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A new view on the kinetics of tricalcium silicate hydration

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ABSTRACT

C_3S hydration is an interesting example of chemical coupling between C_3S dissolution, C–S–H and portlandite precipitation. It occurs because Ca^{2+}, OH^- and silicate ions are present in C_3S, in both hydration products and in the surrounding solution. Various experimental data sets reveal that the undersaturation with respect to C_3S always increases when C_3S hydration enters into the deceleratory phase, leading to the conclusion that C_3S dissolution is at the origin of this deceleration, not C–S–H growth. In addition, as soon as portlandite precipitates, the dissolution limits the hydration already in the acceleratory hydration step. The evolution of the undersaturation cannot account for the hydration peak. Rather, it results from an extension and subsequently a decrease of the C_3S reactive surface area. The formation and coalescence of dissolution etch-pits can provide a reasonable explanation for the C_3S hydration kinetics.

1. Introduction

Tricalcium silicate (C_3S[1]), the main component of ordinary Portland cement, hydrates into calcium-silicate-hydrates (C–S–H) and then possibly into portlandite ($Ca(OH)_2$), as follows:

C_3S dissolution:

$$Ca_3SiO_5 + 5\,H_2O \rightarrow 3Ca^{2+} + 6OH^- + H_4SiO_4 \tag{1}$$

C_x-S-H_y precipitation:

$$x\,Ca^{2+} + 2x\,OH^- + H_4SiO_4 \rightarrow (CaO)_x - (SiO_2) - (H_2O)_b + (2 + x - b)\,H_2O \tag{2}$$

$Ca(OH)_2$ precipitation:

$$y\,Ca^{2+} + 2y\,OH^- \rightarrow Ca(OH)_2 \tag{3}$$

with $x + y = 3$ and x the calcium to silicon molar ratio that is a variable parameter of the C–S–H composition that strongly depends on the concentration of calcium hydroxide in solution. b, the amount of water molecules in C–S–H is also a variable close to the value of 1.8 [1,2] for C–S–H with high Ca/Si ratios. C_3S hydration consists of at least two of these reactions which are the dissolution of C_3S and the precipitation of C–S–H. Using the example of dilute suspensions, it is possible to hydrate C_3S under conditions undersaturated or insufficiently supersaturated with respect to portlandite to lead to the precipitation of portlandite. In such conditions, the solution gets more and more concentrated in calcium and hydroxide ions. If the maximal supersaturation with respect to portlandite is exceeded, the latter precipitates leading to a new kinetic situation, hence resulting in the C_3S dissolution and both C–S–H and $Ca(OH)_2$ precipitation. In all cases, the chemical equations impose the following:

$$x + y + z = 3$$

z being the number of moles of calcium in solution for 1 mol of C_3S. The authors chose H_4SiO_4 as silicate species for balancing the reactions but are aware that the solution consists of a mix of H_4SiO_4, $H_3SiO_4^-$ and $H_2SiO_4^{2-}$, for which the speciation depends on pH.

The hydration of cement today is firmly recognized to be a dissolution–precipitation process, and reaction kinetics has been a prominent research topic for a century. Le Chatelier, being a fervent defender of the “through-solution” theory, was the first to lay the foundations of hydration chemistry [3]. Since then, even if our knowledge considerably increased, the overall picture on hydration is still not complete and some questions are still a matter of debate (see reviews in [4–6]). More recently, our understanding on the dissolution reaction of tricalcium silicate has been increased [7–9]. Under the new light of these results, some critical points regarding alite hydration kinetics are revisited in this paper (the tricalcium silicate phase in cement is commonly called alite).

The hydration of alite is routinely measured by the well-established technique of isothermal conduction calorimetry. $\dot{Q}$, the heat flow released during the hydration of alite is equal to the sum of heat flows

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[1] In cement notation, C, S and H stand for CaO, SiO_2 and H_2O respectively. $C_3S = Ca_3SiO_5$, C–S–H $= (CaO)_x-(SiO_2)-(H_2O)_y$.

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released or stored by each reaction:

$$\dot{Q} = R_{C_3S\,\mathrm{diss.}}\Delta H_{C_3S\,\mathrm{diss.}} + R_{C\text{–}S\text{–}H\,\mathrm{prec.}}\Delta H_{C\text{–}S\text{–}H\,\mathrm{prec.}} + R_{CH\,\mathrm{prec.}}\Delta H_{CH\,\mathrm{prec.}} \qquad (4)$$

with ΔH_i the reaction enthalpy of the reaction i. In paste, the 3 rates become rapidly equal and then $\dot{Q}$ is proportional to the hydration rate. The characteristic heat evolution curve (Fig. 1) obtained during the hydration of C_3S in paste presents different phases:

I *The dissolution peak*: this non-steady state step is difficult to interpret because of the calorimeter inertia and often because of the frictional heat due to the sample introduction.
II *The so-called "dormant" period* or sometimes called the induction period. This period of low activity precedes the acceleration of hydration. It is generally very short in the case of pure C_3S hydration.
III *The acceleratory phase*: this is a relatively short period of time but important for the early mechanical properties. During these first hours, the rate increases until reaching a maximum value.
IV *The deceleratory phase*: with the acceleratory period it forms the main hydration peak. The deceleratory phase continues until the end of hydration.

Among the still-debated issues, two of them have received particular attention during the last two or three decades. The first one is the occurrence of the dormant period. To explain this, two theories are often reported in the literature. One is based on the precipitation of a transient metastable C–S–H phase [10,11] and another one is based on C–S–H nucleation kinetics, which may be hampered by aluminum ions, [12] for instance. An alternative to these theories, recently proposed, suggests that the dormant period results from underlying mechanisms governing the opening of dissolution etch-pits [9].

The second most important issue is the reasons leading to the main hydration peak. The acceleration is generally attributed to the increase of the surface area of C–S–H in a kind of autocatalytic process. The entry into the deceleratory regime following the maximum rate value is more discussed. So far, most of the hypotheses advanced to rationalize the deceleration also rely upon C–S–H growth. There are two assumptions, both of which postulated that C–S–H growth is constrained in space. It is assumed that some constraints limit the growth rate and consequently the hydration rate. They are derived from Avrami's model [13–15] and have been adapted to C_3S (or cement) hydration [16]. Some authors considered that the transformation takes place on the surface of grains [17,18]. The theories arising in these articles are differentiated by the origin of space constraints. The first proposes that C–S–H growth is hindered by existing C–S–H that grows outward from the surrounding cement grains [17], and the second proposes that the hindrance on growth is due to adjacent C–S–H growing on the same grain [18]. Note that in this latter, the consequence is not a decrease but a constant hydration rate.

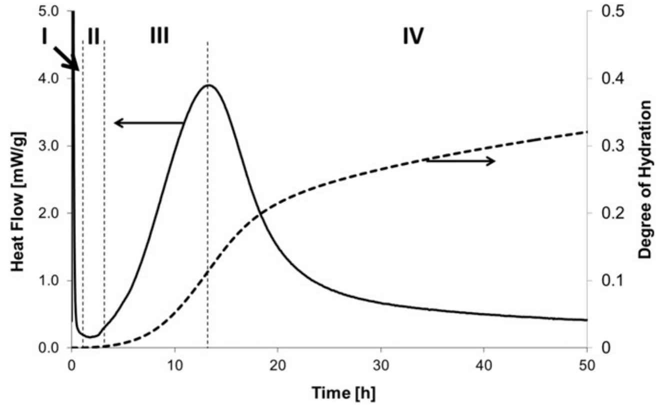

Fig. 1. Very typical evolution of alite hydration at water-to-alite ratio of 0.5. The usual steps are represented: I the pure dissolution peak, II the "dormant" period, III the acceleratory period and IV the deceleratory period.

It is worthwhile mentioning that, to the best of the authors' knowledge, these C–S–H growth-based hypotheses have never been experimentally verified, but rather have been supported by self-consistent fitting. Indeed, the typical hydration curve (as plotted in Fig. 1) has been modeled or fitted using these theories. More generally, many different models (based on C–S–H) can be used to reproduce the sigmoidal hydration curve [17–21] showing in some cases, excellent agreement between experiments and fits. But even a perfect fit does not provide validation of a theory [22]. The C_3S hydration curve is the result of dissolution and precipitation reactions leading to possible dual interpretations if the theory used to produce a curve does not account for both reactions. In addition to the possible space constraints on C–S–H growth, C_3S is depleting over time while C–S–H grows. After a certain time, and as long as water is still available, C_3S will not be able to provide enough material for the C–S–H growth and the hydration rate will be limited. This has been described by Nonat et al. [23] and appears to be indisputable evidence. However, the corresponding hydration time has never been experimentally identified, but has only been predicted to occur.

In this article, a simple approach has been used that consists of the examination of ion concentrations during hydration under various experimental conditions. The data are all extracted from the literature. As explained in the next section, the evolution of ion concentrations allows for the determination of which reaction drives the kinetics, for example through the calculation of the undersaturation with respect to C_3S and the supersaturation with respect to hydration products. In spite of the simplicity of the approach to monitor ion concentrations, the evolution of the characteristics of the pore solution and the consequences on hydration kinetics has never been thoroughly studied, except during the very early period of hydration [24] and in a very recent theoretical study [25]. The relation between the C_3S dissolution rate and its undersaturation has been recently described [7]. Unfortunately, the same kind of work on the C–S–H precipitation is still pending. The role of the dissolution rate on hydration kinetics will be put into perspective, and light will be shed on the phenomena taking place during the main hydration peak shown by calorimetry. An alternative hydration scheme will be then proposed and meanwhile the relevance of the existing theories based on C–S–H growth will be discussed.

2. Notions of heterogeneous kinetics applied to C_3S hydration

C_3S hydration is an example of transformation of solid A into solid B through the solution. As a matter of fact, during C_3S hydration, C_3S dissolves and releases ions into the solution at the flow Φ_{diss}. At the same time, hydrates, i.e. C–S–H and portlandite, precipitate and consume ions from the solution at the flow Φ_{prec}. Because C_3S, C–S–H and portlandite are composed of the same species, dissolution and precipitation rates, i.e., the appearance rate of C–S–H and portlandite and the disappearance rate of C_3S, are linked. Such a connection is the definition of the so-called coupled reactions. In case of a steady state or a quasi-steady state, both flows become equal:

$$\varphi_{\mathrm{diss.}}(t) = \varphi_{\mathrm{prec.}}(t). \qquad (5)$$

In the following, some known concepts about heterogeneous kinetics are described to establish pertinent groundwork for C_3S hydration kinetics and to show that C_3S dissolution and precipitation of C–S–H and portlandite are coupled. Many interesting examples of coupling can be found in geochemistry. Indeed coupling is typical in diagenesis, metamorphism, metasomatism, chemical weathering, and other water-rock reactions [26–28]. In these geochemical transformations, mineral A transforms into mineral B through the surrounding fluid. The dissolution rate of A is equal to the precipitation rate of B and the