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MICROSTRUCTURE DEVELOPMENT OF THE CEMENT PASTE BASED ON THE UNIT CELL MODEL

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Abstract

Microstructure development of the cement paste is closely associated with internal processes such as self-desiccation, shrinkage, creep and other internal processes throughout service life of cement-based materials. The ability to accurately model microstructure parameters is key to predicting internal processes of the cement paste.

Currently, the most frequently used approaches to microstructural modeling of cement paste are vector and discrete. Both approaches generate and process a random structure of the cement paste, but at the same time are characterized by high computational complexity and time-consuming. It accounts for the fact, that simplified structural models still remain relevant. A unit cell model, which can be considered as a particular case of the vector approach, is a geometrically simple model that describes microstructure development based on a representative hydrated cement particle.

The paper presents an advanced microstructural model of the cement paste based on the unit cell model.

Keywords: cement paste, hydration model, unit cell, pore size distribution, percolation threshold.

МОДЕЛИРОВАНИЕ МИКРОСТРУКТУРЫ ЦЕМЕНТНОГО КАМНЯ НА ОСНОВЕ МОДЕЛИ ЭЛЕМЕНТАРНОЙ ЯЧЕЙКИ

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Реферат

Развитие микроструктуры цементного камня тесно связано с такими внутренними процессами, как самовысыхание, усадка, ползучесть и другими процессами на протяжении всего срока службы материалов на основе цемента. Способность точно моделировать параметры микроструктуры является основой прогнозирования внутренних процессов цементного камня.

В настоящее время наиболее часто используемыми подходами к моделированию микроструктуры цементного камня являются векторный и дискретный. Оба подхода генерируют и обрабатывают случайную структуру цементного камня, но в то же время характеризуются высокой вычислительной сложностью и как следствие значительными затратами времени. С точки зрения численного моделирования предпочтительными являются простые в расчетах модели, достаточные для оценки необходимых параметров микроструктуры. Это обуславливает тот факт, что упрощенные модели микроструктуры цементного камня по-прежнему остаются актуальными. Модель элементарной ячейки, которую можно рассматривать как частный случай векторного подхода, представляет собой геометрически простую модель, описывающую развитие микроструктуры на основе репрезентативной гидратирующей частицы цемента.

В статье представлена усовершенствованная модель микроструктуры цементного камня, основанная на модели элементарной ячейки.

Ключевые слова: цементный камень, модель гидратации, элементарная ячейка, распределение пор по размерам, порог перколяции.

Introduction

The cement paste is a crucial phase of cement-based composites whose structure is formed as a result of chemical reactions between cement clinker and water, called a hydration process. During hydration, the cement paste of a plastic consistency turns into a porous solid. Basic properties of cement-based materials, such as mechanical and transport properties, depend heavily on the formed microstructure of the cement paste.

The most effective way to research the microstructure of the cement paste over time is modelling and simulation. Modelling and simulation, taken together, comprise a spectrum of activities that enable the researcher or engineer to compare observations with theory, to extract physical parameters from experimental data, and to predict system behaviors [1].

Despite the fact that a sufficient number of models exist, it remains hard to accurately predict microstructure development of the cement paste due to its extremely complexity.

There are two approaches in modelling microstructure development of the cement paste: discretization and continuous (also called vector) approach.

In the discretization approach the microstructure of the cement paste is approximated as a set of pixels (in two dimensions) or voxels (in three dimensions). Each pixel (voxel) is associated with a specific phase of the cement paste. The key idea of the discretization approach is that at an arbitrary time-step, any pixel (voxel) in a system can change a pre-defined phase state and update it to another according to the taken hydration model. One of the most widely used discretization models was developed at NIST and called CEMHYD3D [2].

In the continuous approach the microstructure of the cement paste is approximated as a set of inclusions in the form of circles (in two dimensions) or spheres (in three dimensions) randomly placed in a representative volume. The circles (spheres) represent an anhydrous phase, and the space between them represents porosity. The hydrate phase appears over time as a layer around each circle (sphere). The key idea of the continuous approach is that at arbitrary time-step, the initial area (volume) of the circles (spheres) in a system decreases, while the hydrate layer increases according to the taken hydration model.

The set of inclusions can consist of either many polydisperse circles (spheres) or a single circle (sphere). The poly-dispersed structure is more preferable, but also much more computationally expensive primarily due to the calculation of the circles (spheres) overlap. Such a structure is used in HYMOSTRUC [3] and μic [4] models.

Meanwhile, there are many observations that point to the agglomeration and flocculation of cement particles, which might result from the adherence of smaller powder particles to the larger ones. In such a case, the average size of the flocculated particles can be considered as the representative size of the particle [5]. DuCOM [5] and unit cell [6] models are based on this idea. Besides, this approach is characterized by a significant reduction in computational costs compared to the polydisperse structure.

This paper presents an advanced microstructural model of the cement paste based on the unit cell model originally described in [6].

Hydration model

A modern model of cement hydration is a complex model that includes at least two parts:

1) Hydration kinetics model.

2) Predicting the volume fractions of the cement paste phases over hydration time.

There are a sufficient number of hydration kinetics models, but all of them are phenomenological. Among the existing models, the Parrot and Killoh model was taken, which provides both sound and practical in spite of its drawbacks [7].

According to the model, the hydration process describes by empirical expressions which varies depending on its stage.

Stage 1. Nucleation and growth:

$$\frac{\partial \alpha_{1,i}}{\partial t} = \frac{k_{1,i}}{n_{1,i}} \cdot (1 - \alpha_i) \cdot (-\ln(1 - \alpha_i))^{1 - n_{1,i}}, \quad (1)$$

Stage 2. Diffusion:

$$\frac{\partial \alpha_{2,i}}{\partial t} = k_{2,i} \cdot \frac{(1 - \alpha_i)^{2/3}}{1 - (1 - \alpha_i)^{1/3}}, \quad (2)$$

Stage 3. Formation of hydration shells:

$$\frac{\partial \alpha_{3,i}}{\partial t} = k_{3,i} \cdot (1 - \alpha_i)^{n_{3,i}}, \quad (3)$$

where $\alpha_{1,i}$, $\alpha_{2,i}$, and $\alpha_{3,i}$ – is the hydration degree of the i-th clinker mineral ($i \in$ {alite, belite, aluminate, and aluminoferrite});

t – is arbitrary time, day;

$k_{1,i}$, $k_{2,i}$, and $k_{3,i}$ – are the rate constants of the i-th phase of the cement clinker, 1/day;

$n_{1,i}$ and $n_{3,i}$ – are the model parameters of the i-th phase of the cement clinker.

A lowest value is taken as the hydration rate of the i-th phase of the cement clinker (α_i):

$$\frac{\partial \alpha_i}{\partial t} = \min\left(\frac{\partial \alpha_{1,i}}{\partial t}, \frac{\partial \alpha_{2,i}}{\partial t}, \frac{\partial \alpha_{3,i}}{\partial t}\right), \quad (4)$$

The kinetics of the pozzolanic reactions is adopted according to the results [8]:

$$\frac{\partial \alpha_i}{\partial t} = \frac{n}{\tau} \cdot \alpha_i^{1 - \frac{1}{n}} \cdot (1 - \alpha_i)^{1 + \frac{1}{n}}, \quad (5)$$

where α_i – is the hydration degree of the i-th phase of the pozzolana ($i \in$ {silica, alumina});

n and τ – are the model parameters, τ in day.

The overall hydration degree (α) of cement (pozzolana) is calculated as a weighted mean by mass fraction of phases.

Predicting the volume fractions of the cement paste phases can essentially be done in only two ways:

1) Based on stoichiometry of hydration reactions of cement (pozzolana) phases [9].

2) Based on the Powers model [10].

In the present study, the first way was taken because it not be related to experimental data, especially since for pozzolana they vary greatly.

The following volume fractions (in m³/m³) are the result of stoichiometry computations: the i-th clinker mineral ($f_{cl,i}$), the j-th hydrate product ($f_{hyd,j}$), and water (f_w).

Proceeding from these fractions, the aggregated phases of the cement paste can be determined:

$$f_c = \sum_i f_{cl,i}; \; f_{hyd} = \sum_j f_{hyd,j}; \; f_{ch} = 1 - f_c - f_{hyd} - f_w. \quad (6)$$

where f_c, f_{hyd}, f_{ch} – is the volume fraction of the unhydrated cement, hydration products, and chemical shrinkage, respectively.

It should be noted, that at the initial moment of hydration ($t = 0$):

$$f_c + f_w = f_c \cdot \left(1 + \frac{f_w}{f_c}\right) = f_c \cdot \left(1 + \frac{\rho_c \cdot w/c}{\rho_w}\right) = 1. \quad (7)$$

where w/c – is the water to cement ratio;

ρ_c and ρ_w – is the density of the cement and water, respectively, kg/m³.

Geometrical model

Basic assumptions

The assumptions of the unit cell model are listed as follows:

1) The cement particles are spherical, uniformly sized, and uniformly distributed over the cement paste.

2) The unhydrated core of each cement particle is equally decreased during hydration.

3) The hydrate products are formed in an equally layer at the surface of each cement particle.

4) Each cement particle is surrounded by the same volume of available free water.

5) A unit cell is a cube with a centred single spherical cement particle surrounded by water.

Geometrical formulation

In the original source [6], the evolution of geometry of the single cement particle inside a unit cell is described by three cases (see Fig. 1).

Case 1: $r_{cp} \leq \frac{1}{2} \cdot l$;

Case 2: $\frac{\sqrt{2}}{2} \cdot l \geq r_{cp} > \frac{1}{2} \cdot l$;

Case 3: $\frac{\sqrt{3}}{2} \cdot l \geq r_{cp} > \frac{\sqrt{2}}{2} \cdot l. \quad (8)$

where r_{cp} – is the average radius of the single cement particle;

l – is the length of unit cell edge.

The unit cell can be considered in absolute dimensions or dimensionless. In the first case, the length of unit cell edge (l) should be expressed in terms of r_{cp}:

$$l = \sqrt[3]{\frac{1}{n}}. \quad (9)$$

where n – is the number density of the cement particles in the cement paste 1/m³, which for the case at hand is determined as:

$$n = \frac{f_c}{V_{cp}} = \frac{f_c}{\frac{4}{3}\pi \cdot r_{cp}^3} \quad (10)$$

where V_{cp} – is the volume of the single cement particle, m³.

In the second case, the inverse problem of finding r_{cp} is solved, since $l = 1$.

The principal drawback of the unit cell model in absolute dimensions is that the average radius of the cement particle can vary greatly depending on the way of its determining.

During the hydration process, the volume of the cement particle is computed using the following geometric expressions:

Case 1: $V_{cp} = \frac{4}{3} \cdot \pi \cdot r_p^3$;

Case 2: $V_{cp} = \frac{4}{3} \cdot \pi \cdot r_{cp}^3 - 6 \cdot \left(\frac{\pi}{3} \cdot h^2 \cdot (3 \cdot r_{cp} - h)\right). \quad (11)$

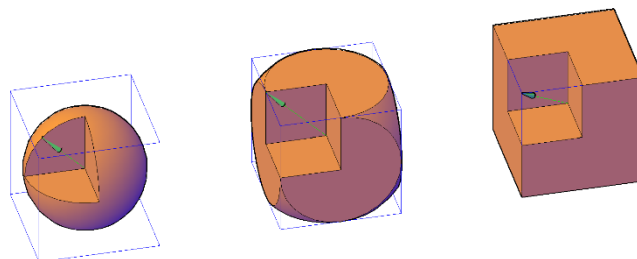where h – is the height of the spherical segment, $h = r_{cp} - \frac{1}{2} \cdot l$.

Figure 1 – The geometry evolution of the single cement particle inside a unit cell

The Case 3 can be neglected, since Case 2 implies $1 - V_{cp}\left(r_{cp} = \frac{\sqrt{2}}{2} \cdot 1\right) = 0{,}035$. Considering the fact that chemical shrinkage in cement-based materials depends on water to cement ratio, but exceeds on average 6%, then the Case 3 is hardly reachable in reality.

One more important geometrical parameter is an available surface of the cement particle (S_{cp}) for contact with water:

Case 1: $S_{cp} = 4 \cdot \pi \cdot r_{cp}^2$;

Case 2: $S_{cp} = 4 \cdot \pi \cdot r_{cp}^2 - 6 \cdot (2 \cdot \pi \cdot r_{cp} \cdot h)$. \hfill (12)

Adjustment of hydration kinetics

The serious problem of the Parrot and Killoh model (as well as other existing models) is that it does not take into consideration several key factors in the hydration process: environment temperature, reduction in available free water and pore space for the deposition of hydration products. Moreover, this model suffers from an inability to account for the fineness of cement.

All these factors heavily affect the hydration rate. The following relation should be used to adjust the original models (4) and (5):

$$\left(\frac{\partial \alpha_i}{\partial t}\right)' = \frac{\partial \alpha_i}{\partial t} \cdot \frac{f_w(t)}{f_w(t=0)} \cdot \frac{S_{cp}(t)}{S_{cp}(t=0)} \cdot \frac{FN}{FN_{ref}} \cdot \exp\left(-\frac{E_{a,i}}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right). \quad (13)$$

where $\left(\frac{\partial \alpha_i}{\partial t}\right)'$ – is the adjusted hydration rate of the i-th phase of the cement clinker (pozzolana);

FN – is the actual fineness of cement, m^2/kg;

FN_{ref} – is the reference fineness of cement, 385 m^2/kg [7];

$E_{a,i}$ – is the activation energy of the i-th phase of the cement clinker, J/mol (it can be taken from []);

R – is the universal gas constant, 8,314 J/(K·mol);

T – is the actual temperature, K;

T_{ref} – is the reference temperature, 293,15 K.

It should be pointed out that the ratio $\frac{f_w(t)}{f_w(t=0)}$ is best suited for modelling at low water-to-cement ratios. At water-to-cement ratios more about than 0,35 water transport processes due to moisture diffusion become increasingly important in the cement paste. Therefore, it is preferable to use a ratio based on relative humidity instead of the ratio $\frac{f_w(t)}{f_w(t=0)}$, for instance, one of the most well-known [1]:

$$\begin{cases} \left(\frac{RH(t)-0{,}55}{0{,}45}\right)^4 \ at \ RH(t) \geq 0{,}55 \\ 0 \qquad\qquad\quad at \ RH(t) < 0{,}55 \end{cases}. \quad (14)$$

However, it also requires to construct a moisture diffusion model to evaluate relative humidity over time in cases like this.

Microstructure evolution

Since, the model is based on a single cement particle, the overall radius of the particle is the sole parameter that needs to be determined during hydration. This is easily done by solving the following equation for r_{cp}:

$$V_{cp}(r_{cp}) = (f_c(t) + f_{hyd}(t)) \cdot l^3. \quad (15)$$

The initial radius of the particle (r_0) is determined from the following equation:

$$V_{cp}(r_0) = f_c(t=0) \cdot l^3. \quad (16)$$

As it has been mentioned, V_{cp} varies depending on the geometric case.

Pore size distribution

The overall pore size distribution ($V_p(r)$) of the cement paste is given by:

$$V_p(r) = \sum_i f_{p,i} \cdot \phi_i(r). \quad (17)$$

where $f_{p,i}$ – is the volume fraction of the i-th type of porosity of the cement paste;

$\phi_i(r)$ – is the distribution fraction of the i-th type of porosity up to pore radius r.

Currently, this issue is the most difficult in modeling microstructure of the cement paste. The measured pore size distribution is dependent on many factors: the laboratory technique used, sample preparation, curing conditions, drying procedure, etc. Typically, the mercury intrusion porosimetry is widely applied to determine the pore size distribution.

However, even the measured values are not always comparable with the actual pore distribution. It is primarily related with «ink-bottle» effect which influences the measurement and distorts the final result. It makes it difficult to establish an analytical function of the porosity distribution, that is why continuous probability functions with minimal parameters are preferred to facilitate calculations.

The simplistic unimodal Raleigh–Ritz distribution function is considered as one of the possible ways to provide the representative pore size distribution [5]:

$$\phi_i(r) = 1 - \exp(-B_i \cdot r). \quad (18)$$

where B_i – is the pore structure parameter corresponding the peak of porosity distribution on a logarithmic scale, 1/m.

One more frequently mentioned function is described in [3]:

$$\phi_i(d) = a_i \cdot ln\left(\frac{d}{d_{min}}\right). \quad (19)$$

where $\phi_i(d)$ – is the distribution fraction of the i-th type of porosity up to pore diameter d;

a_i – is the pore structure parameter;

d_{min} – is the smallest capillary pore, m.

There is no exact solution for the above pore structure parameter B_i and a_i. In practice, the relationship obtained by fitting the pore structure parameter to the measured pore size distribution function is used.

The Raleigh–Ritz distribution was chosen between these two models primarily due to its function to be better than that in (19), where it is assumed to be a straight line in a semi-logarithmic space.

Assuming that pores are cylindrical and no surface other than the inner walls of the pores exists, the follow expression for the representative pore radius can be obtained ($r_{i,peak}$):

$$r_{i,peak} = 2 \cdot \frac{V_{p,i}(r_{peak})}{S_{p,i}} = 2 \cdot \frac{f_{p,i} \cdot \phi_i(r_{peak})}{S_{p,i}}. \quad (20)$$

where $S_{p,i}$ – is the pore surface area per unit volume, m^2/m^3.

Using the equation (18) jointly with (20), the pore structure parameter (B_i) can be approximately computed as:

$$B_i = -\frac{S_{p,i}}{f_{p,i}} \cdot \frac{\ln(1-\phi_i(r_{peak}))}{2 \cdot \phi_i(r_{peak})}. \quad (21)$$

Assuming that the Raleigh–Ritz distribution has a symmetric density function regardless of the type of porosity, it is not difficult to determine $\phi_i(r_{peak}) = 0{,}5$.

From the point of view of moisture transport, the overall porosity of the cement paste can be divided into two components: macropores and micropores. Macropores are empty spaces between partially hydrated cement particles, while micropores are located in the high-density structure (abbreviated HD) of C-S-H particles.

In view of the above, the surface area of macropores ($S_{p,mac}$) and micropores ($S_{p,mic}$) per unit volume can be determined as:

$$S_{p,mac} = \frac{S_{cp}}{l^3}; \qquad S_{p,mic} = S_{hd} \cdot \rho_{hd} \cdot f_{hd} \cdot f_{csh}. \quad (22)$$

where S_{hd} – is the specific surface area of HD C-S-H, 247 m^2/g [11];

ρ_{hd} – is the density of HD C-S-H, 1750 kg/m^3 [11];

f_{hd} – is the volume fraction of HD phase of C-S-H;

f_{csh} – is the volume fraction of C-S-H of the cement paste.

The approach presented in [11] is used to determine the volume fraction of HD phase of C-S-H (f_{hd}).

The volume fractions of porosity are computed by the following expressions:

$$f_{p,mac} = f_w + f_{ch}; \qquad f_{p,mic} = 0{,}28 \cdot f_{csh} . \tag{23}$$

Threshold of solid percolation

The main concept of percolation theory is an idea of connectivity. The percolation threshold is defined by the value of some parameter, say volume fraction of the structure in the box, right at the point where the structure either achieves or loses continuity across the box [12].

Inherently, the percolation threshold is a time point of hydration at which a plastic paste turns into a solid (called the set point).

According to the geometrical representation of the model, the percolation threshold is the value of the hydration degree (α_{per}) at which the radius of the growing particle reaches the unit cell faces:

$$\alpha_{per} = \alpha \left(r_p = \tfrac{1}{2} \cdot l \right). \tag{24}$$

Actually, the above condition is not optimal, since with a decrease of the water to cement ratio, the cement fraction increases. It brings out the fact that at the initial moment of hydration ($t = 0$) the initial radius of cement particle ($r_{p,0}$) may already satisfy the following condition:

$$r_{p,0} \geq \tfrac{1}{2} \cdot l. \tag{25}$$

The most suitable solution to avoid such a problem is to add one more condition:

$$\alpha_{per} = \alpha \left(r_p = \tfrac{1}{2} \cdot l, f_{hyd\_sol} \geq f_{hyd\_sol,cr} \right). \tag{26}$$

where f_{hyd_sol} – is the fraction of hydration products in the solid phase, $f_{hyd\_sol} = \frac{f_{hyd}}{f_{hyd}+f_c}$;

$f_{hyd\_sol,cr}$ – is the critical fraction of hydration products in the solid phase which provides the formation of stable bonds for connectivity when the particle radius reaches with the faces of the unit cell.

The critical fraction of hydration products in modelling is assumed to be 0,1.

Modelling results

Two types of the cement paste based on ordinary Portland cement (OPC) and blended cement (BC) were used for the simulation.

The considered characteristics of the cement paste are reported in Table 1.

Table 1 – Characteristics of the cement paste

Name	Mix proportions, kg/m³			Water to Binder ratio
	Portland Cement	Water	Fly Ash	
OPC	370	185	–	0,5
BC	450	155	50	0,31

The characteristics of cement paste constituents are reported in Table 2.

**Table 2** – The characteristics of cement paste constituents

Name	Density, kg/m³	Fineness, m²/kg	Mineral (chemical) composition (mass %)
Portland Cement	3150	345	C₃S: 54,5; C₂S: 17,3; C₃A: 8,9; C₄AF: 7,6; Gypsum: 5
Fly Ash	2270	337,5	Silica (S): 56,7; Alumina (A): 21,2

The parameters in equations (1)–(5) were taken from the above references for the corresponding model.

Sets of Portland cement hydration reactions and phase characteristics contained in [11] were taken to carry out the stoichiometry calculations.

The principal reaction scheme for pozzolana is S[1]+H+CH=C-S-H and A+CH+H=C-A-H [13].

Based on this, the following chemical reaction were taken for fly ash [7, 8]:

$$S + 1{,}1 \cdot CH + 2{,}8 \cdot H \rightarrow C_{1,1}SH_{3,9} . \tag{27}$$

$$A + 3 \cdot CH + 3 \cdot H \rightarrow C_3AH_6 . \tag{28}$$
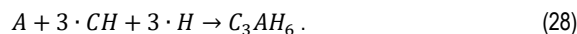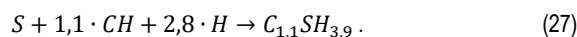
The phase characteristics for pozzolana reactions were used given in [7]. The pozzolanic activity of flay ash is assumed of 60%.

The initial average radius of the single cement particle was computed as expected value of the Rosin-Rammler probability distribution. The parameters of the Rosin-Rammler probability distribution as a function of the cement fineness were taken from [3]

The found value of the initial average radius of the single cement particle was additionally specified by the equation (16).

The actual temperature was assumed to be 20 °C. The hydration degree of blended cement was computed as weighted mean:

$$\alpha = \frac{\alpha_{pc} \cdot m_{pc} + \alpha_{fa} \cdot m_{fa}}{m_{pc} + m_{fa}}. \tag{29}$$

where α_{pc} and α_{fa} – is the hydration degree of Portland cement and reaction degree of fly ash, respectively;

m_{pc} and m_{fa} – is the content of Portland cement and fly ash in the mix, respectively.

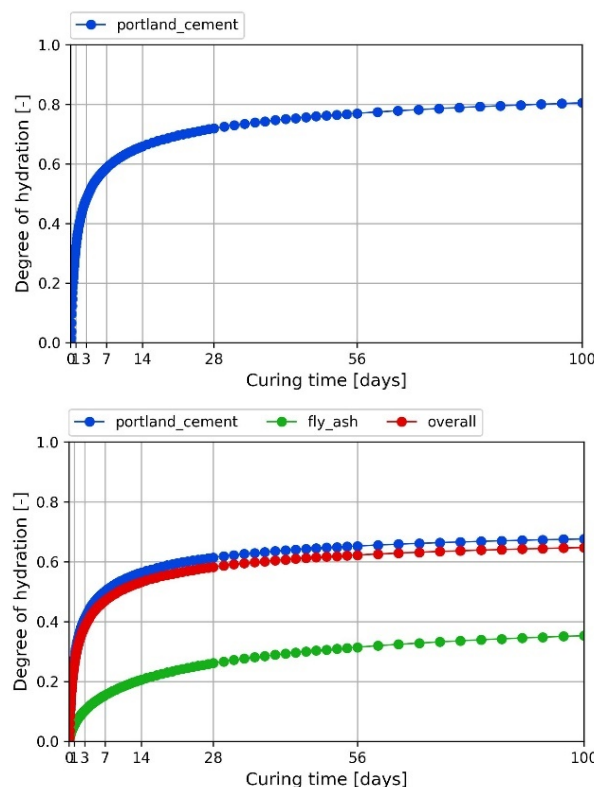The modeling results are presented in Figures 1–5.

Figure 1 – The predicted degree of hydration of the cement paste
(Left: OPC; Right: BC)

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[1] Cement chemistry notation is used here to write chemical compounds
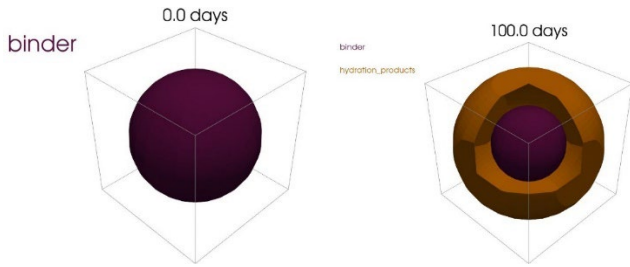
Figure 2 – The evolution of unit cell geometry for OPC
(The estimated percolation threshold $\alpha_{per} = 0,23$)

Figure 3 – The evolution of unit cell geometry for BC
(The estimated percolation threshold $\alpha_{per} = 0,06$)
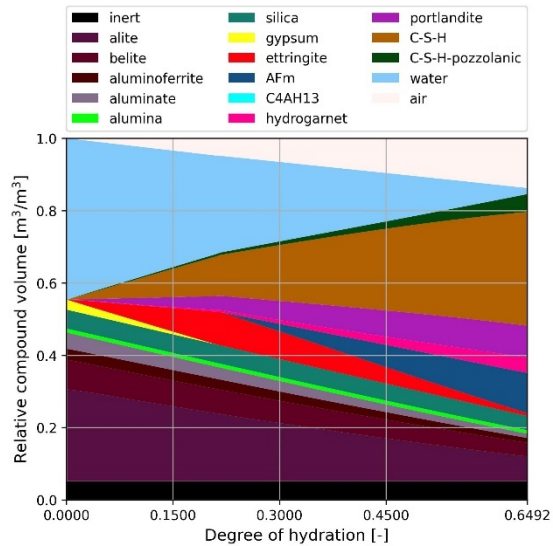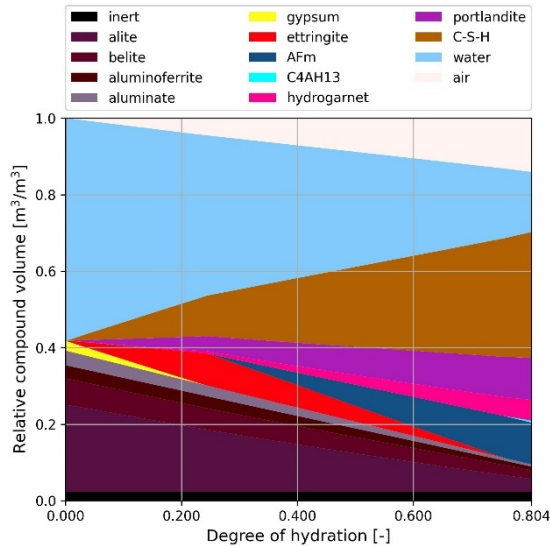

Figure 4 – The predicted phase composition of the cement paste under sealed conditions
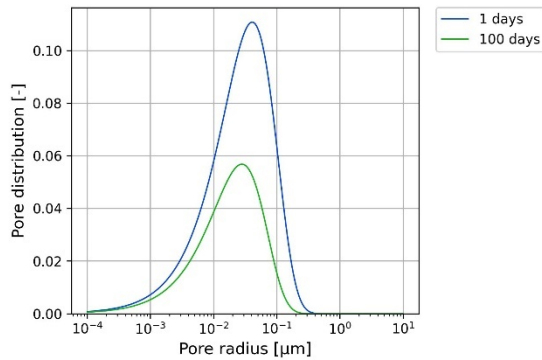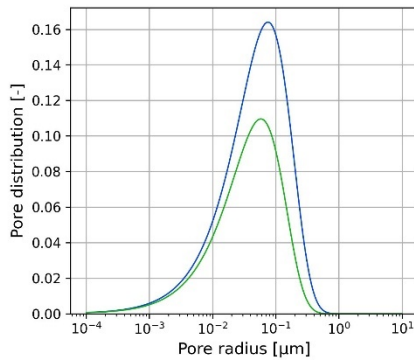(Left: OPC; Right: BC)

Figure 5 – The predicted size distribution of macropores of the cement paste
(Left: OPC; Right: BC)

Conclusions

1. The presented model of microstructure development of the cement paste is characterized by computational simplicity, but provides all the basic structural characteristics: phase volume composition, evolution of geometry, pore size distribution, and percolation threshold. The simplicity of the model is important, because it facilitates to be incorporated into more complex computational models (for instance, to predict the mechanical properties of cement-based composites over time).

2. The model includes considerable assumptions that may decrease its accuracy. Since, the microstructure of the cement paste is extremely complexity and highly heterogeneous, it is quite difficult to validate such a model. It can be said that accuracy of the presented model is an open issue.

3. The principal drawback of the model is lots of types of averages that can be used to determine the radius of the cement particle.

4. It is impossible to extract a histogram of the frequency distribution of pore sizes from the model i.e., the pore size distribution is strictly limited by the given probability distribution function.

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