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Electrokinetic properties of calcium aluminate hydrates

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With 6 figures and 2 tables

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Introduction

Calcium aluminate hydrates are formed when $\text{Ca}_3\text{Al}_2\text{O}_6$, a compound present in Portland cement, reacts with water (1–3). At 25 °C two metastable hydrates $\text{Ca}_2\text{Al}(\text{OH})_6^+$ · OH^- · $3\text{H}_2\text{O}$ and $\text{Ca}_2\text{Al}(\text{OH})_6^+$ · $\text{Al}(\text{OH})_4^-$ · $3\text{H}_2\text{O}$ are formed in the first stage of the reaction; these hydrates, present as hexagonal plates, have a structure consisting of $\text{Ca}_2\text{Al}(\text{OH})_6^+$ sheets with H_2O and respectively OH^- and $\text{Al}(\text{OH})_4^-$ in the interlayer (4). These hexagonal hydrates recrystallize after some time, depending on the conditions (temperature, water/solid ratio, surface area of reactants) into the cubic $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$, the stable hydrate under these conditions, which is (in small amounts) already present in the first stage together with the hexagonal hydrates.

In the past little attention has been paid to the study of the electrokinetic properties of the calcium aluminate hydrates and other hydrates present in hydrating cement (5, 6) although these properties will influence the physico-mechanical properties of these systems.

We studied the electrokinetic properties of the calcium aluminate hydrates and the influence of NaOH on them in the course of an investigation of the influence of Na_2O on the reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ with water (7, 8).

Experimental

$\text{Ca}_3\text{Al}_2\text{O}_6$ was prepared as described by *de Jong et al.* (9). The water used was distilled twice and redistilled under reduced pressure shortly prior to use.

$\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ was prepared in an autoclave from $\text{Ca}_3\text{Al}_2\text{O}_6$ and water as described by *Thorvaldson et al.* (10). NaOH solutions were prepared from titrisol NaOH (Merck). All preparations were performed in a glove box with a N_2 -atmosphere free of CO_2 .

Water and NaOH solutions saturated towards $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ were prepared by dispersing $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ in the solution in a polythene vessel. This vessel was kept in a CO_2 -free atmosphere and shaken mechanically twice daily for 30 minutes. After 3 weeks the dispersion was filtered, with exclusion of CO_2 , through a micropore membrane filter with pore size 0.08 μm (Shandon Nuclepore N 008). This filter was used for other filtrations as well.

$\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ suspensions (0.1 g/l) were prepared by dispersing the material in solutions previously saturated towards it, using an ultrasonic bath (Megason Ultrasonic, Frequency 80,000 Hz) for 30 minutes.

The reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ (1 g) with water and NaOH solutions (100 ml) took place in a polythene vessel at $25^\circ \pm 0.1^\circ \text{C}$, with continued stirring. At predetermined times during the reaction a sample of 11 ml was taken and left standing for 30 minutes to allow the much larger unreacted $\text{Ca}_3\text{Al}_2\text{O}_6$ particles to settle. The ζ -potential of the hydrate crystals present in suspension after the settling was measured electrophoretically using a Smith and Lisse cell (11). The Helmholtz-Smoluchowski relation was used for the calculation of the ζ -potential from the electrophoretic mobility; this is justified by the fact that the radius of the almost spherical icositetrahedral $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ -particles as determined by SEM, ranges from 100 to 1000 nm, while the thickness of the double layer κ^{-1} ranges from 1 to 2.5 nm (12). In the case of the hexagonal hydrates the thickness of the plates was about 200 nm. These values also justify the assumption of a flat double layer (see later).

Calcium was determined in the liquid phase after filtration using a spectrophotometric titration method as described by *Smit and Stein* (13). Aluminium was determined as described by *Pribil and Vesely* (14).

X-ray analyses were performed using a Philips diffractometer PW 1120 with filtered Cu radiation. Scanning electron micrographs (SEM) were made using a Cambridge MK-2A instrument.

Theoretical

Calculation of the surface charge behind the electrokinetic slipping plane.

The formula for calculating the surface charge behind the electrokinetic slipping plane from the ζ -potential as derived from the Gouy-Chapman theory of the diffuse double-layer is based on the assumption that the concentration of each ion in the diffuse double-layer is determined by the electrical macro-potential only. However, using the equality of the electrochemical potential of each type of ions, throughout the double-layer, the number n_i of these ions as function of the distance to the slipping plane is given by:

$$n_i = \frac{f_i^\infty}{f_i} n_i^\infty \exp\left(\frac{-z_i e \psi}{kT}\right) \quad [1]$$

where f_i is the activity coefficient and the index ∞ indicates the value of the quantity in the bulk of the liquid. The other symbols have their usual meaning. Then, the surface charge σ_ζ for flat double layers is given by:

$$\sigma_\zeta = \left\{ 2\epsilon_0 \epsilon_r e \sum_i z_i n_i^\infty \left[\int_0^\zeta \frac{f_i^\infty}{f_i} \exp\left(-\frac{z_i e \psi}{kT}\right) d\psi \right] \right\}^{\frac{1}{2}} \quad [2]$$

The ratio f_i^∞/f_i cannot be determined experimentally. However, it may differ significantly from 1 because the activity coefficient is determined primarily by the atmosphere of ions of opposite charge around any ion. This atmosphere near the interface differs from that in the bulk solution: If the solid has, say, a negative surface charge, anions will be all but absent in its vicinity; the cations will have, near the interface, an activity coefficient higher and the anions an activity coefficient lower than in the bulk solution. The net effect is a decrease in absolute value of σ_ζ as compared with that calculated on the assumption of constant activity coefficients throughout the diffuse double layer.

Because it is essential in the discussion, whether σ_ζ increases with increasing NaOH concentration (see later), we estimated this effect, comparing σ_ζ calculated on the assumption $f_i^\infty/f_i = 1$ throughout the diffuse double

layer with σ_ζ calculated on the following assumptions. For the region $0 < x < \kappa^{-1}$ (x = distance from the slipping plane, κ = the Debye Hückel parameter) f_i was taken equal to f_i at $x = 0$; for $x > \kappa^{-1}$, f_i was taken to be $= f_i^\infty$. Thus:

$$\sigma_\zeta = \left\{ 2\epsilon_0 \epsilon_r kT \sum_i n_i^\infty \left[\frac{f_i^\infty}{f_i^0} \exp\left(-\frac{z_i e \zeta}{kT}\right) + \left(1 - \frac{f_i^\infty}{f_i^0}\right) \exp\left(-\frac{z_i e \psi_\kappa}{kT}\right) - 1 \right] \right\}^{\frac{1}{2}} \quad [3]$$

where $f_i^0 = f_i$ at $x = 0$ and $\psi_\kappa = \psi$ at $x = \kappa^{-1}$. ψ_κ was calculated from the equation for $\psi(x)$ for an electrolyte consisting of uni- and bivalent cations and univalent anions:

$$\frac{\sqrt{(\kappa^2 - \gamma^2) \exp\left(\frac{e\psi}{kT}\right) + \gamma^2} - \kappa}{\sqrt{(\kappa^2 - \gamma^2) \exp\left(\frac{e\psi}{kT}\right) + \gamma^2} + \kappa} = \exp(-\kappa x) \frac{\sqrt{(\kappa^2 - \gamma^2) \exp\left(\frac{e\zeta}{kT}\right) + \gamma^2} - \kappa}{\sqrt{(\kappa^2 - \gamma^2) \exp\left(\frac{e\zeta}{kT}\right) + \gamma^2} + \kappa} \quad [4]$$

where $\gamma^2 = \frac{2e^2 n_{2+}^\infty}{\epsilon_0 \epsilon_r kT}$; this equation can be derived from the Poisson-Boltzmann relation.

Activity coefficients at $x = 0$ were calculated from the Debye-Hückel equation as given by Gimblett and Monk (15); the ionic strength I used in this calculation was taken proportional to the concentration of univalent ions of opposite charge:

$$I_+(x=0) = \frac{c_-(x=0)}{c_-(x=\infty)} I(x=\infty)$$

$$I_-(x=0) = \frac{c_+(x=0)}{c_+(x=\infty)} I(x=\infty) \quad [5]$$

where $I_+(x=0)$ is the ionic strength used for calculating the activity coefficient of the cations etc.

In both equations [4] and [5], concentrations were calculated with $f_i^\infty/f_i = 1$; the approximation involved was considered to be a second order effect.

Fig. 1. The potential and activity coefficients in the liquid phase for $\zeta = -17.4$ mV, $[\text{Ca}^{2+}] = 2,24 \times 10^{-3}$ M and $[\text{Na}^+] = 10^{-2}$ M. —●—●— calculated activity coefficient. — activity coefficient used for the calculation of σ_ζ

The procedure may be illustrated by figure 1 showing for $\zeta = -17.4$ mV at $[\text{Na}^+] = 10^{-2}$ M and $[\text{Ca}^{2+}] = 2,24 \times 10^{-3}$ M the course of: a) the potential as calculated from [4]; b) the activity coefficients as calculated from the Debye-Hückel relation using [5] for the ionic strength; c) the activity coefficients as used in the calculation of σ_ζ .

Results and discussion

The ζ -potential of the hydrates in the two stages of the reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ with water and NaOH solutions is shown in figure 2. Because of the influence of NaOH on the time at which the reaction stages occur (8), samples

Fig. 2. The ζ -potential of the calcium aluminate hydrates during the reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ with NaOH solutions versus the NaOH concentration. I: reaction stage I (both hexagonal hydrates and $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$). II: reaction stage II ($\text{Ca}_3\text{Al}_2(\text{OH})_{12}$)

were taken after different times according to the NaOH concentration (table 1).

Table 1.

NaOH concentration (M)	stage	time	Concentration mmol. l ⁻¹	
			Ca ²⁺	Al(OH) ₄ ⁻
0	I	4 h	11.6	2.5
0	II	8.33 h	6.6	4.5
0.01	I	2.33 h	7.7	2.2
0.01	II	5.50 h	3.4	2.8
0.02	I	2 h	5.3	3.1
0.02	II	4.83 h	2.5	2.4
0.04	I	1 h	2.2	4.1
0.04	II	4 h	2.0	2.0
0.1	I	0.83 h	0.9	6.1
0.1	II	3.50 h	0.9	2.2

The experiments shown in figure 2 in stage I all refer to the ζ -potential of the hexagonal hydrates; in the electrophoresis cell these hydrates were easily distinguishable as platey crystals from $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$. No difference, however, was found in the behaviour of the two types of hydrates. In the second stage only $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ is present, as evidenced by X-ray analysis.

From the ζ -potential and the concentration of ions the surface charge behind the electrokinetic slipping plane was calculated using Eq. [3] (fig. 3). The concentrations of $\text{Ca}(\text{OH})^+$ and Ca^{2+} were calculated using the equilibrium constant $K = \frac{f^\infty(\text{Ca}^{2+})[\text{Ca}^{2+}]f^\infty(\text{OH}^-)[\text{OH}^-]}{f^\infty(\text{CaOH}^+)[\text{CaOH}^+]} = 0,043$ (15), the activity coefficients were

Fig. 3. The net change behind the electrokinetic slipping plane versus the NaOH concentration for both reaction stages

Fig. 4. The ζ -potential of the hydrates during the reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ with a 0.01 M NaOH solution versus time

estimated using the modified Debye-Hückel formula as given by Gimblett and Monk (15).

The ζ -potential of the hydrates during the reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ with an 0.01 M NaOH solution is shown in figure 4. During 140 h the ζ -potential does not change significantly, only in the period short after the recrystallization of the hexagonal hydrates into $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ (after 5 hours), the ζ -potential is lower (this lowering of the ζ -potential is also found for the other NaOH concentrations, compare in fig. 2, stages I and II).

The Ca^{2+} and $\text{Al}(\text{OH})_4^-$ concentrations, however, vary during the reaction (see table 1). A similar change in concentrations had been observed previously (16, 17). In that case the change comes more or less to a standstill after about 20 h reaction, but the Ca^{2+} and $\text{Al}(\text{OH})_4^-$ concentrations at this point still have a value considerably larger than the equilibrium concentrations of these ions in the system $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ (18).

The large positive ζ -potential and the increasing σ_z when the NaOH concentration increases indicate, that a surface layer exists on the hydrate particles in which the charge of the Ca^{2+} ions is not fully compensated by that of the anions (aluminate and OH^- ions). Such a layer can be envisaged to originate either by withdrawal of aluminate ions from $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ and only partial replacement by OH^- , or by chemisorption of Ca^{2+} or $\text{Ca}(\text{OH})^+$ ions from the solution: Chemisorption of Na^+ to the extent required is unknown on oxidic surfaces. It is true that the crystal structure of the hexagonal hydrates would give rise to a positive surface charge if layers with overall composition $\text{Ca}_2\text{Al}(\text{OH})_6^+$ would form the outermost part of the crystals (4). However, the increasing positive surface charge with in-

creasing NaOH concentrations (see fig. 3) can only be explained by withdrawal of aluminate ions from the solid. Moreover, a positive surface charge is observed on $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ as well, at least in non-equilibrium solutions; when equilibrium between $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ and the solution is obtained the surface charge is negative (see later). The layer existing on the surface of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ hinders further growth of the crystals and a solution, supersaturated towards $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ and crystalline $\gamma\text{-Al}(\text{OH})_3$, can be kept for a certain time with $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ present in it. A similar surface layer on the surface of the $\text{Ca}_3\text{Al}_2\text{O}_6$ has been proposed as an important factor in the reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ with NaOH solutions (8) from reaction rate data.

Table 2.

NaOH added (M)	concentration (mmol l^{-1})	
	Ca^{2+}	$\text{Al}(\text{OH})_4^-$
0	2.99	1.64
0.01	2.24	1.53
0.02	1.70	1.31
0.04	1.16	1.08
0.1	0.70	0.74

Figure 5 shows the ζ -potential of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$, prepared separately in an autoclave, and dispersed in water and NaOH solutions which, before the experiment, were saturated towards $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$. The con-

Fig. 5. The ζ -potential and charge behind the electrokinetic slipping plane for $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ when re-dispersed in water and NaOH solutions saturated towards it. ● charge calculated taking $f_i^\infty/f_i = 1$. + charge calculated from Eq. [3]

centrations of Ca^{2+} and $\text{Al}(\text{OH})_4^-$ in these solutions are given in table 2.

The Ca^{2+} and $\text{Al}(\text{OH})_4^-$ concentrations of the liquid phase in water are situated in the phase diagram of the ternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ on the extension of the solubility curve of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ (saturated towards $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ but supersaturated towards crystalline $\gamma\text{-Al}(\text{OH})_3$).

The σ_ζ calculated using both the equation based on the Gouy-Chapman theory and eq. [3] are compared in figure 5. The absolute value of the σ_ζ in the first case is larger than in the latter, where the change of the activity coefficients is taken into account.

As long as OH^- ions are regarded as potential determining ions for the hydrates and oxides (19, 20), the ζ -potential is expected to be negative as is found in the experiments using the "equilibrium" solution; σ_ζ should be negative in that case and become even more so when the $[\text{OH}^-]$ increases (see e.g., the results of *Rutgers* and *de Smet* on pyrex glass (21)).

To elucidate the cause of the difference in ζ -potential of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ in both systems we followed the ζ -potential as a function of time for three conditions (fig. 6):

1. 100 μl of the suspension obtained after 140 h reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ in 0.01 M NaOH were added to 100 ml 0.01 M NaOH solution saturated towards $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ (solution A).
2. $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ dispersed into 0.01 M NaOH solution saturated towards $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ (solution A).
3. $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ dispersed into the liquid phase obtained after 6 h reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ in 0.01 M NaOH (solution B).

In all three experiments the ζ -potential changes sign from positive to negative and reaches a value of about -18 mV. In experiments 1 and 2, $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ from two different sources is brought into a solution saturated towards it. $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ formed during the reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ with water and NaOH solutions needs more time to change sign and reach the "equilibrium value" of the ζ -potential than $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ prepared in advance in an autoclave. This supports the presence of a disordered surface layer in the former case.

Fig. 6. The ζ -potential versus time. A) $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ (autoclave) in solution A. B) $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ (after 140 h $\text{Ca}_3\text{Al}_2\text{O}_6$ reaction) in solution A. C) $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ (autoclave) in solution B

In the third experiment the liquid phase is supersaturated towards both $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ and crystalline $\gamma\text{-Al}(\text{OH})_3$. The result can be interpreted as indicating that the surface layer becomes disordered similar to $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ formed during the reaction. The recrystallization is very slow, but at a certain point it is so far advanced that precipitation from the solution can occur and the concentrations of Ca^{2+} and $\text{Al}(\text{OH})_4^-$ change (after 140 h the Ca^{2+} concentration has decreased from 3.4 to 2.6 mmol l^{-1} , the $\text{Al}(\text{OH})_4^-$ concentration from 2.8 to 2.0 mmol l^{-1}) while the ζ -potential decreases to a value of about -10 mV.

Conclusion

ζ -potential measurements show that the surface charge on Ca-aluminate hydrates in the solution obtained during the reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ with water and NaOH solutions is positive, whereas the surface charge becomes negative in a solution saturated towards $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$. The positive surface charge indicates the presence of a surface layer on the calcium aluminate hydrates with Ca^{2+} ions, whose charge is not completely compensated by that of anions present either in the solid or in its direct vicinity. The presence of this layer can account for the prolonged coexistence of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ and a solution supersaturated towards this compound.

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Summary

The surface charge of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ in water and NaOH solutions is negative when the solution is saturated towards this compound. When $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ is formed during the reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ with water and NaOH solutions a positive surface charge is present. This positive charge is also found for other hydrates existing during this reaction; it indicates a disturbed surface layer with excess Ca^{2+} ions on the solid. Further it was shown that the absolute value of the surface charge calculated with the change of the activity coefficient in the diffuse double-layer taken into account is smaller than calculated with the equation without this correction.

Zusammenfassung

Die Oberflächenladung von $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ in Wasser oder NaOH-Lösungen ist negativ, wenn die Lösung gegenüber der Verbindung gesättigt ist. Dagegen hat $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$, wenn es während der Reaktion von $\text{Ca}_3\text{Al}_2\text{O}_6$ mit Wasser oder NaOH-Lösungen entsteht, eine positive Oberflächenladung. Diese positive Ladung wird auch gefunden bei anderen Hydraten, die während dieser Reaktion entstehen; dieses deutet auf eine gestörte Oberflächenschicht mit einem Überschuß an Ca^{2+} -Ionen. Der absolute Wert der berechneten Oberflächenladung wird anders, wenn für die Veränderung des Aktivitätskoeffizienten in der diffusen Doppelschicht korrigiert wird.

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