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Simulating the hydration of cementitious phases with an oscillating rate of reaction

Cecilie Evju[a], Eskil Hansen[b], Staffan Hansen[a,]*

[a]Inorganic Chemistry 2, Chemical Center, Lund University, P.O. Box 124, S-221 00 Lund, Sweden
[b]F97, Engineering Physics, Lund University, P.O. Box 118, S-221 00 Lund, Sweden

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Abstract

To investigate how an oscillating reaction rate might influence the hydration of cementitious solids, a simple iterative mathematical model that includes recurrent passivation of the surface has been constructed. The algorithm generates a wide variety of hydration curves with a limited number of input parameters: i.e., V_o (volume of unreacted solid after initial reaction), α_o (degree of reaction upon initial wetting), x_o (fraction of particle surface passivated after initial wetting); running index: n (cycle number, with an arbitrary unit of time per cycle); constants: m (number of cycles with constant x, the relative rate of the hydration and passivation reactions), k (maximum linear rate of reaction front), and λ (range 0–1, determines the general passivation behaviour, modelled by the algorithm $x_{\text{new}} = 4\lambda x_{\text{old}}[1 - x_{\text{old}}]$). The hydration process is described by the sequence: (1) $\Delta V = k(1 - x)V^{2/3}$, (2) $V_{\text{new}} = V_{\text{old}} - \Delta V$, (3) $\alpha = 1 - (V/V_o) + \alpha_o$. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In calorimetric measurements on hydrating cementitious phases, one or two peaks are usually observed in the heat evolution curves as a function of time [1]. These maxima in the function $dQ/dt = f(t)$ correspond to steps in the integrated heat curves $Q = f(t)$ or the corresponding reaction curves $\alpha = f(t)$, where α is the fraction of the original anhydrous phase that has been transformed into hydrated phases. These variations in the reaction rate are attributed to (1) temporary passivation of the surface of the anhydrous solid due to the formation of a compact product layer or (2) changes in the nature of the hydration reaction (i.e., intermediate products forming at different rates). Calorimetric curves for hydrating phases with three peaks (steps) are not uncommon [2,3] and even four periods of high reaction rate have been observed in case of the aluminate $CaAl_2O_4$ [4]. This type of behaviour suggests that the reaction rate can oscillate repeatedly between high and low values.

A review [5] of the basic mechanisms involved in the hydration of cementitious phases included the following fundamental processes: (1) nucleation, (2) growth and dissolution, (3) diffusion, (4) adsorption, and (5) solid state phase changes. The typical two-peak hydration curve of Ca_3SiO_5 pastes was then divided into five stages and a critical assessment was undertaken in order to identify the most plausible rate-limiting step for each stage of the reaction. The use of a similar approach to interpret the hydration curves with three or even four peaks would make it necessary to identify several additional rate-limiting steps describing the consecutive formation of the different metastable hydrates.

The mechanistic interpretation of the experimentally observed stages of hydration has been a matter of some controversy (e.g., the hydration of $Ca_3Al_2O_6$ in the presence of calcium sulfate, which gives a two-peak hydration curve with a pronounced dormant period after the initial reaction). A summary of the literature [6] concerning this reaction reveals that the dormant period is usually considered to be caused by a product layer on the surface of the anhydrous aluminate grains. This product layer then acts as a diffusion barrier. Another model involves blocking of dissolution sites by adsorbed sulfate ions. Returning to the product layer, this has been suggested to consist of X-ray amorphous phases (e.g., aluminium hydroxide; different types of AFm), or crystalline AFt, or a combination of an amorphous and a crystalline layer (aluminium hydroxide and AFm). The destruction of the passivating product layer has been attributed to osmotic swelling and subsequent rupture of the amorphous surface layers or crack formation and healing

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* Corresponding author. Tel.: +46-46-2228117; fax: +46-46-222-4012.
E-mail address: staffan.hansen@oorg2.lth.se (S. Hansen)

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due to the volume expansion when the anhydrous aluminate is transformed to a crystalline AFt cover.

In the case of industrial Portland or aluminate cements, the situation is further complicated by the fact that an intergrowth/mixture of at least five cementitious phases, with very different inherent hydration behaviours, are allowed to react in contact with a common pore solution. The hydration and microstructural development of industrial cements with time has also been reviewed [7]. The fact that systems of nonlinear differential equations can have solutions representing oscillating or even chaotic behaviour has been applied in many fields of chemistry, physics, biology, and medicine. However, the differential equation approach to cement hydration [8] is complicated by the lack of detailed knowledge concerning the reaction mechanisms involved.

In the present paper we have attempted to construct a simple theoretical model that reproduces some of the basic features of the hydration curves for single-phase cementitious materials. Our approach has been to avoid the extensive sequences of more or less well-known fundamental steps described above. We have attempted to do this by basing our model on an essentially phenomenological description of the oscillating reaction rate (i.e., we focus on the consequences of an oscillating reaction rate and not its causes).

2. Continuous functions

For a cube with the original half edge length r_o (or a sphere of radius r_o), the degree of reaction α can be expressed as a function of the initial volume of the cementitious material (V_o) and the volume after a certain period of reaction (V), as seen in Eq. (1):

$$\alpha = (V_o - V)/V_o = 1 - (V/V_o) = 1 - (r/r_o)^3 \quad (1)$$

If the linear velocity of the reaction front k is constant, then r can be written as seen in Eq. (2):

$$r = r_o - kt \quad (2)$$

and the degree of hydration can consequently be calculated according to Eq. (3), cf. Ref. [9].

$$\alpha = 1 - [1 - (kt/r_o)]^3 \quad (3)$$

The oscillating behaviour observed in experimental hydration curves of the type $\alpha = f(t)$ indicates that the reaction rate k varies over time t as a step function $k = f(t)$, at least as a first approximation. To introduce suitable step functions $k = f(t)$ into Eq. (3), we utilise the iterative approximation described next.

3. Iterative procedure

A flowchart summarising the sequence of calculations is presented in Fig. 1. We assume cubic or spherical particles of the same size (i.e., the influence of the particle size distribution is neglected), since this phenomenon is well understood [10]. The equally sized particles instantly react upon contact with water, so that a certain fraction ($x = x_o$) of the surface becomes passivated due to the formation of a impenetrable product layer. A schematic drawing depicting the reacting surface of a particle is shown in Fig. 2. If the layer is of negligible thickness, the fraction of cementitious phase (α_o) that has reacted is still zero, or if not, α_o is typically a few percent. The x_{old} value is kept constant through m iterative cycles and then a new value (x_{new}) is calculated using Eq. (4):

$$x_{\text{new}} = 4\lambda x_{\text{old}}(1 - x_{\text{old}}) \quad (4)$$

where λ, x_{old}, and x_{new} are numbers in the range 0–1. The dynamic formation of the passivating layer is considered to be proportional to both the fraction of passivated surface x and the fraction of unpassivated surface $(1 - x)$, cf. Fig. 2. This is reasonable for the formation of thin islands of amorphous reaction products on the surface of the anhydrous grain. The constant λ determines the general behaviour [11] of $x = f(t)$ and λ represents the maximum value that x_{new} can assume during iteration. We can maximise x_{new} by setting $x_{\text{old}} = 0.5$ in Eq. (4), and arrive at $x_{\text{new}} = 4\lambda \cdot 0.5 \cdot 0.5 = \lambda$.

In each cycle, the volume of unhydrated material decreases with an amount ΔV, which is proportional to the area of unpassivated surface $(1 - x)A$ and the specific reaction rate of the surface k_a (suitable unit: μm per iteration).

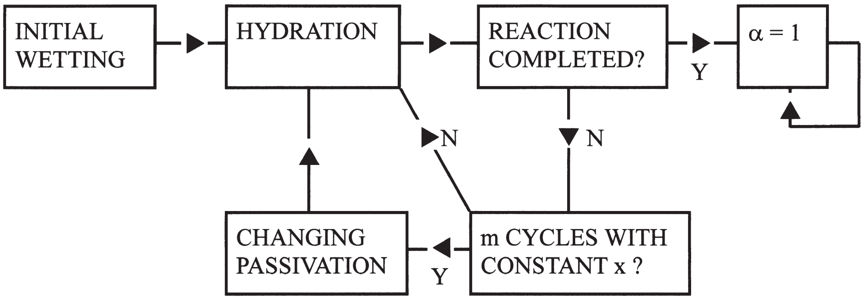

Fig. 1. Flow diagram of the iterative algorithm.

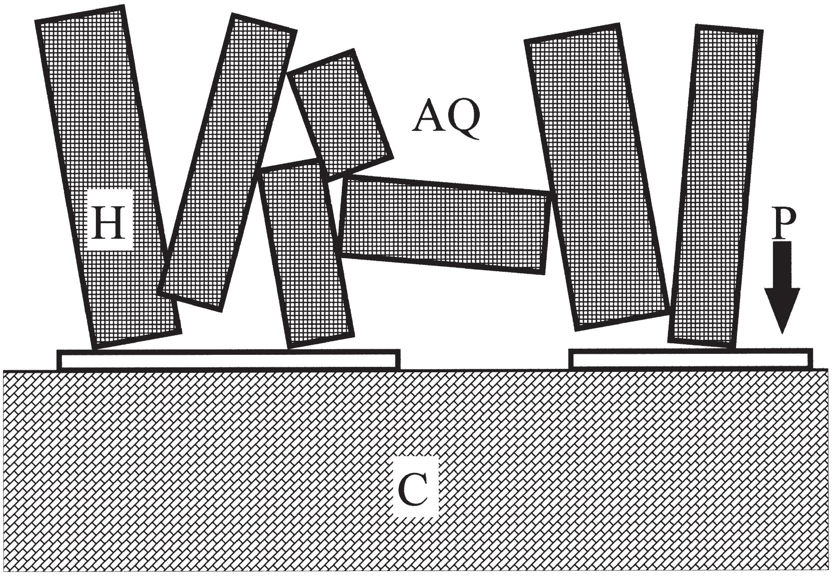

Fig. 2. Schematic drawing of the surface of the reacting cementitious phase (C) in contact with the aqueous solution (AQ). The surface of the anhydrous material is partially covered by a passivating product layer (P), while the bulk hydrates (H) form from the solution.

This is a plausible assumption if the bulk hydrates are formed via a through-solution route resulting in the deposition of a porous precipitate between the reacting particles (Fig. 2). The volume change of the anhydrous grain can then be expressed as shown in Eq. (5):

$$\Delta V = k_a(1-x)A = k(1-x)V^{2/3} \quad (5)$$

Where $k \approx 4.836k_a$ for a sphere (or $k = 6k_a$ for a cube). The new volume after the reaction step becomes [see Eq. (6)]

$$V_{\text{new}} = V_{\text{old}} - \Delta V \quad (6)$$

and the corresponding degree of hydration is calculated according to Eq. (7)

$$\alpha = 1 - (V/V_o) + \alpha_o \quad (7)$$

As long as $\alpha < 1$ the sequence is then repeated according to Eq. (4) through (7); otherwise, the degree of hydration is fixed to unity. Some resulting hydration curves are presented in Figs. 3 and 4. It should be noted that the time scale can be chosen freely since it is possible to assign any suitable period of time per iteration. A logarithmic time scale is also applicable.

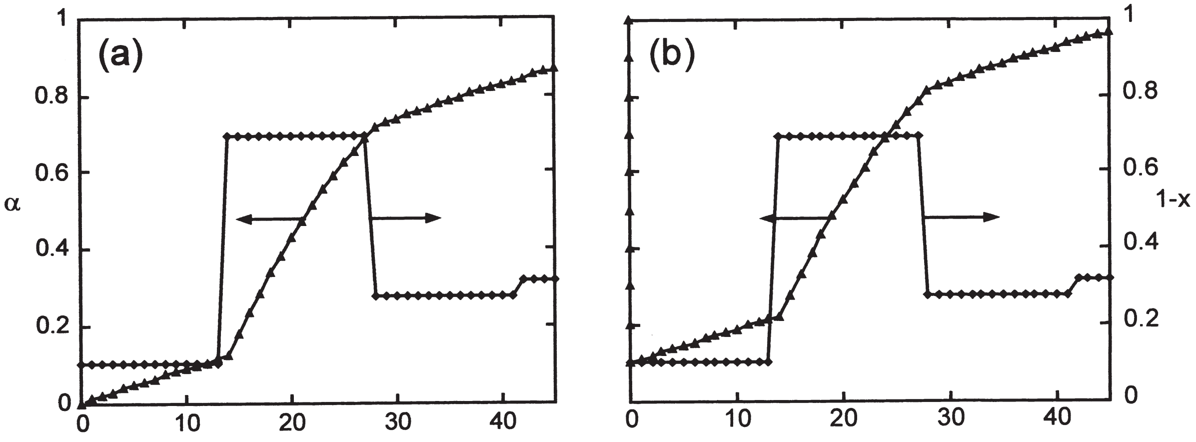

Fig. 3. (a) Degree of reaction α and fraction of active surface $(1-x)$ as a function of cycle number n, with $V_o = 1000\ \mu\text{m}^3$, $x_o = 0.9$, $\alpha_o = 0$, $m = 14$, $k = 0.9\ \mu\text{m cycle}^{-1}$ and $\lambda = 0.85$. (b) The same calculation with $\alpha_o = 0.1$, simulating an instantaneous reaction upon wetting.

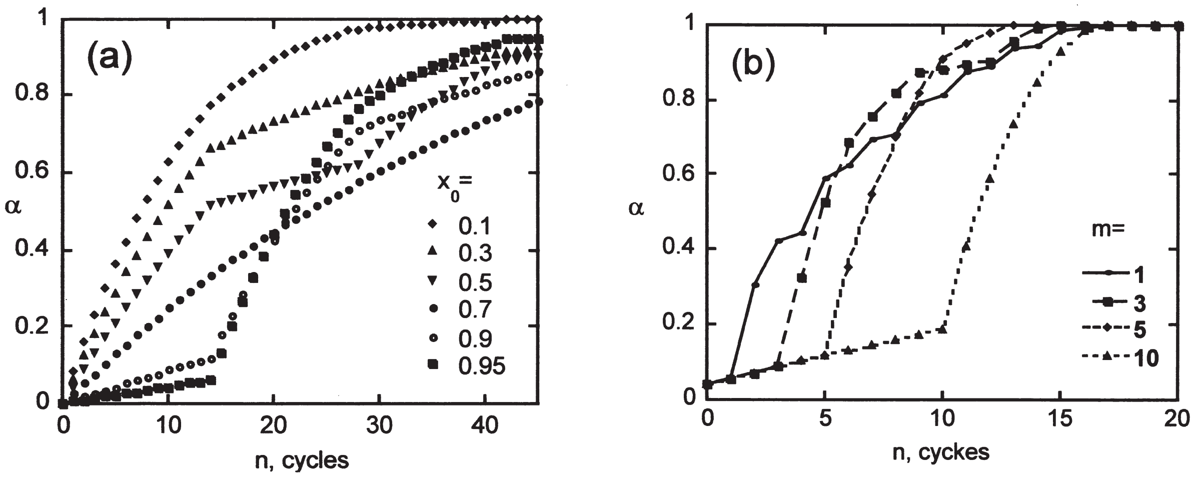

Fig. 4. Degree of hydration α as a function of cycle number n; (a) varying x_o ($V_o = 1000\ \mu m^3$, $\alpha_o = 0$, $m = 14$, $k = 0.9\ \mu m\ cycle^{-1}$ and $\lambda = 0.85$); (b) varying number of cycles m with fixed degree of passivation ($V_o = 1000\ \mu m^3$, $x_o = 0.85$, $\alpha_o = 0$, $k = 1.8\ \mu m\ cycle^{-1}$ and $\lambda = 0.85$).

4. Discussion

In the model in the previous section, we have utilised a description with an oscillating passivation of the surface because this allows us to give Eq. (4) some physical interpretation. But instead of viewing $(1 - x)A$ in Eq. (5) as the amount of reacting surface area, one can instead interpret $k(1 - x)$ as the linear reaction rate relative to the maximum reaction rate k. This is probably a more general interpretation, but it becomes harder to suggest a mechanistic interpretation of Eq. (4). The model can nevertheless handle both passivation phenomena and changes in rate due to intermediate reactions, as well as mixtures of the two.

Eq. (4) is often used in biology to introduce nonlinear growth phenomena in populations of living organisms [11]. For low starting values of x (say 0.1) and λ in the range 0–0.25, x goes to zero with increasing time. In the range 0.25–0.75, x increases towards a stable limiting value. For $\lambda = 0.75$–0.89, x exhibits periodic oscillations at high t and the amplitude of the oscillation increases with λ. In the range 0.89–0.99, nonperiodic (chaotic) oscillation is usually observed, though windows in λ with periodic oscillation is also present. In the chaotic region, the value of x at a certain time becomes very sensitive to its starting value x_o [11]. Our initial results indicate that the algorithm consisting of Eq. (4) through Eq. (7) generates a variety of different hydration curves with a limited number of input parameters and constants. In the reported calculations we used λ values close to the upper limit for periodic oscillations, 0.8925, since our main objective was to investigate the possible influence of an oscillating passivation.

If the initial value of x is high (e.g., 0.9), the following x value becomes low and then the general behaviour is similar to the one described above. This property is relevant in the present context (i.e., an initial passivation associated with a period of slow reaction, which is then followed by a period of rapid reaction). This is illustrated in Fig. 3, where the degree of reaction α and the fraction of nonpassivated surface $(1 - x)$ has been calculated as a function of time. The function $(1 - x) = f(t)$ behaves in a manner similar to $d\alpha/dt = f(t)$ or $dQ/dt = f(t)$. When the initial passivating layer is of negligible thickness and thus $\alpha_o = 0$, the function $\alpha = f(t)$ exhibits an induction period, as seen in Fig. 3(a). If an instantaneous initial reaction affects α_o, the curve mimics the behaviour with a quick wetting reaction followed by a dormant period, as seen in Fig 3(b).

In Fig. 4(a) a set of hydration curves has been calculated using the same input parameters as in Fig. 3(a), but with varying degrees of initial passivation x_o. The variation in the hydration curves that are generated has a striking (qualitative) similarity to the complex $\alpha = f(t)$ graphs that are sometimes observed experimentally. Hydration of Ca_3SiO_5 using varying water-solid ratios [12] or of belite and ferrite in synthetic clinkers of varying composition in the system CaO-MgO-SiO_2-Al_2O_3-Fe_2O_3-SO_3 [13] can serve as examples.

In Fig. 4(b) the influence of changing m, the relative rate of the oscillating passivation and the hydration reaction, has been investigated. With a low m, a large number of oscillations is observed, while a high value of m limits the number of oscillations. The results indicate that it could be difficult to distinguish between experimental noise and an oscillating reaction, especially at the end of the reaction (i.e., at high αs).

The calculations have been implemented using a Microsoft Excel spread sheet (Microsoft Corporation, Redmond, WA, USA). Anyone interested in obtaining a copy of the spreadsheet via e-mail can contact the first author at the address: cecilie.evju@oorg2.lth.se.

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