Evaluating the growth parameters of Ca(OH)$_2$ crystals in a liquid solution on the basis of soft X-ray microscopy imaging

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In this study, we demonstrate a possibility to evaluate the main physical parameters, associated with the growth process of a solid phase in a liquid solution, on the basis of successive recording of a series of soft X-ray images from the solution and theoretical modeling of the growth process. The proposed approach is applied to quantitative analysis of the growth-associated parameters of Ca(OH)$_2$ colloidal crystals at an early stage of their precipitation in a dilute aqueous cement solution. Theoretical modeling of the experimentally established time-dependent variation of characteristic sizes of individual Ca(OH)$_2$ crystals results in evaluation of the supersaturation of solution, kinetic and diffusion coefficients, growth rates of crystal facets as well as the crystal sizes at transition of the growth regime from kinetic to diffusive.

**Keywords:** soft X-ray microscopy; liquid solution; calcium hydroxide; growth parameters

1. Introduction

Soft X-ray microscopy [1,2] is a powerful tool for studying the physicochemical properties of inorganic materials [1–3], biological objects [4] as well as growth processes of solids in liquid solutions [5]. This technique has been particularly successful for in situ observation and analysis of through-solution hydration products and products of topochemical reactions, which form in aqueous cement solutions [5–7]. The soft X-ray microscopy investigations may be conducted not only on a microscope installed at a synchrotron radiation facility [1,3], but also may be carried out on microscopes operating at laboratory conditions [2]. Owing to advances in preparation of Fresnel zone plates [8], it is expected that in near future the spatial resolution in soft X-ray microscopy may be enhanced up to ≈10 nm that considerably exceeds the level of the spatial resolution in above-mentioned earlier studies, = 30–40 nm [2–7]. This may provide a remarkable possibility of tracing the early growth process in a liquid solution of precipitating individual particles in a broad range of variation of their sizes at the nano-size level. Not only could such a high spatial resolution enable the observation and quantitative analysis of the progress in the growth process of a solid phase in a liquid solution, but this methodology could also enable – under certain physical conditions – tracing the shape and size variations of individual molecular clusters and their transformation into critical nuclei of the precipitating phase.

In this study, we demonstrate a possibility to evaluate the physical parameters, associated with the growth process of a solid phase in a liquid solution, on the basis of successive recording of a series of soft X-ray images from the solution and theoretical modeling of the growth process. The proposed approach is applied to quantitative analysis of the growth-associated parameters of the Ca(OH)$_2$ (calcium hydroxide) colloidal crystals at an early stage of their precipitation in a dilute aqueous cement solution. Theoretical modeling of the experimentally established time-dependent variation of characteristic sizes of individual Ca(OH)$_2$ crystals results in evaluation of the supersaturation of solution, growth rates of crystal facets, kinetic and diffusion coefficients, and crystal sizes at transition of the growth regime from kinetic to diffusive. Ca(OH)$_2$ is one of the main hydration products in cementitious materials and understanding of the mechanisms that control precipitation of this phase in cement solutions is of a principle importance in chemistry of cement hydration. Besides, the Ca(OH)$_2$ is a compound of a practical interest driven by its numerous applications in chemical industry, industries of food production and storage, medicine, pharmacology, ecology and environmental safety. In above mentioned industrial and scientific areas, it is of a special interest the peculiarities of precipitation and morphological features of nano- and micron-sized Ca(OH)$_2$ crystals in aqueous solutions and media.

2. Experiment

A dilute cementitious solution with water–to–cement ratio of = 50 was prepared by mixing Type K cement (a blend of ASTM Type II Portland cement with 6% calcium sulfoaluminate expansive admixture, Ca$_4$Al$_6$O$_{12}$SO$_4$) for 50 sec in freshly boiled deionized water preliminarily saturated with respect to Ca(OH)$_2$ and gypsum. The solution was preliminarily saturation to the Ca(OH)$_2$ and gypsum to compensate its dilution and to mimic cement pore solutions more closely in terms of precipitation of the Ca(OH)$_2$ and ettringite phases. Immediately after the preparation procedure, the solution was centrifuged for 15 sec to remove particles larger in size than 10 μm. The removal of large size particles was necessary since, for soft X-rays to be transmitted with sufficient intensity through a sample of aqueous cement solution, the thickness of the sample must be limited to about 10 μm. A small droplet was taken from the supernatant solution and assembled in the sample holder, and then squeezed between two 100 nm thin Si$_3$N$_4$
windows that are transparent for transmission of soft X-rays. During the image recording procedure, these Si$_3$N$_4$ windows are sandwiched between stainless steel plates fitted with rubber o-rings to minimize evaporation and exposure to CO$_2$. The procedure of a solution sample preparation is described in more detail in our earlier study [7].

The soft X-ray imaging of the solution sample was conducted on microscope XM-1 operating at Beamline 6.1.2 of the Advanced Light Source (LBN Laboratory, Berkeley, CA, USA). The X-ray optical setup of this microscope is in detail described in Ref. [9]. In this study, radiation with a wavelength of 2.4 nm (516.6 eV) was used. The radiation transmitted by the sample was detected using an X-ray CCD camera, with a resolution of $\approx 40$ nm and magnification

![Fig. 1](image.jpg)

*Fig. 1* Soft X-ray images recorded from aqueous cement solution during 178 min observation time-interval after the procedure of solution preparation. In all images, both the black and white arrows indicate the growing Ca(OH)$_2$ colloidal crystals. The black arrows indicate two Ca(OH)$_2$ particles (No 1 and N 2) with favorable orientations allowing directly to trace and measure the time-dependent variation of their characteristic sized $L_1$ and $L_2$ specified in Fig. 2. The scale bar in all images is 1 $\mu$m. The time of recording of each image, passed after preparation of the solution, is indicated under the image.
factor of 2000. The recorded images have a circular field of view of approximately 10 μm in diameter, as shown in Fig. 1. The illumination time per image was in the range 5–8 sec. The experimental work was conducted at room temperature $T = 298$ K. Figure 1 shows the soft X-ray images recorded from solution during 178 min observation time-interval after the procedure of solution preparation. On average, during this time-interval the seven images were recorded every 25.4 min.

The colloidal crystals imaged in Fig. 1 do not belong to ettringite phase that typically precipitates in cement solutions as needle-like crystals [7]. According to a motivation presented in our earlier study [7], the colloidal plate-like crystals imaged in Fig. 1a–g may be in a reliable way identified as belonging to Ca(OH)$_2$. These crystals are imaged in Fig. 1a–g in different crystallographic projections that definitely belong to particles with a hexagonal-prism shape, as is schematically depicted in Fig. 2. As specified in Fig. 2, the Ca(OH)$_2$ crystals imaged in Fig. 1 are faceted by morphologically important $\{10\bar{1}0\}$ and $\{0001\}$ type facets and are characterized by linear sizes $L_1$ and $L_2$ along the $<10\bar{1}0>$ and $<0001>$ crystallographic directions, respectively. Under a wide variety of physicochemical conditions [10–12], the Ca(OH)$_2$ crystals precipitate in aqueous solution with aspect ratios $R_L$ satisfying the condition $R_L = L_1/L_2 > 1$. The morphology of the Ca(OH)$_2$ crystals imaged in Fig. 1a–g obeys this condition. The $<10\bar{1}0>$ and $<0001>$ crystallographic directions indicate correspondingly the growth directions of the $\{10\bar{1}0\}$ and $\{0001\}$ type facets of an individual Ca(OH)$_2$ crystal, and the measurements of the time-dependent variation of characteristic sizes $L_1$ and $L_2$ may result in determination of the corresponding growth rates of these facets. The images presented in Figure 1 show that the relative locations and orientation of the growing Ca(OH)$_2$ crystals in solution are preserved in time. That is to say, during the growth process, no strong convective fluxes were generated in the solution and the growing particles remained practically immobile. This provided a possibility in this study to trace and measure the time-dependent variations in the linear sizes of growing Ca(OH)$_2$ crystals. It is clear that a complete analysis of the growth process for an imaged individual Ca(OH)$_2$ crystal may be conducted only for its such a type orientation (projection on plane of the recorded image) that is favorable for simultaneous measurements of the characteristic sizes $L_1$ and $L_2$ specified in Fig. 2. In images presented in Fig. 1, such a type favorable orientation exhibit the two Ca(OH)$_2$ particles numbered as 1 and 2. These particles are viewed (projected) in recorded images along $<1\bar{2}10>$ type crystallographic direction (see Fig. 2b) and for them the sizes $L_1$ and $L_2$ was directly measured in the recorded images. For these particles, Fig. 3 presents the variation of measured sizes $L_i(t = 1, 2)$ and calculated aspect ratio $R_L(t = L_1/L_2)$ versus time. Within accuracy of size measurements, no size variation was detected for imaged Ca(OH)$_2$ crystals in the time interval $t > 158$ min, i.e. after recording of the image presented in Fig. 1f, and this size stabilization was preserved.

![Fig. 2](image)

**Fig. 2** (a) Plate-like morphology of a Ca(OH)$_2$ crystal faceted by $\{0001\}$ basal and $\{10\bar{1}0\}$ prismatic facets. $L_2$ is the characteristic size along the $<0001>$ crystallographic direction. (b) View at a $\{0001\}$ facet along the $<0001>$ direction. $L_1$ is the characteristic size along the $<10\bar{1}0>$ crystallographic directions.

$<10\bar{1}0>$ and $<0001>$ crystallographic directions, respectively. Under a wide variety of physicochemical conditions [10–12], the Ca(OH)$_2$ crystals precipitate in aqueous solution with aspect ratios $R_L$ satisfying the condition $R_L = L_1/L_2 > 1$. The morphology of the Ca(OH)$_2$ crystals imaged in Fig. 1a–g obeys this condition. The $<10\bar{1}0>$ and $<0001>$ crystallographic directions indicate correspondingly the growth directions of the $\{10\bar{1}0\}$ and $\{0001\}$ type facets of an individual Ca(OH)$_2$ crystal, and the measurements of the time-dependent variation of characteristic sizes $L_1$ and $L_2$ may result in determination of the corresponding growth rates of these facets. The images presented in Figure 1 show that the relative locations and orientation of the growing Ca(OH)$_2$ crystals in solution are preserved in time. That is to say, during the growth process, no strong convective fluxes were generated in the solution and the growing particles remained practically immobile. This provided a possibility in this study to trace and measure the time-dependent variations in the linear sizes of growing Ca(OH)$_2$ crystals. It is clear that a complete analysis of the growth process for an imaged individual Ca(OH)$_2$ crystal may be conducted only for its such a type orientation (projection on plane of the recorded image) that is favorable for simultaneous measurements of the characteristic sizes $L_1$ and $L_2$ specified in Fig. 2. In images presented in Fig. 1, such a type favorable orientation exhibit the two Ca(OH)$_2$ particles numbered as 1 and 2. These particles are viewed (projected) in recorded images along $<1\bar{2}10>$ type crystallographic direction (see Fig. 2b) and for them the sizes $L_1$ and $L_2$ was directly measured in the recorded images. For these particles, Fig. 3 presents the variation of measured sizes $L_i(t = 1, 2)$ and calculated aspect ratio $R_L(t = L_1/L_2)$ versus time. Within accuracy of size measurements, no size variation was detected for imaged Ca(OH)$_2$ crystals in the time interval $t > 158$ min, i.e. after recording of the image presented in Fig. 1f, and this size stabilization was preserved.
Fig. 3  (a) Time-dependent variation of the characteristic linear sizes \( L_i \) \((i = 1, 2)\) and aspect ratio \( R_L = L_1/L_2 \) of Ca(OH)$_2$ particles No. 1 and No. 2 imaged in Fig. 1. The symbols (dots, triangles, and squares) represent the experimental data for above indicated parameters as specified in figure. The corresponding theoretical dependences \( L_i(t) \) \((i = 1, 2)\) and \( R_L(t) = L_1(t)/L_2(t) \) are given by solid and dashed lines according to Eq. (1) (Stage 1 of the growth process). At \( t \approx 4\) min, it takes place transition of the growth regime (TGR) from kinetic to diffusive. At \( t > 158 \) min (Stage 2), it was observed the size stabilization (SS) in the morphology of Ca(OH)$_2$ particles. (b) Time-dependent variation of the growth rates \( V_1 \) and \( V_2 \) of Ca(OH)$_2$ particles No. 1 in growth directions \( <10\bar{1}0> \) and \( <0001> \), respectively, according to Eq. (2). The plots \( V_1(t) \) and \( V_2(t) \) are performed for a time-interval \( 0 < t < 158 \) min with the upper limit \( t = 158 \) min at which the sizes of the particle are stabilized (see Fig. 3a).

During several hours, therefore, in our further analysis of the growth process of Ca(OH)$_2$ crystals, we distinguish two specific stages: Stage 1 and Stage 2 (see Fig. 3a). At Stage 1 with duration \( t < 158 \) min, the Ca(OH)$_2$ crystals grow in size, whereas at Stage 2, \( t > 158 \) min, the growth process of these crystals is practically suppressed.
3. Theorectica model

According to a theoretical model used in our earlier study [7], variation of characteristic sizes \( L_i(i = 1, 2) \) of a growing Ca(OH)\(_2\) crystal may be expressed as follows:

\[
L_i(t) = \left( \frac{2D}{\beta_i} \right)^2 + 8\Omega (C - C_{\text{eq}}) D t - \frac{2D}{\beta_i} \quad (i = 1, 2),
\]

where the subscript values \( i = 1 \) and \( i = 2 \) correspond to \( <1\overline{1}0\overline{1}> \) and \( <0001> \) growth directions (i.e., to \{1\overline{1}0\overline{1}\} and \{0001\} facets), respectively; \( \Omega \) is the unit cell volume of the Ca(OH)\(_2\), \( C \) is the actual concentration of dissolved Ca(OH)\(_2\) molecules in solution, \( \beta_i \) and \( C_{\text{eq}} \) are the growth kinetic coefficient and the equilibrium concentration of Ca(OH)\(_2\) molecules in solution at facets of the type \( i \), respectively, \( D \) is the effective diffusion coefficient of Ca\(^{2+}\) and OH\(^-\) ions, and \( t \) is the time. Equation 1 yields the growth rates of \{1\overline{1}0\overline{1}\} and \{0001\} type facets of a Ca(OH)\(_2\) crystal

\[
V_i(t) = \frac{1}{2} \frac{dL_i}{dt} = \frac{2\Omega (C - C_{\text{eq}}) D}{\left( \frac{2D}{\beta_i} \right)^2 + 8\Omega (C - C_{\text{eq}}) D t} \quad (i = 1, 2)
\]

where, again, the subscript values \( i = 1 \) and \( i = 2 \) correspond to growth rates in directions \( <1\overline{1}0\overline{1}> \) and \( <0001> \), respectively.

Analysis of Eqs. (1) and (2) yields that, during the growth process, transition of the growth regime from kinetic to diffusive takes place at particle sizes (for details, see Ref. [13])

\[
L_i^{(k\rightarrow d)} = \frac{2D}{\beta_i} \quad (i = 1, 2)
\]

At sizes \( L_i \) satisfying the condition

\[
L_i \ll L_i^{(k\rightarrow d)} = \frac{2D}{\beta_i} \quad (i = 1, 2),
\]

Eq. (1) reduces to a relationship

\[
L_i(t) = 2\Omega \beta_i (C - C_{\text{eq}}) t \quad (i = 1, 2),
\]

whereas in the size range

\[
L_i \gg L_i^{(k\rightarrow d)} = \frac{2D}{\beta_i} \quad (i = 1, 2),
\]

Eq. (1) may be approximated by an expression

\[
L_i(t) = \sqrt{8\Omega (C - C_{\text{eq}}) Dt} \quad (i = 1, 2).
\]

Accordingly, Eqs. (5) and (7) are valid with a sufficient accuracy for analysis of the growth process at kinetic and diffusion growth regimes, respectively. From Eq. (5) it follows that, at kinetic growth regime, the growth rate of \{1\overline{1}0\overline{1}\} and \{0001\} type facets is expressed as

\[
V_i(t) = \Omega \beta_i (C - C_{\text{eq}}) t \quad (i = 1, 2).
\]

4. Evaluation of the growth-associated parameters

In this section, we present the procedure of determination of the physical parameters of interest with the use of the obtained experimental data and the theoretical expressions given by Eqs. (1)–(3). This procedure is applied to Stage 1 of the growth process specified in Sec. 2 (see also Fig. 3a). In the modeling of the growth process of Ca(OH)\(_2\) crystals on the basis of Eq. (1), we assume that the actual concentration \( C \) of dissolved Ca(OH)\(_2\) molecules in solution was kept constant throughout the observation (imaging) time of the growth process. In the first approximation, this assumption seems valid since (i) solution under investigation was initially (prior to observation time) saturated with respect to Ca(OH)\(_2\), (ii) in dilute cement solutions, the supersaturation with respect to this phase reaches its maximal level during first several minutes of the cement hydration [14], and (iii) the consumption of Ca\(^{2+}\) and OH\(^-\) ions by growing Ca(OH)\(_2\)
crystals is presumably compensated by a release of the same type of ions in the solution as a result of hydration of cement grains. Within the theoretical model applied to this study (see Sec. 3), it is also assumed that the diffusion coefficient for dissolved constituent Ca\(^{2+}\) and OH\(^{-}\) ions in the solution is the same both throughout the solution and in the vicinity of growing \{10\(\bar{1}\)0\} and \{0001\} crystal facets. In the fitting procedure of the theoretical dependences \(L_i(t)(i = 1, 2)\), expressed by Eq. (1), to the corresponding experimental data presented in Fig. 3a, parameters \(C\), \(C_{si}(i = 1, 2)\), \(\beta_i (i = 1, 2)\), and \(D\) are considered as fitting parameters. With the use of a value \(5.488 \times 10^{-29}\) m\(^3\) for the unit cell volume \(\Omega\) of the Ca(OH)\(_2\), the data obtained for above specified parameters from the best fits are presented in Table 1. It is important to note that in spite of a large number of fitting parameters, the achievement of the best fits was favored by different parametric dependences of the sizes \(L_i(t)(i = 1, 2)\) (see Eq. (1)) on kinetic and diffusion coefficients: at an early stage of the growth process, the sizes \(L_i(t)(i = 1, 2)\) depend predominantly on kinetic coefficient (see Eq. (5)), whereas at later stage of the growth process, the sizes \(L_i(t)(i = 1, 2)\) depend predominantly on diffusion coefficient (see Eq. (7)). Besides, taking into account the results of our previous study [7], in the choice of the fitting values for concentrations \(C_{si}\) \((i = 1, 2)\), it was expected that these values are close to saturation (equilibrium) concentration \(C_e\) of Ca(OH)\(_2\) molecules in the solution under study. On the bases of results reported in study [15], this saturation concentration \(C_e\) is estimated to be \(1.156 \times 10^{-22}\) m\(^3\). With the use of the data for concentrations \(C\) and \(C_{si}(i = 1, 2)\) presented in Table 1, the supersaturation of solution \(S_i (i = 1, 2)\) at facets of Ca(OH)\(_2\) particles is calculated from expression \(S_i = (C - C_{si}) / C_{si}\). Figure 3b shows the time-dependent variation of the growth rates \(V_1\) and \(V_2\) of Ca(OH)\(_2\) particles No. 1 in growth directions <10\(\bar{1}\)0> and <0001>, respectively. The dependences \(V_1(t)\) and \(V_2(t)\) presented in Fig. 3b are plotted according to Eq. (2) with the use of the necessary data listed in Table 1. Equation (3) yields the data for the size parameter \(L_i^{(k \to d)}(i = 1, 2)\), which is associated with transition of the growth regime from kinetic to diffusive. As show the data in Table 1, achieved for parameter \(L_i^{(k \to d)}(i = 1, 2)\), and the plots in Fig. 3a, the transition of the growth regime from kinetic to diffusive takes place at \(t = 4\) min when the particle sizes are at a submicron level. For kinetic growth regime \((t < 4\) min\), the growth rates of facets \(V_{i,k}(i = 1, 2)\), which remain practically

### Table 1

<table>
<thead>
<tr>
<th>Parameter (unit)</th>
<th>Particle No. 1</th>
<th>Particle No. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C \times 10^{-25}) (m(^3))</td>
<td>1.173</td>
<td>1.173</td>
</tr>
<tr>
<td>(C_{si} \times 10^{-25}) (m(^3))</td>
<td>1.146</td>
<td>1.145</td>
</tr>
<tr>
<td>(C_{e2} \times 10^{-25}) (m(^3))</td>
<td>1.169</td>
<td>1.168</td>
</tr>
<tr>
<td>(S_1) (%)</td>
<td>2.36</td>
<td>2.40</td>
</tr>
<tr>
<td>(S_2) (%)</td>
<td>0.34</td>
<td>0.39</td>
</tr>
<tr>
<td>(\beta_1) ((\mu)m/min)</td>
<td>1800</td>
<td>2200</td>
</tr>
<tr>
<td>(\beta_2) ((\mu)m/min)</td>
<td>5165</td>
<td>5165</td>
</tr>
<tr>
<td>(D) ((\mu)m/(\mu)m)</td>
<td>270</td>
<td>270</td>
</tr>
<tr>
<td>(V_{1,k}) (nm/(\mu)m)</td>
<td>27</td>
<td>33</td>
</tr>
<tr>
<td>(V_{2,k}) (nm/(\mu)m)</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>(&lt;V_{1,d}&gt;) (nm/(\mu)m)</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>(&lt;V_{2,d}&gt;) (nm/(\mu)m)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>(l_{1}^{(k \to d)}, l_{2}^{(k \to d)}) ((\mu)m)</td>
<td>(= 0.17, = 0.07)</td>
<td>(= 0.19, = 0.08)</td>
</tr>
<tr>
<td>(l_{1}^{(eq)}, l_{2}^{(eq)}) ((\mu)m)</td>
<td>1.87, 0.77</td>
<td>2.02, 0.86</td>
</tr>
<tr>
<td>(p_{L}^{(eq)} (= l_{1}^{(eq)}/l_{2}^{(eq)}))</td>
<td>2.4</td>
<td>2.3</td>
</tr>
</tbody>
</table>
constant, may be determined either from Eq. (2) or from the approximate expression given by Eq. (8). During the diffusive growth regime (4 min < t < 158 min), the growth rates of facets considerably decrease with time (see Fig. 3b), and the average growth rates during this growth regime, \( V_{i,d} \) (i = 1, 2), are calculated with the use of Eq. (2). The data determined for above specified physical parameters are presented in Table 1. As specified in Sec. 2, within accuracy of size measurements, no size variation was detected for imaged Ca(OH)\(_2\) crystals in the time interval \( t > 158 \) min, i.e. after recording of the image presented in Fig. 1f, and this size stabilization was preserved during several hours (it should be noted that the size stabilization was achieved for all Ca(OH)\(_2\) particles indicated in Fig. 1f by arrows). The observed size stabilization may be interpreted as formation of conditions, at which the driving force of the growth process is suppressed and the Ca(OH)\(_2\) crystals preserve equilibrium sizes \( L_{i}^{eq} \) (i = 1, 2). According to plots in Fig. 3a, the equilibrium sizes \( L_{i}^{eq} \) (i = 1, 2) for Ca(OH)\(_2\) particles No. 1 and No. 2 are achieved at \( t = 158 \) min (Fig. 1f). The experimental data for sizes \( L_{i}^{eq} \) (i = 1, 2) and corresponding aspect ratio \( R_{i}^{eq} = \left( L_{i}^{eq} / W_{i}^{eq} \right) \) (i = 1, 2) are also presented in Table 1.

5. Discussion and conclusions

Because of limited contrast in the imaging of the crystal ribs (see Fig. 1), the relative error in the Ca(OH)\(_2\) crystal size measurements on the recorded images is estimated to be of about 3%. This error results in relative error at the level \( \approx 5 \) % in evaluating the growth parameters from fitting procedure of theoretical curves to experimental data (Sec. 4). The data presented in Table 1 show that, for two examined Ca(OH)\(_2\) particles, the values determined for all parameters either coincide or are very close to each other., as expected from the physical standpoint This in a certain degree is the evidence of a high sensitivity of the proposed approach in the analysis of the growth process of colloidal crystals in a liquid solution.

As discussed in our previous study [7], in the theoretical model [13] that results in Eq. (1), it is assumed that the saturation (equilibrium) concentration \( C_{eq} \) of solute molecules for a through-solution and homogeneously growing particle is the same at all its facets, \( C_{si} \) (i.e., is independent of the crystallographic orientation/type of a facet i). Accordingly, the theoretical model discussed in Ref. [13] assumes in Eqs. (1), (2), (5), (7), and (8) the replacement \( C_{si} = C_{eq} \). However, the results reported in our previous work [7] and this study show that, within accuracy of the fitting procedure for concentrations, \( \Delta C_{si} = \pm 10^{22} \) m\(^{-3}\), the equilibrium concentrations \( C_{s1} \) and \( C_{s2} \) determined correspondingly for \{10\(\bar{0}\)\} and \{0001\} type facets of a Ca(OH)\(_2\) crystal substantially differ from each other (see Table 1). It is reasonable to assume that the anisotropy in the parameters \( C_{s1} \) and \( C_{s2} \) results from anisotropy in the physical properties of \{10\(\bar{0}\)\} and \{0001\} surfaces of a Ca(OH)\(_2\) crystal. According to results reported in study [16], the adsorption energy of a Ca(OH)\(_2\) molecule on the \{10\(\bar{0}\)\} and \{0001\} surfaces of a Ca(OH)\(_2\) crystal is \(-2.13\) and \(-0.15\) eV, respectively. This means that the activation energy of desorption of the Ca(OH)\(_2\) molecules from \{0001\} type facets is considerably smaller than that from \{10\(\bar{0}\)\} type facets. Therefore, it may be expected that, at a given temperature of the solution saturated with respect to Ca(OH)\(_2\), the equilibrium concentration of Ca(OH)\(_2\) molecules in solution in the vicinity of the \{0001\} type facets, \( C_{s2} \), exceeds that in the vicinity of the \{10\(\bar{0}\)\} type facets, \( C_{s1} \). This argumentation in a certain degree explains the difference between the equilibrium concentrations \( C_{s1} \) and \( C_{s2} \) in the data presented in Table 1. Interestingly, for both examined Ca(OH)\(_2\) particles, the evaluated surface concentrations \( C_{s1} \) and \( C_{s2} \) and the saturation concentration \( C_{eq} = 1.165 \times 10^{25} \) m\(^{-3}\) of Ca(OH)\(_2\) molecules in the solution under study (see Sec. 4) are in a relation \( C_{s1} < C_{eq} < C_{s2} \). This means that the value of the saturation concentration far from the surface of a Ca(OH)\(_2\) particle (i.e., the bulk concentration), \( C_{eq} \), is changed at \{10\(\bar{0}\)\} and \{0001\} type facets in opposite ways.

The value determined for diffusion coefficient in this study, \( D = 270 \) \(\mu\)m\(^2\)/min = \(4.5 \times 10^{-12}\) m\(^2\)/sec (see Table 1), falls in the range of diffusivities that are exhibited by ionic species in cement solutions [17].

The suppression of the growth process of Ca(OH)\(_2\) crystals at Stage 2 (see Fig. 3a), may in potential result from the following physical factors: (i) drop of the solution supersaturation with respect to this phase, \( C > C_{si} \), down to the saturation level, \( C = C_{si} \) [see Eq. (2)], (ii) a drastic decrease in the diffusion coefficient of Ca\(^{2+}\) and OH\(^-\) ions [see Eq. (2)] because of possible increase of the internal pressure in the solution as a result of spatial confinement of the solution and phase transformations in it, and (iii) crystal surface poisoning with absorbed non-stoichiometric ions. A realistic analysis of the influence of above specified physical factors on growth process of Ca(OH)\(_2\) crystals at Stage 2 assumes the additional experimental and theoretical investigations, which will be conducted in our next study.
We did not observe in recorded images the homogeneous precipitation of the ettringite, which is one of the main hydration products in cement solutions. This phase presumably precipitated heterogeneously on some hydrating cement grains imaged as darkest areas at the left-hand side of Figs. 1a-g.

The idea of using successively recorded images of a crystal, precipitating in a liquid solution (not necessarily in aqueous solution), for theoretical quantitative evaluation of the growth-associated physical parameters is universal. This approach may be effective to study both homogeneous and heterogeneous precipitation of a solid phase in a liquid solution provided positions and orientations of the growing particles of interest remain stable during the imaging time-interval. In the analysis of the growth process of a precipitate by applying the approach described in this study, the choice of an appropriate theoretical model of the growth process is needed and this choice is dictated by physicochemical properties both of the precipitate and solvent [13].

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