



Mitigating the effects of system resolution on computer simulation of Portland cement hydration

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ABSTRACT

CEMHYD3D is an advanced, three-dimensional computer model for simulating the hydration processes of cement, in which the microstructure of the hydrating cement paste is represented by digitized particles in a cubic domain. However, the system resolution (which is determined by the voxel size) has a prominent influence on the simulation results and, thus, is difficult to choose a priori. In this paper, it is shown that the effects of system resolution on the simulation results are mainly due to the lack of considerations of the diffusion-controlled reactions in the model. A new concept “hydration layer” is proposed for mitigating the effects of system resolution on the model predictions. By performing simulations with different system resolutions, the robustness of the improved model is demonstrated. Comparisons of model predictions with experimental measurements further demonstrate that the use of hydration layer can successfully mitigate the bias brought by the system resolution.

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1. Introduction

Computer models for cement hydration have been proven to be a useful tool for understanding the chemistry of cement hydration, simulating the microstructure development of hydrating paste and predicting the properties of the hydration process [17]. Currently, several computer models for simulating the cement hydration are available [1,9,16,18]. Factors affecting the hydration process such as the water/cement (w/c) ratios, curing temperature, particle size distribution (PSD) and water-accessibility are considered in most models. Properties of the hydration process such as heat evolution and chemical shrinkage are predicted. Most of the models are used to predict long-term properties of cement-based materials as well such as durability, permeability and volume changes.

CEMHYD3D is one of the most advanced and well-known models for cement hydration [1,17]. It has at least three major advantages: (a) it uses fundamental knowledge about hydration reactions and hydration products in the hydrating pastes; (b) the algorithm employed in the model is very flexible. New types of reactions and hydration products can be added into the computer model by extending or modifying corresponding modules (e.g. modules of dissolution and reaction) without changing the others and (c) the system is represented by a digitized microstructure; hence, microstructural characteristics are easily evaluated, e.g. vol-

ume fraction of phases, percolation properties and contact areas between different phases [18].

However, the smallest size handled in CEMHYD3D, called “system resolution”, is important to such a digitized model. Features smaller than the voxel size cannot be represented since the model works based on the movement and phase change of each discrete voxel. This model is thus not able to represent the microstructure of hydrated cement paste at levels smaller than the voxel size used [12]. Furthermore, the system resolution determines the amount of computing time needed for a specific simulation task. Besides, it may affect the model prediction significantly [8]. The selection of system resolution in CEMHYD3D is based on the computing power available and hence, bias brought by the different system resolutions has not been investigated sufficiently, yet. This work is thus focused on methods for mitigating the effects of system resolution on model predictions. The original model used as the starting point of this study is the version modified by Van Eijk [18], in which the hydration kinetics is calibrated with some Dutch cements and modules for modeling the pore solution are incorporated.

The concept of hydration layer is proposed to simulate the diffusion-controlled reactions in the cement hydration process, which is not considered in the original model. It is demonstrated that the use of hydration layer concept mitigates the effects of system resolution on the model predictions, especially on the hydration degree of cement. The time conversion factors fitted from experimental data obtained with a wide range of cements are very close to each other, demonstrating the robustness of the updated model.

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2. Modelling the cement hydration with CEMHYD3D

CEMHYD3D is a digitized computer model that uses voxels to represent the phases in the hardening paste/concrete. Each voxel is assigned to a phase that is susceptible to move and to transform into another phase. A procedure consisting of dissolution, diffusion, reaction, and precipitation processes is followed to simulate the gradual growth of grains and disappearance of reactants. Results of the simulation such as hydration degree, phase distribution, porosity and phase connectivity are used to predict the performance of the hardened cement pastes. Good accordance between the model predictions and experimental results has been found [1,18]. Furthermore, the computer model is extended for simulating the pore solution composition of hydrating Portland cement paste [18].

2.1. Principles of the model

The simulation starts with a microstructure representing the fresh paste and proceeds by using the cellular automation and random walk algorithms to simulate the reactions of cement. Hydration products are formed in the pore spaces or on the particle surfaces. Heat evolution and volumetric changes are calculated based on the hydration degree of cement, amounts of hydration products, and physical/chemical properties of solids. These properties are compared to experimental measurements for validating the model.

The model starts with an initial 3D microstructure reconstructed from information of the cement powder such as the distribution of clinker phases (via SEM images) and PSD. The hydrating cement paste is represented by a cube divided into cubic voxels. The size of one voxel, i.e. the system resolution, may represent different physical dimension. Most particles of a typical type of cement are smaller than 90 μm . The dimension of the simulated microstructure is thus often set to be $100 \times 100 \times 100 \mu\text{m}^3$, and preferably $200 \times 200 \times 200 \mu\text{m}^3$. System resolutions of 0.5 μm and 1 μm are commonly used for simulation. Larger system sizes and smaller voxel sizes represent the structures more accurately. However, the computing time augments remarkably due to the increase of the voxel number.

The cement particles are built within the cube by putting voxels in an approximately spherical shape called “digitized particle”. An example of a digitized 3- μm particle (system resolution 1 μm) is shown in Fig. 1 which contains 19 voxels [18]. Particles of other sizes are generated in a similar way by placing the voxels in the best possible particle-forming positions. A 1- μm particle is represented by 1 voxel if the system resolution is 1 μm .

An initial microstructure is generated preserving the correct particle size distribution and phase distributions taking use of periodic boundaries (Fig. 2). A detailed routine for placing digitized particles and assigning phases to all voxels is given by Bentz [1]

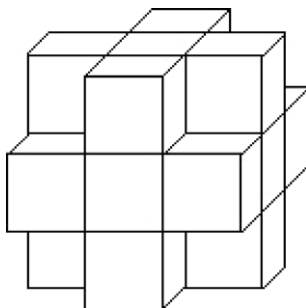
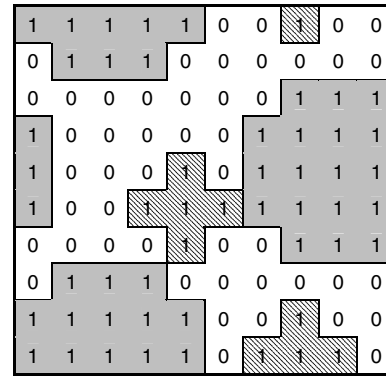


Fig. 1. Digitized 3 μm particle in CEMHYD3D (system resolution 1 μm) [18].



0: Porosity, 1: Solid

1 Voxels in a 5 μm particle

Voxels in a 3 μm particle

Fig. 2. 2D schematic illustration of an initial microstructure in CEMHYD3D with periodic boundary conditions for a 2D system with size $10 \mu\text{m} \times 10 \mu\text{m}$ (system resolution 1 μm).

and Van Eijk [18]. Periodic boundaries are used to eliminate the sparsity effect due to the presence of boundaries [1]. It is noteworthy that to assign phases to the voxels by using the autocorrelation method proposed by Bentz [1] is not possible if the 2D SEM images and that detailed phase distribution information are not available for some cements. A random distribution method is then used. The phases are assigned randomly to the voxels preserving the appropriate volume fractions, resulting in a homogeneous phase distribution. It appears that the randomly assigned phases and those based on 2D images yield almost identical simulation results [18].

Hydration of the initial microstructure is simulated in an iterative process consisting of discrete cycles. Each cycle consists of three processes: dissolution, diffusion and reaction. The phases dissolve from the surface of the cement particles, diffuse in the space available up to a certain number of steps, and may react to form hydration products.

The dissolution step is executed by scanning the entire 3D microstructure for identifying all reactant phases which are soluble and enabling those voxels to dissolve if certain conditions are met. A dissolution probability is used in the model to define the likelihood of each phase to dissolve. The cement phases (such as C_3S , C_2S , C_3A , C_4AF , and gypsum) have different dissolution probabilities so that they dissolve at different rates. The hydraulic reactivity of each phase is considered in this way. All solid voxels in contact with water are marked as being able to dissolve. In a second scan, all marked voxels take a one-step random walk. The dissolution is allowed if (a) this step is into porosity, (b) the phase of the voxel is currently soluble and (c) a randomly chosen number is higher than the dissolution probability of this phase. The solid voxel dissolved is then converted to one or more diffusing voxels preserving the appropriate volume equations. After the scan, the number of dissolved voxels of each reactant is counted, and the corresponding diffusing species are added randomly in the water-filled spaces (porosity). The volume stoichiometry of the reactions is preserved statistically. For example, if 100 voxels of C_3S dissolve in a cycle, 152 diffusing C–S–H voxels and 61 diffusing CH voxels are added.

Each of these diffusing voxels executes a random walk in the water after the diffusing species have been created. The voxel moves into one of the neighboring porosity voxels in one step. Three types of changes of the voxels are possible during the

diffusion process: nucleation, precipitation and reaction. The direction of diffusion is randomly chosen. Most of the diffusing species turn into solid products after a large number of diffusion steps.

Diffusing species such as FH_3 , CH, and ettringite may nucleate and are converted to corresponding solid products. The likelihood for the species to nucleate is called “nucleation probability”, which is exponentially proportional to the number of diffusing species remaining in the microstructure.

Precipitation takes place if the diffusing voxel collides with certain types of solids. For example, a diffusing CH voxel precipitates if it collides with solid CH. The gradual growth of hydration products on the surface of solid particles in the microstructure is simulated in the precipitation process.

Reactions obeying a series of rules take place if the diffusing species collide with other solid/diffusing species. The possibility of the chemical reaction depends on the nature of the two species colliding. The diffusing voxels are converted into hydration products preserving the volume stoichiometry.

The microstructure is updated after each hydration cycle. Properties related to the hydration process such as the hydration degree, amount of combined water, heat development and chemical shrinkage are calculated. The hydration degree of cement is computed by using the numbers of voxels in the initial and changed microstructure as:

$$\alpha_j^i = \frac{[I]_j^0 - [I]_j^i}{[I]_j^0} \quad (1)$$

in which α_j^i is the hydration degree of phase j in cycle i , $[I]_j^0$ is the number of voxels in the initial microstructure, $[I]_j^i$ is the number of remaining voxels of phase j in cycle i . The overall hydration degree of the cement is calculated from the total numbers of initial and remaining cement voxels on a volume basis, which is further converted into the degree on a mass basis by using the densities of phases. Temperature of the paste in each hydration cycle is calculated by using the enthalpy changes.

2.2. Reaction kinetics considered in the original CEMHYD3D

CEMHYD3D runs on a cycle basis and no time dependent factors are included in the model. So, the model results are not ready for use if the time factor needs to be considered. The calculation cycles are related to time by using a quadratic relation given by Bentz [1] and based on the parabolic hydration kinetics:

$$t = t_0 + B \cdot (\text{cycles})^2, \quad (2)$$

where t is the hydration time (in hour), t_0 corresponds to the duration of the dormant period (in hour), B is the time conversion factor (in h/cycle^2) and cycles are the number of executed calculation or model cycles. The kinetic Eq. (2) is completely empirically based and has been calibrated for US CCRL, French Montalieu Portland cement [1] and for two Dutch cements ENCI CEM I 32.5 and CEM I 52.5 [18]. The calibration was done by using different experimental techniques to measure the hydration degrees of cement and relating the results to the degree of hydration predicted with the model. The values of “ B ” range from 0.3×10^{-3} to $1.7 \times 10^{-3} \text{ h}/\text{cycles}^2$ [1,18].

Three different mechanisms are used to explain the hydration kinetics of a cement particle [3,12]: nucleation and growth, phase-boundary reaction and diffusion-controlled reaction. The first mechanism considers the formation of solid products from the solution and its nucleation or precipitation. The second mechanism considers the process of dissolution of solid at the surface, its diffusion in the neighboring locations and precipitation on the grain. The difference between these two mechanisms is that the nucleation takes place throughout the available pore space filled with solutions while boundary reaction occurs close to the dissolu-

tion source. The third mechanism corresponds to diffusion through the C–S–H and other colloidal products coating the anhydrous core. The reaction rate is controlled by the capability of species to diffuse through the layer formed by the hydration products.

The original CEMHYD3D simulates the phase-boundary reactions by allowing the voxels on the surface of the digitized particles to dissolve. After the dissolution, the voxel diffuses in the neighboring locations and nucleates in the pores, or reacts with other species to form solid products, or precipitates on the surface of solids. The nucleation mechanism is also simulated in CEMHYD3D by putting some diffusing species randomly throughout the microstructure and by enabling possibilities for nucleation or growth on some solids.

However, considerations to the diffusion-controlled reactions are not included in the original CEMHYD3D. This causes remarkable variations of the time conversion factor, the kinetic parameter of the model, which should be avoided. More comprehensive methods for simulating the different mechanisms are expected to give the model a more chemically sound basis and make the model more robust.

3. Effects of system resolution in CEMHYD3D

It was found that changing the system resolution affects the model predictions significantly [8], which should be avoided in a robust system. The reason for this effect of system resolution on the model predictions is discussed in details.

The physical size of one real cement particle is irrelevant to the resolution of the system representing it. However, the fraction of voxels on the surface of a particle to its total volume is changed if different system resolutions are used to reconstruct the particle. A cement particle of the size $7 \mu\text{m}$ is chosen as example. The particle is reconstructed in two systems with resolutions of $1 \mu\text{m}$ and $7 \mu\text{m}$, respectively (Fig. 3). The two particles have the same areas in the two different systems ($49 \mu\text{m}^2$), representing the same particle sizes. The voxels on the edge of the particle are marked in the figure as well. The fraction of voxels on the surface layer that are susceptible to dissolve is 1.0 in system (b) and is 0.41 in system (a). Furthermore, only the voxels on the surface of the particles are able to dissolve. Hence, for the same dissolution probability (for example 1.0), the hydration degree of particle in system (b) is higher than that in system (a) in one cycle. Therefore, increasing the size of the system resolution of the model increases the amount of hydrated cement in one cycle [8], and results in larger hydration degrees if the same time conversion factors are used.

This bias brought by the system resolution is caused by the mechanisms used in the model. As discussed in Section 2.2, only two reaction mechanisms are considered in the original CEMHYD3D (nucleation and boundary reactions). Therefore, only cement voxels in direct contact with water are able to react. In other words, only cement voxels on the surfaces of particles can hydrate and those coated by hydration products are inert. However, due to the fact that the main hydration product C–S–H is porous and water as well as other substances can penetrate through it, the anhydrous cement cores covered by hydration products are also able to hydrate, although the rate is affected by the thickness and nature of the coating layer. So, the diffusion-controlled reactions should be simulated in CEMHYD3D. In the next Section this update of CEMHYD3D is introduced

4. Hydration layer: a method to mitigate the effects of system resolution

A new method for the dissolution process of cement voxels in CEMHYD3D is proposed, which simulates both the phase-boundary

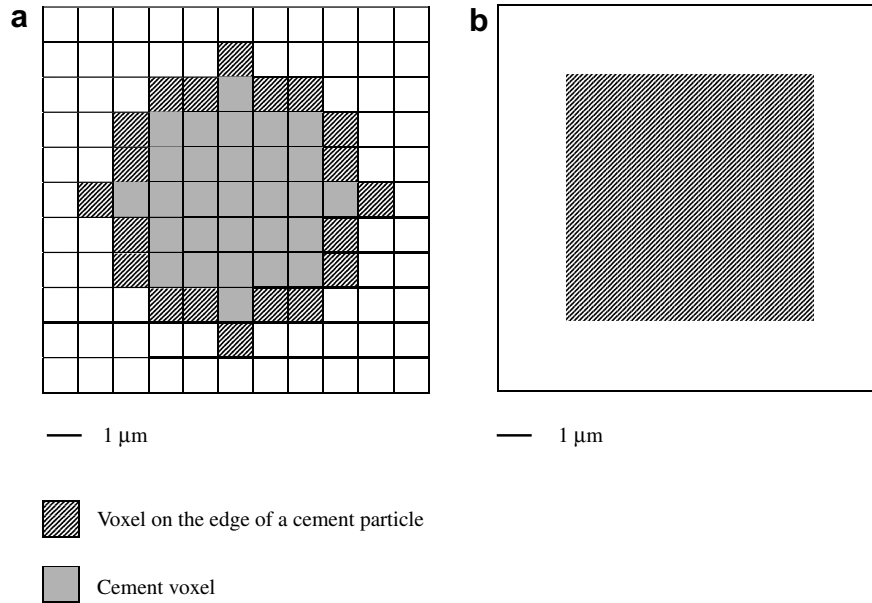


Fig. 3. 2D illustration of effects of system resolution on the ratio of surface voxels to the total of a 7- μm particle. (a) System resolution 1 μm , and (b) system resolution 7 μm . The two particles have the same areas ($49 \mu\text{m}^2$) indicating the same physical sizes.

and diffusion-controlled reactions. The nucleation of products remains unchanged. The major extension is that cement voxels coated by hydration products are allowed to hydrate in the updated model.

4.1. Definition of hydration layer

The definition of hydration layer is first introduced. The dissolution of a cement voxel in the CMEHYD3D is determined by its hydraulic reactivity and the voxels surrounding it. The cement voxel to dissolve is called “source voxel” and the surrounding voxels which are checked are called “target voxel”. Each target voxel is marked with a number called “layer number”, which physically represents its relative location to the source. The “hydration layer” is the group of target voxels with the same distance to the source voxel. Voxels on the same hydration layer have the same layer number. For example, the layer number of voxels next to the source is 1 and that of the further layer is 2 (Fig. 4). A concept “layer thickness” is also defined which physically represents the distance of the target voxel to the source. For example, the voxels in direct contact with the source voxel have a layer thickness of 1 μm (when the system resolution is 1 μm).

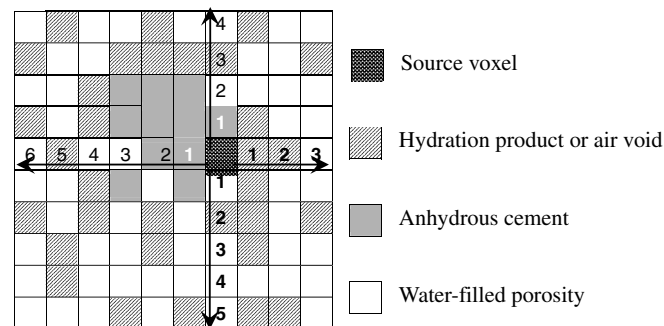


Fig. 4. 2D schematic illustration of hydration layer concept in two directions with the layer number indicated. The arrows indicate the directions that the check takes place.

4.2. Dissolution in the updated model

The dissolution step starts by checking the phase of the adjacent voxel next to the cement voxel (source voxel). A random number is generated with the value of 1, 2, 3, 4, 5 or 6, representing the six direction in which the check occurs. In this way, the preferential dissolution in one direction is avoided. Dissolution of the source voxel is possible if the adjacent voxel is water. The likelihood for the dissolution is further controlled by a randomly generated number whose value is smaller than the predefined dissolution probability.

The check continues for other voxels surrounding the cement if all the adjacent voxels are checked and the source voxel does not dissolve. Target voxels on the same layer are checked in each step, starting from the close ones. The procedure is similar to that for the adjacent voxels. The exception is that the check is terminated in directions in which the adjacent voxel to the source is cement. The major reason for this configuration is that the cement voxel is regarded as being impermeable and diffusion of substances in this direction is not possible. Hence, dissolution in this direction is not allowed. Periodic boundary conditions are used in the check procedure above to eliminate the boundary effect. The check procedure continues till the source voxel dissolves or the layer number reaches the system size. The latter case corresponds to a complete check of all target voxels in the selected direction.

It is noteworthy that the check of phases is carried out in only six directions in the dissolution process above. Check in other directions (for example, diagonals) is possible. But, the computing time is drastically increased with a typical personal computer. Therefore, only the six neighboring voxels are checked for dissolution of a cement voxel in the original CEMHYD3D. The same principle is taken over in this study, but extended for more voxels in each direction.

4.3. Dissolution probabilities in the updated model

The dissolution probabilities of cement voxels are modified in the updated model. Voxels in direct contact with porosity are taken the same as those used in the original CEMHYD3D [1], which are empirically determined and calibrated using some experimental

results. The discussion is thus focused on the method for determining the dissolution probabilities when the cement voxel is coated by hydration products.

The hydration rate of a cement voxel coated by hydration products is governed by two factors: the transport rate of the reaction-controlling substances through the coating layer and the reactivity of the cement voxel. The transport rate is considered by the flux of substances through the coating layer and the reactivity is considered with the dissolution probability (set a priori).

4.3.1. Diffusion of substances through the coating layer

Cement particles are partially or completely coated by hydration products shortly after they are mixed with water. The hydration can still proceed because substances diffuse through the coating layer. The substance that controls the reaction rate could be water moving toward the anhydrous cement core or ions (Ca^{2+} , $H_3SiO_4^-$, $Al(OH)_4^-$ etc.) moving outward [14]. Considering a hydrating C_3S particle and at the surface, the Ca^{2+} and $H_3SiO_4^-$ ions enter the solution and ultimately precipitate along with the OH^- ions released from the H_2O molecules as CH and outer product C–S–H. Migration of silicon is suggested as the probable rate-determining step by Taylor [14]. The effects of coating layer on the diffusion are discussed.

According to the Fick's law:

$$J = -D \frac{10^3 \times \partial C}{\partial x_p} \tag{3}$$

in which J is the diffusion flux of a substance through the product layer ($mol/(s\ m^2)$), C is the concentration of the limiting substance (mol/L), D is the diffusion coefficient (m^2/s), and x_p is the particle size (m) of cement. It is assumed in Eq. (3) that the diffusion of controlling substance through the coating layer is a steady state process.

The flux of water through the coating layer is used as example for facilitating the discussion. This does not imply that the diffusion of water is the rate-controlling mechanism in this stage. Diffusion of other substances is also possible, but the fluxes of substances other than water are analyzed in a similar way. Assuming the concentration gradient of water in the coating layer is constant, the rate of water diffusion to the reaction front is calculated as:

$$J_0 = \frac{D(C_\infty - C_0) \times 10^3}{\delta} \tag{4}$$

in which C_0 (mol/L) is the concentration of water at the reaction front (surface of the anhydrous cement core); C_∞ (mol/L) is the concentration of water in the pore solution surrounding the hydrating cement particle, set to be a constant value assuming that the pore solution is a homogenous mixture of substances, and is independent of the thickness of the coating layer. C_0 equals to zero if an instant reaction of cement with water is assumed; and δ (m) is the thickness of the coating layer (Fig. 5).

It is taken in Eq. (4) that the flux of diffusion at the reaction front is proportional to the concentration difference across the coating layer ($C_\infty - C_0$) and is inversely proportional to the thickness of the coating layer (δ). The dissolution probability for the surface layer (voxels in direct contact with porosity) follows the same procedure as that used in original CEMHYD3D. The dissolution probability of a source voxel coated by hydration products is calculated as:

$$P_i = P^0 \cdot \frac{J_0}{J_0^{max}} = P^0 \cdot \frac{D(C_\infty - C_0) \times 10^3}{J_0^{max} \cdot \delta} \tag{5}$$

in which J_0^{max} is the maximum flux of water diffusion, corresponding to the case that the voxel is in direct contact with porosity and is a

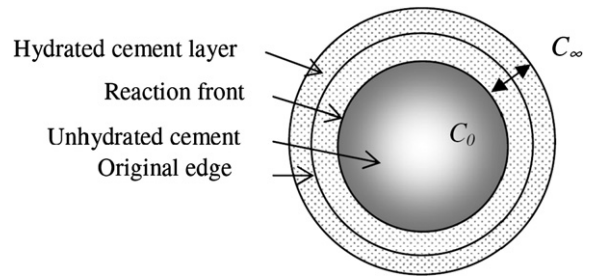


Fig. 5. Schematic illustration of a hydrating cement particle.

constant; P_i (dimensionless) is the dissolution probability of the source voxel when the layer number is i , P_0 (dimensionless) is the base dissolution probability (i.e. when the source voxel is in contact with water). Separating the constants in Eq. (5) and rewriting it gives:

$$P_i = P^0 \cdot \frac{D(C_\infty - C_0) \times 10^3}{J_0^{max}} \cdot \frac{1}{\delta} = \frac{P^0 \cdot \Omega}{\delta} \tag{6}$$

in which:

$$\Omega = \frac{D(C_\infty - C_0) \times 10^3}{J_0^{max}} \tag{7}$$

Ω (m) is a model parameter independent of the layer thickness. One can see that the method for computing the dissolution probability as Eq. (7) is similar to that used in HYMOSTRUC for computing the penetration depth by comparing Eq. (7) to the Eq. (6.45b) by Van Breugel [16]. The parameter Ω represents the effect of water accessibility to the cement voxel.

4.3.2. Effects of water consumption

During the hydration process, the capillary pores that are initially filled with water gradually become desiccated due to the continuous consumption of water by the cement hydration. It causes a drop of the internal relative humidity that further impedes the hydration process.

Another effect of the initial water in the paste on the cement hydration rate is the gel/space ratio. Higher water/cement ratios result in larger gel-space ratios. Research has shown that the relative hydration rate of cement is clearly affected by the gel-space ratio of the paste [7]. Berliner et al. [2] found that the w/c ratio of the C_3S paste influences the diffusion constant of the hydration product C–S–H. Larger w/c ratios result in higher diffusion constants. A log-linear relationship was found between the diffusion constants and the initial w/c ratios (Fig. 6).

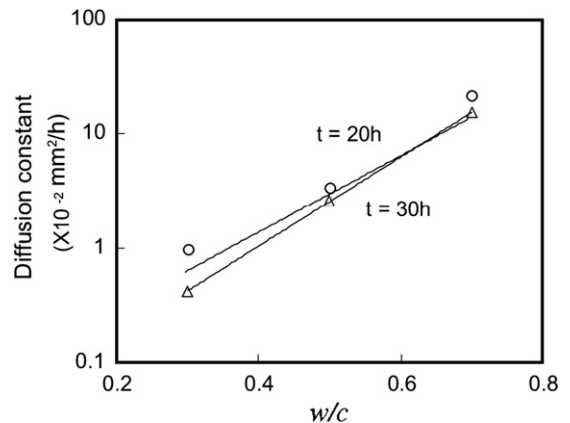


Fig. 6. Diffusion constant of C–S–H produced from C_3S hydration as a function of initial w/c ratios [2].

The effect of w/c ratio on the diffusion constant could be explained by its influence on both the morphology and the composition of hydration products. The C/S ratio of the major product C–S–H in a C_3S paste increases with decreasing water/solid ratios [16] and C–S–H with a higher C/S ratio has lower porosity [4]. Surface area measurements with the BET method by Mikhail and Selim [10] confirmed that the w/c ratio has dominant effects on the internal structure of the hydration products (Table 1). Higher surface areas correspond to more porous internal microstructure via which substances diffuse through. Therefore, it is more likely easier in pastes with higher w/c ratios that the substances diffuse through the coating layer.

4.3.3. Determination of Ω

The parameter Ω in Eq. (7) is an inherent property of the paste depending on the diffusion coefficient of substances in the hydration layer. A major conclusion drawn from the discussion above is that it depends on the w/c ratio of the starting paste. Furthermore, the diffusion coefficient at the beginning of the hydration is large because of the small amount of hydration product in the paste.

The chemical principles about the diffusion of substances via the coating layer as used in HYMOSTRUC are adopted in this study. It provides the inclusion of the third mechanism with a solid chemical background. Van Breugel [16] proposed in HYMOSTRUC the following factor to account for the water shortage as a function of the w/c ratio as:

$$\Omega = \frac{w/c - 0.4\alpha}{w/c} = 1 - \frac{0.4\alpha}{w/c} \quad (8)$$

in which w/c is the water/cement ratio; α is the overall hydration degree of cement in the paste ranging from zero to unity. A schematic representation of the parameter Ω as a function of the hydration degree and for different w/c ratios is shown in Fig. 7(a and b). The value of Ω decreases with increasing hydration degrees and decreasing w/c ratios.

It is important to compute the parameter Ω accurately in each hydration cycle. The coefficient 0.4 used in Eq. (8) is actually very close to the amount of retained water in the saturated and com-

pletely hydrated Portland cement paste, namely 0.42–0.44 g water per g original cement [15]. Hence, the expression $w/c - 0.4\alpha$ corresponds to the amount of water left in the paste (per unit mass of cement) in the saturate state. So, Eq. (8) is the fraction between the amount of water left in the paste and that in the starting paste. However, the coefficient 0.4 is largely an generalization in Eq. (8) and the hydration degree (α) of cement is an overall degree of all phases. Since the computer model CEMHYD3D represents the hydrating microstructure digitally and all phases are distinguished, it is expected that the parameter Ω is computed in a more accurate way based on the simulation results.

A new expression for determining Ω is proposed taking use of the model outputs and the water contents of the hydration products in the saturated state as:

$$\Omega = \frac{w/c - \frac{M_w}{m} \cdot \sum_i n_i \cdot H_i}{w/c}, \quad (9)$$

where M_w is the molar mass of water (1 g/mol), n_i is the moles of hydration products i (C–S–H, C_4AH_{13} , CH etc.) that are predicted with CEMHYD3D, H_i is the water content in each of the products (mol per mol product). The values of n_i are computed from the predictions in the previous cycle.

Note that systems with higher resolutions have larger values of dissolution probabilities according to the new method as Eq. (6) for the same layer due to the smaller value of δ . One of the advantages of this extension is that the dissolution probabilities take into account the effects of system resolution. The physical size of one hydration layer in a system with the resolution of 2 μm is larger than that in the system with the resolution of 1 μm . Therefore, a smaller value of P_i is calculated, half of that in a system with the resolution of 1 μm . In this way, the effects of the system resolution on the model predictions are effectively mitigated.

5. Validation of the updated model

5.1. Comparison with experiments

Two series of simulations are carried out using the updated model. The simulation results are compared to the experimental results in two independent studies [7,11], which are well documented.

The properties of the two cements used in the two studies, Cement A and Cement B from Mounanga et al. [11], and Copeland et al. [7], respectively, are listed in Table 2. The clinker composition of Cement A is derived from its oxide composition by using Bogue's equations and that of Cement B is given in the literature. Mounanga et al. [11] measured the hydration degree of cement pastes with various w/c ratios. The cement pastes are cured at different temperatures (10, 20, 30 and 40 °C). The hydration degree is

Table 1
Surface area of hydrated cement paste at 28 days as a function of the initial w/c ratio [10]

w/c ratio	N_2 BET (m^2/g)
0.35	56.7
0.4	79.4
0.5	97.3
0.57	132.2
0.7	139.6

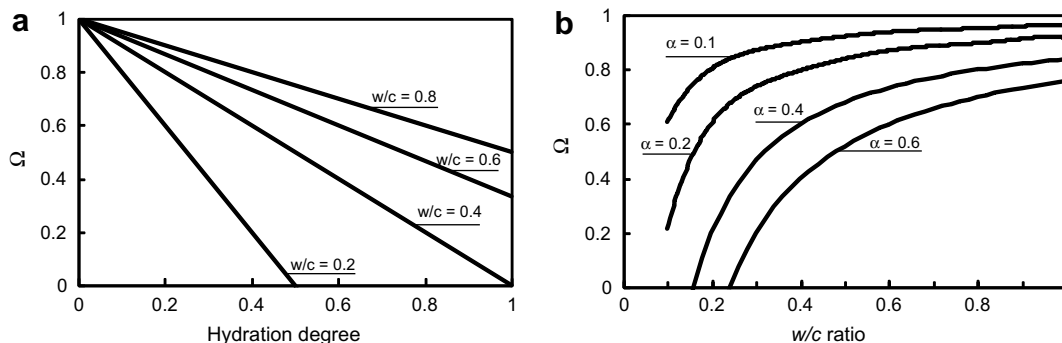


Fig. 7. Values of Ω as function of the hydration degree of cement (a) and w/c ratios (b), computed with Eq. (8).

Table 2

Chemical composition of cements used in experiments (m/m%) and the Blaine fineness

Oxide	A ^a	B ^b
CaO	66.39	
SiO ₂	21.17	
Al ₂ O ₃	2.69	
MgO	0.65	
SO ₃	2.43	
Fe ₂ O ₃	1.96	
Na ₂ O	0.3	
K ₂ O	0.22	
Loss on ignition	2.26	
Insoluble residue	0.96	
Free lime	0.84	
<i>Bogue composition</i>		
Phase	m/m%	
C ₃ S	70.15	53.1
C ₂ S	7.77	25.9
C ₃ A	3.81	6.9
C ₄ AF	5.95	9.7
Gypsum	5.22	3.0 ^c
Total	92.9	98.6
Fineness (Blaine, m ² /kg)	332	380

^a Mounanga et al. [11].

^b Copeland et al. [7].

^c Estimated value.

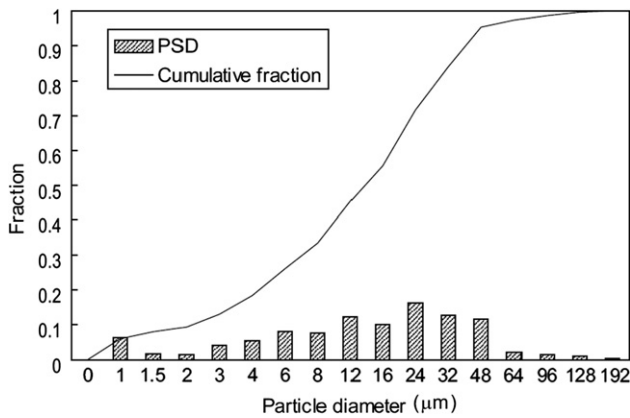


Fig. 8. Differential and cumulative particle size distribution of Cement A used in the experiments of Mounanga et al. [11].

derived from the non-evaporable water measurement by using thermogravimetric analysis. The amount of non-evaporable water for complete cement hydration is estimated by Mounanga et al. [11]

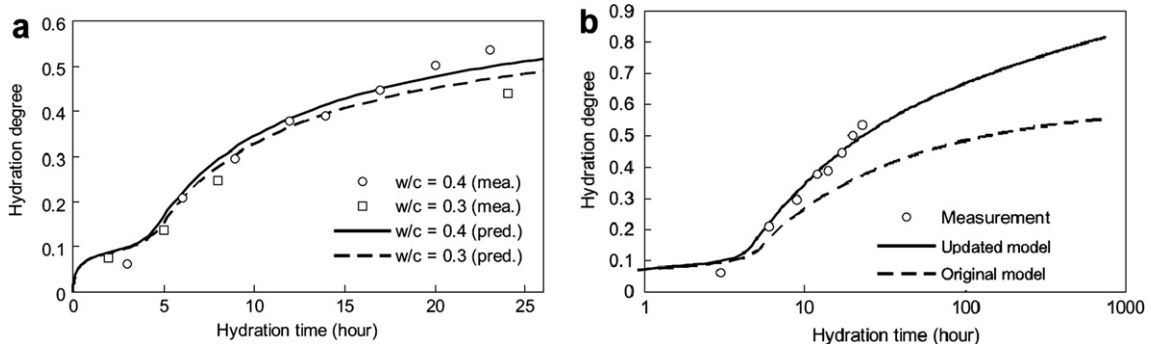


Fig. 9. Predicted and measured hydration degree of Cement A. Experimental data from Mounanga et al. [11], $T = 30\text{ }^\circ\text{C}$, time conversion factor B is $3.8 \times 10^{-3}\text{ h/cycle}^2$.

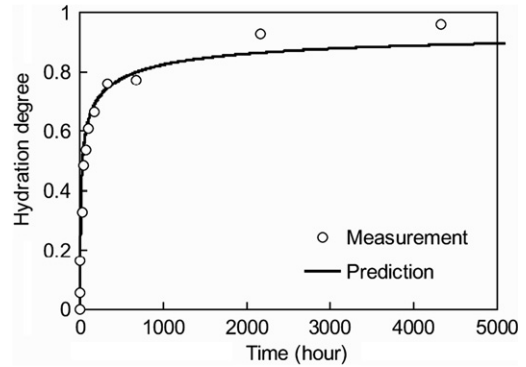


Fig. 10. Measured and predicted hydration degree of Cement B; $w/c = 0.4$, $T = 21\text{ }^\circ\text{C}$, $B = 3.8 \times 10^{-3}\text{ h/cycle}^2$, experimental data from Copeland et al. [7].

from its Bogue composition to be 0.23 g per g cement. The PSD of the cement is presented in Fig. 8.

Simulations are carried out for pastes cured at $30\text{ }^\circ\text{C}$. The influence of the w/c ratio on the hydration degree of the cement during the first 24 h is shown in Fig. 9a. The time conversion factor B used for relating the cycles to time is fitted as $3.8 \times 10^{-3}\text{ h/cycle}^2$ (see Eq. (2)).

It can be seen that the w/c ratio has very limited influence on the hydration degree of cement during the early ages. As the hydration proceeds, the hydration degrees differ from each other due to the different w/c ratios. The observation of the influence of w/c ratios on the hydration degree is in line with that by Taplin [13]. The hydration degree is mainly controlled by the surface of cement particles in contact with water at early hydration ages. As hydration proceeds, water is combined in the hydration product and thus less water is available for the hydration. Hence, the hydration process is impeded for pastes with low w/c ratios.

The hydration degrees of the cement pastes with w/c ratio of 0.4 and cured at $30\text{ }^\circ\text{C}$ are predicted by using both the original CEM-HYD3D and the updated model and are shown in Fig. 9b. The time conversion factors (B) for both models are $3.8 \times 10^{-3}\text{ h/cycles}^2$. It can be seen that the updated model predicts the hydration degree of Cement A more accurately than the original model. Furthermore, it takes less computing time as well (less hydration cycles).

The hydration of Cement B is simulated as well. The cement pastes are made with a w/c ratio of 0.4 and are cured for different ages ranging from 2 hours to 6 months. The hydration degree of each phase was measured by Copeland et al. [7]. The particle size distribution of Cement B is unknown and is assumed to follow that of a CEM I 32.5R cement [5]. The gypsum content in the cement is not known and is assumed to be 3% (m/m). The simulation is carried out in the same curing condition with the same w/c ratios.

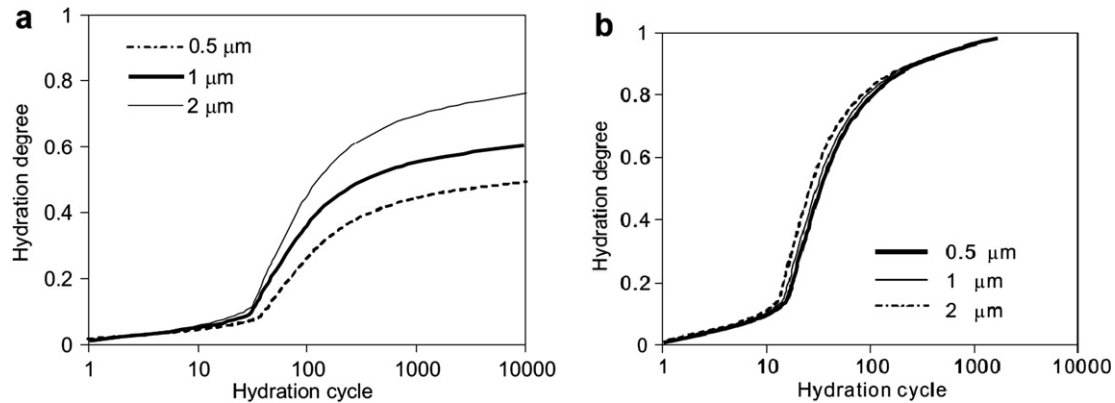


Fig. 11. Simulated hydration degrees of Cement A using the original version (a) and the updated one (b) of CEMHYD3D with three different system resolutions, $T = 21\text{ }^{\circ}\text{C}$, $w/c = 0.4$.

The cycle-time conversion factor for Cement B is set to be $3.8 \times 10^{-3}\text{ h/cycle}^2$ as well. The predicted and measured hydration degrees of the model cement are shown in Fig. 10.

The predicted hydration degree of cement agrees well with the measurements using the same time conversion factor ($3.8 \times 10^{-3}\text{ h/cycle}^2$) as that for Cement A although the two experiments are significantly different. The compositions and fineness of the two cements are different. The w/c ratio of the pastes and the curing temperatures are different as well. Therefore, it appears that the most essential factors that affect the hydration rate of the cement (such as clinker composition, fineness, w/c ratio, temperature) are appropriately handled by the updated model. It is found that this time conversion factor is applicable for several other Portland cement and slag cement pastes as well, which is published elsewhere [5,6]. This factor appears to be appropriate for simulating the hydration of cement if there are no experimental data available for calibrating the simulations.

5.2. Effect of system resolution in the updated model

Simulations by using the updated model with three different system resolutions ($0.5\text{ }\mu\text{m}$, $1\text{ }\mu\text{m}$ and $2\text{ }\mu\text{m}$) are carried out with cement A in Table 2. The pastes are cured in the saturated state. The predicted hydration degrees of the cement with the three different system resolutions with the original CEMHYD3D (“hydration layer” function disabled) are plotted in Fig. 11a. It is shown that the system resolution plays a significant role in the original CEMHYD3D, as discussed earlier.

Simulations using the updated model with three different resolutions are carried out again and the results are plotted in Fig. 11b. The predicted hydration degrees of models with the three resolutions are almost identical. Hence, it appears that the effects of system resolution on the model performance are successfully mitigated.

6. Conclusions

The work presented in this study is focused on methods to mitigate the effects of system resolution on the model predictions in CEMHYD3D. Although the voxel size effectively defines the smallest microstructural features/processes that can be represented by the model, addressing this inherent limitation of digital models is beyond the scope of this study. However, the bias of predicted hydration degrees brought by using different system resolutions is mitigated in the updated model. Furthermore, the implementation of algorithms for modelling the diffusion-controlled reactions makes the background of CEMHYD3D more chemically sound. Pre-

dictions can be made with system resolutions as small as possible without the need of changing the time conversion factor (the major fitting parameter in CEMHYD3D). This enables representation of the microstructure of hydrating cement paste with the finest scale by using the computing power available.

Several conclusions are drawn based on the investigations in this study, which are summarized as follows:

- The system resolution is important for modelling the cement hydration process in CEMHYD3D. It affects the model predictions significantly. The predicted hydration degrees with larger system resolutions are lower than those with smaller resolutions.
- The background of this effect is the lack of consideration to the mechanism of the diffusion-controlled reaction in the simulation, which is the dominant mechanism in the late stages of cement hydration process.
- A new method for the dissolution process in the model by using the hydration layer concept is proposed that accounts for different reaction mechanisms during the hydration process. The computer model CEMHYD3D is updated accordingly with this new development. It is shown that the effects of system resolution on the model predictions are mitigated in the updated model.
- The time conversion factor $3.8 \times 10^{-3}\text{ h/cycle}^2$ appears to be appropriate for simulating the hydration of a wide range of cements. This value is thus recommended if experimental data of cement are not available for calibrating the simulation of such cement.

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