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# Hydration of Cement and its Mechanisms

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***Abstract:*** *The current state of knowledge of cement hydration mechanisms is reviewed, including the origin of the period of slow reaction in alite and cement, the nature of the acceleration period, the role of calcium sulfate in modifying the reaction rate of tricalcium, aluminate, the interactions of silicates and aluminates, and the kinetics of the deceleration period. In addition, several remaining controversies or gaps in understanding are identified, such as the nature and influence on kinetics of an early surface hydrate, the mechanistic origin of the beginning of the acceleration period, the manner in which microscopic growth processes lead to the characteristic morphologies of hydration products at larger length scales, and the role played by diffusion in the deceleration period. The review concludes with some perspectives on research needs for the future.*

***Keywords:***
- Hydration (A)
- Kinetics (A)
- Microstructure (B)

## I. Introduction

Understanding the kinetic mechanisms of cement hydration intersects both academic and practical interests. From an academic standpoint, the chemical and microstructural phenomena that characterize cement hydration are quite complex and interdependent, making it difficult to resolve the individual mechanisms or the parameters that determine their rates. Fundamental study of hydration therefore offers significant scientific challenges in experimental techniques and multi-scale theoretical modeling methods. From a more practical standpoint, the drive to produce more sustainable concrete materials is leading to more complex mix designs that include increased amounts of secondary mineral additions, often originating as by-products of other industrial processes, and a wide variety of chemical admixtures that can enhance concrete performance. More complete knowledge of basic kinetic mechanisms of hydration is needed to provide a rational basis for mixture proportioning as well as the design and selection of chemical admixtures.

Several detailed reviews have been written about the mechanisms that are thought to govern the kinetics of hydration [1], [2], [3] and [4]. At the time they were published, several important issues – the mechanistic origin of the induction period, the rate-controlling mechanisms during the acceleration period, the most important factors responsible for the subsequent deceleration of hydration, etc. – were addressed but left unresolved due to either lack of data or seemingly equivocal evidence for different viewpoints. But significant strides have been made both in experimental techniques and in theoretical models in the intervening years. Our intention is to focus on these more recent developments, thereby providing an updated picture of the current state of knowledge and identifying the remaining controversies or gaps in understanding. Finally, we then propose a road map for future cement hydration research that targets the remaining gaps and could have the greatest impact toward supporting the development of more sustainable concrete materials.

## II. Background

Models of chemical kinetics that are based on fundamental chemistry and physics at the molecular scale have been feasible for gas-phase systems [5], for nucleation of crystals from a melt or aqueous solution [6], and even for dissolution and growth at crystal surfaces [7], [8], [9], [10] and [11] by analyzing and modeling the individual kinetic steps in detail. Similarly, a fundamental approach to understanding cement hydration would involve breaking the problem down to the study of the kinetics of the individual mechanistic steps. This approach is desirable because it would provide a foundation for understanding the interactions among the coupled processes, and for establishing how the microscopic kinetics lead to the development of the microstructure at higher length and time scales. Furthermore, mechanistic understanding at the molecular scale would provide knowledge of the dependence of rates of reaction and diffusion on temperature and the state of saturation, that is, the effect of curing conditions.

Cement hydration involves a collection of coupled chemical processes, each of which occurs at a rate that is determined both by the nature of the process and by the state of the system at that instant. These processes fall into one of the following categories:

1. *Dissolution/dissociation* involves detachment of molecular units from the surface of a solid in contact with water. A good comprehensive review of dissolution kinetics was performed by Dove et al. [12] and [13].
2. *Diffusion* describes the transport of solution components through the pore volume of cement paste [5] and [14] or along the surfaces of solids in the adsorption layer [15] and [16].
3. *Growth* involves surface attachment, the incorporation of molecular units into the structure of a crystalline or amorphous solid within its self-adsorption layer [17].
4. *Nucleation* initiates the precipitation of solids heterogeneously on solid surfaces or homogeneously in solution, when the bulk free energy driving force for forming the solid outweighs the energetic penalty of forming the new solid–liquid interface [6].
5. *Complexation*, reactions between simple ions to form ion complexes or adsorbed molecular complexes on solid surfaces [18] and [19].
6. *Adsorption*, the accumulation of ions or other molecular units at an interface, such as the surface of a solid particle in a liquid [15], [16] and [19].

These processes may operate in series, in parallel, or in some more complex combination. For example, even simple crystal growth from solution involves diffusion of solute to the proximity of an existing solid surface, adsorption of the solute onto the surface, complexation of several solute species into a molecular unit that can be incorporated into the crystal structure and, finally, attachment and equilibration of that molecular unit into the structure [9] and [19]. When in series, these steps are coupled in the sense that the products of one step are the reactants of the next step, and so on. Often, but not always, one step has a significantly lower rate than any of the other steps in the sequence. In that case, all but the slowest step, *the rate-controlling step*, can reach equilibrium conditions and will determine the activities of the reactants and products of the rate-controlling step [19]. In this simple case where one step is rate-controlling, that step alone is responsible for the observed kinetic rate equation, the rate constant, and their temperature dependences. When the rates of two or more fundamental steps are comparable, then the rate equations and their dependence on system variables can be significantly more complicated and difficult to determine experimentally [19].

Unfortunately, the rigorous application of these concepts to cement hydration continues to be elusive because of the difficulty of isolating the individual chemical processes for detailed study. Even a task as seemingly simple as determining a fundamental rate law for the dissolution of $Ca_3SiO_5$, consistent with thermodynamics and the principle of mass action, is quite challenging because of the competing effects of rapid precipitation of less soluble phases from solution, the difficulty of adequately characterizing the surface at which dissolution is occurring and, even more basically, because rate data are usually acquired on polydispere particle suspensions without a complete characterization of the particle size distribution or absolute reactive surface area. The problem becomes exponentially more difficult to analyze when more complex systems like portland cement are contemplated. Therefore, for cement one has been forced to accept only partial knowledge about the net kinetic effects of multiple interacting processes.

The key to eventually building more mechanistic, less empirical models of hydration, capable of embracing its full range of chemical and structural complexity, is to develop strategies to isolate and study the individual rate processes that govern cement hydration. Such strategies will inevitably involve a close collaboration among a wide variety of experimental techniques, along with mathematical models and numerical simulation methods that can provide an intellectual framework for interpreting the data. This kind of collaboration has born fruit for unravelling the kinetics of certain processes in environmental geochemistry [10], [20] and [21] and other branches of materials science [22], [23], [24] and [25].

### 2.1. Scope of this review

Nearly every review of portland cement (PC) hydration kinetics [1], [2] and [4] spends the majority of its attention on the hydration characteristics tricalcium silicate, $Ca_3SiO_5$, or $C_3S$ according to conventional cement chemistry notation. One reason is that the impure monoclinic polymorph of $C_3S$, referred to as alite, constitutes about 50% to 70% of PC by mass. Progress in basic understanding of kinetics is made more feasible by restricting attention to this simpler chemical subsystem because the analysis of chemical kinetics becomes increasingly complex with increasing number of components and phases. In addition, alite tends to dominate the early hydration period that comprises setting and early strength development because it is the component most responsible for formation of the calcium silicate hydrate gel (C–S–H), the principle product of hydration.

In keeping with this trend, much of the new progress in cement hydration research has been made either on pure $C_3S$ or on alite itself. Recent research shows that triclinic $C_3S$ has significantly different microstructure and hydration kinetics than impure, monoclinic alite [26]. Pure $C_3S$ powders tend to be much finer grained than alite powders prepared and ground under similar conditions [26] because impurities in alite, mostly Mg and Al, promote grain growth during cooling from clinkering temperatures. In addition, some have speculated that the different crystal structure or impurity levels in alite alter the density of reactive sites at the surface, (e.g. screw dislocations or stacking faults) which can modify dissolution rates. Finally, there is some evidence that the growth morphology of C–S–H hydration products may be less porous, and therefore more resistant to mass transport, in $C_3S$ pastes than in alite pastes [26]. This may be related to the experimental observation that hydration of $C_3S$ often slows down markedly at lower degrees of hydration [27] than does hydration of alite [26].

Recent research on hydration of the $C_3A$ + gypsum subsystem of PC will also be reviewed because of its importance in determining the calcium sulfate requirements of PC with and without replacement by mineral admixtures. This will include a discussion of the interactions among the silicate and aluminate subsystems that are important for understanding the influence of sulfate levels on the hydration kinetics of PC with partial replacement by fly ash or blast furnace slag.

In closing this section, it is helpful to mention the experimental techniques that have been used to monitor hydration kinetics, because these techniques will be referenced repeatedly in the remainder of the paper. Most of the techniques used to date monitor the *net rate* of hydration, that is the overall progress of hydration without regard to the action of individual chemical reactions. Such methods include isothermal calorimetry, continuous monitoring of chemical shrinkage, in situ quantitative X-ray diffraction, semi-continuous analysis of pore solution composition, nuclear magnetic resonance spectroscopy (NMR), quasi-elastic neutron scattering (QENS) and small angle neutron scattering (SANS). The relative merits and weaknesses of such methods have been thoroughly assessed elsewhere; being outside the scope of this review, the interested reader is referred to [28] for more details. For now, we note that none of these techniques resolves the details of any particular mechanism, but they have proven useful for comparing the hydration of different cements, for characterizing the influence of variables such as cement fineness, water-to-solids mass ratio (w/s), cement composition, temperature, and the type and dosage of admixtures. More importantly, comparison of different methods, such as calorimetry and SANS data [29] and [30], calorimetry and QENS data [31] and [32], or calorimetry and chemical shrinkage on parallel specimens can provide insights into the hydration process that cannot be obtained by any one method alone. For example, the SANS surface area tracks closely with the cumulative heat measured by calorimetry at very early times, up to about the peak hydration rate, but then diverges as the morphology of the C–S–H phase is not constant with time. The same is true of the constrained water component of the QENS signal.

## III. Mechanisms of $C_3S$ (or) Alite Hydration

The rates of hydration of (triclinic) $C_3S$, alite, and even PC have long been observed to vary with time by orders of magnitude in a complicated, nonmonotonic fashion. Historically, this fact has led to the division of the overall progress of hydration into four or five stages, defined by somewhat arbitrary points on a plot of hydration rate versus time [4]. For our purposes in discussing kinetic mechanisms, we find it helpful to consider the four periods indicated in the calorimetry plot of hydration rate versus time shown in Fig. 1: (1) initial reaction, (2) period of slow reaction, (3) acceleration period, and (4) deceleration period. The beginning and ending of these stages are still difficult to pinpoint precisely, but they provide a more accurate picture of the current state of knowledge.

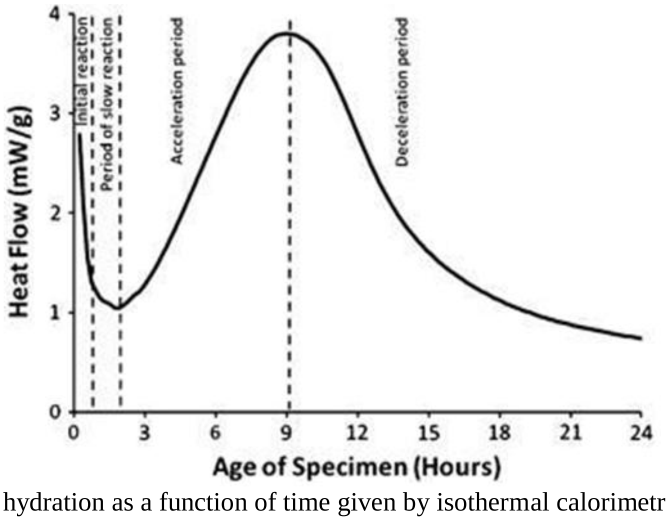

**Fig. 1.** Rate of alite hydration as a function of time given by isothermal calorimetry measurements.

In this section we undertake a review of recent progress in experimental and theoretical research on cement hydration in terms of its mechanism(s) and implications for microstructure development. Attention is focused on results that have come to light in the last decade, with limited review of earlier work only where necessary for historical context. The interested reader may refer to [4] and references therein for a more comprehensive review of earlier work.

### 3.1. Initial reaction

The initial period is characterized by rapid reactions between $C_3S$ and water that begin immediately upon wetting, characterized by a large exothermic signal in isothermal calorimetry experiments [26]. The heat released by wetting the cement powder contributes to this early exothermic signal, but significant heat is also released by dissolution of $C_3S$. The enthalpy of congruent $C_3S$ dissolution is − 138 kJ/mol, based on the reaction [33] and [34]:

**Equation(1)**

$$\mathbf{C_3S + 3H_2O \rightarrow 3Ca^{2+} + H_2SiO_4^{2-} + 4OH^-}$$

Chemical analyses of the solution phases [35], [36], [37], [38] and [39] have furnished persuasive evidence that $C_3S$ dissolves congruently and quite rapidly in the first seconds after wetting. In dilute suspensions of $C_3S$, for example, the increase in silicate concentration over the first 30 s suggests that the dissolution rate may be at least 10 μmol $m^{-2}$ $s^{-1}$[27]. Stein [40] calculated a theoretical solubility product for $C_3S$ of $K_{sp} \approx 3$, when referenced to Eq. (1), which would imply that $C_3S$ should continue to dissolve until reaching equilibrium calcium and silicate concentrations in solution of several hundred mmol/L. In fact, it is well known that $C_3S$ dissolution rates decelerate very quickly while the solution is still undersaturated, by about 17 orders of magnitude with respect to the ion activity product of Reaction (1) compared to the equilibrium calculation, by the end of this period [27], [40] and [41]. The mechanism of this early deceleration of $C_3S$ has been a subject of considerable debate over the years, and many hypotheses have been proposed. The reader is referred to [4] and references therein for a description of the proposed mechanisms. Here we will focus on three mechanistic explanations that continue to have the greatest plausibility in light of recent experimental and theoretical research.

### 3.1.1. Metastable barrier hypothesis

Stein [42] and others [43] have argued that the deceleration is caused by the rapid formation of a continuous but thin metastable layer of a calcium silicate hydrate phase, which Gartner [2] has called C–S–H(m), that effectively passivates the surface by restricting its access to water, or restricts diffusion of detaching ions away from the surface. This thin layer is proposed to reach equilibrium with the solution at the end of the intial reaction period. Jennings [44] reviewed solution composition data from several decades of literature and showed that they tend to lie along one of two curves on a plot of calcium concentration versus silicate concentration, as shown in Fig. 2. The curve with higher Ca and Si concentrations was interpreted as reflecting equilibrium of the solution with a *metastable* hydrate layer having a variable Ca:Si molar ratio, and Gartner and Jennings [41] subsequently used the Gibbs–Duhem relation to estimate the Ca:Si molar ratio of this metastable hydrate as a function of calcium concentration in solution.

The metastable barrier hypothesis implies that the metastable hydrate isolates the underlying alite from the solution, which then comes into equilibrium with the hydrate. However, the mechanism for the end of the delay period is not evident. The fact that the time of the end of the slow reaction period has such a precise and repeatable value indicates that there must be some critical process acting during that period. This must take the form of some continuing chemical reaction or reactions that eventually destabilize the metastable layer in some way [2] and [4]. Indeed, calorimetry measurements show that the rate of heat output never decreases all the way to zero during the period of slow reaction.

Bullard [45] recently simulated the metastable barrier hypothesis for $C_3S$ hydration, using a kinetic cellular automaton model of coupled reactions and diffusion phenomena using the principles of mass action and detailed balances. Simulations using the metastable barrier hypothesis adopted assumptions about the composition variability both of the passivating layer and of the more stable forms of C–S–H, based on limited and indirect experimental evidence. Even so, the simulations quantitatively reproduced a number of experimental observations of the evolution of the solution composition, the composition variablity of C–S–H, and the hydration rate of $C_3S$ at two different water–cement mass ratios and initial conditions of the solution [27], [46] and [47].

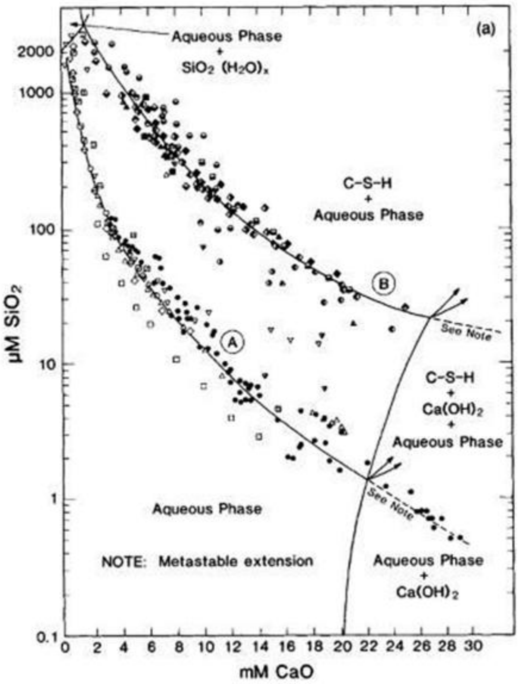

**Fig. 2.**

Concentrations of silica ($y$-axis in μmol/L) and calcium ($x$-axis in mmol/L) reported for cement paste pore solution, collected from an extensive literature search in [44], and interpreted as indicating that either of two types of C–S–H can establish equilibrium with the solution.

One difficulty with the metastable barrier hypothesis has been the scant direct experimental evidence of the existence of such a layer. However, the last several years have witnessed significant progress in this area. Nuclear resonance reaction analysis (NRRA), based on the $^{1}\mathrm{H}(^{15}\mathrm{N}, \alpha, \gamma)^{12}$ resonance, has been used to measure the hydrogen depth profile at and below the surface of a specimen, with a depth resolution of a few nm and a sensitivity to hydrogen of a few μg/g [48] and [49]. By probing below surfaces of cementitious phases immersed in aqueous solution for different times, they have observed changes in the hydrogen depth profile as a function of time. Some typical depth profiles for hydrating triclinic $C_3S$ are presented in Fig. 3. The profile is characterized by a Gaussian peak at the surface and a diffusion-like curve into the depth of the sample. The Gaussian peak has been interpreted as a thin but continuous hydrated layer [49]. Based on ideas from the glass corrosion literature, the overall hydrogen depth profile measured by NRRA has been interpreted as a set of layers with differing degrees of calcium/hydrogen exchange, as shown in Fig. 4. Although the Gaussian peak remains essentially fixed at later times (Fig. 3), the profile extends progressively deeper into the solid, reaching appreciable hydrogen concentrations as deep as 0.4 μm after 45 min at 30 °C. This increasing average penetration depth of hydrogen indicates that significant hydration reactions are still occurring during the slow reaction period. These conclusions are not too different from the mechanisms proposed in earlier publications [1], [2], [4] and [50].

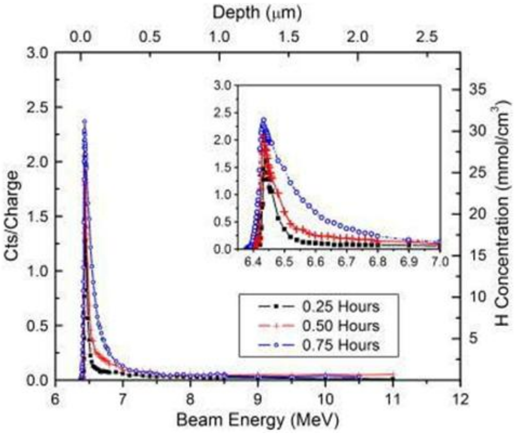

**Fig. 3.** Progression of hydrogen concentrations with depth and time during the initial and slow reaction

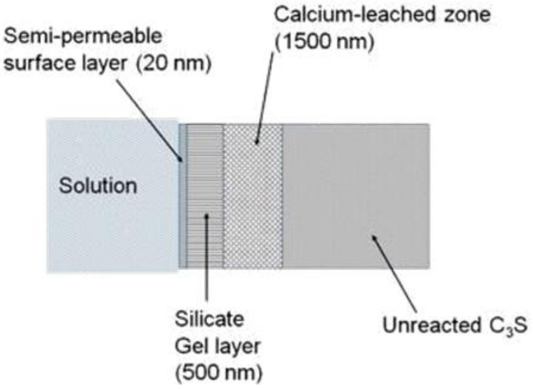

**Fig. 4.** Schematic diagram of the arrangement of surface layers on a $C_3S$ grain during the slow reaction period based on the hydrogen depth profile measured by nuclear resonance reaction analysis (NRRA).

More recently, Bellmann et al. [51] have examined pastes and very dilute suspensions of $C_3S$ nanoparticles in water. Using $^{29}Si$ NMR, they observed that an intermediate calcium silicate phase containing hydrated silicate monomers forms very early during hydration, a result that is consistent with earlier research on $C_3S$ [50], [52], [53] and [54]. Their data demonstrate that, at least for nanoparticulate $C_3S$, hydration proceeds in two stages: formation of an intermediate silicate hydrate phase followed by conversion of this phase into C–S–H once the solution becomes sufficiently concentrated with calcium.

With greater direct evidence of the existence of an early hydrate phase, the challenge still remains to demonstrate that the phase has the necessary passivating influence on $C_3S$ to explain the transition to the slow reaction period. NRRA data have been interpreted as indicating a thin surface hydrate that is permeable to calcium and water but not to silicates, although this latter idea is a conjecture because NRRA does not measure either calcium or silicate species. Moreover, the length of the slow reaction period has been correlated with the time required to achieve a critical hydrogen depth in NRRA experiments. For example, increasing temperature both shortens the slow reaction period and increases the rate of penetration of hydrogen below the surface (Fig. 3). And when sucrose, known to be a strong retarder, is added to the solution, the penetration rate of hydrogen below the surface occurs much more slowly than without sucrose [49]. All of these studies therefore provide strong evidence of a direct correlation between the length of the slow reaction period and the rate of development of the surface hydrate. A remaining challenge is to determine if the development of that surface hydrate controls the rate of hydration or if the rate of hydration controls the development of the surface hydrate.

If the metastable barrier hypothesis is correct, the layer must cover the great majority of the $C_3S$ surfaces and be fairly dense if it is to effectively block the diffusion of one or more dissolved components. There are examples of nanoscale metal oxides such as alumina being able to passivate aluminum surfaces and limit further oxidation, but in those instances the layer is extremely stable thermodynamically and mechanically and has a close crystallographic relationship with the underlying metal, in contrast with the metastable C–S–H phase. Both atomic force microscopy conducted on flat $C_3S$ surfaces under water [55] and high-resolution electron microscopy on dried samples [56] have been used to search for evidence of a continuous film of this kind. However, although patches of some kind of precipitate are often observed on the surfaces at very early times, evidence for a continuous layer has not been found using these direct methods of surface examination.

### 3.1.2. Slow dissolution step hypothesis

The metastable barrier hypothesis discussed in the last section assumes either explicitly or implicitly that the rate of $C_3S$ dissolution in the period of intial reaction would continue to be rapid up to much higher solution concentrations of calcium and silicates if not for the formation of the passivating hydrate layer. However, other researchers have assumed that $C_3S$ dissolution rates decrease rapidly for some other reason. Barret et al. [35] and [36] originally proposed that a―superficially hydroxylated layer‖ forms on $C_3S$ surfaces in contact with water, and that the dissociation of ions from this layer occurs much more slowly than would be otherwise expected for a mineral in highly undersaturated solutions. Nonat et al. [27], [39], [47], [55] and [57] have adopted this explanation for slow dissolution of $C_3S$ and subsequently developed an alternative mechanistic explanation for the initial reactions that is based on a steady state balance between slow dissolution of $C_3S$ and initially slow growth of C–S–H. According to these authors, the apparent solubility of the superficially hydroxylated $C_3S$ is much lower than the one calculated for $C_3S$, and the dissolution rate decreases very rapidly when the calcium hydroxide concentration increases due to dissolution. When the solution exceeds a maximum supersaturation with respect to C–S–H, C–S–H nucleates very rapidly on $C_3S$ surfaces and begins to grow slowly because of its initially low surface area. Growth of C–S–H causes the silicate concentration in solution to decrease and the Ca:Si molar ratio in solution to increase. Within minutes, a steady state condition is set up in which the solution is supersaturated with respect to C–S–H but undersaturated with respect to $C_3S$. Fig. 5 shows this behavior by superimposing the changes in solution concentration on a cross-section of a solubilty diagram in the system $CaO–SiO_2–H_2O$, with curves for both $C_3S$ and C–S–H indicated in the figure. The dashed arrow in the figure indicates the trajectory of the solution concentration for pure congruent dissolution, which continues until a maximum supersaturation is reached with respect to C–S–H (point A in the figure). Nucleation of C–S–H causes the silicate concentration to decrease (bold arrow in the figure) as the solution composition approaches the solubility curve for C–S–H.

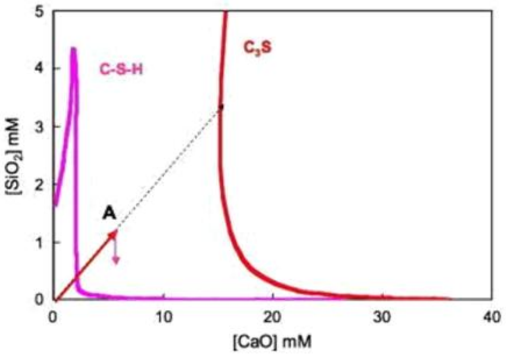

**Fig. 5.** Cross-section of a solubility diagram in the system $CaO–SiO_2–H_2O$. The arrow shows the path followed by the concentrations in solution during the congruent dissolution of $C_3S$. The concentration increases beyond the solubility of C–S–H until the maximum supersaturation from which C–S–H precipitates immediately is reached (point A). From [35] and [126].

Evidence supporting this view comes from studies of dissolution rates of $C_3S$ in stirred suspensions [58]. Increases in Ca and Si concentrations in solution were monitored continuously in suspensions of $C_3S$ so dilute (w/s = 50,000) that, theoretically, the solution should never become supersaturated with respect to C–S–H. Without the complicating factor of C–S–H nucleation and growth, congruent dissolution caused the concentrations of Ca and Si to increase continuously in a 3:1 ratio. With this technique, initial $C_3S$ dissolution rates were measured as approximately 10 μmol $m^{-2}$ $s^{-1}$ and the steady-state ion activity product (IAP) was estimated to be $\log IAP = -17$ when referenced to Reaction (1), nearly 17 orders of magnitude less than the solubility product calculated from the Gibbs free energy of the reaction.

Along the same lines, the dissolution rates of many natural minerals in aqueous solutions do not follow a smooth relationship with respect to the saturation state of the solution [10], [11] and [20]. Briefly, different mechanisms of dissolution are rate controlling depending on the saturation state of the solution. Far from equilibrium, high rates of dissolution are enabled by etch pit opening at surface defects, whereas closer to equilibrium but still significantly undersaturated, the driving force is insufficient to activate the etch pit opening and dissolution occurs primarily by a retreating step mechanism that is much slower.

The slow dissolution step hypothesis for the onset of the period of slow reaction is supported by the observed roles of crystallographic defects in the early hydration processes of cementitious material, which have been studied by several researchers [62], [63] and [64]. Maycock et al. [64] as well as Odler and Schüppstuhl [63] studied the effect of quenching rate on the reactions of alite and found that faster quenching, likely to induce more crystal defects, resulted in shorter induction periods. Fierens and Verhaegen [62] cooled $C_3S$ at different rates from 1600 °C to 1300 °C before quenching, and similarly found that the duration of the induction period was related to the length of the thermal treatment. More recently, Juilland et al. [61]. performed a post-thermal annealing treatment at 650 °C on alite of narrow particle size distribution as a way to decrease the defect density. A change of polymorphism from monoclinic M3 to triclinic T1 occurred without any significant change of the particle size distribution. Isothermal calorimetry data for the annealed samples show the presence of a very long induction period for the thermally treated samples (Fig. 6), supporting the hypothesis that surface defects control the rate of dissolution and thereby influence the length of the induction period.

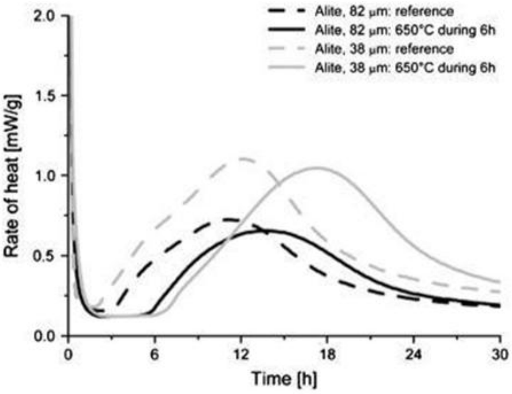

**Fig. 6.** Heat evolution of alite untreated (reference, dashed line) and treated at 650 °C for 6 h (plain lines) of narrow particle size distribution. All measurements were performed at 20 °C and the w/s ratio was kept at 0.4.

A difficulty with this slow dissolution step hypothesis is in reconciling the dissolution rates with the observed time dependence of silicate concentrations in the first minutes of hydration. Most experiments show a sharp peak in silicate concentration in the first minutes after wetting, which decreases almost as rapidly and is followed by a longer period of very slowly decreasing concentrations during the period of slow reaction. Before the peak, increases in silicate concentration can be interpreted as pure $C_3S$ dissolution. The sharp decrease has been interpreted as the consumption of silicates due to nucleation of C–S–H [27]. Within 20 min, the silicate concentration decreases to about half its original value and continues to decrease much more slowly for the next 20 min. Therefore, one should expect the $C_3S$ dissolution rates after 20 min to be comparable to the rates on the left side of the peak at the same silicate concentration in experiments where the calcium concentration is held fixed at 11 mmol/L, because at both those times the solution has basically the same composition and, therefore, the same driving force for dissolution [27] and [47]. However, such rapid $C_3S$ dissolution rates are not experimentally observed after the initially sharp decrease in silicate concentration until the acceleration period begins. One possible explanation is that the $C_3S$ surfaces on the right side of the silicate peak are already significantly covered with C–S–H precipitates, so that the dissolution rate per unit area may be rapid but the overall dissolution rate low.

### 3.2. Acceleration period

In unretarded, unannealed $C_3S$ and alite systems, the delay period is just the minimum in the hydration rate that is reached after the initial reaction but before the beginning of accelerated growth of hydration products [4]. A true induction period appears to exist as a distinct stage only when chemical retarders are added or materials have been annealed. Furthermore, this delay seems to be just the consequence of the slow reaction (due to one of the mechanisms described previously) until a critical point is reached when the rate of nucleation and growth starts to accelerate. Therefore, we have made the unconventional choice of omitting a separate section for the period of slow reaction, preferring instead to consider its aspects only in terms of the consequences for the onset of the acceleration period, which is generally agreed to be related to a nucleation and growth (N + G) mechanism.

Throughout this N + G period of hydration of $C_3S$ and alite, the hydration rate, expressed as the time derivative of the degree of hydration,[2] $d\alpha/dt$, increases as $\alpha^r$, where $2/3 < r < 1$ [4]. By analogy to autocatalytic chemical reactions, this behavior implies that the rate of hydration in this stage depends on the amount of some hydration product, presumably C–S–H. Supporting this idea, a large and growing body of experimental and modeling evidence [4], [27], [30], [35], [37], [55], [65], [66], [67] and [68] indicates that the rate-controlling step of hydration during this period is related to the heterogeneous nucleation and growth of C–S–H on alite and perhaps on other mineral surfaces as well. The evidence for this comes from a number of sources. C–S–H is observed to be formed primarily on surfaces of $C_3S$ or alite [4], [69] and [70] when observed by scanning, atomic force, or transmission electron microscopy. In addition, Zajac [71] has reported experimental measurements showing that the hydration rate of $C_3S$ is proportional to the surface area of C–S–H as measured by nuclear magnetic resonance (NMR) spectroscopy. If growth of C–S–H is rate-controlling, the hydration rate is expected to be proportional to the number of active growth sites for C–S–H (i.e., its surface area). Another paper in this issue [72] describes the application of various modeling and simulation methods that strongly support the underlying mechanism as being one of nucleation and growth and discusses in detail various hypotheses regarding the nucleation process (initial or ongoing); growth (isotropic, anisotropic or diffuse) and other mechanisms.

### 3.3. Deceleration period

Even though the period of ―post-peak‖ decelerating hydration progress (Fig. 1) is important in concrete technology because of the slower strength development, there have been comparatively few quantitative studies of this later period. It is widely considered that at later ages the rate of hydration is controlled by a diffusion process. However, several other factors may also be important, namely:

1. Consumption of small particles, leaving only large particles to react;
2. Lack of space, or
3. Lack of water.

The third factor is particularly important in practice. The total volume of hydrates is slightly less than the combined volume of the reacting cement plus water (by about 5% to 10%). This decrease in total volume, known as chemical or le Chatelier shrinkage, leads to the formation of gas-filled porosity after setting and a decrease in internal relative humidity, which will decrease the hydration rate. Therefore, the analysis of kinetic data in this period must consider whether the system was in contact with a water reservoir or was sealed from external sources of water.

The effect of particle size distribution is not only important during the main hydration peak, but after it as well. In a typical cement, the size of the initial particles ranges from around 50 μm to 60 μm down to smaller than 1 μm. Particles less than about 3 μm are completely consumed by about 10 h and particles below 7 μm by 24 h [92]. Knudsen argued in 1980 [93] that the simultaneous hydration of different particle sizes obscures the rate controlling mechanism. His argument is probably applicable only at later times, because the mechanisms of nucleation and unobstructed growth of C–S–H depend only on the total surface area and are therefore not obscured by a range of particle sizes. Nevertheless, to eliminate complications due to broad particle size distributions, Costoya [26] and Bishnoi and Scrivener [86] adopted the practice of studying alite divided into different particle size fractions.

The time dependence of the cumulative amount of reaction sometimes has a distinct―knee‖, as shown by a plot of the bound water index (BWI) inferred from QENS measurements in Fig. 7. This knee, when observed, is often assumed to correspond to the onset of diffusion. Supporting this idea, mathematical fits of BWI versus time often indicate a transition to a parabolic time dependence at the knee. On the other hand, the transition is not always as obvious as in Fig. 7. Even in QENS studies, the knee is not as exaggerated as in Fig. 7 when three populations of bound water are considered [74], [82] and [94] when calculating BWI instead of only two [31]. The transition is even less evident from cumulative data. In fact, neutron scattering data track calorimetry data closely until shortly after the main peak, but the two curves sometimes diverge afterward [29], [31] and [74]. One reason may be that calorimetry primarily measures the exothermic dissolution of $C_3S$, while neutron scattering tracks microstructural features of the hydration products (e.g. states of water) as a proxy for reaction progress. This difference in the way changes are measured may mean that the knee observed in QENS data may reflect the onset of some change in the hydrated microstructure rather than a transition in the rate of reaction. But it is important to note that the knee *does not* coincide with the maximum observed rate of hydration, $d\alpha/dt$. The $d\alpha/dt$ maximum is in fact the inflexion point in the cumulative curve, where there is no indication of a change in rate controlling mechanism.

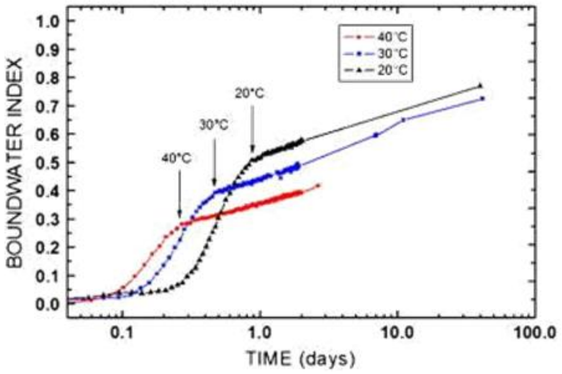

**Fig. 7.** Plots of bound water index (BWI) versus time for $C_3S$ hydration measured by quasi-elastic neutron scattering [31].

From this and other evidence, it now seems very unlikely that a transition to diffusion rate control is responsible for the first period of deceleration immediately after the main peak, although diffusion may becom rate controlling at later ages. The inevitable impingement of different domains of the growing hydration product, which is a fundamental feature of nucleation and growth transformations, reduces the surface available for growth and readily explains the shift from accelerating to decelerating hydration rate (see full discussion in [72]). Based on hydration simulations conducted according to boundary nucleation and growth conditions [65], Bishnoi and Scrivener [85] recently proposed that the shape of the main hydration peak results from the fast outward growth of a diffuse, highly porous C–S–H product.

The transition to diffusion controlled kinetics, if it occurs at all, likely happens well after this period of initial impingement and when heat release rates decrease to nearly zero. Such a transition in rate control would occur due to the formation of thick product layers that hinder the transport of reactants. Because this is a microstructural effect, it is useful to look at the overall development of micro- and nanostructure for clues. Allen et al. [30], [95] and [96] have shown using SANS that there are surface fractal and volume fractal length scale regimes associated with the deposition of nanoscale C–S–H onto the hydrating particles, and Mori et al. [97] have inferred a gradual change in fractal dimension of C–S–H gel from a surface fractal at early ages to a volume fractal at the transition point, which they associate with thickening of the layer of hydration products around the hydrating $C_3S$. In addition, examination of microstructures by scanning electron or scanning-transmission electron microscopy often indicate either gaps or regions of low-density product adjacent to the reacting grain surfaces [98], [99] and [100], while hydration products evidently deposit further away from the grains. These kinds of microstructural features imply that there may not always be a significant barrier to the transport of chemical species to and from the reacting grains. Other indirect evidence against the hypothesis of pure diffusion control can be found in the work of Peterson and Juenger [74], who used QENS to examine the hydration of $C_3S$ in water and in solutions of $CaCl_2$ or sucrose. They analyzed the cumulative progress of reaction characterized by the bound water index (BWI) and fit the curves with an empirical model, in the spirit of the Avrami model, that divided hydration kinetics into three stages: (1) an induction period at early times, (2) a nucleation and growth period at intermediate times, and (3) a diffusion-controlled period at later times. In this case, the later time period extended only to about 48 h after mixing, which is still relatively early in the hydration process. Their fits indicated that the diffusion coefficient for C–S–H must vary by more than an order of magnitude depending only on whether triclinic or monoclinic $C_3S$ is used as the starting powder. A similar point was made by Bishnoi and Scrivener [86]. They found that, to model the kinetic data for alite powder with different particle sizes, it was necessary to assume that the diffusion constant varied considerably with particle size. Since C–S–H grows by a through-solution process, it is difficult to explain how the source of the solute species or the particle size distribution could influence the properties of C–S–H so strongly. This suggests instead that the pure diffusion model used to fit the data is incorrect.

Other QENS data seem to indicate that filling of the capillary pore space cannot entirely account for the later age kinetics of $C_3S$ hydration. The available pore space in cement paste is essentially defined by the initial amount of water in the mix [50]. The reaction progress variable $\beta(t)$ described by Livingston et al. [101] is the ratio of water consumed to the initial water in the mix, so this variable should reach unity when the pores are finally all filled, assuming that the cement mix has the ideal molar $H/C_3S$ ratio of 3.1 which provides just enough capillary pore volume to accommodate the hydration products at complete hydration. However, the experimental evidence contradicts this; for example, the value of $\beta(t_D)$ for the curves presented in Fig. 7 never exceeds about 0.51. Thus the asymptotic kinetic behavior apparently cannot be explained by complete filling of the capillary pore space with hydration product. Livingston et al. used QENS to further investigate the effect on the asymptotic behavior of varying the w/s ratio. They found that the transition time, $t_D$, was independent of the w/s ratio and, in fact, that the individual curves could be collapsed into a single master curve by a simple vertical scaling that has a linear correlation with the w/s ratio. They concluded that the pore-filling mechanism could not be solely responsible for the transition to parabolic kinetics at later times. These same authors went on to propose an alternative mechanism for the transition point based on the hypothesis of rapid surface layer development that is complete at the end of the initial reaction period. If this interpretation were correct, the degree of reaction progress achieved at later times would be largely determined by the extent of the reaction during the delay period.

## IV. Perspectives for future research

### Motivation

As discussed in this review, cement hydration kinetics has been the subject of extensive investigation and yet the controlling mechanisms remain controversial. It is worth reviewing a couple of reasons for the importance of studying and understanding kinetics, apart from simple intellectual curiosity, as this helps motivate specific questions and research directions. Because the study of kinetics is a tool for elucidating mechanisms, it complements microstructure analysis by indicating which processes are predominant when structural changes occur. There are at least two broad areas of practical impact: 1) defining ways of controlling the rate of reaction, and therefore the rates of hardening and heat generation, and 2) finding ways of controlling and monitoring the structure and distribution of products; in short, controlling the microstructure and therefore *all* the material properties as a function of time. The first impact is related to controlling the length of time concrete remains fluid before it begins to gain strength and then the rate of subsequent strength development. The second has a more subtle, and potentially equally important, impact in the quest to control properties by manipulation of the micro- and nanostructure of concrete.

As for the rate of reaction, it is often stated that an ideal concrete should stay fluid during transport and placing and then very rapidly gain strength and other engineering properties. Both the mineralogy of cement and the addition of admixtures are used to control the kinetics of setting and hardening, but there is little consensus on the mechanisms, and chemicals are tested largely by trial and error. A mechanistic understanding would provide a powerful tool in the quest for new chemicals that are inexpensive, effective, noncorrosive toward steel reinforcing bars, and able to control equally the length of time before hardening starts and the rate of property development afterward.

Control of the microstructure of concrete has advanced remarkably in recent years, with the development of ultra-high strength products, such as Ductal where the particle size distribution has been optimized on the basis of theoretical models. In contrast, the ability to control the microstructure of C–S–H has received relatively little direct attention, with a few exceptions [67] and [109]. Thus the morphology and spatial distribution of the products formed during the hardening of cement paste cannot yet be controlled with the same precision as for metals and other materials, but a mechanistic understanding should provide new strategies for predicting the evolution of microstructure and properties, and ultimately designing microstructure and properties.

While the control of microstructure has not been investigated very much, a few studies have correlated morphology with time of formation, i.e. the stage during which the product seems to form. During the 1980s, several papers [110], [111], [112], [113], [114] and [115] reported that specific morphological features seem to form during each stage of reaction. The C– S–H needle morphology that typically forms preferentially during the early stages was once seen as a clue to the reaction mechanism [110] and [113], but this has not stood the test of time. Gartner [83] and others [69] and [100] have analyzed morphology and established plausible relationships between kinetics and atomic structure.

An important aspect of recent progress on hydration kinetics is that the proposed mechanisms have been described in increasingly quantitative terms, which enables better comparisons to data. However, some very important questions remain almost completely unanswered. For example, with a few isolated exceptions [30], knowledge of the mechanisms that control the rate of reaction have not been applied to explain the sometimes dramatically altered rate of reaction, as well as altered microstructure and properties, which often accompany the use of admixtures. This includes accelerators and retarders, mineral admixtures of all kinds and variation in cement composition.

This review has identified several rate phenomena that can control hydration kinetics at different times:

1. Dissolution of cement
2. Diffusion of reactants to site of chemical reaction
3. Nucleation of first product
4. Growth of product, perhaps by ―autocatalytic‖ formation of grains of product and which may be limited by chemical reaction or by diffusion of reactants to reaction site

The fact that more than one step can control the rate of reaction, depending on the stage of the reaction and perhaps on the presence of admixtures, in itself makes the mapping of the overall hydration process more complex than it would be if the rate were controlled by one step with a single activation energy. This suggests that the reaction kinetics might be best analyzed using a flow chart type of approach, an example of which is shown in Fig. 8, where the rate controlling step can be identified from among several candidates by evaluating several ―if–then‖ type of statements. For example, the presence of seed clearly removes the nucleation step as being rate controlling, and also stimulates growth of product in the volume of water filled as opposed to just on the surface (at least this is one interpretation of the kinetic data). Neither dissolution of cement nor diffusion of reactants appears to be rate controlling throughout most of hydration, but rather the rate of product growth appears to control the rate at least until the product becomes congested in the capillary pore space at later ages.

As the modern drive for more sustainable concrete pushes the formulation of cement toward increased use of supplementary cementitious materials (SCMs) like fly ash and slag, concrete producers are faced with an ever more complex chemical and structural design space within which to formulate binders. Responding to the demand to replace greater volumes of portland cement with SCMs, producers are increasingly faced with ―incompatibility‖ in the mixes, that is, unexpected and unexplained acceleration or retardation in the kinetics, combined with undesirable strength gain, shrinkage, and cracking. The impact of SCMs on hydration and kinetics is considered in more detail in another paper in this issue [116]. However, it is worth noting that scientific understanding of the influence of SCMs on cement hydration is still in its infancy, even though some general engineering principles, such as the importance of sulfate balance, are developing. Even so, with concrete technology steadily moving toward these more complex mix designs, it is critical that an engineering/scientific basis be established for understanding and ameliorating compatibility issues.

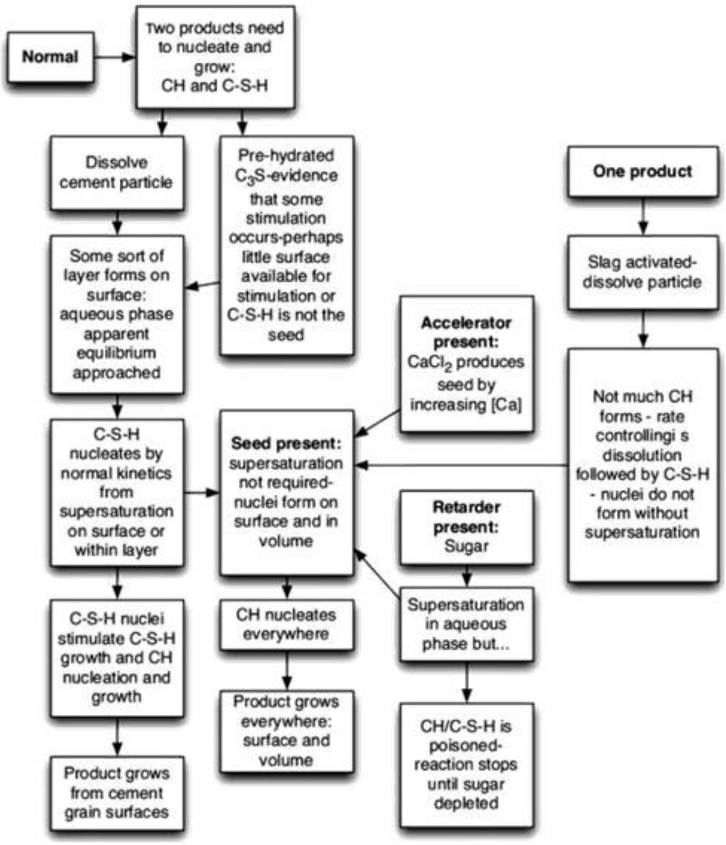

**Fig. 8.** Flowchart for organizing thinking about hydration kinetics and mechanisms.

## References

[1]. H.F.W. Taylor, P. Barret, P.W. Brown, D.D. Double, G. Frohnsdorff, V. Johansen, D. Ménétrier-Sorrentino, I. Odler, L.J. Parrott, J.M. Pommersheim, M. Regourd, J.F. YoungThe hydration of tricalcium silicateMater. Struct., 17 (1984), pp. 457–468|

[2]. E.M. Gartner, J.M. GaidisHydration mechanisms, IJ. Skalny (Ed.), Materials Science of Concrete, Vol. 1American Ceramic Society, Westerville, OH (1989) pp. 95–125

[3]. J.M. Gaidis, E.M. GartnerHydration mechanisms, IIJ. Skalny, S. Mindess (Eds.), Materials Science of Concrete, Vol. 2American Ceramic Society, Westerville, OH (1989), pp. 9–39

[4]. E.M. Gartner, J.F. Young, D.A. Damidot, I. JawedHydration of portland cementJ. Bensted, P. Barnes (Eds.), Structure and Performance of Cements (2nd Edition), Spon Press, New York (2002), pp. 57 -113

[5]. S. Glasstone, K.J. Laidler, H. EyringThe Theory of Rate ProcessesMcGraw-Hill, New York (1941)

[6]. D. Kaschiev, G.M. van RosmalenReview: nucleation in solutions revisitedCryst. Res. Technol., 38 (2003), pp. 555–574

[7]. H.H. Teng, P.M. Dove, J.J.D. YoreoThe kinetics of calcite growth: interpreting chemical affinity-based rate laws through the lens of direct observationMorphology and Dynamics of Crystal Surfaces in Complex Molecular Systems, Mater. Res. Soc. Symposium Proc, 620 (2000), p. M2.6

[8]. K.J. Davis, P.M. Dove, J.J.D. YoreoResolving the control of magnesium on calcite growth: thermodynamic and kinetic consequences of impurity incorporation for biomineral formationMorphological and Dynamics of Crystal Surfaces in Complex Molecular Systems, Mater. Res. Soc. Symposium Proc., 620 (2000), p. M.9.5.1

[9]. A.C. LasagaRate laws of chemical reactionsA.C. Lasaga, R.J. Kirkpatrick (Eds.), Kinetics of Geochemical Processes, No. 8 in Reviews in Mineralogy, Mineralogical Society of America (1981), pp. 1–68|

[10]. A.C. Lasaga, A. LuttgeVariation of crystal dissolution rate based on a dissolution step wave modelScience, 291 (2001), pp. 2400–2404 |

[11]. R.S. Arvidson, I.E. Ertan, J.E. Amonette, A. LuttgeVariation in calcite dissolution rates: a fundamental problem?Geochim. Cosmochim. Acta, 67 (9) (2003), pp. 1623–163

[12]. P.M. Dove, N. Han, J.J.D. YoreoMechanisms of classical crystal growth theory explain quartz and silicate dissolution behaviorProc. Nat. Acad. Sci. U.S.A., 102 (43) (2005), pp. 15357– 15362

[13]. P.M. Dove, N. HanKinetics of mineral dissolution and growth as reciprocal microscopic surface processes across chemical driving forceAIP Conference Proceedings, Vol. 916 (2007), pp. 215–234

[14]. R. Mills, V.M.M. LoboSelf-Diffusion in Electrolyte SolutionsElsevier, Amsterdam (198

[15]. G.A. SomorjaiIntroduction to Surface Chemistry and CatalysisWiley-Interscience, New York (1994)

[16]. A.W. Adamson, A.P. GastPhysical Chemistry of Surfaces(6th Edition)Wiley-Interscience, New York (1997)

[17]. W.K. Burton, N. Cabrera, F.C. FrankThe growth of crystals and the equilibrium structure of their surfacesPhil. Trans. R. Soc. Lond. A, 243 (866) (1951), pp. 299–3

[18]. W. Stumm, J.J. MorganAquatic ChemistryWiley-Interscience, New York (1972)

[19]. F.M.M. MorelPrinciples of Aquatic ChemistryWiley-Interscience, New York (1983)

[20]. R.S. Arvidson, C. Fischer, A. LuttgeResolution of crystal dissolution and growth processes at multiple scalesGeochim. Cosmochim. Acta, 72 (12) (2009), p. A34

[21]. J. Cama, L. Zhang, G. De Guidici, J.M. Soler, R.S. Arvidson, A. LuttgeDissolution of fluorite (111) cleavage surface in acid pH: VSI, AFM, and Monte Carlo simulationsGeochim. Cosmochim. Acta, 73 (2009), p. A187

[22]. C.C. Battaile, D.J. Srolovitz, J.E. ButlerA kinetic Monte Carlo method for the atomic-scale simulation of chemical vapor deposition: application to diamondJ. Appl. Phys., 82 (12) (1997), pp. 6293–6300

[23]. V.B. Shenoy, R. Miller, E.B. Tadmor, R. Phillips, M. OrtizAn adaptive finite element approach to atomic-scale mechanics—the quasicontinuum methodJ. Mech. Phys. Solids, 47 (3) (1999), pp. 611–642

[24]. L. Gránásy, T. Pusztai, T. Borzsonyi, J.A. Warren, J.F. DouglasA general mechanism of polycrystalline growthNat. Mater., 3 (9) (2004), pp. 645–650

[25]. K. Muralidharan, J.H. Simmons, P.A. Deymier, K. RungeMolecular dynamics studies of brittle fracture in vitreous silica: review and recent progressJ. Non-Cryst. Solids, 351 (18) (2005), pp. 1532–1542

[26]. M.M. Costoya, Effect of particle size on the hydration kinetics and microstructural development of tricalcium silicate, PhD dissertation, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland, 2008.

[27]. S. Garrault, A. NonatHydrated layer formation on tricalcium and dicalcium silicate surfaces: experimental study and numerical simulationsLangmuir, 17 (2001), pp. 8131–8138

[28]. V. Kocaba, Development and evaluation of methods to follow microstructural development of cementitious systems including slags, PhD dissertation, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland, 2009.

[29]. J.J. Thomas, H.M. Jennings, A.J. AllenThe surface area of cement paste as measured by neutron scattering — evidence for two C–S–H morphologiesCem. Concr. Res., 28 (1998), pp. 897–905

[30]. J.J. Thomas, A.J. Allen, H.M. JenningsHydration kinetics and microstructure development of normal and CaCl$_2$-accelerated tricalcium silicate (C$_3$S) pastesJ. Phys. Chem. C, 113 (2009), pp. 19836–19844

[31]. S.A. FitzGerald, D.A. Neumann, J.J. Rush, D.P. Bentz, R.A. LivingstonIn situ quasi-elastic neutron scattering study of the hydration of tricalcium silicateChem. Mater., 10 (1998), p. 397

[32]. J.J. Thomas, S.A. FitzGerald, D.A. Neumann, R.A. LivingstonState of water in hydrating tricalcium silicate and portland cement pastes as measured by quasi-elastic neutron scatteringJ. Am. Ceram. Soc., 84 (8) (2001), pp. 1811–1816

[33]. D.L. ParkhurstUser's guide to PHREEQC—a computer program for speciation reaction-path, advective-transport, and geochemical calculationsWater-Resources Investigations Report 95-4227, U.S. Geological Survey (1995)

[34]. W. Hummel, U. Berner, E. Curti, F.J. Pearson, T. ThoenenNagra/PSI Chemical Thermodynamic Data Base 01/01Universal Publishers, Parkland, Florida (2002)

[35]. P. Barret, D. MénétrierFilter dissolution of C$_3$S as a function of the lime concentration in a limited amount of lime waterCem. Concr. Res., 10 (1980), pp. 521–534

[36]. P. Barret, D. Ménétrier, D. BertrandieMechanism of C$_3$S dissolution and problem of the congruency in the very initial period and later onCem. Concr. Res., 13 (1983), pp. 728–73

[37]. J.B. Ings, P.W. Brown, G. FrohnsdorffEarly hydration of large single crystals of tricalcium silicateCem. Concr. Res., 13 (1983), pp. 843–848

[38]. D. Damidot, A. NonatC$_3$S hydration in dilute and stirred suspensions: (I) study of the two kinetic stepsAdv. Cem. Res., 6 (21) (1994), pp. 27–35

[39]. D. Damidot, F. Bellmann, B. Möser, T. SovoidnichCalculation of the dissolution rate of tricalcium silicate in several electrolyte compositionsCement Wapno Beton, 12/74 (2) (2007), pp. 57–67

[40]. H.N. SteinThermodynamic considerations on the hydration mechanisms of Ca$_3$SiO$_5$ and Ca$_3$Al$_2$O$_6$Cem. Concr. Res., 2 (2) (1972), pp. 167–177

[41]. E.M. Gartner, H.M. JenningsThermodynamics of calcium silicate hydrates and their solutionsJ. Am. Ceram. Soc., 80 (10) (1987), pp. 743–749

[42]. H.N. Stein, J.M. StevelsInfluence of silica on the hydration of 3CaO, SiO2J. Appl. Chem., 14 (1964), pp. 338–346

[43]. H.M. Jennings, P.L. PrattAn experimental argument for the existence of a protective membrane surrounding portland cement during the induction periodCem. Concr. Res., 9 (1979), pp. 501–506

[44]. H.M. JenningsAqueous solubility relationships for two types of calcium silicate hydrateJ. Am. Ceram. Soc., 69 (8) (1986), pp. 614–618

[45]. J.W. BullardA determination of hydration mechanisms for tricalcium silicate using a kinetic cellular automaton modelJ. Am. Ceram. Soc., 91 (7) (2008), pp. 2088–2097

[46]. R. Kondo, S. UedaKinetics and mechanisms of the hydration of cementsProceedings of the Fifth International Symposium on the Chemistry of Cement, Volume 2 (1968), pp. 203–212

[47]. S. Garrault-Gauffinet, A. NonatExperimental investigation of calcium silicate hydrate (C–S– H) nucleationJ. Cryst. Growth, 200 (1999), pp. 565–574

[48]. R.A. Livingston, J.S. Schweitzer, C. Rolfs, H.W. Becker, S. KubskyCharacterization of the induction period in tricalcium silicate hydration by nuclear resonance reaction analysisJ. Mater. Res., 16 (3) (2001), pp. 687–693

[49]. J.W. Schweitzer, R.A. Livingston, C. Rolfs, H.W. Becker, S. Kubsky, T. Spillane, M. Castellote, P.G. de ViedmaIn situ measurements of the cement hydration profile during the induction periodProceedings of the Twelfth International Congress on the Chemistry of Cement, National Research Council of Canada, Montreal, Canada (2007)

[50]. H.F.W. TaylorCement Chemistry(2nd Edition.)Thomas Telford, London (1997)

[51]. F. Bellmann, D. Damidot, B. Möser, J. SkibstedImproved evidence for the existence of an intermediate phase during hydration of tricalcium silicateCem. Concr. Res., 40 (2010), pp. 875– 884

[52]. N.J. Clayden, C.M. Dobson, C.J. Hayes, S.A. RodgerHydration of tricalcium silicate followed by solid-state $^{29}$Si NMR spectroscopyJ. Chem. Soc. Chem. Commun., 21 (1984), pp. 1396–1397

[53]. S.A. Rodger, G.W. Groves, N.J. Clayden, C.M. DobsonHydration of tricalcium silicate followed by $^{29}$Si NMR with cross polarizationJ. Am. Ceram. Soc., 71 (1988), pp. 91–96

[54]. X.D. Cong, R.J. Kirkpatrick$^{17}$O and $^{29}$Si MAS NMR study of β-C$_2$S hydration and the structure of calcium silicate hydratesCem. Concr. Res., 23 (1993), pp. 1065–1077

[55]. S. Garrault, E. Finot, E. Lesniewska, A. NonatStudy of C–S–H growth on C3S surface during its early hydrationMater. Struct., 38 (2005), pp. 435–442

[56]. P. Juilland, E. Gallucci, R. Flatt, K. ScrivenerDissolution theory applied to the induction period in alite hydrationCem. Concr. Res., 40 (2010), pp. 831–844

[57]. D. Damidot, A. Nonat, P. BarretKinetics of tricalcium silicate hydration in diluted suspensions microcalorimetric measurementsJ. Am. Ceram. Soc., 73 (11) (1990), pp. 3319– 3322

[58]. A. NonatModelling hydration and setting of cementCeramics, 92 (2005), pp. 247–257

[59]. T. Sakurai, T. Sato, A. YoshinagaThe effect of minor components on the early hydraulic activity of the major phases of portland cement clinkerProceedings of the Fifth International Symposium on the Chemistry of Cement,Vol. 1 Tokyo, Japan (1968), pp. 300–321

[60]. D. Ménétrier, I. Jawed, T.S. Sun, J. SkalnyESCA and SEM studies on early $C_3S$ hydrationCem. Concr. Res., 9 (1979), pp. 473–482

[61]. J.M. Makar, G.W. ChanEnd of induction period in ordinary portland cement as examined by high-resolution scanning electron microscopyJ. Am. Ceram. Soc., 91 (2008), pp. 1292–1299

[62]. P. Fierens, J.P. VerhaegenInduction period of hydration of tricalcium silicateCem. Concr. Res., 2 (1976), pp. 287–292

[63]. I. Odler, J. SchüppstuhlEarly hydration of tricalcium silicate 3. Control of the induction periodCem. Concr. Res., 11 (1981), pp. 765–774

[64]. J.N. Maycock, J.P. Skalny, R.S. KalyoncuSolid-state defects and clinker mineral hydrationAm. Ceram. Soc. Bull., 53 (1974), p. 326

[65]. J.J. ThomasA new approach to modeling the nucleation and growth kinetics of tricalcium silicate hydrationJ. Am. Ceram. Soc., 90 (10) (2007), pp. 3282–3288

[66]. S. Bishnoi, K.L. Scrivener$\mu$ic: A new platform for modelling the hydration of cementsCem. Concr. Res., 39 (4) (2009), pp. 266–274

[67]. J.J. Thomas, H.M. Jennings, J.J. ChenInfluence of nucleation seeding on the hydration mechanisms of tricalcium silicate and cementJ. Phys. Chem. C, 113 (11) (2009), pp. 4327–4334

[68]. J.W. Bullard, R.J. FlattNew insights into the effect of calcium hydroxide precipitation on the kinetics of tricalcium silicate hydrationJ. Am. Ceram. Soc., 93 (2010), pp. 1894–1903

[69]. S. Gauffinet, E. Finot, R. Lesniewska, A. NonatDirect observation of the growth of calcium silicate hydrate on alite and silica surfaces by atomic force microscopyC. R. Acad. Sci. Paris Earth Planet. Sci., 327 (4) (1998), pp. 231–236

[70]. I.G. RichardsonTobermorite/jennite- and tobermorite/calcium hydroxide-based models for the structure of C–S–H: applicability to hardened pastes of tricalcium silicate, β-dicalcium silicate, portland cement, and blends of portland cement with blast-furnace slag, metakaolin, or silica fumeCem. Concr. Res., 34 (2004), pp. 1733–1777

[71]. M. Zajac, Étude des relations entre vitesse d'hydratation, texturation des hydrates et résistance méchanique finale des pâtes et micro-mortiers de ciment portland. PhD dissertation, Universite de Bourgogne, Dijon, France, 2007.

[72]. J.J. Thomas, J.J. Biernacki, J.W. Bullard, S. Bishnoi, J.S. Dolado, G.W. Scherer, A. LuttgeModeling and simulation of cement hydration kinetics and microstructure developmentCem. Concr. Res., 41 (2011), pp. 1257–1278

[73]. A.J. Allen, J.C. McLaughlin, D.A. Neumann, R.A. LivingstonIn situ quasi-elastic scattering characterization of particle size effects on the hydration of tricalcium silicateJ. Mater. Res., 19 (11) (2004), pp. 3242–3254

[74]. V.K. Peterson, M.C.G. JuengerHydration of tricalcium silicate: effects of $CaCl_2$ and sucrose on reaction kinetics and product formationChem. Mater., 18 (2006), pp. 5798–5804

[75]. G.W. Scherer, J. Zhang, and J.J. Thomas, Nucleation and Growth Models for Hydration of Cement, in preparation.

[76]. J. Zhang, E.A. Weissinger, S. Peethamparan, G.W. SchererEarly hydration and setting of oil well cementCem. Concr. Res., 40 (2010), pp. 1023–1033

[77]. Z.Q. Wu, J.F. YoungThe hydration of tricalcium silicate in the presence of colloidal silicaJ. Mater. Sci., 19 (1984), pp. 3477–3486

[78]. A.J. Allen, R.C. Oberthur, D. Pearson, P. Schofield, C.R. WildingDevelopment of the fine porosity and gel structure of hydrating cement systemsPhilos. Mag. B, 56 (1987), pp. 263–268

[79]. H.M. JenningsA model for the microstructure of calcium silicate hydrate in cement pasteCem. Concr. Res., 30 (2000), pp. 101–116

[80]. A.J. Allen, J.J. Thomas, H.M. JenningsComposition and density of nanoscale calcium– silicate–hydrate in cementNat. Mater., 6 (2007), pp. 311–316

[81]. H.M. Jennings, J.J. Thomas, J.S. Gevrenov, G. Constantinides, F.-J. UlmA multi-technique investigation of the nanoporosity of cement pasteCem. Concr. Res., 37 (2007), pp. 329–336

[82]. H.M. Jennings, J.W. Bullard, J.J. Thomas, J.E. Andrade, J.J. Chen, G.W. SchererCharacterization and modeling of pores and surfaces in cement paste: correlations to processing and propertiesJ. Adv. Concr. Technol., 6 (1) (2008), pp. 1–25

[83]. E.M. GartnerA proposed mechanism for the growth of C–S–H during the hydration of tricalcium silicateCem. Concr. Res., 27 (5) (1997), pp. 665–672

[84]. G. Constantinides, F.-J. UlmThe effect of two types of C–S–H on the elasticity of cement-based materials: results from nanoindentation and micromechanical modelingCem. Concr. Res., 34 (2004), pp. 67–80

[85]. G. Constantinides, F.-J. UlmThe nanogranular nature of C–S–HJ. Mech. Phys. Solids, 55 (2007), pp. 64–90

[86]. S. Bishnoi, K.L. ScrivenerStudying nucleation and growth kinetics of alite hydration using $\mu$ icCem. Concr. Res., 39 (2009), pp. 849–860

[87]. J.F. Young, H.S. Tong, R.L. BergerComposition of solutions in contact with hydrating tricalcium silicate pastesJ. Am. Ceram. Soc., 60 (1977), pp. 193–198

[88]. I. Jawed, J. SkalnySurface phenomena during tricalcium silicate hydrationJ. Colloid Interface Sci., 85 (1) (1982), pp. 235–243

[89]. I. Odler, H. DörrEarly hydration of tricalcium silicate II. The induction periodCem. Concr. Res., 9 (1979), pp. 277–284

[90]. P.W. Brown, C.L. Harner, E.J. ProsenThe effect of inorganic salts on tricalcium silicate hydrationCem. Concr. Res., 16 (1985), pp. 17–22

[91]. J.G.M. de Jong, H.N. Stein, J.M. StevelsHydration of tricalcium silicateJ. Appl. Chem., 17 (1967), pp. 246–250

[92]. K.L. Scrivener, The development of microstructure during hydration of portland cement. Ph.D. Dissertation, University of London, 1984.

[93]. T. KnudsenKinetics of the reaction of β-$C_2S$ and $C_3S$ with $CO_2$ and water vaporJ. Am. Ceram. Soc., 63 (1980), pp. 114–115

[94]. V.K. Peterson, D.A. Neumann, R.A. LivingstonHydration of tricalcium and dicalcium silicate mixtures studied using quasielastic neutron scatteringJ. Phys. Chem. B, 109 (2005), pp. 14449–14453

[95]. A.J. Allen, R.C. Oberthur, D. Pearson, P. Schofield, C.R. Wildin Development of the fine porosity and gel structure of hydrating cement systemsPhilos. Mag. B, 56 (1987), pp. 263–288

[96]. A.J. AllenTime-resolved phenomena in cements, clays, and porous rocksJ. Appl. Cryst., 24 (1991), pp. 624–634

[97]. K. Mori, *et al.*Observation of microstructure of hydrated $Ca_3SiO_5$Phys. B Condensed Matter, 385 (2006), pp. 517–519

[98]. D.W. Hadley, W.L. Dolch, S. DiamondOn the occurrence of hollow-shell hydration grains in hydrated cement pasteCem. Concr. Res., 30 (2000), pp. 1–6

[99]. K.O. Kjellsen, B. LagerbladMicrostructure of tricalcium silicate and portland cement systems at middle periods of hydration-development of Hadley grainsCem. Concr. Res., 37 (2007), pp. 13–20

[100]. E. Gallucci, P. Mathur, K.L. ScrivenerMicrostructural development of early age hydration shells around cement grainsCem. Concr. Res., 40 (2010), pp. 4–13

[101]. R.A. Livingston, N. Nemes, D.A. Neumann, The transition point in the hydration kinetics of tricalcium silicate determined by quasi-elastic neutron scattering, unpublished.

[102]. W.A. Corstanje, H.N. Stein, J.M. Stevels Hydration reactions in pastesC3S + C3A + CaSO4.2aq + H2O at 25°C Cem. Concr. Res., 3 (1973), pp. 791–806

[103]. W.A. Corstanje, H.N. Stein, J.M. Stevels Hydration reactions C3S + C3A + CaSO4.2aq + H2O at 25 °C IIICem. Concr. Res., 4 (1974), pp. 417–431

[104]. E. Breval$C_3A$ hydrationCem. Concr. Res., 6 (1976), pp. 129–138

[105]. H. Minard, S. Garrault, L. Regnaud, A. NonatMechanisms and parameters controlling the tricalcium aluminate reactivity in the presence of gypsumCem. Concr. Res., 37 (2007), pp. 1418–1426

[106]. N. TenoutasseThe hydration mechanism of $C_3A$ and $C_3S$ in the presence of calcium chloride and calcium sulphateProceedings of the Fifth International Symposium on the Chemistry of Cement, Volume IIThe Cement Association of Japan, Tokyo, Japan (1968), pp. 372–378

[107]. K.L. Scrivener, P.L. PrattMicrostructural studies of the hydration of $C_3A$ and $C_4AF$ independently and in cement pasteF.P. Glasser (Ed.), Brit. Ceram. Proc. 35, Stoke-on-Trent, British Ceramic Society (1984), pp. 207–219

[108]. W. LerchThe influence of gypsum on the hydration reactions of portland cementProc. ASTM, 46 (1946), pp. 1252–1292

[109]. D.P. BentzInfluence of silica fume on diffusivity in cement-based materials. I. Experimental and computer modeling studies on cement pastesCem. Concr. Res., 30 (2000), pp. 953–962

[110]. D.D. DoubleNew developments in understanding the chemistry of cement hydrationPhil. Trans. R. Soc. Lond. A, 310 (1983), pp. 53–66

[111]. H.M. Jennings, B.J. Dalgleish, P.L. PrattMorphological development of hydrating tricalcium silicate as examined by electron microscopy techniquesJ. Am. Ceram. Soc., 64 (10) (1981), pp. 567–572

[112]. P.L. Pratt, H.M. JenningsThe microchemistry and microstructure of portland cementAnn. Rev. Mater. Sci., 11 (1981), pp. 123–149

[113]. R.D. Coatman, N.L. Thomas, D.D. DoubleStudies of the growth of silicate gardens and related phenomenaJ. Mater. Sci., 15 (1980), p. 2017-2026

[114]. E.E. Lachowski, S. DiamondInvestigation of the composition and morphology of individual particles of portland cement paste. 1. C–S–H gel and calcium hydroxide particlesCem. Concr. Res., 13 (1983), pp. 177–185

[115]. S. Diamond, E.E. LachowskiInvestigation of the composition and morphology of individual particles of portland cement paste. 2. Calcium sulfoaluminatesCem. Concr. Res., 13 (1983), pp. 335–340

[116]. B. Lothenbach, *et al.*Supplementary cementitious materialsCem. Concr. Res., 41 (2011), pp. 1244–1256

[117]. A. Lasaga, G.V. GibbsAb initio quantum mechanical calculations of water–rock interactions: adsorption and hydrolysis reactionsAm. J. Sci., 290 (1990), pp. 263–295

[118]. S.C. Parker, N.H. de Leeuw, E. Bourova, D.J. CookeApplication of lattice dynamics and molecular dynamics techniques to minerals and their surfacesin: R.T. Cygan, J.D. Kubicki (Eds.), Molecular Modeling Theory: Applications in the Geosciences, Reviews in Mineralogy and Geochemistry, 42, Mineralogical Society of America, Washington, D.C (2001), pp. 63–82

[119]. A. LuttgeCrystal dissolution kinetics studied by vertical scanning interferometry and Monte Carlo simulationsX.-Y. Liu, J.J. De Yoreo (Eds.), Interfacial Structures versus Dynamics, Series on Nanoscience and Technologies, Vol. IKluwer Academic Pu

[120]. P. Bénard, S. Garrault, A. Nonat, C. Cau-dit-CoumesInfluence of orthophosphate ions on the dissolution of tricalcium silicateCem. Concr. Res., 38 (2008), pp. 1137–1141

[121]. M.C.G. Juenger, V.H.R. Lamour, P.J.M. Monteiro, E.M. Gartner, G.P. DenbeauxDirect observation of cement hydration by soft X-ray transmission microscopyJ. Mater. Sci. Lett., 22 (19) (2003), pp. 1335–1337

[122]. M.C.G. Juenger, P.J.M. Monteiro, E.M. Gartner, G.P. DenbeauxA soft X-ray microscope investigation into the effects of calcium chloride on tricalcium silicate hydrationCem. Concr. Res., 35 (1) (2005), pp. 19–25

[123]. D.A. Silva, P.J.M. MonteiroHydration evolution of $C_3S$–EVA composites analyzed by soft X-ray microscopyCem. Concr. Res., 35 (2005), pp. 351–357

[124]. R.B. WilliamsonConstitutional supersaturation in portland cement solidified by hydrationJ. Cryst. Growth, 3 (1968), pp. 787–794

[125]. L. Gránásy, T. Pusztai, G. Tegze, J.A. Warren, J.F. DouglasGrowth and form of spherulitesPhys. Rev. E, 72 (2006), p. 011605

[126]. P. Barret, D. Ménétrier, D. Bertrandie, M. RegourdComparative study of C–S–H formation from supersaturated solutions and $C_3S$ solution mixtures7th International Congress on the Chemistry of Cement, Paris, France (1980)