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A reaction zone hypothesis for the effects of particle size and water-to-cement ratio on the early hydration kinetics of C_3S

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Abstract

The hydration kinetics of tricalcium silicate (C_3S) have been the subject of much study, yet the experimentally observed effects of the water-to-cement (w/c) ratio and particle size distribution have been difficult to explain with models. Here we propose a simple hypothesis that provides an explanation for the lack of any significant effect of w/c on the kinetics and for the strong effect of the particle size distribution on the amount of early hydration associated with the main hydration peak. The hypothesis is that during the early hydration period the calcium-silicate-hydrate product forms only in a reaction zone close to the surface of the C_3S particles. To test the hypothesis, a new microstructure-based kinetics (MBK) model has been developed. The MBK model treats the C_3S size distribution in a statistical way to save computation time and treats the early hydration as essentially a boundary nucleation and growth process. The MBK model is used to fit kinetic data

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from two published studies for C_3S with different size distributions, one for alite (impure C_3S) pastes and one for stirred C_3S suspensions. The model is able to fit all of the datasets with the same values of the growth rate and nucleation rate, and, for each study, the thickness of the reaction zone shows no significant trend with particle size, providing strong support for the reaction zone hypothesis.

Key words: cement, hydration, kinetics, calorimetry, modeling, boundary nucleation and growth

1. Introduction

The kinetics of hydration of the constituent minerals in Portland cement has been the subject of significant experimental and modeling work, and the state of the field has been recently reviewed [1, 2]. Kinetic data obtained by, for example, isothermal calorimetry, are typically characterized by a peak of hydration (at ~ 10 hours in Fig. 1), followed by a slow continued reaction for days or weeks. It is well accepted that the acceleration stage prior to the peak is generated as a result of nucleation and growth of hydration products, primarily calcium-silicate-hydrate (C-S-H) gel. However the transition to the subsequent deceleration, i.e. the cause of the peak, is more controversial. This transition has traditionally been attributed to a switch to diffusion-controlled kinetics [3], caused by the requirement of transporting reactants through a product layer around the particles that becomes thicker with time. However, based on new experimental evidence and modeling work, the hypothesis of an early transition to diffusion-controlled kinetics has in recent

years become more controversial, as summarized in [1]. For example, Bishnoi and Scrivener [4] performed fitting simulations showing that if diffusion control was responsible for the initial deceleration, the diffusion constant for transport of reactants through the product layer would have to vary strongly with the average particle size of the cement, which is unlikely. Additionally, Thomas [5] showed that the activation energy for hydration remains constant across the main hydration peak, which argues against a change in the rate-controlling mechanism.

An alternative explanation for the initial deceleration is that it is a natural consequence of the same nucleation and growth process responsible for the acceleration period. The mathematical boundary nucleation and growth (BNG) model, in which nucleation is only permitted to occur on the surface of the cement or C_3S grains, can be used to accurately fit the shape of the kinetic data well past the peak in hydration rate [6, 7, 8, 9, 10] (see Fig. 1). In fact, it is a common feature of nucleation and growth (NG) models, that deceleration in the overall rate occurs as regions of the transformed phase (i.e. hydration product) impinge on each other as they fill the available space.

However, there are problems with the above NG interpretation of the kinetics related to specific experimental observations. These problems lie not with the shape of the kinetic curve, but in the amount of hydration that occurs during the early hydration period. We summarize these problems as three distinct points:

1. It has long been recognized that the amount of hydration accounted

for by NG fits to kinetic data for cement or C_3S usually represents a degree of hydration of less than 0.5. The problem is that more than half of the total hydration occurs during a period of very slowly declining hydration rate after the main hydration peak (after 20 hours in Fig. 1) not captured by the fits. As correctly pointed out by Bishnoi and Scrivener [4], this presents a challenge to the hypothesis that the main hydration peak is controlled only by NG, because, unless the w/c of the paste is unusually low, there is enough space available for complete hydration to occur.

2. The early hydration kinetics (both the amount of hydration and the shape of the rate curve) are almost unaffected by the water-to-cement mass ratio (w/c) of the paste [6, 11]. It is difficult to reconcile this observation with a hypothesis of a NG process filling the available pore space during the early hydration period, since this available volume scales with the w/c . This point is discussed in detail by Kirby and Biernacki [11]. In fact, even stirred suspensions with w/c much greater than 1 show a rate peak [12].
3. The amount of early hydration is strongly affected by the average particle size of the cement or C_3S , increasing with the specific surface area of the powder [12, 13, 14]. In fact, although an acceleration is expected due to the greater amount of nucleation that can occur on finer particles, the *amount* of early hydration (which is proportional to the area under the peak) should not change if the available volume for

precipitation is the same.

To solve point (1) above, Bishnoi and Scrivener [4] proposed a modified two-step hydration process which they call nucleation and densified growth (NDG). In the first step, hydration product forms with a low bulk density (i.e. with a large amount of internal porosity), such that it fills the available pore space at a relatively low degree of hydration. Impingement of this low-density product generates a main hydration peak that is complete after a relatively low degree of hydration, as is experimentally observed. In the second step, the hydration product gradually densifies, providing space for further hydration. However, while the NDG hypothesis is attractive in some respects [11], it does not explain (and is in fact contradicted by) points (2) and (3) above.

Here we propose a hypothesis to explain all three of the points noted above. This hypothesis is simply that during the early reaction period the calcium-silicate-hydrate (C-S-H) product is restricted to form only within a region close to the cement or C_3S particles, which we call the “reaction zone”. Within the reaction zone, hydration follows the BNG process. This hypothesis reduces the initial volume available to be filled by hydration product, which addresses point (1). It also effectively decouples the volume available for early hydration from the total pore volume (as determined by the w/c) and links it instead to the surface area of the powder. This addresses both points (2) and (3). At later times, after the main peak, hydration can continue to fill the remaining space outside the reaction zone. We note that

the reaction zone hypothesis is proposed on a purely empirical basis; that is, its justification is that it reconciles a number of important observations regarding the early kinetics, as discussed above. We do not attempt here to provide a full mechanistic explanation for why the hydration process should occur in this way, although we suggest possible mechanisms in the Discussion section.

The reaction zone hypothesis is quantitatively tested using a new microstructure based kinetics (MBK) model for early hydration that accounts for the size distributions of both the cement or C_3S grains and of the of inter-grain pores. These distributions are handled on a statistical basis, so the model does not require a detailed description of the spatial arrangement of the individual grains, which reduces the computational cost. The model is described in more detail in the next section. In the Results section we use the MBK model to fit published kinetic data obtained for alite (impure C_3S) pastes with $w/c = 0.4$ and different particle sizes [13], and published kinetic data for stirred suspensions of C_3S with $w/c = 50$ and different particle sizes [12]. The ability to fit these disparate datasets, using similar values for key input parameters such as the growth rate and nucleation rate, provides support for the reaction zone hypothesis.

2. Model description

The MBK model is divided into three basic steps. The first step is to set fixed input quantities such as the growth rate and to define the initial

geometry of the system (microstructure). The second step is dissolution of the C_3S grains, which provides ions to the solution and reduces the volume of the grains. The third step is the precipitation of hydration product (C-S-H and CH) according to specified nucleation and growth rates for the C-S-H phase. Steps 2 and 3 are repeated iteratively until the simulation is complete.

2.1. System description

Fig. 2 illustrates how the MBK model handles the initial geometry of the system, which consists of spherical C_3S grains surrounded by water-filled pores. While the model currently considers only spherical grains, generalization to non-spherical grains would be reasonably straightforward. The dotted lines in Fig. 2 show how the pore volume can be partitioned to associate each location in the pore space with the closest possible grain. The shape of the partitioned pore volumes is irregular, and their size distribution is directly related to the way in which the C_3S grains are distributed. The MBK model operates using a statistical description of the size and shape of these pore volumes, and therefore does not require as input the positions of the individual grains, which saves considerably on computation time.

Each C_3S grain and its associated pore volume is divided into pyramidal volume elements with vertices at the center of the grain. As shown in Fig. 2, each pyramid has a "semi-pore" associated with it, with size defined as L_{pp} . While all of the pyramids associated with a particular C_3S grain have the same grain radius R_c , the size of the semi-pores will have a distribution

denoted $p(L_{pp})$. The number of pyramids per grain $N_{p,i}$ is chosen to describe with sufficient accuracy the distribution $p(L_{pp})$. The hydration steps of the model (dissolution and precipitation) occur within these pyramidal volume elements.

As noted above, the position of each C₃S grain is not considered explicitly. Instead, the configuration of the just-mixed paste is described with three parameters: the w/c , the C₃S grain size distribution, and the semi-pore size distribution $p(L_{pp})$. To model the grain size distribution, the range of grain diameters is divided into $n_{c,bin}$ bins and the number of grains in each bin, $N_{c,i}$, is defined to match an experimentally measured distribution. $p(L_{pp})$ is the most difficult quantity to evaluate in practice, but digital images, detailed microstructural evolution simulators, and insights from the statistical physics of particle aggregates can be useful to this end.

Since all of the grains within a particular bin are statistically equivalent, it is only necessary to explicitly simulate the hydration of one grain per bin. This is a key to the computational efficiency of the MBK model. Hydration of a particular grain is performed by modeling the hydration process within pyramidal volume elements with different semi-pore sizes that follow $p(L_{pp})$. The results from different-size grains are then combined according to $N_{c,i}$ to give the hydration results for the paste. Care is taken to ensure that the total volume of semi-pores associated with all the elements matches the total pore volume calculated from the global w/c .

2.2. Dissolution step

The degree of hydration $\alpha(t)$ is the fraction of the initial total volume of C_3S grains that has dissolved at time t during hydration. Consequently $\alpha(0) = 0$ and, if the w/c is sufficiently large to attain full hydration at time t^* , then $\alpha(t \geq t^*) = 1$. The MBK model operates iteratively, with each iteration consisting of the dissolution of a fixed amount of C_3S followed by the growth of the corresponding amount of hydration product. The dissolution step is defined by a fixed increment of the total amount of hydration, $\Delta\alpha$, which reduces linearly the total volume of unreacted C_3S . The hydration kinetics are modeled by calculating, at each iteration, the time required for the dissolved C_3S to be transformed into product by nucleation and growth, as discussed in Section 2.4.

The total volume of C_3S dissolved at each step is distributed between the grains by assuming that the radius $R_{c,i}(\alpha)$ of each grain decreases by the same distance, denoted d_d . This implies that the dissolution rate is the same for all grains, independent of their size. This is in general not true for pure dissolution of isolated grains, but for a hydrating paste where the solution concentrations are controlled by the presence of hydrated phases we consider this reasonably accurate. The computed value of d_d defines the new position of the C_3S -pore interface in each volume element, and the newly formed empty space is now available to be occupied by hydration product. As hydration proceeds some grains will dissolve completely, which of course shuts off their hydration.

2.3. Stoichiometry, mass, and volume balance

Hydration is assumed to everywhere obey the following global stoichiometric balance between C_3S , water, solid calcium-silicate-hydrate (C-S-H), and calcium hydroxide (CH):

For the purpose of modeling a space-filling reaction, it is necessary to include additional water associated with the C-S-H phase that is trapped in nanopores and does not contribute further to the reaction. Here we take the volume fraction of such nanopores in the C-S-H phase to be 34.5%, which is the amount present in the low-density (LD) C-S-H phase defined by the Jennings colloid model [15, 16]. This increases the H/S molar ratio of the C-S-H from 1.8 to 3.9, so the hydration reaction effectively becomes:

The density and molar volume of each phase participating in Eq. 2 is given in Table 1. There is a volume decrease of 8.1% associated with Eq. 2. This is the chemical shrinkage, which can empty internal pores if no external water is available. The model assumes that water can percolate from the larger capillary pores into the nanopores so that the C-S-H product remains saturated.

Table 1: Density and molar volumes of the phases in Eq. 2.

Phase	Density (g/cm ³)	Molar volume (cm ³ /mol)
C ₃ S	3.15	72.5
H ₂ O	1.0	18.1
C-S-H	2.05 ^a	110.1
Ca(OH) ₂	2.24	33.1

^aDensity of saturated C-S-H from ref. [17]

2.4. Precipitation step

The precipitation step involves the formation of new hydration product inside the pyramidal volume elements by a process of nucleation and growth. This is driven by the two fundamental parameters of the BNG process, which are the nucleation rate per unit area of C₃S surface, I_b , and the linear growth rate of existing regions of product, G . This product consists of the C-S-H gel with 35% nanoporosity and CH, in the stoichiometry defined by Eq. 2.

Based on the previous dissolution step where a fixed amount of C₃S has dissolved, the volume of product that must form during the precipitation step is known from Eq. 2. The time required to form this product is not calculated directly, but is determined in an iterative manner, as follows. A trial time increment Δt^{try} is chosen, and the amount of hydration product that forms during Δt^{try} is calculated. This amount is compared to the calculated amount, and the value of Δt^{try} is then adjusted accordingly. This process is repeated until the correct amount of product is formed, to a specified degree of accuracy.

The configuration of each pyramidal volume element at the start of a precipitation step consists of the regions of hydration product resulting from the previous precipitation step, along with newly exposed C_3S surface resulting from the dissolution step (see Fig. 3). The first step is to precipitate new C-S-H nuclei on the C_3S surface. The number of new nuclei formed in volume element k of grain i is

$$n_{i,k}(\alpha, \Delta t^{try}) = I_b S_{i,k}(\alpha) \Delta t^{try} \quad (3)$$

where $S_{i,k}(\alpha)$ is the area of the C_3S surface in element k of grain i . These new nuclei are distributed randomly on the surface. In a minor deviation from a standard nucleation and growth model, the nuclei are modeled as flat patches with zero volume but finite area d_0^2 , rather than as points. This variation was adopted to enable a better fitting of the calorimetry data at very early age (< 3 hours), and plays a similar role to the time-shift parameter often used with nucleation and growth models [2]. Physically, this can be interpreted as the rapid formation of closely spaced point nuclei on an active region of the C_3S surface. The location of the initial nucleation patch does not change with time, so the product regions that grow from each patch do not translate inward to follow with the dissolving C_3S surface.

During the time increment Δt^{try} the new C-S-H nuclei and the pre-existing regions of C-S-H product all grow by a distance $G\Delta t^{try}$ in the directions perpendicular to the grain surface, both inward and outward, and

in the tangential direction. This results in product regions with the shape of a truncated pyramid, rather than a sphere (see Fig. 3). As is typical of NG models, the MBK model first calculates the extended volume of each product region ignoring the impingement of neighboring regions. This extended volume scales with $G^3(t - t_f)^3$, where t_f is the time at which it formed, as required by the standard BNG model. Next the impingements are calculated and subtracted from the extended volume to give the true volume of C-S-H product. Then the CH product is added to the system, assuming homogeneous nucleation throughout the pore system and ensuring that the stoichiometrically correct amount of CH has formed after accounting for impingement. Finally, the amount of new hydration product that has formed is compared to the correct value calculated from the dissolution step. If these do not match, the value of Δt^{try} is adjusted and the precipitation step is repeated.

2.5. Reaction Zone

The model as described above essentially simulates a pure boundary nucleation and growth process for which all the pore space is available. As discussed in the Introduction, such a simulation will over-predict the amount of early hydration and will not correctly model the effects of the w/c or grain size distribution on the hydration kinetics. We therefore impose the presence of a reaction zone around the C_3S grains, within which the C-S-H hydration product is restricted to form during the early hydration period considered by

the model. The outer boundary of the reaction zone is defined to be a fixed distance from the current C_3S grain surfaces, so the reaction zone follows the surface of the shrinking grains as hydration proceeds. This distance is varied as a fitting parameter. The reaction zone does not apply to the CH, which forms by homogeneous nucleation everywhere in the pore system.

3. Results

To test the MBK model and the reaction zone hypothesis, the model was used to fit kinetic data from two published studies for the hydration of C_3S with different grain sizes. The first study is from the PhD thesis of Costoya [13], where alite (impure C_3S) pastes with different grain size distributions were hydrated at a fixed w/c of 0.4 at room temperature. The second study is that of Garrault et al. [12], where C_3S powders with different grain size distributions were hydrated as suspensions with very high w/c of 50, also at room temperature. In both studies a strong effect of the grain size distribution on the kinetics was observed, but the general shape of the hydration rate curves is always similar to Fig. 1. In this section we show that the MBK model, with the reaction zone implemented, is able to fit all of these datasets in a satisfactory way.

3.1. Case study #1: alite pastes

Costoya [13] studied the hydration kinetics of alite pastes with different particle size distributions. From the reported volume fractions obtained by

sieving, we estimated the grain size distributions as shown in Fig. 4. The mean particle sizes, which we use to label the different batches, are 13 μm , 18 μm , 38 μm , and 82 μm . The size distributions were accounted for in the MBK model by the binning method described in Section 2.1. The rate of hydration as measured by isothermal calorimetry for the first 24 h of hydration is shown as the dotted lines in Fig. 5(a). Note that the initial rapid heat release in the first few minutes has been removed, since this is not treated by the model. While the time of the maximum hydration rate decreases slightly with decreasing mean particle size, the most striking effect is the significant increase in the area under the hydration peak with decreasing mean particle size. Fig. 5(b) shows the degree of hydration, obtained by integrating the calorimetry rate data and dividing by the reaction enthalpy of -517 J per gram of C_3S [13].

Because the semi-pore size distribution $p(L_{pp})$ is not known, and to simplify the modeling procedure, we made the simplest possible assumption, which is that the semi-pores in each paste have a single size, which is the value that gives the correct w/c value of 0.4. This assumption is clearly an oversimplification, since even in a well-dispersed paste the pores will be irregular in shape, and some amount of agglomeration can always be expected. On the other hand, the assumption of a reaction zone makes the MBK model much less sensitive to the semi-pore size distribution than would otherwise be the case. The calculated semi-pore size increases with the mean particle size, ranging from 2.31 μm for the finest PSD to 23 μm for the coarsest PSD.

The independent (fitting) parameters in the MBK model are the nucleation rate, growth rate, nucleation patch size, and reaction zone thickness. However, in conducting the fits to the data shown in Fig. 5, the nucleation rate, growth rate, and nucleation patch size were kept constant for all of the datasets, since these values would not be expected to depend on the alite grain size. The thickness of the reaction zone was allowed to vary for each individual dataset, but with the expectation that the fitted values should not vary excessively with particle size if the reaction zone hypothesis has merit.

The solid lines in Fig. 5 show the MBK model fits. The agreement is quite good, particularly when the many simplifying assumptions and potential sources of error are considered. For all these fits, the nucleation rate is $I_b = 0.09 \mu\text{m}^{-2} \text{ h}^{-1}$, the growth rate is $G = 0.04 \mu\text{m h}^{-1}$, and the nucleus patch size is $d_0 = 1 \mu\text{m}$. These nucleation and growth rates are similar to those previously obtained [6, 7] by fitting the mathematical BNG model to calorimetry data obtained at 20°C ($G = 0.07 - 0.09 \mu\text{m h}^{-1}$, $I_b = 0.06 - 0.12 \mu\text{m}^{-2} \text{ h}^{-1}$). The fitted values of the reaction zone thickness obtained for the different alite PSDs are plotted in Fig. 6. The reaction zone thickness varies around a value of about $1 \mu\text{m}$ without a clear trend. We consider that this result provides support to the reaction zone hypothesis as an empirical tool to explain the measured hydration kinetics.

3.2. Case study #2: stirred C_3S suspensions

Garrault et al. [12] studied the hydration of stirred suspensions of C_3S with $w/c = 50$, using 5 different grain size distributions. From the reported volume fractions obtained by sieving, we estimated the grain size distributions as shown in Fig. 7. In this study, the concentration of calcium ions in the hydration solution was maintained at a constant value of 22 mmol/L, which corresponds to the equilibrium solubility of calcium hydroxide. This was achieved by continuously removing calcium ions from the solution as needed during the run. This procedure was adopted to ensure a constant Ca/Si ratio of the precipitating C–S–H and also to prevent the formation of calcium hydroxide.

From the measured amount of calcium removed from the solution, Garrault et al. [12] calculated the amount of C–S–H formed in the C_3S suspensions over time. This provided the measurement of the hydration kinetics, as isothermal calorimetry could not be conducted under these experimental conditions. Based on the stoichiometry of Eq. 2, we converted these results into the degree of hydration of the C_3S with time. This is shown as the dashed lines in Fig. 8(b). We also converted these degree of hydration curves into simulated heat release rate curves by taking the derivative and assuming a fixed reaction enthalpy of -517 J/g.

As with case study 1, the grain size distributions in Fig. 7 were simulated in the MBK model by binning and a single value of the semi-pore size was used. Due to the very high w/c , the modeled hydration process is insensitive

to the semi-pore size, because the reaction zone thickness is much smaller than the semi-pore size. Therefore, to reduce computation time these runs were performed with a nominal w/c of 5, which was still high enough to ensure that C-S-H product always reached the reaction zone before reaching the semi-pore boundary. It should be noted that for case study #2, the model will over-predict the amount of CH that forms inside the reaction zone, since the formation of CH was suppressed in the experiment. However, the volume fraction of CH inside the reaction zone was found to be less than 2% after all the simulations, so this would have minimal effect on the results.

The solid lines in Fig. 8 show the results of the model fits. As with the first case study, the agreement is good. This is perhaps more surprising for this case study since the experimental conditions were much different from a paste. For these simulations, the same nucleation and growth rates (I_b , G) were used as for the alite pastes of case study #1. (While we were prepared to change these values for case study 2, we found it unnecessary). Compared to case study #1, a larger nuclei patch size was required to capture the sharper increase in rate at very early times ($1.5\ \mu\text{m}$ vs. $1\ \mu\text{m}$). Fig. 9 shows the reaction zone thicknesses for the different grain size distributions, which vary around a value of $0.5\ \mu\text{m}$ without a clear trend. These values are about half those found for case study #1 (see Fig. 6). Interestingly, Garrault et al. [12] estimated the thickness of the C-S-H layer covering the C_3S grains to be $\approx 0.4\ \mu\text{m}$ once a complete layer had formed. In their interpretation, this initiated a transition to diffusion-controlled kinetics. On the other hand, they

found that the layer thickness decreased as the mean particle size increased, while our results for the reaction zone show no such trend. This might be because the MBK model considers the size distribution of C_3S grains while the calculations in [12] are based only on the median grain size.

4. Discussion

4.1. The reaction zone hypothesis

The most significant finding of this paper is that the strong, experimentally measured effect of the C_3S grain size distribution on the early hydration kinetics can be modeled as a BNG process modified with the additional constraint of a reaction zone around the individual grains. The newly developed MBK model was programmed to simulate this conceptually simple process and then used to fit two sets of previously published kinetic data, for pastes at $w/c = 0.4$ and for stirred suspensions at $w/c = 50$. For each case study, good fits to the data for the different grain size distributions were obtained with the same fixed values of the nucleation rate, growth rate, and nucleation patch size. Furthermore, although the reaction zone thickness was varied to give the best fit to each individual dataset, the resulting values of the reaction zone thickness show limited variation with C_3S grain size. These results make good physical sense, since none of these parameters should vary strongly with the grain size, and other relevant parameters such as temperature were fixed. On the other hand, it would be unlikely for the fit results to work in this way if the underlying assumptions are fundamentally incorrect.

As discussed in the Introduction, the reaction zone hypothesis also provides a natural explanation for the lack of an effect (or very weak effect) of w/c on the hydration kinetics. The reaction zone effectively decouples the hydration process from the w/c during the early hydration period, as long as the reaction zone is small compared to the average distance between the grains. This was found to be the case: the paste with the smallest mean semi-pore size of $2.31\text{ }\mu\text{m}$ has a reaction zone thickness of $0.9\text{ }\mu\text{m}$. The reaction zone hypothesis also explains why only a fraction (usually less than half) of the C_3S hydrates during early hydration period associated with the main hydration peak.

Comparison of the experimental results from the two case studies shows that the early hydration is faster in the C_3S suspensions at high w/c than in the alite pastes, even when the grain size distribution is similar. Specifically, the acceleration of the hydration rate is more rapid, and the peak time is earlier, for the C_3S suspensions. In the model fits, this effect was captured by using different nuclei patch sizes. The use of nuclei patches with a finite area effectively specifies that a certain number of C-S-H nuclei are present at the time of mixing, or form very rapidly just after mixing. This concept was introduced to account for the fact that in both the of case studies the acceleration period initiates more quickly than traditional NG models would predict, unless a negative time-shift parameter is used. From a physical perspective, the C-S-H nuclei patches could represent active regions of the grain surface where nucleation occurs very easily, possibly due to atomic

defects. In this light, the larger fitted patch size for the C_3S suspensions as compared to the alite pastes implies the presence of more active surface regions in the former case.

The reaction zone was imposed as an empirical concept to force hydration product to form close to the grains during the early hydration period. While the exact physical mechanisms that cause the hydration to occur in this way are not clear, the results of the MBK model provide some possible insights. There is a strong correlation between the time at which the outermost regions of growing C-S-H reach the reaction zone boundary and the time at which the regions closer to the particle surface impinge tangentially on each other to form a continuous layer of product. Thus C-S-H product initially grows outward in an unconstrained way until the reaction zone is reached, and then after that the remaining space inside the reaction zone fills in while outward growth stops. The most straightforward physical explanation is that once tangential impingement forms a complete layer, the outermost C-S-H regions no longer are supplied with enough ions to continue growing, i.e. they reach thermodynamic equilibrium with the solution. This would signal the onset of a period of mixed rate control, with nucleation and growth controlling the rate at which the remaining space inside the reaction zone fills in, and diffusion controlling, or limiting, the rate of outward growth. As the space close to particles fills in, the overall rate would increasingly be controlled by diffusion.

The ability of mixed mathematical models that combine nucleation and

growth at early times with diffusion control at later times to fit experimentally measured kinetics for C_3S and cement hydration is well established [14, 18, 19, 20, 21, 22, 23]. Nevertheless the reasonable fits are not sufficient to confirm these models, due to the large number of fitting parameters involved. Furthermore, the fitted values of the diffusion constants sometimes show unreasonable trends [1]. An exception is a recent study by Pang [23] who analyzed the stirred suspension results of Garraut et al. (case study 2) finding very similar values of the diffusion constant for all the grain size distributions. On the other hand, Bishnoi and Scrivener [4] applied a similar combined model to fit the paste hydration results of Costoya (case study 1) and found that, while good fits could be obtained, the fitted diffusion constants varied by more than an order of magnitude depending on the grain size distribution, leading them to conclude that diffusion control was not responsible for the early deceleration. Also, measurements of the instantaneous activation energy at different hydration times indicates that the activation energy does not change during the early hydration period even after the deceleration period [5]. This argues against a change in rate-controlling mechanism, but is not conclusive since the activation energies for growth and for diffusion could coincidentally be very similar. We therefore draw no firm conclusions about the underlying mechanism for a reaction zone. In the future, sophisticated hydration simulators that take into account the solution chemistry, such as Hydratica [24, 25], and simulations of the formation of C-S-H at the nanoscale [26] should shed more light on this issue.

An interesting phenomenon that we observed from the MBK model results is the formation of a less-dense region of hydration product close to the C_3S surface during the rapid hydration period, such that at some locations there is a gap between the C_3S surface and the hydration product (see Figs. 10 and 11). This situation arises because new pore space is always being created by the dissolution of C_3S , which cannot immediately be filled by inward growth of hydration product and new nucleation. Because this phenomenon was unexpected, we considered a few options to prevent this from occurring, such as forcing product to form preferentially in this newly created space, or by having regions of already-formed product move inward to follow the receding C_3S surface. However, such modifications do not seem to have any physical justification based on our assumed hydration mechanisms. Our calculations indicate the maximum size of the gap is 0.1-0.2 μm for the conditions simulated here. Interestingly, gaps of comparable size have been systematically observed in portland cement pastes, where they are termed Hadley grains [27, 28, 29], and can also be seen, but are less obvious, in alite pastes [30, 31].

4.2. The MBK model

The microstructure-based kinetics (MBK) model introduced here incorporates the fundamental mechanisms of nucleation and growth and combines them with microstructural information in the radial direction of the hydrating grains (see Fig. 10). The statistical binning approach for handling the

grain size distribution and pore size distribution enables the simulations to be computationally very efficient, in that the number of different particles that must be considered is greatly reduced. For the results presented here, only between 9 and 13 different grain sizes were explicitly modeled to simulate each dataset. The required number of pyramidal volumes per grain will depend on the pore size distribution and how accurately it must be captured. Here we considered a single-valued pore size distribution, so only one pyramid per grain was required.

As a result of the statistical approach used by the MBK model, a high degree of spatial resolution can be obtained with relatively short computation times. Each simulation reported in this paper required less than 1 hour to complete on a single-processor computer, yet spatial resolutions ranging from 1 to 26 nm in the radial direction were obtained. Such high spatial resolution makes the model well suited to exchange information with atomistic and meso-scale models that can simulate processes taking place at smaller scales ranging from 1 nm to 1 μm . Important local information that can be imported from these smaller-scale models includes the time evolution of structural parameters (e.g. chemical composition and nanoporosity), physical properties (e.g. permeability), and mechanical properties (e.g. elastic moduli and strength). Eventually, the MBK model could be used to link the nano- and the macro- scales, enabling the application of homogenization techniques and poromechanics to extract macroscopic properties such as sorption curves, setting, stress development, and strength.

In its current form the MBK model considers only C–S–H and CH hydration products. From a technical point of view, extension of the model to include additional phases should be straightforward. However, to simulate hydration kinetics correctly, the nucleation and growth mechanisms of all the phases and their effect on the system chemistry must be known, which considerably complicates the task.

5. Conclusions

The experimentally observed effects of the w/c and the grain size distribution on the amount of early hydration of C_3S or cement associated with the main hydration rate peak can be explained in a qualitative way by the simple hypothesis that during the early hydration period the C–S–H product is constrained to form within a region close to the hydrating grains, which we call the reaction zone. To quantitatively test this hypothesis, a new microstructure-based kinetics (MBK) model was developed. The MBK model treats the C_3S size distribution in a statistical way to save computation time and treats the early hydration as essentially a boundary nucleation and growth process. The reaction zone was implemented in the simplest possible way, which was to allow new C–S–H product to form only within a fixed distance of the current surface of a hydrating grain. This thickness was varied as a fitting parameter. The MBK model was used to fit kinetic data from two published studies for C_3S with different size distributions, one for alite (impure C_3S) pastes and one for stirred C_3S suspensions. The model

was able to fit all of the datasets from both studies with the same values of the growth rate and nucleation rate, and, for each study, the thickness of the reaction zone shows no significant dependence on the particle size. These results provide strong support for the reaction zone hypothesis, indicating a strategy for further research on Portland cements.

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Figure 1: Example of an isothermal calorimetry curve for the hydration of C_3S paste at 25°C (open circles), along with a mathematical boundary nucleation and growth fit (solid line), after [7]. The numbered hydration stages are described in the text. The amount of hydration described by the fit is about 35% of the total.

Figure 2: Left: Schematic of C₃S grains (gray circles) suspended in water (blue). The dashed lines illustrate the partitioning of the pore space to assign all locations to the nearest C₃S grain. The pore space assigned to each grain is divided into pyramidal volume elements (example in red). Right: Each volume element contains both grain and pore space.

Figure 3: Conceptual illustration of the precipitation step for the MBK model inside a single volume element. (a) First hydration step, from $\alpha = 0$ to $\alpha = \Delta\alpha$. The dashed red line is the current location of the C_3S grain surface, while dashed line A shows the initial location of the surface. A region of C-S-H gel (B) nucleated on the original surface with finite footprint d_0 and zero thickness (red line segment), and then grew in all directions between $\alpha = 0$ and $\alpha = \Delta\alpha$. Regions of CH (C) also nucleated homogeneously throughout the pore space. (b) Later precipitation step from the same simulation. “E” shows the tangential growth of the already existing C-S-H gel, and its outward normal growth until reaching the boundary of the pyramid (or the reaction zone, which is not shown here). “F” shows inward growth of C-S-H gel that does not reach the C_3S surface, which has dissolved away from it. “G” represents impingement between C-S-H and CH, while “H” indicates impingement between existing and new CH. “J” shows the nucleation and growth of new C-S-H gel, and “K” the impingement between previously and newly formed C-S-H.

Figure 4: Alite grain size distributions considered in case study #1, calculated from data in Costoya [13]. The median grain sizes (weighted by the grain volume) are indicated in the legend.

Figure 5: Experimentally measured kinetics (dashed lines, adapted from [13]) and MBK model fits (solid lines) for case study #1 (alite pastes at $w/c = 0.4$). a) Rate of heat release, b) degree of hydration as determined from the cumulative heat evolved. All fits used the same growth rate ($G = 0.0396 \mu\text{m h}^{-1}$), nucleation rate ($I_b = 0.09 \mu\text{m}^{-2} \text{h}^{-1}$), and nuclei patch size ($d_0 = 1 \mu\text{m}$). The reaction zone thickness used for each fit is shown in Fig. 6.

Figure 6: Fitted values of the reaction zone thickness used by the MBK model as applied to case study #1 for alite pastes with $w/c = 0.4$.

Figure 7: C_3S grain size distributions considered in case study #2, calculated from data in Garrault et al. [12]. The median grain sizes (weighted by the grain volume) are indicated in the legend.

Figure 8: Experimentally measured kinetics (dashed lines, adapted from [12]) and MBK model fits (solid lines) for case study #2 (C_3S suspensions at $w/c = 50$). a) Rate data, converted to units of heat release. For better legibility, rates for three out of the five PSDs considered are shown. b) Cumulative data converted to degree of hydration (original data from Fig. 8 plotted on right axis). All fits used the same growth rate ($G = 0.0396 \mu\text{m h}^{-1}$), nucleation rate ($I_b = 0.09 \mu\text{m}^{-2} \text{h}^{-1}$), and nuclei patch size ($d_0 = 1.5 \mu\text{m}$). The reaction zone thickness used for each fit is shown in Fig. 9.

Figure 9: Fitted values of the reaction zone thickness used by the MBK model as applied to case study #2 for C_3S suspensions at $w/c = 50$.

Figure 10: Illustration of microstructure output from the MBK model at different hydration times, for the PSD 18 sample in case study #1. Volume fractions of C-S-H (red), CH (green), and pore space (blue) at each radial distance (vertical direction in the figure) are indicated by the horizontal thickness of the corresponding colored region. The reaction zone boundary is indicated by the horizontal black line that follows the grain surface (gray) inwards as hydration proceeds. At 11 hours, the growing front of C-S-H first touches the reaction zone. At 15 hours the tangential (here horizontal) impingement of C-S-H is very significant. At 21 hours the reaction zone is entirely filled by product. Note that the C-S-H product that extends outside the reaction zone at later times was inside the reaction zone at the time it formed.

Figure 11: Selected microstructure outputs from the MBK model illustrating the more-porous region, or gap, close to the grain surface. The illustrations follow the same conventions as Fig. 10. (a) Snapshot from the PSD $13 \mu\text{m}$ simulation of case study #1 (alite paste at $w/c = 0.4$). (b) Snapshot from the PSD $7 \mu\text{m}$ simulation of case study #2 (C_3S suspensions at $w/c = 50$).