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Discussion

Discussion of the paper “Accelerated growth of calcium silicate hydrates” by Luc Nicoleau

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ABSTRACT

Some of the limitations of the model recently used by Nicoleau in a recent article [Accelerated growth of calcium silicate hydrates: experiments and simulations, Cement Concr. Res. 21 (2011) 1339 -1348.] are discussed.

1. Introduction

In a recent paper, Nicoleau [1] presented a study of accelerated alite hydration modelled using a scheme presented earlier by Garrault and Nonat [2]. Although this model is relatively simple to apply, its over-simplicity can lead to some serious limitations in its ability to correctly represent cement hydration. Some of these limitations are discussed here. Most importantly, it is shown that the values of the “permeability” parameter obtained from the fits are sensitive to the other parameters chosen to fit the first part of the curve.

2. Use of a single cement particle

In the numerical scheme used for modelling hydration a single two-dimensional surface is used to represent the entire cementitious system. The validity of this assumption is questionable since it has been shown in an earlier article [3] that impingements with C-S-H originating from different cement particles will affect nucleation and growth kinetics. Since these impingements are the cause of setting and strength-gain in cements, they must not be negligible. Such impingements have been considered also in analytical models, such as that by Cahn [4], which was one of the first models to be derived for systems where nucleation occurs on a surface, rather than homogeneously in a solution.

3. Effect of shape on post-peak deceleration

Nicoleau has reported significant deceleration in hydration kinetics originating from the nucleation and growth model developed by Garrault and Nonat [2], before changing to diffusion controlled kinetics. However, this deceleration is a side-effect of the choice of the growth pattern of C-S-H chosen by the authors.

Nicoleau and earlier Garrault and Nonat [2] have chosen to use cuboidal nuclei that form at the same instant and remain cuboidal as they grow. With this form of precipitate, when two nuclei “collide” the surface of both nuclei where they “join” disappears, leading to a large reduction in the surface area available for further growth. After a certain time, a continuous layer is produced, and the remaining surface for growth equals the initial surface area. This effect can be seen in the third step of Fig. 1.

In most other studies, the nuclei are considered to be spherical or ellipsoidal (e.g. Refs. [4–6]). If this is the case, as shown in Fig. 2, the surface area available for growth is higher than the initially available surface even when the entire surface gets covered by the product, reducing the deceleration after the peak. Another artefact of the cuboidal scheme is that, although the user specifies the parallel and perpendicular growth rates (G_1 and G_2), the highest rate of growth will be in the diagonal direction (G_3), as seen in Fig. 3. This is not the case for ellipsoidal nuclei since it is possible to specify the maximum rate of growth to be either perpendicular to the surface or parallel to the boundary of nucleation.

To demonstrate that the deceleration obtained from the ellipsoidal growth is less than cuboidal growth, simplified equations that can replicate the results from cuboidal nucleation and growth are derived below. The volume of the product can be calculated using an equation which can be derived using the same principles as those used by

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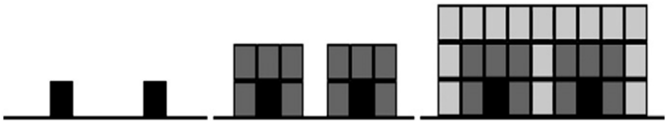

Fig. 1. Growth of cuboidal nuclei completely removing surface area on the sides of the cuboids. Black squares show the initial nuclei and the lighter grey squares show the subsequent layers of growth.

Avrami [6] and Cahn [4]. In the derivation below we use the concept of the extended volume or area, which means the sum of the volumes or areas of all nuclei, neglecting the overlaps or impingements between neighbouring nuclei. This volume can later be converted to the actual volume or area, taking the overlaps into account.

If the total surface area under consideration is written as A_0, the extended area of the nuclei as A^*, the initial number of nuclei as n, the parallel growth rate as G_1 and the perpendicular growth rate as G_2, the total extended area of all the nuclei at any time t after the nucleation event can be written as below:

$$A^* = n\left(2G_1 t + \frac{x_0}{2}\right)^2 \tag{1}$$

where x_0 is the initial dimension of the nuclei parallel to the surface. The actual fraction of the area covered by nuclei, A_c, can therefore be written as:

$$A_c = A_0\left(1 - e^{\frac{-A^*}{A}}\right) \tag{2}$$

If z_0 is the initial dimension of the nuclei perpendicular to the surface, the total volume of the products, V_p, can be written as:

$$V_p = A_c(G_2 t + z_0) \tag{3}$$

The degree and rate of hydration calculated from the above equations have been plotted in Fig. 4, using the same fit parameters used by Nicoleau for blank alite (see Table 1) and assuming that 100% hydration occurs when 3.3×10^8 pixels of C-S-H have been produced. The results using the above equations for cuboidal growth compare well with those presented in Fig. 8 by Nicoleau when the diffusion part of the model is not applied.

Similarly, the volume of the product from the growth of ellipsoidal nuclei can be derived to be as below:

$$V_{p,\text{ellipsoidal}} = A_0 \int_0^{G_2 t} \left[1 - \exp\left(-\pi N G_1^2 \left(t^2 - y^2/G_2^2\right)\right)\right] \partial y \tag{4}$$

Fig. 4 compares the post-peak deceleration obtained using cuboidal and ellipsoidal shapes. The curve for the ellipsoidal growth was simulated by varying the parameters so that the acceleration obtained closely matches that from cuboidal growth. The parameters used for the fit are listed in Table 1. The peaks for both shapes occurred at 12.5 hours. It was found that at the end of 20 hours, i.e. 7.5 hours after the peak, while the rate of hydration reduces by 21.7% in the cuboidal case, it reduces by 11.5% in the ellipsoidal case.

Fig. 2. Growth of ellipsoidal nuclei. The initial nuclei are shown in black and the subsequent layers in lighter shades of grey.

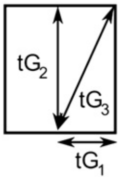

Fig. 3. In cuboidal growth the diagonal rate of growth is higher than both the parallel rate and the perpendicular rate.

4. Permeability parameter

To get around the fact that the rate of reaction does not continue to slow down after the meeting of the nuclei in a uniform layer, Nicoleau introduces a "permeability" parameter which aims to capture the effect of ion transport through the layer of hydrates. It is claimed that the similar values fitted for this parameter support the case that transport control plays a role in the deceleration part of the reaction.

However, the supposed similarity in the "permeability" parameter listed in Table 1 of the article under discussion only results from the choice of the other parameters, particularly the available area which seems to be varied in an arbitrary manner. It will be shown below that by increasing the available area for nucleation, as the author has done, the permeability parameter can be controlled to fall within a given range.

In Fig. 5, the degree and rate of hydration using the equations derived above and the parameters listed by Nicoleau for 100 mM $CaCl_2$ have been shown as set 1 in Table 1. In these calculations an additional area for nucleation as assumed by Nicoleau was used and the obtained trends are similar to those in the original article. In order to show the sensitive the layer-thickness is to this additional surface area, similar curves were obtained without using any additional surface area for nucleation only by modifying the rates of growth. The values of the parameters for these fits are listed as Set-2 in the table. Since the outward rate of growth for the second set is more than 2.5 times that in set 1, in set 2 the thickness of the C-S-H layer at peak and at the point where the entire surface is covered will be more than 2.5 times the thickness in set 1. This means that the thickness of C-S-H layer at the point where the so-called "diffusion controlled" mechanism starts and therefore the permeability parameter used also depend on the additional surface used. Therefore, by modifying the initial surface area and the initial number of nuclei, the permeability parameter can be easily controlled to be within a given range.

Furthermore, due to the slower deceleration obtained when an ellipsoidal growth is used to simulate nucleation and growth, diffusion control would have to become the controlling mechanism

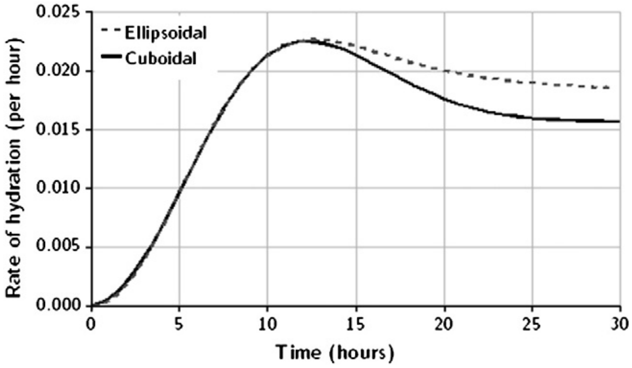

Fig. 4. Comparison of deceleration obtained after peak using ellipsoidal and cuboidal growths.

Table 1
Values of parameters used in simulations shown in Fig. 5.

Parameter	Blank	Ellipsoidal growth	Set 1 100 mM $CaCl_2$ from Nicoleau [1]	Set 2 100 mM $CaCl_2$—alternative values
A_0 (N^2/100)	3000	1304	3000	3000
G_1 (pixels/hour)	6.1	8.2	6.8	5.5
G_2 (pixels/hour)	17.2	44.7	13.0	33.0
x_0 (pixels)	1	–	1	1
z_0 (pixels)	1	–	1	1
n (pixels)	20	9	14	20
Additional surface (N^2/100)	0	0	4600	0
Additional nuclei (pixels)	0	0	30	0

earlier than when cuboidal growth is used. As noted in the article under discussion, the earlier diffusion becomes rate-controlling, the higher is the variability in the values of permeability obtained. Therefore, the choice of the shape of growth of nuclei, also has an important role to play in the obtained values of permeability.

5. Cryo-SEM images and thickness of C-S-H layer

Nicoleau has used cryo-SEM to study C-S-H layer thickness around cement particles and a comparison with simulated thickness is given in Fig. 7 of the article. Although this technique offers the advantage of not disturbing cement morphology, it is still difficult to measure the layer thickness. As can be seen in Fig. 6 of the article under discussion, the layer of C-S-H is uneven and “fibres” of C-S-H make this measurement even more subjective. Furthermore, it is known that fracture surfaces cannot be used to accurately measure dimensions, and even polished sections suffer from the so-called “sectioning effect” [7]. Therefore, the thickness of the C-S-H layers measured from SEM images cannot be compared with the simulated layer thickness for validation of the model.

In fact, to this writer, the cryo-SEM images give further evidence of a diffuse growth as the aforementioned “fibres” clearly show the growth of a loosely packed C-S-H, as has been argued by the authors in an earlier article [3].

Nicoleau further uses this measured thickness to estimate the actual thickness of a simulation block and then uses that to calculate the actual area of the particle being simulated. It is then shown that the equivalent surface area matches well with experimental results. However, once the degree of hydration, and therefore the volume of the product, is fixed through fitting and the thickness is fixed, the surface area is automatically fixed. The good correlation between the measurements and the calculations is therefore not surprising.

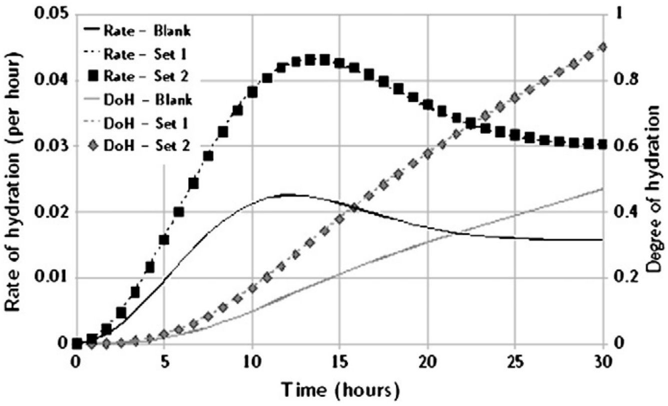

Fig. 5. Calculated rate degree of hydration and rate of increase in degree of reaction per hour using described equations for blank alite and 100 mM $CaCl_2$ using two sets of fit parameters listed in Table 1.

6. Conclusions

It has been shown above that the numerical scheme and model used by Nicoleau suffer from limitations that can significantly affect the simulation results. Also, the observed variation in the permeability parameter can be higher than that reported depending on the parameters used in the first part of the fit. The reliability of the SEM images provided to support the simulation results is also questionable.

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