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Effect of pH and impurities on the surface charge of zinc oxide in aqueous solution

Andrej Degen*, Marija Kosec

Ceramic Department, Jozef Stefan Institute, Jamova 39, Ljubljana, Slovenia

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Abstract

The surface charge on some commercially available zinc oxide powders in aqueous solution has been studied. Aqueous suspensions of zinc oxide could not be stabilized electrostatically because of the decreasing pH of suspensions in the region between 7.2 and 12 as a result the transformation of colloidal $Zn(OH)_{2(S)}$ particles to $Zn(OH)_{2(aq)}$ ions. The major cationic impurity in the zinc oxide powders is lead, whereas in the aged suspensions of the same powders, zinc and sulphate ions dominate. These ions have the the most significant effect in creating an electrical double layer shell around the zinc oxide particles. The effect of these ions on the surface potential of zinc oxide was studied and the point of zero charge and charge reversal were found to be a direct function of the zinc and sulphate ions' concentration in the supernatant. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Varistors are electronic devices that are used as surge arrestors. The major component of the oxide varistor is ZnO, this is used in combination with some other metal oxides which are determined by the intended application of the varistor. The processing of a stable suspension is an important technological step in varistor production.[1] The stability of the suspension is, to a large extent, dependent on the surface charge of the constituent oxides. Since the charge and surface potential of the pure oxide are primarily pH dependent it is possible, in some cases, to adjust the pH conditions of the slurry in such a way that all the particles exhibit the same charge polarity. If the surface charge of the particulate is high enough, a stable suspension without the formation of hard agglomerates is prepared[1,2] The surface charge can also originate from the presence of mineral impurities such as oxo ions or multivalent (and especially transition) metal ions.[3–5]

Many metal oxides will hydrolyze in the presence of water to form hydroxide layers at the surface (≡M–OH). Water molecules may be both physically and chemically adsorbed onto the surface of the dispersed oxide particles. The polar hydroxyl (-OH) groups may cause the surface to attract and physically adsorb a single or several additional layers of polar water molecules. An oxide or hydroxide surface (≡M–OH) can become charged by reacting with H^+ or OH^- ions due to surface amphoteric reactions [Eqs. (1) and (2)]. At low pH, hydroxide surfaces adsorb protons to produce positively charged surfaces ($\equiv M\text{–}OH_2^+$). At high pH they lose protons to produce negatively charged surfaces ($\equiv M\text{–}O^-$).[1]

$$\equiv M-OH + H^+ \leftrightarrow \equiv M-OH_2^+ \tag{1}$$

$$\equiv M-OH + OH^- \leftrightarrow M-O^- + H_2O \tag{2}$$

The number of these sites and the surface charge of the oxide particles are determined by the pH of the solution. The useful pH range may be limited because the solubility of oxides and hydroxides is strongly pH dependent, especially when the cation can form hydroxyl complexes.[1,6]

When the zinc oxide is immersed in the water the surface of the oxide is hydrolyzed and a layer of hydroxide is built up. It is well established that zinc hydroxide is slightly soluble in water, becoming more soluble as the pH is either lowered or raised.[7] Zinc oxide

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* Corresponding author.

E-mail address: andrej.degen@ijs.si (A. Degen).

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and zinc hydroxide are amphoteric, dissolving in acids to form salts containing the hydrated zinc (II) cation which may be more or less complexed with the acid anion depending upon the affinity for zinc and on the concentration. Hydrolysis can also occur, for example, species such as $[Zn_4(OH)_4]^{4+}{}_{(aq)}$ and $[Zn_2(OH)]^{3+}_{(aq)}$ have been identified in hydrolyzed solutions. Zinc oxide dissolves in alkalis to form zincates such as $[Zn(OH)_3]^-_{(aq)}$ and $[Zn(OH)_4]^{2-}_{(aq)}$. In solution the quasicolloidal particles, based on $Zn(OH)_{2(aq)}$ and hydrating water molecules, are also present. These undergo a first-order decay to yield a solution containing the species $[Zn(OH)_2(H_2O)_2]$, $[Zn(OH)_3(H_2O)]^-_{(aq)}$, and $[Zn(OH)_4]^{2-}_{(aq)}$, the actual composition depending on the concentration.[8]

In water suspension of zinc oxide the surface hydroxide $\equiv$Zn–OH or $Zn(OH)_{2(S)}$ is in equilibrium with the solution which contains species that can be represented by $Zn^{2+}_{(aq)}$, $Zn(OH)^+_{(aq)}$, $Zn(OH)_{2(aq)}$, $Zn(OH)_3^-{}_{(aq)}$ and $Zn(OH)_4^{2-}{}_{(aq)}$. Fig. 1 represents the fraction of zinc species existing as $Zn^{2+}_{(aq)}$, $Zn(OH)^+_{(aq)}$, $Zn(OH)_{2(aq)}$, $Zn(OH)_3^-{}_{(aq)}$ and $Zn(OH)_4^{2-}{}_{(aq)}$ over a range of pH at 25°C. The hydroxide complexes can be also represented by the formula $Zn(OH)_i^{2-i}$ ($i = 1$ to 4). The diagram was redrawn from the data reported by Reichle et al.[7]

The establishment of a surface charge on the metal oxide in water may occur by two distinct but essentially equivalent mechanisms: (i) the adsorption of protons or hydroxyls onto amphoteric surface sites [Eqs. (1) and (2)] or (ii) the formation of hydroxylated metal species in solution which deposit on the solid surfaces [2,4]. For zinc the corresponding equations [Eqs. (3)–(8)] are as follows.[7,9]

$$Zn^{2+}_{(aq)} + OH^- \leftrightarrow Zn(OH)^+_{(aq)} \quad (3)$$

$$Zn(OH)^+_{(aq)} + OH^- \leftrightarrow Zn(OH)_{2(S)} \quad (4)$$

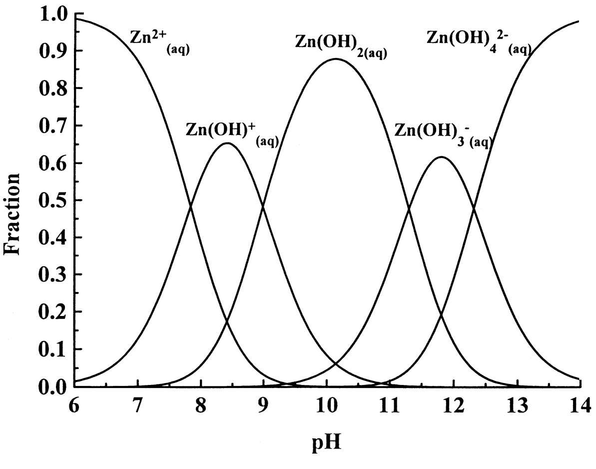

Fig. 1. Fraction of Zn (II) ions species existing as $Zn^{2+}_{(aq)}$, $Zn(OH)^+_{(aq)}$, $Zn(OH)_{2(aq)}$, $Zn(OH)^-_{3(aq)}$ and $Zn(OH)^{2-}_{4(aq)}$ over a range of pH at 25°C.[7]

$$Zn(OH)_{2(S)} \leftrightarrow Zn(OH)_{2(aq)} \quad (5)$$

$$Zn(OH)_{2(S)} \leftrightarrow Zn^{2+}_{(aq)} + 2OH^- \quad (6)$$

$$Zn(OH)_{2(S)} + OH^- \leftrightarrow Zn(OH)_3^-(aq) \quad (7)$$

$$Zn(OH)_{2(S)} + 2OH^- \leftrightarrow Zn(OH)_4^{2-}(aq) \quad (8)$$

Alternatively the species $Zn(OH)_{2(aq)}$ may be considered to form directly on the solid surface.

For most oxide/aqueous solution systems the generation of surface charge due to amphoteric surface reactions may be described by Eqs (1)–(8), if only H^+, OH^- and $M(OH)_i^{2-i}$ ($i = 1$ to 4) ions are present in the solution. If other species are included in the surface charge formation then a simple interpretation such as surface amphoteric ionization is not sufficient. In this case a large number of hydrolytic processes and a variety of ionic equilibrium determine the species in solution. Each of these species could be adsorbed at the solid surface depending on the pH, composition and concentration of the electrolyte.[2]

The purpose of our research is to investigate in more detail the nature of the impurities responsible for the surface charge on the zinc oxide particles dispersed in water. In this study, the effect of pH and impurity ions on the zeta potential of zinc oxide powders of different purity commonly used in varistor production, has been investigated. The surface charge of the zinc oxide was measured in deionized water and in the supernatant. The supernatant solution prepared from the aged suspension contains multivalent metal ions and different anionic species. Ionic as well as solid impurities in the suspension can change the sign and magnitude of the zeta potential due to specific and electrostatic adsorption on the oxide surface. This, in turn, will allow us to show that knowledge of the type of impurities facilitates the preparation of the concentrated zinc oxide suspension.

2. Experimental procedure

The model zinc oxide powders chosen for this study were: powder A (Johnson Matthey Company — Alfa, purity 99.99%, BET specific surface area of 3.02 $m^2\ g^{-1}$, average diameter 1.18 mm), powder B (BBU Zinkweiss Pharma A, 99.9%, 4.18 $m^2\ g^{-1}$, 0.82 μm), powder C (Grillo Zinkoxid GmbH, 99.6%, 3.63 $m^2\ g^{-1}$, 1.8 μm) and powder D (SLOVLAK Košeca, 99.78%, 3.57 $m^2\ g^{-1}$, 1.46 μm). HCl, NaOH and all salts used were of reagent grade or better.

An aqueous zinc oxide suspension was produced by adding a specific weight of zinc oxide powder to distilled water that contained no additives. If the effect of electrolytes ($PbCl_2$, $ZnCl_2$, Na_2SO_4) and solid ($PbSO_4$) is tested, the distilled water contains a specific amount of these chemicals in the solution. Suspensions were homogenized using a magnetic stirrer for 1 h and ultrasonificated for 5 min. Preliminary experiments showed that these conditions are suitable for almost complete adsorption of the additives.

The zeta potential of the zinc oxide powder in a dilute suspension (< 1 vol%) was measured using a zeta meter (Model 501 Lazer Zee Meter^{TM}, PenKem Inc.). Prior to the measurement, the 1 vol% zinc oxide suspensions with or without addition of the additives were centrifuged. The supernatant was carefully decanted into a beaker, subsequently a very minute amount of the suspension was remixed with the supernatant. pH adjustment was achieved by dilute HCl or NaOH solution when the zeta potential was measured as a function of pH.

The concentration of cations in the solid and aged supernatant solution was determined by inductive coupled plasma–atomic emission spectroscopy, whereas the anionic species were determined by ionic exchange chromatography (Atomscan 25 Thermo Jarrell Ash).

3. Results and discussion

It is well known from the literature that a stable aqueous suspension of metal oxide can be prepared by changing the pH of the suspension if the solubility of the oxide and its hydroxide are not strongly dependent on pH, e.g. Al_2O_3, ZrO_2.[10,11] As a consequence of this the experiment was carried out with a 5 vol% zinc oxide aqueous suspension with dilute solutions of HCl and NaOH used to preset the initial pH. The initial pH was monitored as a function of time with the suspension mixed continuously for 3 days. The preset value of pH was in the range from 6.6 to 12. Fig. 2 represents the difference observed between initial and final pH values of the zinc oxide suspension with time.

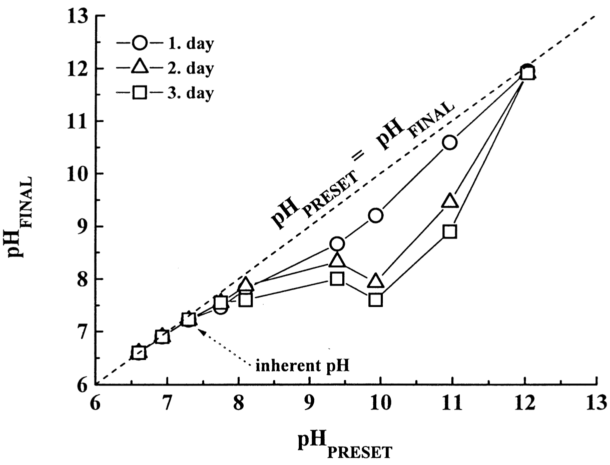

Fig. 2. Initial and final pH of the 5 vol% zinc oxide (powder D) aqueous suspension as a function of time.

In this experiment two stable regions were determied where the difference between the initial and final pH is not significant: pH $<$ 7.2 and pH $>$ 12. Between these two stable regions, there is a pH unstable region with the greatest difference obtained for an initial pH = 9.9. All experiments carried out in this region showed a decrease of the final pH with time. From Fig. 2 it can be seen that the inherent pH of the zinc oxide suspension at pH = 7.2 is very stable.

The decrease of the final pH with time can be explained by a small dissolution of the zinc oxide or surface hydroxide $Zn(OH)_{2(S)}$ and the formation of different zinc species.[7] From Fig. 1 it can be seen that zinc hydroxide dissolves at pH $<$ 6.3, which is in agreement with the experimental results. Below this pH the $Zn^{2+}_{(aq)}$ ions are the only stable form in the solution. The lowest preset pH value that could be adjusted by the addition of the of hydrochloric acid solution was 6.6. There is an equilibrium between $Zn^{2+}_{(aq)}$ and $Zn(OH)^{+}_{(aq)}$ species in the solution and the surface hydroxide in the pH range 6.6–7.2 (Fig. 1). The stable pH was reached immediately after the addition of the acid and there was no decrease of pH with time. Very similar conditions take place at pH $>$ 12 where we have an equilibrium between surface hydroxide and zincate ions $[Zn(OH)^{-}_{3\,(aq)}, Zn(OH)^{2-}_{4\,(aq)}]$.

The most dramatic decrease in the final pH takes place in the region 7.2 $<$ pH $<$ 12 due to different species in solution, which are in equilibrium with the hydrated zinc oxide surface. The preset pH = 9.9 of the suspension decreased to 7.6 after 3 days. At pH = 10 around 90% of the species in the solution, which are in equilibrium with the solid surface, belong to the “quasikoloidal” particles of $Zn(OH)_{2(aq)}$ (Fig. 1). When the zinc oxide powder was immersed in the water, the surface of the oxide particles was hydrolyzed because of the physically and chemically adsorbed polar water molecules and a layer of zinc hydroxide is formed.[1] By the addition of the sodium hydroxide solution we preset the pH of the suspension to 9.9 and the surface hydroxide $Zn(OH)_{2(S)}$ transformed [Eq. (5)] to the additionally hydrated particles of $Zn(OH)_{2(aq)}$, which is the most stable species at this pH. Coloidal particles of $Zn(OH)_{2(aq)}$ leave the metal oxide surface.[4] Zinc oxide surface is hydrolyzed again in the reaction of the OH^- ions with the surface zinc atoms. Because of this the concentration of OH^- ions decrease until the final pH = 7.6 is reached after 3 days.

The final pH value of 7.6 after 3 days is very stable (Fig. 2). At that pH the concentration of $Zn(OH)_{2(aq)}$ is negligible, the only stable species in the solution are $Zn^{2+}_{(aq)}$ and $Zn(OH)^{+}_{(aq)}$ ions. Because of this there is no transformation of $Zn(OH)_{2(aq)}$ particles and no decrease in the pH. We can conclude that the pH of the suspension decreases in the pH region where the $Zn(OH)_{2(aq)}$ particles are present the solution. The $Zn(OH)_{2(aq)}$ particles are present in the region 7.4 $<$ pH $<$ 12.6 (Fig. 1), which agrees very well with our experimental results from the region $7.3 < \text{pH} < 12$, where a significant time dependent difference between initial and final pH of the suspension takes place (Fig. 2).

This experiment shows that electrostatic stabilization of a zinc oxide suspension in water is not possible in the range $7.2 < \text{pH} < 12$, because of a decrease in pH with time. For this reason all further experiments were performed at the inherent pH of the aqueous ZnO suspension, which for powder D is approximately pH = 7.2.

The zeta potential of the aqueous suspension of ZnO was also measured. Fig. 3 shows zeta potential as a function of pH for ZnO (powder C) determined in the deionized water and in the supernatant solution. The zeta potential of the ZnO in the deionized water could be explained by Fig. 1 and Eqs. (3)–(8). Only H^+ and OH^- ions are present in deionized water and so the surface charge is affected only by the chemical reaction between the surface of the zinc oxide and the liquid medium according to the Eqs. (3)–(8). The adsorption of the resulting zinc species affects the sign and the magnitude of the surface charge of the zinc oxide particles. It is clear that in the pH range 7–9 where our results showed a highly positive zeta potential, the dominant species are Zn^{2+} and $Zn(OH)^{+}_{(aq)}$ ions (Fig. 1). At higher pH the dominant species are $Zn(OH)_{2(aq)}$ which could precipitate giving a new solid phase, $Zn(OH)_{2(S)}$. By raising the pH, the negative species, such as $Zn(OH)_3^-{}_{(aq)}$ and $Zn(OH)_4^{2-}{}_{(aq)}$ dominate and determine the overall negative charge. The isoelectric point (IEP) for zinc oxide at pH = 9.5, found in this work, coincides well with the pH of the transition from positive, over neutral, to negative zinc hydroxo species, as shown in Fig. 1. The IEP of zinc oxide found in the literature ranges from 8.7 to 10.3.[1,12]

In addition, we also measured the zeta potential as a function of pH of the zinc oxide (powder C) in the supernatant solution (Fig. 3). In the supernatant solution, prepared by aged suspension centrifugation, impurity ions from the starting zinc oxide are present. The zeta potential of the zinc oxide in the supernatant exhibits lower values in the pH range 7–12. The IEP is changed from 9.5 in the deionized water, to 9.2 in the supernatant solution. Charge reversal at pH = 7 also occurred.

The zeta potential versus pH of zinc oxide can be partly explained by the zinc species present at different pH (Fig. 1). A slight shift of the IEP by 0.3 pH units could be because of specific adsorption of negatively charged impurity ions. Specific or coordination adsorption of anions can lead to a decrease in positive surface charge and an increase in negative surface charge on the oxide.[5] However the same effect can be obtained due to compression of the electrical double layer by an increase in the cation's impurities.

In the pH region 7–8 the $Zn^{2+}_{(aq)}$ ions become the dominant species and may slowly lower the zeta potential, due to compression of the electrical double layer, to zero. The $Zn^{2+}_{(aq)}$ ions have a much more profound effect on the compression of the electrical double layer at pH 7–8 than $Zn(OH)^{+}_{(aq)}$ ions, because of the higher ionic charge and a higher concentration, in accordance with Schulze–Hardy's rule.[2,13,14] A similar conclusion can be made at $\text{pH} > 12$. The compression of the electric double layer takes place at pH = 12 because of the high concentration of the $Zn(OH)^{2-}_{4(aq)}$ ions in the solution. However the charge reversal can not be explained by an increase in the concentration of the $Zn^{2+}_{(aq)}$ species with lowering of pH, but must be a consequence of the negatively charged impurities.

To identify the type and the concentration of the impurity ions in the supernatant solution, a chemical analysis was performed. Fig. 4 shows the results of the time dependent concentration of ions in the supernatant of powder C. Major ions in the supernatant solution are zinc, lead, sulphate and chloride ions. During the suspension ageing the concentration of ions in the solution

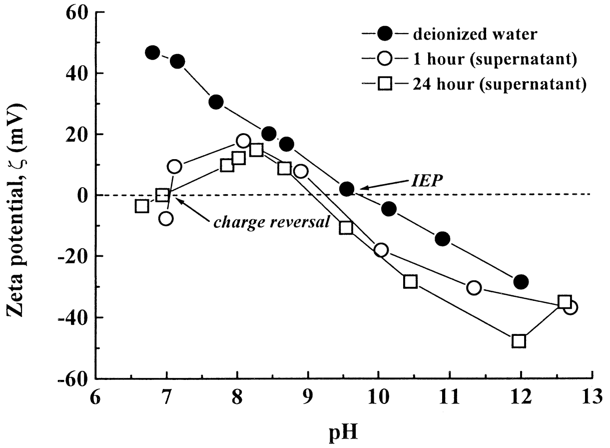

Fig. 3. Zeta potential of zinc oxide (powder C) as a function of pH in deionized water and in supernatant solution.

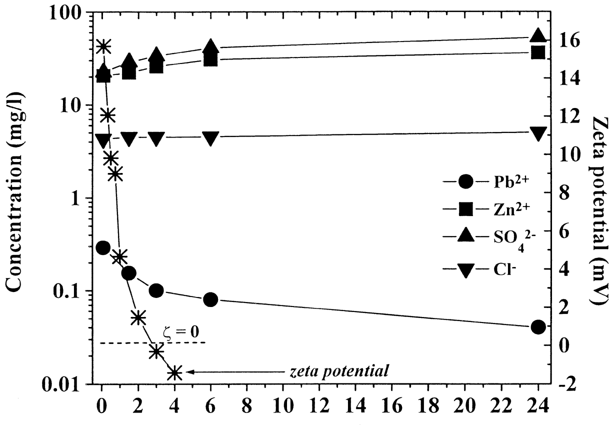

Fig. 4. Concentration of the ions and zeta potential in the supernatant solution of the zinc oxide (powder C) suspension as a function of time.

changes. The concentration of the zinc and sulphate ions increases with time and reaches equilibrium after approximately 24 h. In contrast the concentration of the chloride ions is constant and the concentration of lead ions decreases slightly with time. The concentration of the zinc and sulphate ions is more than an order of magnitude greater than the chloride and lead ions, so they probably have a more pronounced effect on the surface properties of the zinc oxide particles. The decreasing concentration of lead ions could be explained by the formation of sparingly soluble lead sulphate [15] during ageing or by adsorption of lead species on the solid surface. The adsorption of lead species on the surface of zinc oxide would increase the zeta potential, however a decrease with time is observed (Fig. 4), implying the adsorption of the negatively charged species. Therefore lead sulphate formation is the most probable process responsible for decreasing the concentration of lead ions in the solution. The amount of lead in the bulk zinc oxide, determined chemically, was 0.11 wt%. After 5 min of ageing the concentration of lead ions in the supernatant was only 0.45% of the total lead in the solid, and after 24 h the concentration was even lower (0.06%). From this we can conclude that the majority of lead ions are incorporated into the crystal lattice of zinc oxide, with only a very minute amount present at the surface of the solid.

The zeta potential of zinc oxide in the supernatant decreased and changed sign after 3 h (Fig. 4). This charge reversal indicates the specific adsorption of anions. The time dependent zeta potential, also shown in Fig. 3, exhibits a small decrease in the positive zeta potential and an acidic shift of the IEP from 9.2 to 9 between 1 and 24 h for the aged suspension of zinc oxide in the supernatant (Fig. 3).

By the addition of different salts to the suspension of 99.99% zinc oxide (powder A) we examined the effect of major impurity ions, found in the supernatant solution, on the zeta potential. Ultra pure zinc oxide was selected because of the low content of impurities. Fig. 5 shows the effect of $PbCl_2$, $ZnCl_2$, Na_2SO_4 and $PbSO_4$ on the zeta potential of ultra pure zinc oxide (powder A) as a function of pH. The concentration of Pb^{2+}, Zn^{2+}, SO_4^{2-} ions in the suspension was 3×10^{-3} mol l^{-1}. Solid $PbSO_4$ was prepared in situ by mixing $PbCl_2$ and Na_2SO_4 in such a proportion that the concentration of the $PbSO_4$ in suspension was also 3×10^{-3} mol l^{-1}. In Fig. 5, the zeta potential of 99.99% pure zinc oxide (powder A) as a function of pH is shown for comparison.

The increase in zeta potential and the shift in IEP of zinc oxide in a solution of lead and zinc ions to more alkaline values demonstrate the adsorption of positive lead and zinc species on to the zinc oxide surface. In agreement with Ref. 2, in the pH range 7–9, $Pb^{2+}_{(aq)}$ and $Pb(OH)^{+}_{(aq)}$ exist in salt solution, whereas $Zn^{2+}_{(aq)}$ and $Zn(OH)^{+}_{(aq)}$ ions are the dominant species in zinc salt solution in that pH range (Fig. 1). The influence of lead and zinc ions in the pH range 10–12 is not significant, resulting in a similar zeta potential as that determined for powder A.

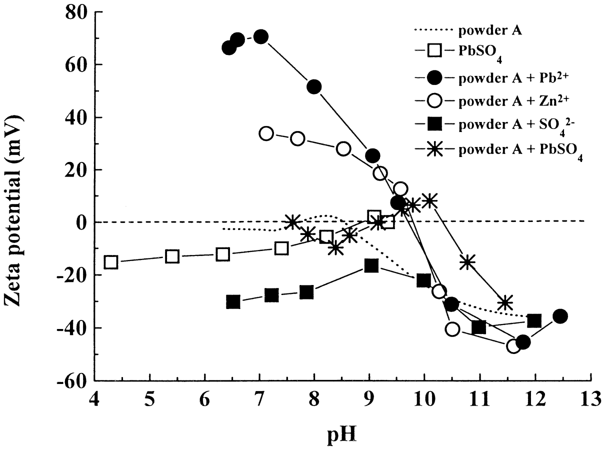

Fig. 5. Effect of Pb^{2+}, Zn^{2+}, SO_4^{2-} ions and solid $PbSO_4$ addition on zeta potential of 99.9% zinc oxide (powder A) in supernatant solution as a function of pH. Zeta potential of solid $PbSO_4$ as a function of pH was also measured.

In Fig. 5, it can be seen that the zeta potential of zinc oxide with the addition of sulphate ions is negative in the pH region 6.5–12. In the solution sulphate ions give a multivalent conjugate bases of sulfuric acid ($pK_1\cong-3$, $pK_2=1.9$). The significant lowering of zeta potential may be due to strong surface adsorption which occurred as a result of high negative charge density associated with this multivalent acid. The apparent surface affinity of the sulphate ions for zinc oxide is probably very similar to that found for iron oxide.[16]

The zeta potential of the solid $PbSO_4$ was also measured as a function of pH in Fig 5. The surface charge of the $PbSO_4$ is negative with an IEP at 9, and above the IEP the dissolution of the solid begins. In the pH region 7.5–9 the zinc oxide and $PbSO_4$ have opposite surface charges. Because of this solid $PbSO_4$ can be adsorbed on the surface of the metal oxide due to electrostatic attraction and the surface becomes negatively charged. In this pH region, the zeta potential and IEP of zinc oxide with the addition of lead sulphate compare very well with lead sulphate. This is a well known effect of precipitate adsorption on the electrokinetical properties of metal oxides.[4,12] At pH > 9, lead sulphate dissolves slowly and lead ions adsorb on the surface of oxide. Adsorbed lead species increase the positive zeta potential and shift the IEP of the zinc oxide to 10.3. Sulphate ions from dissolved lead sulphate may also be adsorbed at the oxide surface but their effect on zeta potential at pH > 9 is not significant, as shown before.

We can conclude that the major impurities as shown in Fig. 4, namely zinc ions, will shift the IEP of the zinc oxide to higher pH values and will increase the zeta potential of the oxide, whereas the charge reversal of zinc oxide at pH values around 7 (Figs. 3–5) is the effect of specific adsorption of sulphate ions and/or electrostatic attraction of lead sulphate precipitate on the surface of the zinc oxide.

Fig. 6 shows the zeta potential of zinc oxide powders of different purity as a function of pH. It can be seen from Fig. 6 that all the zeta potential versus pH curves have very similar shapes with two charge reversals, however the value of zeta potential at different pH depends on the purity of the zinc oxide.

In Table 1 a chemical analysis of the solid zinc oxides and supernatant solution after 1 h of ageing is reported. The impurities in the solid, determined by the producers are lead, copper, cadmium, iron and manganese ions. The measurement of lead, as the major impurity, determined by the chemical analysis differs from the results of the producers. The concentrations of zinc, lead, sulphate, chloride, nitrate and phosphate ions were also determined in the supernatant after 1 h of suspension ageing. The concentration of zinc and sulphate ions is approximately 100 times higher than that of the other ions in the solution. There is good agreement with the results from Fig. 6 and the chemical analysis in Table 1. The higher the concentration of zinc ions in the supernatant solution, the more alkaline is the shift of the IEP, and the higher the concentration of the sulphate ions, the more acidic is the first charge reversal of zinc oxide. We can also speculate that the higher the concentration of zinc ions, the higher the zeta potential of the zinc oxide in the pH range 6.5–10. The maximum positive surface charge increases from +4 mV for 99.99% (powder A) zinc oxide to +20 mV in the case of less pure zinc oxide.

The effect of the concentration of different ions and lead sulphate precipitate was also tested by means of quantified zeta potential of 99.99% zinc oxide (powder A). Fig. 7 shows the zeta potential of 99.99% zinc oxide in the supernatant as a function of $ZnCl_2$, Na_2SO_4 and $PbSO_4$ concentration. The increase in the concentration of zinc ions up to a certain point increases the zeta potential of the zinc oxide. The effectiveness of sulphate ions and lead sulphate is very similar. In both cases zeta potential reverses sign. Zinc species can be specifically adsorbed on the oxide surface in the form of $Zn^{2+}_{(aq)}$ or/and $Zn(OH)^{+}_{(aq)}$ ions. The specific adsorption of zinc

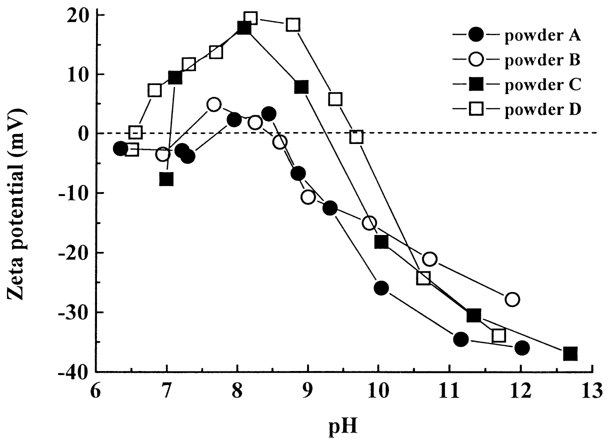

Fig. 6. Zeta potential of A, B, C and D zinc oxide powders in their supernatant solution as a function of pH.

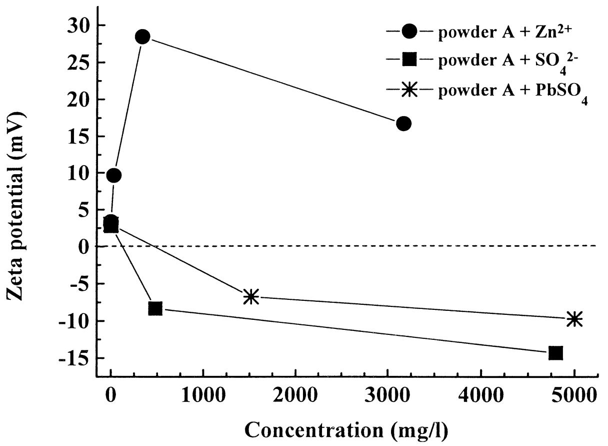

Fig. 7. The zeta potential of 99.99% zinc oxide (powder A) in the supernatant as a function of the concentration of $ZnCI_2$, Na_2SO_4 and $PbSO_4$.

Table 1
Chemical analysis of solid A, B, C and D zinc oxide powders and their supernatant solutions after 1 h of ageing

Solid (wt%)							Supernatant (mg/l)					
ZnO	Purity	Pb	Cu	Cd	Fe	Mn	Zn^{2+}	Pb^{2+}	SO_4^{2-}	Cl^-	NO_3^-	PO_4^{3-}
A	99.99	– 9×10^{-4}[b]	–	–	–	–	6.7	<0.01	0.3	0.3	0.3	<0.1
B	99.9	2×10^{-3}[a] 5×10^{-4}[b]	1×10^{-4}	2×10^{-4}	5×10^{-4}	1×10^{-4}	7.3	<0.01	2.3	0.3	0.2	<0.1
C	99.6	0.11[a] 0.10[b]	1×10^{-4}	17×10^{-4}	17×10^{-4}	1×10^{-4}	27	0.17	24.5	4.3	0.2	<0.1
D	99.78	0.08[a] 0.18[b]	2×10^{-4}	9×10^{-4}	1×10^{-3}	–	38.4	0.06	68.6	1.9	0.2	<0.1

[a] Producer's specification.

[b] Chemical analysis.

species on to the oxide surface follow these reaction equations:[5]

$$\equiv \mathrm{M{-}OH} + \mathrm{Zn}^{2+} \leftrightarrow \equiv \mathrm{M{-}OZn}^{+} + \mathrm{H}^{+} \quad (9)$$

$$\equiv \mathrm{M{-}OH} + \mathrm{ZnOH}^{+} \leftrightarrow \equiv \mathrm{M{-}OZnOH} + \mathrm{H}^{+} \quad (10)$$

In the case of Eq. (9) the surface of the metal oxide becomes positively charged or the positive surface charge is increased. On the other hand, when the $\mathrm{Zn(OH)}^{+}_{(aq)}$ form is adsorbed on the oxide surface [Eq. (10)], there is no increase in positive charge. From the experimental results in Fig. 7, we can conclude that zinc species mostly adsorbed on the surface of the zinc oxide in the form of $\mathrm{Zn}^{2+}_{(aq)}$, because an increase in the positive surface charge appears. There is also a good agreement with Fig. 1, because at the inherent pH = 7.2 of the zinc oxide suspension the ratio $\mathrm{Zn(OH)}^{+}_{(aq)}/\mathrm{Zn}^{2+}_{(aq)}$ of zinc species in solution is approximately 1:4. When the concentration of the added $\mathrm{ZnCl_2}$ in the suspension is greater than 330 $\mathrm{mgl^{-1}}$ (5×10^{-3} $\mathrm{moll^{-1}}$), a compression of an electrical double layer takes place.

Fig. 7 also shows specific adsorption of sulphate on the surface of the zinc oxide, because charge reversal appears.[5,16]

Because of the negative zeta potential of the lead sulphate precipitate (Fig. 5) electrostatic adsorption on the zinc oxide takes place as well (Fig. 7). When the particles of zinc oxide become fully covered with lead sulphate, the sign of the zeta potential is reversed.

4. Summary

The influence of the initial pH on the aqueous suspension of the zinc oxide was studied in terms of electrostatic stabilization. It was found that the zinc oxide suspension could not be electrostatically stabilized in the preset pH range between 7.2 and 12 due to formation of unstable colloidal particles of $\mathrm{Zn(OH)_{2(aq)}}$. During $\mathrm{Zn(OH)_{2(aq)}}$ transformation, consumption of hydroxyl ions from the solution takes place and lowers the final pH of the zinc oxide suspension. The zeta potential of the zinc oxide particles was examined. The surface charge of the solid in distilled water is governed by the adsorption of different zinc hydroxo species. In the supernatant solution, adsorption of impurity ions also influenced the surface charge of the zinc oxide. The major impurity ions are lead, zinc, sulphate and chloride ions. Lead and sulphate ions form a sparingly soluble lead sulphate. The predominant impact of these species on the surface charge was confirmed by a model experiment in which the influence of major impurity ions on the surface charge of 99.99% pure zinc oxide was examined as a function of pH and concentration. It was found that lead and zinc ions increase the positive surface charge of the solid and shift the IEP to more alkaline values due to specific adsorption. Adsorbed sulphate ions increase the negative surface charge and the zinc oxide exhibits no measurable IEP because of strong specific adsorption. Negatively charged lead sulphate also increases negative surface charge on the metal oxide. Zinc ions in the supernatant shift the IEP the zinc oxide to more alkaline values, whereas sulphate ions and lead sulphate cause a charge reversal.

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