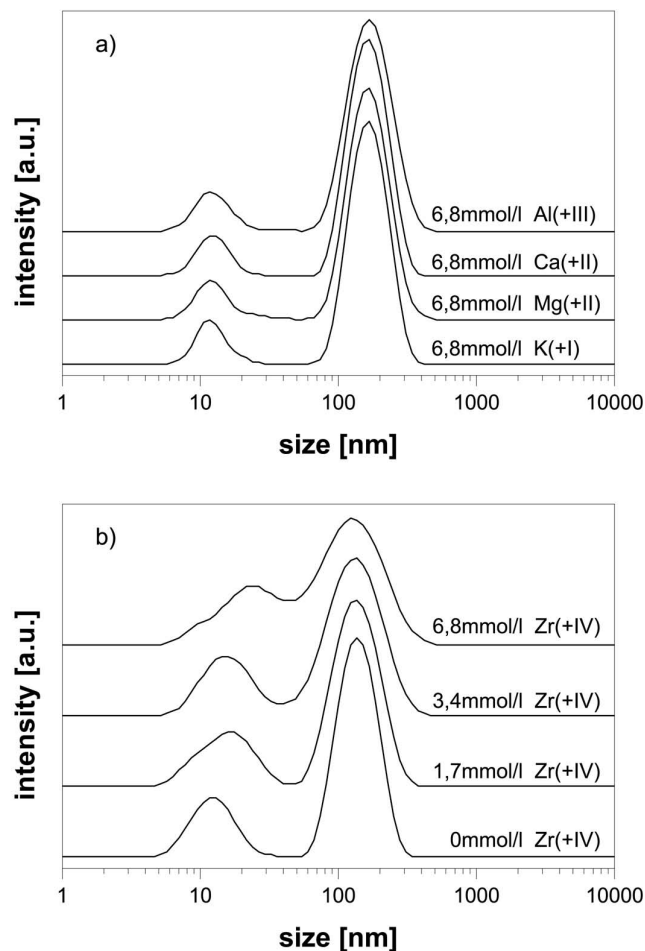
Fig. 9: Effect of cation type on the size distribution of PVA molecules (7.4 mmol/l in water equal to 3 wt% in the alumina suspension) at a constant cation concentration of 6.75 mmol/l (a) and for an increasing Zr (+IV) concentration (b) (relative standard deviation of the size 1.5 %).

The PVA/Zr (+IV) interactions were studied in greater detail through analysis of the change in PVA molecule size distribution with increasing cation concentration (Fig. 9). The PVA size distribution was not influenced by K (+I), Mg (+II), Ca (+II) or Al (+III) even at the highest concentration. In contrast, addition of Zr (+IV) caused a distinct shift. As the Zr (+IV) concentration was increased from 0 to 6.68 mmol/l, the average hydrodynamic diameter rose from 12 nm to 25 nm. The second peak at around 105 nm was caused by residues from polymer manufacture (technical-grade) and disappeared completely after the volume-weighted size distribution was calculated. It can be assumed that the change in polymer size was associated with a change in polymer configuration with sev-

eral PVA molecules attached to a single Zr (+IV) polyca-tion. This result leads to the conclusion that interactions between PVA and Zr (+IV) polycations occurred in the continuous phase and were independent of the alumina particle surface. Moreover the combinable stabilizing ef-fects of the polyacrylate dispersant and the PVA/Zr (+IV) complex are further indications of the absence of a reaction at the particle surface (Fig. 6). The increased PVA adsorp-tion density (Fig. 4) could be explained by an increase in sedimentation tendency of complexed PVA molecules in the centrifugal field, making the result affected by sample preparation.

The differences in sedimentation properties of these suspensions in comparison with other multivalent elec-trolyte-containing suspensions can be explained by a hin-drance of particle migration (Fig. 3). The hydrodynamic diameter of a PVA/Zr (+IV) complex is larger than that of a single PVA molecule and therefore leads to a decrease in sedimentation velocity. Additionally the distinctive de-crease in sediment height can be explained by the forma-tion of sliding layers between the particles, thus resulting in closer packing through particle rearrangement during sedimentation. The decrease in suspension viscosity in the presence of the PVA/Zr (+IV) complex could not be explained in detail until now (Fig. 2). The probability of particle-particle contact is probably reduced in the pres-ence of the PVA/Zr (+IV) complex and thus a reduction in viscosity occurs.

Statements about the macroscopic stability of ceramic suspensions cannot be derived from determination of sur-face potential by means of electroacoustics alone. Rather, it is necessary to identify the complex interactions be-tween all of the suspension's components. Therefore the use of complementary measuring techniques such as sur-face potential, adsorption, viscosity and sedimentation measurement techniques is essential for obtaining infor-mation about the state of interactions in ceramic suspen-sions with complex compositions.

V. Conclusions

A systematic investigation of the interactions between multivalent cations and a PVA binder in alumina suspen-sions was performed using surface potential, adsorption, viscosity and sedimentation measurement techniques. The results showed significant changes in macroscopic sus-pension properties, whereas only small changes in PVA adsorption were detectable. Hence the strong effects of the multivalent cations on the extent of compression of the electric double layer and the formation of hydroxides were identified as reasons for the changes in surface po-tential, viscosity and sedimentation stability. Owing to the increasing tendency towards hydroxide formation with increasing oxidation number, the destabilizing activities of the electrolyte species in the PVA-binder-containing alumina suspensions increased as follows: K<Al<Mg<Ca. However, it was not possible to determine the magnitude of the destabilizing effect solely by means of the oxidation state.

In contrast, the results indicated a significant improve-ment in suspension stability owing to interactions be-tween the Zr (+IV) cations and the PVA binder. With in-

creasing Zr (+IV) concentration, an increase in sedimenta-tion stability and a decrease in suspension viscosity were observed. The altered suspension properties could be at-tributed to strong interactions between the PVA alkoxide groups and the Zr (+IV) polycations, leading to a change in the polymer configuration. Obviously this complex was not attached to the alumina surface. In combination with a surface-affine polyacrylate dispersant, this state-ment could be proved while no competitive reaction could be observed. Furthermore it was possible to combine the stabilizing effects of the dispersant and the PVA/Zr (+IV) complex.

Our investigation clearly shows that it is not sufficient to study the interactions of one single additive or the in-termolecular competition between different organic sub-stances at the ceramic/water interface. Moreover it is es-sential to identify the chemical interactions of common-ly used organic additives in the presence of multivalent cations. Finally, the interactions between additives and electrolytes can even improve the suspension properties, as the example for Zr (+IV) cations impressively illus-trates.

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