Electrokinetic properties of calcium aluminate hydrates

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Introduction

Calcium aluminate hydrates are formed when Ca$_3$Al$_2$O$_6$, a compound present in Portland cement, reacts with water (1-3). At 25 °C two metastable hydrates Ca$_2$Al(OH)$_6$·OH$^-$·3H$_2$O and Ca$_2$Al(OH)$_6$·Al(OH)$_6$·3H$_2$O are formed in the first stage of the reaction; these hydrates, present as hexagonal plates, have a structure consisting of Ca$_2$Al(OH)$_6$ sheets with H$_2$O and respectively OH$^-$ and Al(OH)$_6$ 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 Ca$_3$Al$_2$(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$_2$O on the reaction of Ca$_3$Al$_2$O$_6$ with water (7, 8).

Experimental

Ca$_3$Al$_2$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. Ca$_3$Al$_2$(OH)$_12$ was prepared in an autoclave from Ca$_3$Al$_2$O$_6$ and water as described by Thorrildson 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 Ca$_3$Al$_2$(OH)$_12$ were prepared by dispersing Ca$_3$Al$_2$(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.

Ca$_3$Al$_2$(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 Ca$_3$Al$_2$O$_6$ (1 g) with water and NaOH solutions (100 ml) took place in a polythene vessel at 25° ± 0.1 °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 Ca$_3$Al$_2$O$_6$ particles to settle. The ζ-potential of the hydrate crystals present in suspension after the settling was measured electro-photometrically 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 Ca$_3$Al$_2$(OH)$_12$ particles as determined by SEM, ranges from 100 to 1000 nm, while the thickness of the double layer ζ$^{-1}$ 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 \( \zeta \)-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:

\[
m_i = \frac{f_i^\infty}{f_i} \cdot n_i^\infty \cdot \exp \left( -\frac{z_i \psi}{kT} \right)
\]

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

\[
\sigma_z = \left( 2e_0 \epsilon_r \epsilon \sum_i z_i n_i^\infty \right) \int_0^\infty \frac{f_i^\infty}{f_i} \cdot \exp \left( -\frac{z_i \psi}{kT} \right) \, d\psi
\]

The ratio \( f_i^\infty/f_i \) 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 \( \sigma_z \) 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 \( \sigma_z \) increases with increasing NaOH concentration (see later), we estimated this effect, comparing \( \sigma_z \) calculated on the assumption \( f_i^\infty/f_i = 1 \) throughout the diffuse double layer with \( \sigma_z \) calculated on the following assumptions. For the region \( 0 < x < \infty^{-1} \) (\( x \) distance from the slipping plane, \( x = \) the Debye-Hückel parameter) \( f_i \) was taken equal to \( f_i^\infty \) at \( x = 0 \); for \( x > \infty^{-1} \), \( f_i \) was taken to be \( = f_i^\infty \). Thus:

\[
\sigma_z = \left( 2e_0 \epsilon_r \epsilon \sum_i z_i n_i^\infty \right) \left( \frac{f_i^\infty}{f_i} \cdot \exp \left( -\frac{z_i \psi}{kT} \right) \right) \left( 1 - \frac{f_i^\infty}{f_i} \right) \exp \left( -\frac{z_i \psi x}{kT} \right)\right]\]

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

\[
\frac{\sqrt{(x^2 - \gamma^2)} \exp \left( \frac{\psi x}{kT} \right) + \gamma^2 - x}{\sqrt{(x^2 - \gamma^2)} \exp \left( \frac{\psi x}{kT} \right) + \gamma^2 + x}
\]

\[
= \exp(-\psi x) \frac{\sqrt{(x^2 - \gamma^2)} \exp \left( \frac{\psi x}{kT} \right) + \gamma^2 - x}{\sqrt{(x^2 - \gamma^2)} \exp \left( \frac{\psi x}{kT} \right) + \gamma^2 + x}
\]

where \( \gamma^2 = \frac{2e_0 \epsilon_r \epsilon^\infty}{e_0 \epsilon_r \epsilon \infty} \); 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:

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

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

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.
The procedure may be illustrated by figure 1 showing for $\zeta = -17.4$ mV at $[Na^+] = 10^{-2}$ M and $[Ca^{2+}] = 2.24 \times 10^{-3}$ 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 $\sigma_z$.

Results and discussion

The $\zeta$-potential of the hydrates in the two stages of the reaction of $Ca_3Al_2O_6$ 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 were taken after different times according to the NaOH concentration (table 1).

Table 1.

<table>
<thead>
<tr>
<th>NaOH concentration (M)</th>
<th>stage</th>
<th>time</th>
<th>$Ca^{2+}$</th>
<th>$Al(OH)_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>I</td>
<td>4 h</td>
<td>11.6</td>
<td>2.5</td>
</tr>
<tr>
<td>0</td>
<td>II</td>
<td>8.33 h</td>
<td>6.6</td>
<td>4.5</td>
</tr>
<tr>
<td>0.01</td>
<td>I</td>
<td>2.33 h</td>
<td>7.7</td>
<td>2.2</td>
</tr>
<tr>
<td>0.01</td>
<td>II</td>
<td>5.50 h</td>
<td>3.4</td>
<td>2.8</td>
</tr>
<tr>
<td>0.02</td>
<td>I</td>
<td>2 h</td>
<td>5.3</td>
<td>3.1</td>
</tr>
<tr>
<td>0.02</td>
<td>II</td>
<td>4.83 h</td>
<td>2.5</td>
<td>2.4</td>
</tr>
<tr>
<td>0.04</td>
<td>I</td>
<td>1 h</td>
<td>2.2</td>
<td>4.1</td>
</tr>
<tr>
<td>0.04</td>
<td>II</td>
<td>4 h</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>0.1</td>
<td>I</td>
<td>0.83 h</td>
<td>0.9</td>
<td>6.1</td>
</tr>
<tr>
<td>0.1</td>
<td>II</td>
<td>3.50 h</td>
<td>0.9</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The experiments shown in figure 2 in stage I all refer to the $\zeta$-potential of the hexagonal hydrates; in the electrophoresis cell these hydrates were easily distinguishable as platey crystals from $Ca_3Al_2(OH)_{12}$. No difference, however, was found in the behaviour of the two types of hydrates. In the second stage only $Ca_3Al_2(OH)_{12}$ is present, as evidenced by X-ray analysis.

From the $\zeta$-potential and the concentration of ions the surface charge behind the electrokinetic slipping plane was calculated using Eq. [3] (fig. 3). The concentrations of $Ca(OH)^+$ and $Ca^{2+}$ were calculated using the equilibrium constant $K = \frac{f^\infty(Ca^{2+})[Ca^{2+}]}{f^\infty(OH^-)[OH^-]} = 0.043$ (15), the activity coefficients were
estimated using the modified Debye-Hückel formula as given by Gimblett and Monk (15).

The \( \zeta \)-potential of the hydrates during the reaction of Ca\(_3\)Al\(_2\)O\(_6\) with a 0.01 M NaOH solution is shown in figure 4. During 140 h the \( \zeta \)-potential does not change significantly, only in the period short after the recrystallization of the hexagonal hydrates into Ca\(_3\)Al\(_2\)(OH)\(_12\) (after 5 hours), the \( \zeta \)-potential is lower (this lowering of the \( \zeta \)-potential is also found for the other NaOH concentrations, compare in fig. 2, stages I and II).

The Ca\(^{2+}\) and Al(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 Al(OH)\(_4\) concentrations at this point still have a value considerably larger than the equilibrium concentrations of these ions in the system CaO–Al\(_2\)O\(_3\)–H\(_2\)O (18).

The large positive \( \zeta \)-potential and the increasing \( \sigma_\zeta \) 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 Ca\(_3\)Al\(_2\)(OH)\(_12\) and only partial replacement by OH\(^-\), or by chemisorption of Ca\(^{2+}\) or Ca(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 Ca\(_3\)Al(OH)\(_9\) would form the outermost part of the crystals (4). However, the increasing positive surface charge with increasing 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 Ca\(_3\)Al\(_2\)(OH)\(_12\) as well, at least in non-equilibrium solutions; when equilibrium between Ca\(_3\)Al\(_2\)(OH)\(_12\) and the solution is obtained the surface charge is negative (see later). The layer existing on the surface of Ca\(_3\)Al\(_2\)(OH)\(_12\) hinders further growth of the crystals and a solution, supersaturated towards Ca\(_3\)Al\(_2\)(OH)\(_12\) and crystaline \( \gamma \)-Al(OH)\(_3\), can be kept for a certain time with Ca\(_3\)Al\(_2\)(OH)\(_12\) present in it. A similar surface layer on the surface of the Ca\(_3\)Al\(_2\)O\(_6\) has been proposed as an important factor in the reaction of Ca\(_3\)Al\(_2\)O\(_6\) with NaOH solutions (8) from reaction rate data.

<table>
<thead>
<tr>
<th>NaOH added concentration (M)</th>
<th>Ca(^{2+}) (mmol l(^{-1}))</th>
<th>Al(OH)(_4) (mmol l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.99</td>
<td>1.64</td>
</tr>
<tr>
<td>0.01</td>
<td>2.24</td>
<td>1.53</td>
</tr>
<tr>
<td>0.02</td>
<td>1.70</td>
<td>1.31</td>
</tr>
<tr>
<td>0.04</td>
<td>1.16</td>
<td>1.08</td>
</tr>
<tr>
<td>0.1</td>
<td>0.70</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Figure 5 shows the \( \zeta \)-potential of Ca\(_3\)Al\(_2\)(OH)\(_12\), prepared separately in an autoclave, and dispersed in water and NaOH solutions which, before the experiment, were saturated towards Ca\(_3\)Al\(_2\)(OH)\(_12\). The con-
centrations of Ca\(^{2+}\) and Al(OH)\(_4\) in these solutions are given in table 2.

The Ca\(^{2+}\) and Al(OH)\(_4\) concentrations of the liquid phase in water are situated in the phase diagram of the ternary system CaO-Al\(_2\)O\(_3\)-H\(_2\)O on the extension of the solubility curve of Ca\(_3\)Al\(_2\)(OH)\(_12\) (saturated towards Ca\(_3\)Al\(_2\)(OH)\(_12\) but supersaturated towards crystalline \(\gamma\)-Al(OH)\(_3\).

The \(\sigma_z\) calculated using both the equation based on the Gouy-Chapman theory and eq. [3] are compared in figure 5. The absolute value of the \(\sigma_z\) 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 \(\zeta\)-potential is expected to be negative as is found in the experiments using the "equilibrium" solution; \(\sigma_z\) should be negative in that case and become even more so when the [OH\(^-\)] increases (see e.g., the results of Rutgers and de Smet on pyrex glass (21)).

To elucidate the cause of the difference in \(\zeta\)-potential of Ca\(_3\)Al\(_2\)(OH)\(_12\) in both systems we followed the \(\zeta\)-potential as a function of time for three conditions (fig. 6):

1. 100 \(\mu\)l of the suspension obtained after 140 h reaction of Ca\(_3\)Al\(_2\)O\(_6\) in 0.01 M NaOH were added to 100 ml 0.01 M NaOH solution saturated towards Ca\(_3\)Al\(_2\)(OH)\(_12\) (solution A).
2. Ca\(_3\)Al\(_2\)(OH)\(_12\) dispersed into 0.01 M NaOH solution saturated towards Ca\(_3\)Al\(_2\)(OH)\(_12\) (solution A).
3. Ca\(_3\)Al\(_2\)(OH)\(_12\) dispersed into the liquid phase obtained after 6 h reaction of Ca\(_3\)Al\(_2\)O\(_6\) in 0.01 M NaOH (solution B).

In all three experiments the \(\zeta\)-potential changes sign from positive to negative and reaches a value of about \(-18\) mV. In experiments 1 and 2, Ca\(_3\)Al\(_2\)(OH)\(_12\) from two different sources is brought into a solution saturated towards it. Ca\(_3\)Al\(_2\)(OH)\(_12\) formed during the reaction of Ca\(_3\)Al\(_2\)O\(_6\) with water and NaOH solutions needs more time to change sign and reach the "equilibrium value" of the \(\zeta\)-potential than Ca\(_3\)Al\(_2\)(OH)\(_12\) prepared in advance in an autoclave. This supports the presence of a disordered surface layer in the former case.

![Fig. 6. The \(\zeta\)-potential versus time. A) Ca\(_3\)Al\(_2\)(OH)\(_12\) (autoclave) in solution A. B) Ca\(_3\)Al\(_2\)(OH)\(_12\) (after 140 h Ca\(_3\)Al\(_2\)O\(_6\) reaction) in solution A. C) Ca\(_3\)Al\(_2\)(OH)\(_12\) (autoclave) in solution B](image)

In the third experiment the liquid phase is supersaturated towards both Ca\(_3\)Al\(_2\)(OH)\(_12\) and crystalline \(\gamma\)-Al(OH)\(_3\). The result can be interpreted as indicating that the surface layer becomes disordered similar to Ca\(_3\)Al\(_2\)(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 Al(OH)\(_4\) change (after 140 h the Ca\(^{2+}\) concentration has decreased from 3.4 to 2.6 mmol 1\(^{-1}\), the Al(OH)\(_4\) concentration from 2.8 to 2.0 mmol 1\(^{-1}\) while the \(\zeta\)-potential decreases to a value of about \(-10\) mV.

**Conclusion**

\(\zeta\)-potential measurements show that the surface charge on Ca-aluminate hydrates in the solution obtained during the reaction of Ca\(_3\)Al\(_2\)O\(_6\) with water and NaOH solutions is positive, whereas the surface charge becomes negative in a solution saturated towards Ca\(_3\)Al\(_2\)(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 Ca\(_3\)Al\(_2\)(OH)\(_12\) and a solution supersaturated towards this compound.
Acknowledgement

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Summary

The surface charge of Ca$_3$Al$_2$(OH)$_{12}$ in water and NaOH solutions is negative when the solution is saturated towards this compound. When Ca$_3$Al$_2$(OH)$_{13}$ is formed during the reaction of Ca$_3$Al$_2$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 Ca$_3$Al$_2$(OH)$_{12}$ in Wasser oder NaOH-Lösungen ist negativ, wenn die Lösung gegenüber der Verbindung gesättigt ist. Dagegen hat Ca$_3$Al$_2$(OH)$_{13}$, wenn es während der Reaktion von Ca$_3$Al$_2$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; dies deutet auf eine gestörte Oberflächenrichtung 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.

References


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