Cement and Concrete Research 42 (2012) 881–887

Contents lists available at SciVerse ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Discussion

A reply to the discussion "Accelerated growth of calcium silicate hydrates: Experiments and simulations" by S. Bishnoi and K. Scrivener[☆]

Luc Nicoleau[a,*], André Nonat[b,1]

[a] BASF Construction Chemicals GmbH, Global Research Polymers for Inorganics, 32 Albert Frank Straße, D-83308 Trostberg, Germany
[b] Institut Carnot de Bourgogne UMR5209 CNRS, 9 avenue Alain Savary, BP 47870, 21078 Dijon Cedex, France

ARTICLE INFO

Article history:
Received 20 November 2011
Accepted 9 February 2012

Keywords:
Alite hydration
Kinetics
Nucleation and growth

We sincerely thank Dr. Bishnoi and Prof. Scrivener for their comments [1] on Nicoleau's paper [2]. This discussion contributes significantly in clarifying the current debate about alternatives to model the cement hydration kinetics. In spite of our initial interest on the accelerating part of the hydration [2], the main point discussed by Bishnoi and Scrivener concerns the limitation of growth kinetics of C-S-H during the alite hydration, leading to the post-peak deceleration in isothermal calorimetry. Our reply will therefore also focus on this part of the hydration process, where different models are today in opposition. Doing so, we answer the five different points claimed by Bishnoi et al. in [1].

1. On factors limiting the growth

The cornerstone condition for a proper description of the alite hydration kinetics is to take into account (1) the nucleation and growth of C-S-H and (2) the dissolution of alite [3]. The hydration kinetics cannot be described only by a nucleation and growth process as in Bishnoi's model [4] and in other models based on "Avrami-like" equations discussed later in this reply. Besides in the original Garrault and Nonat's model [5], the dissolution was also not considered since only the accelerating part of the hydration was addressed in this paper. In this part, the limitation by the dissolution is negligible. An extension of this model including also the dissolution rate and the grain size distribution was recently proposed [6].

In order to generate a limitation of the hydration rate, models based on Avrami-like equations introduce some impingements to the C-S-H growth. In particular, the Bishnoi's model asserts that the deceleration of the growth originates with "*impingements with C-S-H originating from different particles will affect nucleation and growth kinetics*" as it has been first proposed in [4] and also questionably assumed in [1]. This configuration is schematically depicted by the case 1 in Fig. 1. This hindrance undergone by the C-S-H growth is termed as an inter-layers impingement. On the contrary, in the Garrault and Nonat's model [5], there is also a hindrance but due to the collision of growing clusters located on same grains. This can be termed as an intra-layer impingement (case 2 in Fig. 1). Nevertheless, the hindrance is not sufficient to account for the complete deceleration; it is actually considered that the main contribution to this deceleration is the decrease of the dissolution rate due to the coverage of the alite surface by C-S-H [2,3,5]. The limitation of the dissolution is described in Nicoleau's paper through a diffusion barrier resulting from the coverage of alite grains by C-S-H and parameterized by a permeability coefficient.

The free space between cement grains is strongly affected by the grain size distribution, as the water to alite ratio also does. The grain size distribution has therefore a considerable effect in case 1 (Bishnoi's model) since the C-S-H growth and its limitation is described by the filling of the free space around the cement grains as it has been proposed in [4] and mentioned in [1]. As far as early hydration times are considered, the particle size distribution is not important in case 2 since the growth is described by clusters growing onto a single grain. The first point debated by Bishnoi et al. is therefore strictly dependent to their model. The question is now to consider which model is more relevant for a proper description of alite hydration. We recall in the following section several experimental facts in favor of case 2.

2. Effect of the water to cement ratio

More than 20 years ago, it was experimentally demonstrated first by Damidot [7–9] in stirred and diluted suspensions and confirmed later [10] by others that the water to cement (or the water to alite/C_3S) ratio (denoted W/C) does not noticeably affect the calorimetric curve of cement hydration (or alite/C_3S) if the hydration is started in a solution saturated with respect to the Portlandite $Ca(OH)_2$. The

---

[☆] A. Nonat joined L. Nicoleau for this reply because the discussion by Bisnoï et al. mainly concerns the model originally proposed by Nonat and Garrault.

[*] Corresponding author. Tel.: +49 8621862734; fax: +49 862166502734.
E-mail addresses: luc.nicoleau@basf.com (L. Nicoleau), andre.nonat@u-bourgogne.fr (A. Nonat).

[1] Tel.: +33 380396166.

0008-8846/$ – see front matter
doi:10.1016/j.cemconres.2012.02.014

Table 1
Sets of parameters used for the simulations shown in Fig. 5.

	Alite matrix size $N^2/100$	Nuclei on alite (blocks)	Rate //[BL/t_i]	Rate [BL/t_i]	Induction time [hours]	Permeability P/100 [BL]	Additional matrix size	Additional nuclei
Blank	3000	20	6.1	17.2	3.5	1		
100mM $CaCl_2$ SET 1 from Nicoleau [2]	3000	14	6.8	13	2	0.6	4600	20
100 mM $CaCl_2$ SET 2 proposed by Bishnoi [1]	3000	20	5.5	33	2	0.6	0	0

saturated solution is representative of a pore solution in paste. The curves corresponding to different W/C are even almost identical if pre-hydrated C_3S is used additionally to the saturated lime solution [11]. The short pre-hydration aims to fix the number of C-S-H nuclei onto the C_3S surface. Experiments done by Damidot were carried out in a Tian-Calvet microcalorimeter with a specially designed cell allowing the monitoring of C_3S hydration in highly diluted conditions. The Tam Air calorimeter used in [2] with Admix-cells enables also to record the heat released in moderately diluted suspensions. An example of alite hydration is shown in Fig. 2. Again, as long as the diluted suspension is hydrated in a saturated lime solution, the water to cement ratio has no influence on the hydration.

During the hydration of alite at W/C = 10 shown in Fig. 2, the grains are dispersed in 20 times more water than at W/C = 0.5, i.e. the free space for C-S-H growth is 20 times larger. Even if impingements of C-S-H from different grains claimed by Bishnoi et al. remain a theoretical possibility at W/C = 0.5, this possibility is vanishing at higher W/C due to the significantly increased distances between the grains. Because the post-peak deceleration is seen in all cases and more importantly that the shape of curves are almost identical, it is hard to believe that the impingement of C-S-H layers is a reasonable hypothesis to explain the deceleration occurring independently of the W/C ratio.

3. On the mechanical consequence of C-S-H impingement

Bishnoi and Scrivener [1] claim that "*since these* (inter-layers) *impingements are the cause of setting and strength-gain in cements, they must not be negligible*". In paste, i.e. at low water to cement ratio, it is undisputed that contacts between C-S-H layers growing from different alite grains are the main cause of strength development in cement. However, this effect on mechanical properties does not allow concluding on hydration kinetics. In paste, cement grains aggregate in few minutes to form a solid network revealed by a gel point in dynamic rheometry [12]. The C-S-H growing around neighboring grains will inevitably overlap (due to the already formed points of contact); hence the increase of the elastic modulus [12]. The overlapping of C-S-H layers and the consecutive impingement is occurring from the first minutes until the end of hydration. Nevertheless, even if C-S-H layers are in contact, it does not mean that overlaps are large enough to have a significant role on hydration kinetics and especially at early times i.e. before the hydration becomes limited by the dissolution as it has been presented in [2]. Moreover, assuming that the peak deceleration in calorimetry would be caused by the meeting of C-S-H layers from neighboring alite grains, this should be manifested in the evolution of the elastic modulus by a steep increase. Such an increase has never been observed (see for examples [13–15])

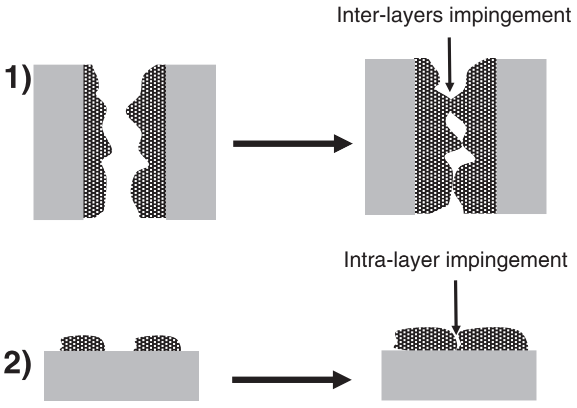

Fig. 1. Schematic representations of the existing models for the explanation of the limitation of the C-S-H growth. The C-S-H growing on alite/cement grains are depicted in dark grey. The model 1 is argued by Bishnoi and Scrivener, the growth of C-S-H is hindered by the growth coming from neighboring grains. The model 2 is defended by Nicoleau. The growth of C-S-H is partially hindered due to the meet of different C-S-H clusters growing on same grain.

4. On the evolution of the C-S-H surface during the hydration

Referring to case 1, C-S-H should fill the space between the grains at constant rate. It clearly means that, according to the ellipsoidal growth proposed by Bishnoi [1,4], the surface area of C-S-H will continuously increase until the collision of C-S-H layers and then continuously decrease due to the inter-layers impingement. This is experimentally invalidated. Indeed, experiments carried out by Zajac [16] described the typical evolution of the surface area during alite hydration. The C-S-H surface area was estimated *in situ* using ^{1}H NMR experiments [17,18] without any sample preparation and almost continuously during the hydration of alite at various temperatures. Zajac's data are plotted in Fig. 3. Undoubtedly, the evolution of the surface area is strongly non-monotonic. The $S_{pNMR} = f(t)$ curves in Fig. 3b can be divided in three distinct parts: (1) a first increase of the surface area corresponding to the accelerating part of the hydration until (2) a drop occurring exactly at the inflexion point of the hydration curve which is then (3) followed by a further increase of the surface area. The drop is undoubtedly related to a partial extinction of the C-S-H surface, i.e. to an impingement of C-S-H. As the surface decrease is only temporary, this is only compatible with the case 2. The subsequent increase of the surface is due to the further growth of C-S-H onto the continuous layer, observed also by atomic force

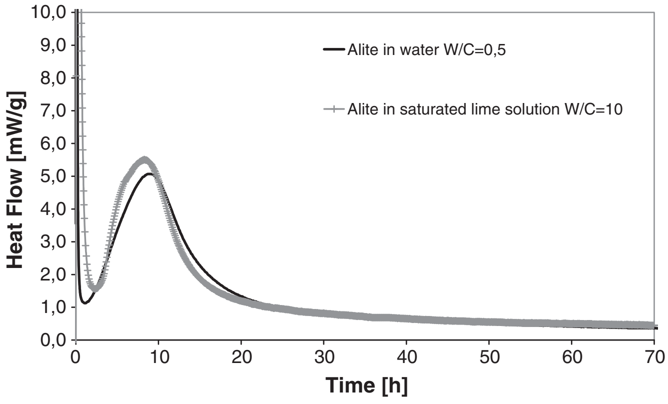

Fig. 2. Heat flow released during the hydration of alite in water at W/C = 0.5 and in a solution saturated with respect to calcium hydroxide at W/C = 10.

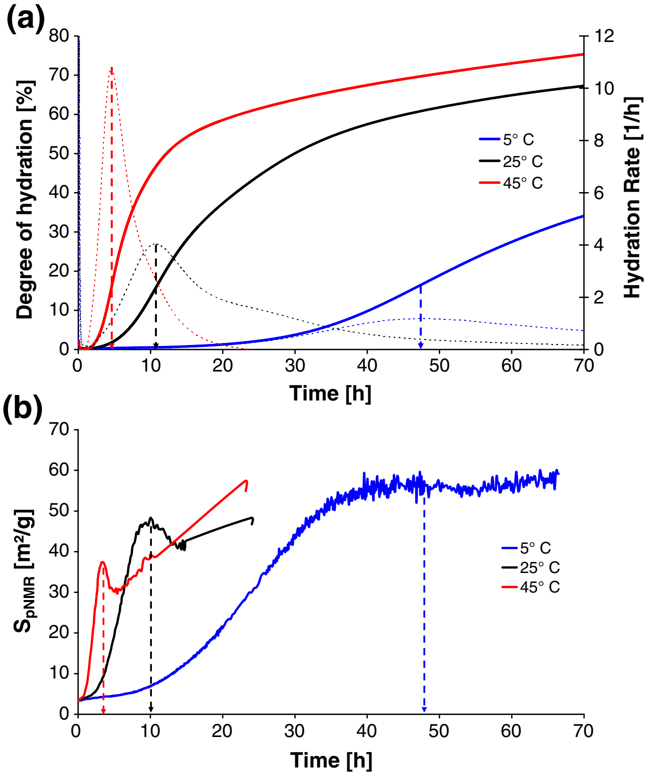

Fig. 3. Evolution of (a) the degree of hydration of C_3S pastes (W/C = 0.375) at different curing temperatures and (b) of the surface area developed in these pastes as measured by ^1H NMR.

microscopy [19]. The Bishnoi's model (case 1) cannot reproduce the double change in the monotony of the surface evolution; on the contrary this is well simulated using the Garrault and Nonat's model [15]. The choice of an ellipsoidal or cuboidal shape for the C-S-H growth is of secondary importance if the limitation of the dissolution is taken into account.

5. Incompatibily of Avrami-like equations with the modeling of cement hydration

In spite of the convenience and the easiness to use Avrami-like equations to fit the hydration of cementitious materials, it implies some hypotheses non-satisfied in the case of the alite hydration. The Johnson-Mehl-Avrami-Kolmogorov equation (JMAK) was often successfully applied in the past (see for examples [20–23]) to account for nucleation and growth reactions. Its generalized form, giving the fraction of transformed product α as a function of time t for isothermal reactions, is:

$$\alpha = 1 - \exp\left(-k \cdot t^{n}\right) \tag{1}$$

where k is a constant depending on temperature and n referred to as the Avrami exponent. This equation was even extended to non-isothermal phase transformations [24,25]. However, many cases of deviation from the standard JMAK kinetics were reported. It was established that nonrandom nucleation [26] and possible impingements [27] lead to important deviations from the standard JMAK model. The last limitation was the motivation for improved models taking into account all possible impingements. As an example, it has been solved by Cahn [28] who derived the JMAK equation and demonstrated its relevance for grain boundary nucleation reactions. First used by Thomas [29], the boundary nucleation model was also applied in cementitious systems. Several variations based on these initial works were proposed. For the purpose of this reply, we have termed all these variations as Avrami-like equations since the main feature of the initial Avrami equation is preserved. Nevertheless, the most important pre-condition assumed in Avrami-like equations, is that the transformation must not be influenced by any time-dependent process [23,30]. In other words, the basis of these equations is that the interfacial growth rate is constant over the time. This condition obviously limits the use in crystallization processes to those with a crystallization rate which does not vary with other reactions. To the best of our knowledge, the heuristic Avrami theory was never used for describing a multi-reaction process. The mentioned pre-condition is clearly not fulfilled for the C-S-H growth since the growth rate is depending on the alite dissolution rate, due to the fact that the precipitation of C-S-H occurs (1) from the ions provided by the dissolution and (2) onto alite particles. Such a type of derivation from the JMAK model is used by Bishnoi in [1] and [4] as an attempt to describe the hydration of alite. Equivalent equations were also used by different authors [31–34]. Even if fits can be always done, the significance of these mathematical fits is limited and questionable.

The main reason generally put forward for using such Avrami-like equations [4] is that the C-S-H nucleation-growth kinetics is controlling the entire hydration. This is only true at the very early age, i.e. before the deceleration. In the following, we will demonstrate the variation of the interfacial C-S-H growth rate and the changes in kinetics during the hydration. In general terms, the hydration is the dissolution of a phase A which leads to the precipitation of a phase B, A and B are constituted of the same elements. In our case, A is alite and B C-S-H. If there is no accumulation of ions in solution, the *sine qua non* condition of hydration kinetics is that the rates of dissolution R_A and precipitation R_B have to be equal at any time t [2,3,6]:

$$R_B = R_B^i S_B = R_A^i S_A = R_A \text{or} \frac{R_A^i(t)}{R_B^i(t)} = \frac{S_B(t)}{S_A(t)} \tag{2}$$

with R_j^i the interfacial reaction rate and S_j the surface area related to the phase j. In other words, the ratio between the interfacial rates has to evolve during the hydration as the inverse of surfaces. Typically, during the cement hydration the surface of B (C-S-H) increases whereas the surface of A (alite) decreases which will naturally lead to an increase of the ratio S_b/S_a. Because the interfacial rates increase with the deviation from equilibrium [35,36]:

$$R_A^i(t) = f(\beta_A) \text{ and } R_B^i(t) = g(\beta_B) \tag{3}$$

where β_A and β_B are respectively the undersaturation with respect to A and the supersaturation with respect to B ($0 < \beta_a < 1$ and $\beta_b > 1$). To satisfy the equality 2 the interfacial dissolution rate will increase and the interfacial precipitation rate will decrease. It is difficult to presume about the two functions *f* and g but at least we know they are monotonic: the higher the supersaturation/undersaturation, the faster the precipitation/dissolution. Therefore, the necessary decrease of the precipitation rate and increase of the dissolution rate will be achieved by a decrease of the supersaturation and meanwhile an increase of the undersaturation. In other words, the ion concentrations depart more and more from the solubility of A to move closer and closer to the solubility of B. For the alite hydration, we have to consider the following reactions:

$$Ca_3SiO_5 + 3H_2O \rightarrow 3Ca^{2+} + 4OH^- + H_2SiO_4^{2-} \qquad \text{(alitedissolution)}$$
$$1,7Ca^{2+} + 1,4OH^- + H_2SiO_4^{2-} \rightarrow (CaO)_{1,7}-(SiO_2)-(H_2O)_y \quad \text{(C – S – Hprecipitation)}$$

Even if the solubilities are uncertain, the super- and undersaturation are proportional to the ion activity product:$\beta_{CSH} \propto (Ca^{2+})$

$^{1,7}(\mathrm{OH}^-)\ ^{1,4}(\mathrm{H_4SiO_4})$ and $\beta_{C3S} \propto \frac{1}{(\mathrm{Ca}^{2+})\ ^{3}(\mathrm{OH}^-)\ ^{4}(\mathrm{H_4SiO_4})}$ with (i) the activity of the ion i.

In the literature, various data are available, we chose to use those published by Lothenbach et al. [37]. In this paper, Lothenbach et al. followed the hydration of an ordinary Portland cement by semi-quantitative XRD and by ICP-OES. Using the ion concentrations available in Table 3 of the cited reference in the time range of interest, i.e. between one half hour and ~14 days and assuming for the sake of simplicity the equivalency between concentrations and activities, we may calculate the ion activity products related to the dissolution of alite and to the C-S-H precipitation. Fig. 4a represents the evolution of the supersaturation with respect to C-S-H during the hydration and Fig. 4b the ratio between the undersaturation and the supersaturation as well as the evolution of the surface area of alite. The surface area evolution is calculated and normalized from the XRD data from Lothenbach assuming monodisperse spherical alite grains, i.e. Surface∝Volume$^{2/3}$.

Referring to the evolution of the supersaturation with respect to C-S-H, we distinguish two domains separated by a clear rupture in the evolution. This rupture occurs after ca. 10 h, i.e. after the inflexion point (or post-peak deceleration). The supersaturation with respect to C-S-H is divided by a factor 3. Assuming the proportionality between the supersaturation and the interfacial growth rate, this would mean that the growth rate after 10 h represents about only one third of the growth rate before 10 h. It is at least far to be constant. This steep change results in the collapse of the first assumption attached to the Avrami-like equations. Despite the fact, as expected, that the decrease of the alite surface is strictly monotonic, strong variations are further observed in the ratio β_a/β_b after 10 h indicating a more complex kinetics at later times.

6. Characteristics of the C-S-H layer formed around the grains

(a1) It is today recognized that a C-S-H layer is formed around the particles of alite after a certain degree of hydration. Nevertheless, for lack of experimental data, there are still a lot of questions concerning this layer. To the best of our knowledge, the article under discussion [2] is the only one reporting experimental work geared towards a characterization of the C-S-H layer. Once formed, this layer has to be porous and permeable to ions and water in order to further enable the hydration reaction. In models proposed in [2] or [4], the porosity is not treated explicitly since compact objects are replicated to account for the C-S-H growth. In order to describe the intra-gel porosity, a parameter called "permeability" is additionally used in [2]. This parameter represents the restraint to the diffusion through the C-S-H layer compared to the free diffusion in solution, as it has been also introduced in [38].

(a2) Bishnoi put forward in [1] that the permeability parameter is introduced "*to get around the fact that the rate of reaction does not continue to slow down after the meeting of the nuclei*". In fact, it is the contrary. Since the rate of hydration becomes lower with a layer restraining the diffusion than with a layer not restraining the diffusion as it is shown in Fig. 8 of the article under discussion. It is also questioned that the

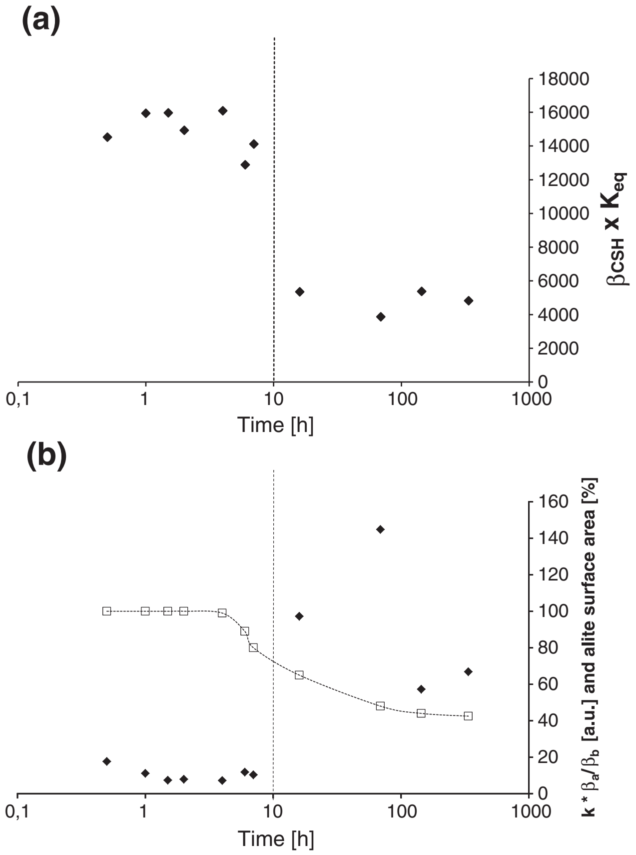

Fig. 4. (a) Evolution of the supersaturation with respect to the C-S-H during the hydration of a typical ordinary Portland cement. (b) Evolutions of the ratio ba/bb as well as the relative surface of alite. Data are from [37] and further used with the courtesy of Barbara Lothenbach.

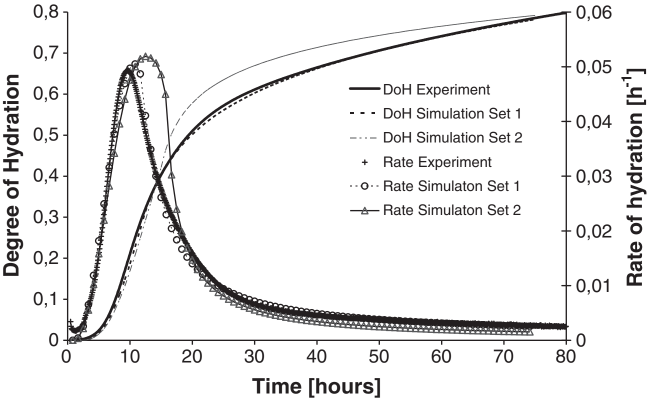

Fig. 5. Experimental and simulated degrees of hydration and their respective rate of hydration. The experimental curves are related to the hydration of alite (W/C = 0.5) with 100 mM of $CaCl_2$ from [2]. The simulated curves used two sets of parameters listed in Table 1 and referred to what was questioned by Bishnoi in [1].

permeability parameter could vary depending on other fitting parameters. This is hopefully an expected feature since the porosity is not simulated explicitly in Nicoleau's first model, but we intended to explain the variation of the permeability looking at the other parameters, as for instance the density of nuclei on alite. It is actually one of the purposes of the article under discussion [2].

(a3) Bishnoi called the variation of the fitting parameters "*arbitrary*" in [2] what came basically out from the best fitting. As an attempt to demonstrate an apparent random choice of the available area for nucleation, Bishnoi compared two sets of parameters resulting in the same curve (Fig. 5 in [1]). However, using an Avrami-like equation, oversimplifies the original model presented in [2]. His simplified growth model takes away and excludes the roles played by the dissolution rate and the diffusion through the C-S-H layer. We have already demonstrated in this current article the misuses of Avrami-like equation to describe the hydration. Fig. 5 shows the original experimental curve as well as the two simulated curves corresponding to the parameter data set 1 (originally presented in [2] as the best fitting set) and the parameter data set 2 alternatively proposed by Bishnoi in [1]. Even if the two sets give identical curves in the simplistic model of Bishnoi [1], they differ significantly enough in our simulations to clearly exclude the set 2 as relevant. Moreover, as Bishnoi did not include the diffusion in his model, we decided to keep the permeability parameter constant in order to make a fair comparison. An additional exclusion of the role played by the diffusion would have given a much larger deviation from the experimental curve. The thickness of the C-S-H layer on alite particles (and only on alite particles) and the porosity of this layer are the two most important parameters controlling the hydration rate at later ages, i.e. when the hydration has drastically decelerated. It refers to times longer than 50 h in the case of Fig. 5. At this time, the set 1 fits very well the experimental curve. However, set 2 gives about only one half of the experimental rate. This is trivial since the perpendicular growth rate, and therefore the thickness of the layer, has been increased compared to the set 1. A thicker layer results in a lower hydration rate at this stage. It is worthwhile to note also that the simulated curves of Bishnoi presented in Fig. 5 of his discussion [1] are far from reproducing the experimental curve. Furthermore, they are poorly comparable with our simulations in spite of opposite claims by the authors.

(b) An original cryo-SEM technique was proposed in [2] in order to evaluate the thickness of C-S-H layer in various samples. In spite of possible artifacts inherent in the technique, it was decided to compare the experimental thicknesses to the simulated ones. We expected proportionality between both as an acceptable model validation. Aware of the possible artifacts related to the SEM microscopy, we carried out the experiments with reasonable statistics: at least 20 relevant sections were gathered and 20 thicknesses measured to average the value, which enabled also the presentation of results with a standard deviation. Small standard deviations confirm that the number of analyzed sections is high enough in order to be representative of a real layer thickness evolution and to consequently invalidate the vague quantitative argument of Bishnoi. Nevertheless, we will numerically demonstrate that our conclusion, based on the proportionally between simulated and experimental thicknesses, is still clearly valid.

Considering spherical alite particles, it is possible to evaluate the mean deviation between the real thickness and the apparent thickness after sectioning measured by imaging. In Fig. 6, the concept schematically is presented. The original alite grain is represented by a sphere of radius R_t where a layer of thickness R_2 has been converted. The non-reacted core keeps a radius R_1. We assume a random sectioning plan symbolized by

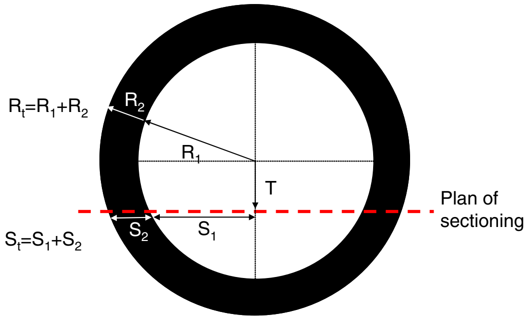

Fig. 6. Schematic representation of a spherical grain randomly sectioned by a plan.

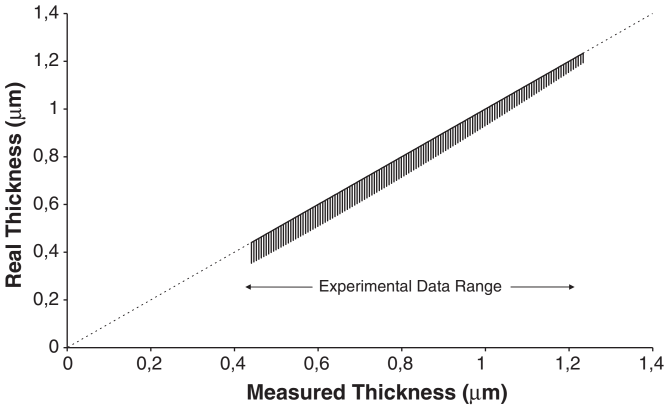

Fig. 7. Evolution of the mean experimental error for the possible averaged experimental thickness. This error is represented by bars.

the dashed line. The cryo-SEM picture corresponds to the image of the spherical cap cut by a plan. The thickness measured by microscopy is the dimension S_2 and can be calculated with the following equation:

$$S_2 = \sqrt{(R_1 + R_2)^2 - T^2} - \sqrt{R_1^2 - T^2}$$

The experimental thickness corresponds to an average on the possible values taken by T, i.e. $T \in]0; T_{max}[$. It results from the above equations that the higher T, the higher S_2, or in other words the higher the overestimation of the thickness, as it has been depicted in [39]. Within a set of experiments, we get the average:

$$\overline{S_2} = \frac{1}{T_{max}} \int_0^{T_{max}} S_2(T).dT = \frac{T_{max}\sqrt{(R_1 + R_2)^2 - T_{max}^2} + \arctan\left(\frac{T_{max}}{\sqrt{(R_1+R_2)^2 - T_{max}^2}}\right)(R_1 + R_2)^2 - T_{max}\sqrt{R_1^2 - T_{max}^2} + R_1^2 \arctan\left(\frac{T_{max}}{\sqrt{R_1^2 - T_{max}^2}}\right)}{2T_{max}}$$

it yields that ΔR_2 the relative experimental overestimation of R_2 is:

$$\Delta R_2 = \frac{\overline{S_2} - R_2}{R_2}$$

Aware of such an overestimation of the thickness, we chose in [2] to reduce the relevant data set to measures where S_2 did not exceed 33% of S_1, or :

$$\frac{\sqrt{R_1^2 - T_{max}^2}}{\sqrt{(R_1 + R_2)^2 - T_{max}^2} - \sqrt{R_1^2 - T_{max}^2}} = 3 \ \text{since} \ S_1 = \sqrt{R_1^2 - T^2}\ \text{, itgives} T \in \left[0; \frac{\sqrt{7(R_1 + 3R_2)(R_1 - 3R_2)}}{7}\right]$$

Coming back to experimental values, the grain size distribution of the alite was measured in [2]; the mean diameter obtained was 11.75 µm which gives $R_t = 5.87$ µm. Taking this data, considering all possible values of R_2, we may easily calculate the error done on R_2 by measuring $\overline{S_2}$. In the article under discussion, we see that the experimental thicknesses measured by cryo-SEM, i.e.$\overline{S_2}$, varied between about 420 and 1200 nm. We will focus only on this range. In Fig. 7, we plotted the straight-line $y = x$ and the possible error done on experimental thickness for each point of the line included in the experimental data range. We see that the possible error remains always acceptable and could not change at all the tendency. In the data set, the maximum relative error, i.e. the maximum ΔR_2 is about 20%. A less constraining initial condition, as for instance $S_2 < 0.5\ S_1$ would have yielded to a maximum ΔR_2 equal to 24%.

(c) The conclusion of this demonstration is that, under the spherical grain approximation, the linear tendency shown in Fig. 7 in [2] is preserved even if some technical artifacts exist. We may trustfully validate the simulations done in [2]. The qualitative opposite argument of Bishnoi et al. is not admissible. It is interesting also to point out that the experimental standard deviation plotted in Fig. 7 of the article under discussion if following the same evolution as plotted in Fig. 7 of this reply, i.e. the experimental values dispersion is following the theoretical one.

The last argument of authors of [1] to question the coherence between simulations and experiments is to let appear trivial the accordance between the simulation data set and the experimental mean diameter of alite. We recall that:

(1) In the simulation data set, the thicknesses and the degrees of hydration can vary independently because of possible C-S-H growth in bulk (with some accelerators).
(2) The experimental thicknesses and the grain size of alite were measured with two different techniques. This latter was never taken into account for the simulations.

Instead of *not surprising*, the close values between simulated and experimental areas of alite should be better qualified of consistent. More interestingly, we see that simulations running onto the surface of a single particle of alite, matches closely the mean grain size obtained by granulometry, i.e. the grain size distribution may be occulted as a very first approximation.

References

[1] S. Bishnoi, et al., Discussion of the paper "Accelerated growth of calcium silicate hydrates" by Luc Nicoleau, Cem. Concr. Res. 42 (2012) 878–880 (this issue).

[2] L. Nicoleau, Accelerated growth of calcium silicate hydrates: experiments and simulations, Cem. Concr. Res. 41 (2011) 1339–1348.

[3] K.L. Scrivener, et al., Hydration of cementitious materials, present and future, Cem. Concr. Res. 41 (7) (2011) 651–665.

[4] S. Bishnoi, et al., Studying nucleation and growth kinetics of alite hydration using µic, Cem. Concr. Res. 39 (2009) 849–860.

[5] S. Garrault, et al., Hydrated layer formation on tricalcium and dicalcium silicate surfaces: experimental study and numerical simulations, Langmuir 17 (2001) 8131–8138.

[6] A. Nonat, et al., Tricalcium silicate hydration modeling and numerical simulations, Proceedings of Conmod, 10, 2010, pp. 91–94.

[7] D. Damidot, et al., C_3S hydration in diluted and stirred suspension: I Evidence of two C-S-H precipitation steps, Adv. Cem. Res. 21 (1994) 27–35.

[8] D. Damidot, et al., C_3S hydration in diluted and stirred suspension: II Properties of two C-S-H precipitation steps, Adv. Cem. Res. 22 (1994) 83–91.

[9] D. Damidot, et al., Kinetics of tricalcium silicate hydration in diluted suspensions by nmicrocalorimetric measurements, J. Am. Ceram. Soc. 73 (11) (1990) 3319–3322.

[10] S.A. Grant, et al., Effect of the temperature on hydration kinetics and polymerization of tricalcium silicate in stirred suspensions of CaO-saturated solutions, Cem. Concr. Res. 36 (2006) 671–677.

[11] D. Damidot, Etude de l'hydratation du silicate tricalcique en suspensions diluées par microcalorimétrie isotherme, Thesis of the Univesité de Bourgogne, Speciality Physical Chemistry, 1990, Dijon.

[12] L. Nachbaur, et al., Dynamic mode rheology of cement and tricalcium silicate paste from mixing to setting, Cem. Concr. Res. 31 (2001) 183–192.

[13] A. Nonat, Du gâchage à l'état durci, ce sont les mêmes liaisons qui sont à l'œuvre, Rev. Fr. Génie Civ. 2 (7) (1998) 759–765.

[14] A. Boumiz, et al., Mechanical properties of cement pastes and mortars at early age: evolution with time and degree of hydration, Adv. Cem. Based Mater. 3 (3–4) (1996) 94–106.

[15] S. Garrault, et al., Hydration of silicate phase and mechanical evolution in 'alite-tricalcium aluminate-gypsum' complex system, in: J.J. Beaudoin, J.M. Makar, L. Raki (Eds.), Proceedings of the 12th ICCC, Montreal 2007, 2007.

[16] M. Zajac, et al., Effect of the temperature on the developement of CSH during early hydration of C_3S, in: J.J. Beaudoin, J.M. Makar, L. Raki (Eds.), Proceedings of the 12th ICCC, Montreal 2007, 2007.

[17] F. Barberon, et al., What is the surface specific area of porous cement-based material? A N.M.R. dispersion approach, Magn. Reson. Imaging 21 (3–4) (2003) 355–357.

[18] F. Barberon, et al., Probing the surface area of cement based materials by NMR dispersion, Phys. Rev. Lett. 90 (2003) 116103.

[19] S. Garrault, et al., Study of C-S-H growth on C_3S surface during its early hydration, Mater. Struct. 38 (2005) 435–442.

[20] J.W. Christian, The theory of transformation in metals and alloys, Pergamon Press, Oxford, 2002, p. 529.

[21] D.H. Bratland, et al., Modeling of precipitation reactions industrial processing, Acta Mater. 45 (1) (1997) 1–22.

[22] I. Shimizu, A stochastic model of grain size distribution during dynamic recrystallization, Philos. Mag. A 79 (1999) 1217–1231.

[23] R.A. Ramos, Test of the Kolmogorov-Johnson-Mehl-Avami picture of metastable decay in a model with microscopic dynamics, Phys. Rev. B 59 (14) (1999) 9053–9069.

[24] Z.-Z. Yuan, Kinetics on non-isothermal crystallization of the metallic $Co_{43}Fe_{20}$-$Ta_{5,5}B_{31,5}$ glass, J. Alloys Compd. 407 (2006) 163–169.

[25] D.W. Henderson, Thermal analysis of non-isothermal crystallization kinetics in glass forming liquids, J. Non-Cryst. Solids 30 (1979) 301–315.

[26] V. Sessa, et al., Validity of Avramis kinetics for random et nonrandom distributions of germs, Physical review B 54 (2) (1996) 836–841.

[27] M.J. Starink, On the meaning of the impingement parameter in kinetic equations for nucleation and growth reactions, J. Mater. Sci. 36 (2001) 4433–4441.

[28] J.W. Cahn, The kinetics of grain boundary nucleated reactions, Acta Metall. 4 (1956) 449–459.

[29] J.J. Thomas, A new approach to modeling the nucleation and growth kinetics of tricalcium silicate hydration, J. Am. Soc. 90 (2007) 311–316.

[30] J. Málek, Kinetic analysis of crystallization processes in amorphous material, Thermochim. Acta 355 (2000) 239–253.

[31] F. Ridi, et al., Hydration kinetics of tricalcium silicate by calorimetric methods, J. Colloids Interface Sci. 364 (2011) 118–124.

[32] A. Damasceni, et al., A novel approach based on differential scanning calorimetry applied to the study of tricalcium silicate hydration kinetics, J. Phys. Chem. B 106 (2002) 11572–11578.

[33] P.W. Brown, et al., A kinetic model for the hydration of tricalcium silicate, Cem. Concr. Res. 15 (1985) 35–41.

[34] R. Berliner, et al., Quasielastic neutron scattering study of the effect of water-to-cement ratio on the hydration kinetics of tricalcium silicate, Cem. Concr. Res. 28 (2) (1998) 231–243.

[35] A.C. Lasaga, Fundamental approaches in describing mineral dissolution and precipitation rates, Rev. Mineral. Geochem. 31 (1995) 23–86.

[36] J. Schott, et al., The link between mineral dissolution/precipitation kinetics and solution chemistry, Rev. Mineral. Geochem. 70 (2009) 207–258.

[37] B. Lothenbach, et al., Thermodynamic modeling of the hydration of Portland cement, Cem. Concr. Res. 36 (2006) 209–226.

[38] J.W. Bullard, A determination of hydration mechanisms for tricalcium silicate using a kinetic cellular automaton model, J. Am. Ceram. Soc. 91 (7) (2008) 2088–2097.

[39] K.L. Scrivener, Backscattered electron imaging of cementitious microstructures: understanding and quantification, Cem. Concr. Compos. 26 (2004) 935–945.