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A MODELLING FRAMEWORK OF PORTLAND CEMENT HYDRATION

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Modelling the hydration process of Portland cement is a critical stage for predicting the mechanical properties of cement-based materials, since the modelling results are actually the initial data for prediction models. Incorrect modelling at this stage is high likely to lead to inadequate values of mechanical properties. The main difficulty of modelling is that cement hydration is an extremely complex process, the features of which are still not clearly understood. This determines the fact that hydration modelling is currently based on a phenomenological approach including a sufficient number of coefficients depending on experimental results.

This paper presents basic principles of hydration modelling and analyses the most widely used models to estimate the degree of cement hydration to identify their assumptions and limitations.

Keywords: portland cement, hydration kinetics, volumetric composition, modelling.

Introduction. Cement hydration is a physical and chemical process of interaction between cement clinker phases and water. The hydration process is a long time and extremely complex which is still considered from the point of hypotheses and assumptions. As a result of the hydration process, the microstructure of the cement paste with mechanical strength is formed.

The microstructure of the cement paste is composed of individual phases such as unhydrated cement, hydrate products and pores randomly distributed throughout its volume. The volumetric composition of these phases highly affects the mechanical properties of cement-based materials, such as compressive strength and Young's modulus.

Currently, a widely used approach is that the mechanical properties of cement-based materials can be predicted by a combination of the hydration model and micromechanical analysis, which originates from a representative elementary volume. The most significant part of the approach is a hydration model which evaluates the volume or volume fraction of all phases of the cement over time as a function of a degree of cement hydration. Essentially, it is a starting point for modeling the mechanical properties of cement-based materials and incorrect modelling at this stage may risk producing inadequacy results.

This paper presents the modelling framework of Portland cement hydration over time including an analysis of existing models to estimate the degree of hydration and volumetric composition of the cement paste at arbitrary time.

Hydration modelling. Actually, the cement hydration model is a complex model that integrates at least two parts:

- 1) Hydration kinetics of cement;
- 2) Predicting the volume (or volume fraction) of each phase of the cement paste over time.

Hydration kinetics of cement is described by the following evolution equations:

$$\frac{\partial \alpha}{\partial t} = f(\alpha) \text{ or } \frac{\partial r}{\partial t} = f(r), \quad (1)$$

where α – is degree of cement hydration;

r – is the radius of the cement particle;

t – is arbitrary time.

It should be pointed out that the function f may vary depending on a hydration stage.

In the first case, the rate equation refers to the overall kinetics model, in the second case to the particle kinetics model [1]. The difference between the models is that the overall kinetics model neglects the particle size distribution of cement.

The particle kinetics model is expressed in term of the rate of decrease in a radius of cement particles, in a way the degree of cement hydration is determined as:

$$\alpha = 1 - \left(\frac{r}{r_0}\right)^3, \quad (2)$$

where r_0 – is the initial radius of the cement particle.

The basic equations (1) are often applied separately for each clinker phase or each cement particle in the cement paste. In this case, the hydration degree of cement is computed as weighted mean:

$$\alpha = \frac{\sum_i \alpha_i m_i}{\sum_i m_i}, \quad (3)$$

where α_i – is the degree of the i -th phase of the cement clinker (alite, belite, aluminate, ferrite) or of the i -th cement particle;

m_i – is the weight fraction of the i -th phase of the cement clinker or of the i -th cement particle.

Predicting the volumetric composition of the cement paste can be done in a few ways:

1) Based on stoichiometry of hydration reactions [2], that makes it possible to determine the volumetric composition of all phases involved in hydration reactions. The volume of each phase is computed as a function of the molar volume ratio of the phase to the clinker phase and the hydration degree of the clinker phase. This way is highly dependent on the chemical reactions of hydration adopted for the clinker phases. One of the well-known sets of hydration reactions which accurately reflects theories on cement hydration is presented in [3].

2) Based on the Powers model [4]. It is a simple approach using experimental data to compute the volumes of unhydrated cement, hydrated solid, porosity, and chemical shrinkage as a function of the hydration degree of cement.

3) Based on the model of the hydrated cement particle [5]. The typical model of the hydrated cement particle is a decreasing cement core around which a layer of hydration products is formed. Having taken the volume ratio of unhydrated cement to hydration products, it is possible to compute the volumes of unhydrated cement, hydrated solid, and porosity. This approach is computationally expensive due to lots of calculations required to check all particle interactions. The main difficulty in such computations is the overlap of cement particles.

Hydration kinetics. As it has been mentioned, cement hydration is an extremely complex process which is still not clearly understood. That is why all the existing hydration kinetics models are phenomenological and based on experimental results. It should be understood that empirical models are designed to fit the experimental results and are not necessarily accurately describing the hydration processes from a physical point of view.

The following models are currently most widely used:

1) The Avrami model [3] describes the nucleation and growth crystals at random locations in a porous media at a constant rate:

$$\frac{\partial \alpha_i}{\partial t} = a_i \cdot c_i \cdot t^{c_i-1} \cdot e^{-(a_i \cdot (t-b_i)^{c_i})}, \quad (4)$$

where α_i – is the degree of hydration of the i -th phase of the cement clinker;

t – is arbitrary time, day;

a_i , b_i , and c_i – are empirical constants of the i -th phase of the cement clinker, a in $\frac{1}{day^c}$ and b in day.

2) The Bernard at al. model [6] describes the hydration process by normalized chemical affinity equations. The expression of the normalized affinity depends on the physical process at the hydration stage.

Stage 1. Dissolution of the clinker phases:

$$\tau_i \cdot \frac{\partial \alpha_i}{\partial t} = \frac{t_{0,i}}{\alpha_{0,i}} \cdot \frac{\partial \alpha_i}{\partial t} = 1. \quad (5)$$

Stage 2. Nucleation and growth-controlled hydration of the clinker phases:

$$\tau_i \cdot \frac{\partial \alpha_i}{\partial t} = \frac{1}{\kappa \cdot k} \cdot \frac{\partial \alpha_i}{\partial t} = \frac{1 - (\alpha_i - \alpha_{0,i})_+}{(-\ln(1 - (\alpha_i - \alpha_{0,i})_+))^{\frac{1}{\kappa} - 1}}. \quad (6)$$

Stage 3. Nucleation and growth:

$$\tau_i \cdot \frac{\partial \alpha_i}{\partial t} = \frac{r_0^2}{3 \cdot D} \cdot \frac{\partial \alpha_i}{\partial t} = \frac{(1 - \alpha_i)^{2/3}}{(1 - \alpha_{cr,i})^{1/3} - (1 - \alpha_i)^{1/3}}, \quad (7)$$

where τ_i – is the characteristic time associated with the reaction, h;

$t_{0,i}$ – is the duration of the induction period, h;

$\alpha_{0,i}$ – is the degree of the hydration threshold of the i -th phase of the cement clinker at the end of the induction period;

κ – is the coefficient defining the reaction order;

k – is the rate constant, 1/h;

D – is the diffusion coefficient, cm^2/h ;

r_0 – is the average initial radius of cement particles, cm;

$\alpha_{cr,i}$ – is the critical hydration degree corresponding to a critical thickness of hydration products formed around cement particles;

$(\alpha_i - \alpha_{0,i})_+$ – is the positive part of the expression.

3) The Parrot and Killoh model [7] is similar to the previous one and describes the hydration process by empirical expressions for three stages of hydration.

Stage 1. Nucleation and growth:

$$\frac{\partial \alpha_i}{\partial t} = \frac{k_{1,i}}{n_{1,i}} \cdot (1 - \alpha_i) \cdot (-\ln(1 - \alpha_i))^{1-n_{1,i}}. \quad (8)$$

Stage 2. Diffusion:

$$\frac{\partial \alpha_i}{\partial t} = k_{2,i} \cdot \frac{(1 - \alpha_i)^{2/3}}{1 - (1 - \alpha_i)^{1/3}}. \quad (9)$$

Stage 3. Formation of hydration shells:

$$\frac{\partial \alpha_i}{\partial t} = k_{3,i} \cdot (1 - \alpha_i)^{n_{3,i}}, \quad (10)$$

where 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 of $\frac{\partial \alpha_i}{\partial t}$ is considered as the stage rate.

4) The Tomosawa model¹ describes the hydration process of a single cement particle, dividing it into three stages: a dormant stage, a phase boundary reaction stage, and a diffusion stage:

$$\frac{\partial r_{in,j}}{\partial t} = \frac{C_w \cdot \rho_w}{v \cdot \rho_c \cdot r_{in,j}^2} \cdot \frac{1}{\frac{1}{k_d \cdot r_{in,j}^2} + \frac{1}{D_e} \cdot \frac{1}{r_{in,j} \cdot r_{out,j}} + \frac{1}{k_r \cdot r_{in,j}^2}}, \quad (11)$$

where $r_{in,j}$ – is the radius of the inner unhydrated core of the j -th individual cement particle, μm ;

t – is arbitrary time, h;

ρ_w and ρ_c – is the density of water and cement respectively, m^3/kg ;

C_w – is the water concentration at the outer region of the gel;

v – is the stoichiometric ratio by mass of water to cement;

$r_{out,j}$ – is the radius of the outer hydrated products of the j -th individual cement particle, μm ;

D_e – is the effective diffusion coefficient, $\mu\text{m}^2/\text{h}$;

k_d – is the effective mass transfer coefficient, $\mu\text{m}/\text{h}$;

k_r – is the coefficient of reaction rate of cement, $\mu\text{m}/\text{h}$.

5) The Navi and Pignat model [8] also describes the hydration process of a single cement particle, in which the rate of reduction of the radius of the inner core is controlled by two hydration mechanisms.

Phase boundary mechanism:

$$\frac{dr_{in,j}}{dt} = -k_1. \quad (12)$$

Diffusion-controlled mechanism:

$$\frac{dr_{in,j}}{dt} = -k_2 \cdot \frac{1}{r_{out,j} - r_{in,j}}, \quad (13)$$

where k_1 and k_2 – are the rate and diffusion constants respectively, k_1 in $\mu\text{m}/\text{h}$ and k_2 in $\mu\text{m}^2/\text{h}$.

As can be clearly seen from the mathematical expressions of the presented models, all of them include a sufficient number of empirical constants needed to fit the experimental results.

The Avrami model is best suited to describe nucleation and growth reactions and is poorly suited to describe the hydration process of Portland cement as a whole. It provides with a simple kinetic model that allows good fits for kinetics for the initial stage of the hydration process up to about one day [3].

The Tomosawa and Navi–Pignat models assume that the cement particles are spheres, which is a considerable assumption. These models have high computational complexity, which increases with an increase in the number of spheres in a representative volume. Moreover, the particle radii are determined from the particle size distribution, which is approximated by a probability function (commonly the Rosin–Rammler distribution). This makes it necessary to predetermine parameters of the distribution function fitting to the fineness of cement.

The similar problem is shared by the Bernard et al. model, which depends on the average initial radius of cement particles. Furthermore, the recommended kinetic parameters of the model are strictly related to the fixed average radius of $5 \mu\text{m}$.

The Parrot–Killoh model does not depend on the radius of cement particles, but at the same there is no nucleation growth step for belite, and no diffusion-controlled step for alite and belite when using the recommended model parameters [9].

Adjustment of hydration kinetics. The serious problem of existing hydration models is that they do not consider some physical phenomena that heavily affect the rate of the hydration process.

Three main phenomena can be distinguished: temperature, available capillary water (or relative humidity in a pore space), and the available pore space for the deposition of hydration products. In addition, the fineness factor should be introduced in overall kinetics models (the Avrami and Parrot–Killoh model).

¹ Maruyama I., Matsushita T., Noguch T. Numerical modelling of Portland cement hydration / I. Maruyama, T. Matsushita, T. Noguch // International RILEM Symposium on Concrete Modelling, Delft, 26–28 May 2008 / Delft University. – Delft, 2008. – P. 155–162.

In view of the above, the follow expression can be written to adjust for the hydration rate:

$$\left(\frac{\partial\alpha}{\partial t}\right)' = \frac{\partial\alpha}{\partial t} \cdot k_T \cdot k_w \cdot k_{por} \cdot k_{fn}, \quad (14)$$

where $\left(\frac{\partial\alpha}{\partial t}\right)'$ – is the adjusted hydration rate;

k_T – is the temperature correction factor;

k_w – is the correction factor for available free (capillary) water;

k_{por} – is the correction factor for available pore space;

k_{fn} – is the fineness correction factor.

Influence of temperature on hydration kinetics is well described by the Arrhenius law [7].

The effect of available free water on hydration kinetics can be described by the following ratio:

$$k_w = \frac{V_{cap}(t)}{V_{cap}(t=0)}, \quad (15)$$

where $V_{cap}(t)$ – is the volume of capillary water in the cement paste at any arbitrary time t ;

$V_{cap}(t=0)$ – is the initial volume of water in the cement paste.

In turn, a similar ratio describes the effect of the available pore space:

$$k_{por} = \frac{SA(t)}{SA(t=0)}, \quad (16)$$

where $SA(t)$ – is the available surface area of cement particles at any arbitrary time t , m^2 ;

$SA(t=0)$ – is the initial available surface area of cement particles, m^2 .

The effect of cement fineness in particle kinetics models is controlled by the particle size distribution, in overall kinetics models by the following ratio:

$$k_{fn} = \frac{FN}{FN_{ref}}, \quad (17)$$

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

FN_{ref} – is the reference fineness of cement, kg/m^2 .

The determination of the factor k_w and k_{por} is associated with certain difficulties. Firstly, the factor k_w can be determined in the two previously mentioned ways: using the Powers model or stoichiometry of hydration reactions. These ways determine the volume of capillary water in the cement paste only for sealed conditions and do not consider the moisture diffusion and evaporation into the environment. Actually, the sealed conditions can be considered if the water to cement ratio is about less 0,35, otherwise the factor k_w should determine jointly with modelling of moisture transport in the cement paste.

Secondly, the factor k_{por} can only be determined if the geometric shape and size of cement particles are known. In fact, using particle kinetics models (the Tomosawa and Navi–Pignat model) is the only way to directly determine k_{por} . In cases of using the overall kinetics models, there is no over way to determine k_{por} than by co-modelling of hydration kinetics and microstructure development of the cement paste. The advantage of this approach is a possibility of using computationally simple microstructure models, such as the Unit Cell model [4], instead of a polydisperse system of cement particles.

Modelling results. Numerical simulation of hydration kinetics models described above has been carried out. The aim of simulation is to estimate the basic hydration degree over time without the influence of correction factors, in order to clearly show significant differences of the presented models.

The recommended parameters in equations (4)-(13) were taken from the original references to the corresponding model.

Characteristics of the cement paste used in numerical simulation: cement content: 370 kg/m^3 ; water content: 185 kg/m^3 ; the density of cement: 3150 kg/m^3 .

Numerical simulation of particle hydration kinetics models was carried out for a single spherical particle in order to reduce a number of calculations. The particle radius was determined as the 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 [1].

To predict the volumetric composition of the cement paste, the Powers model was taken with the parameters presented in [4].

The modeling results are presented in Figures 1–3.

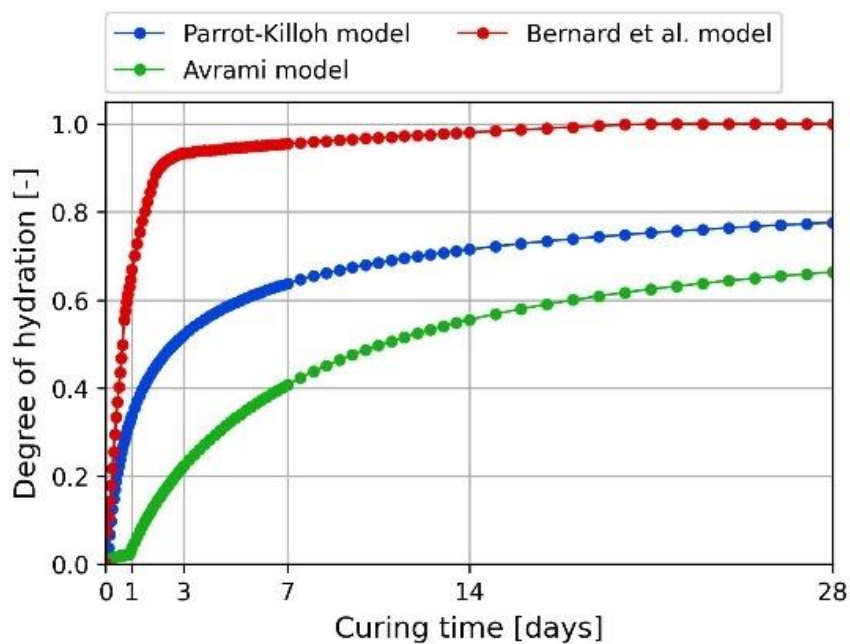
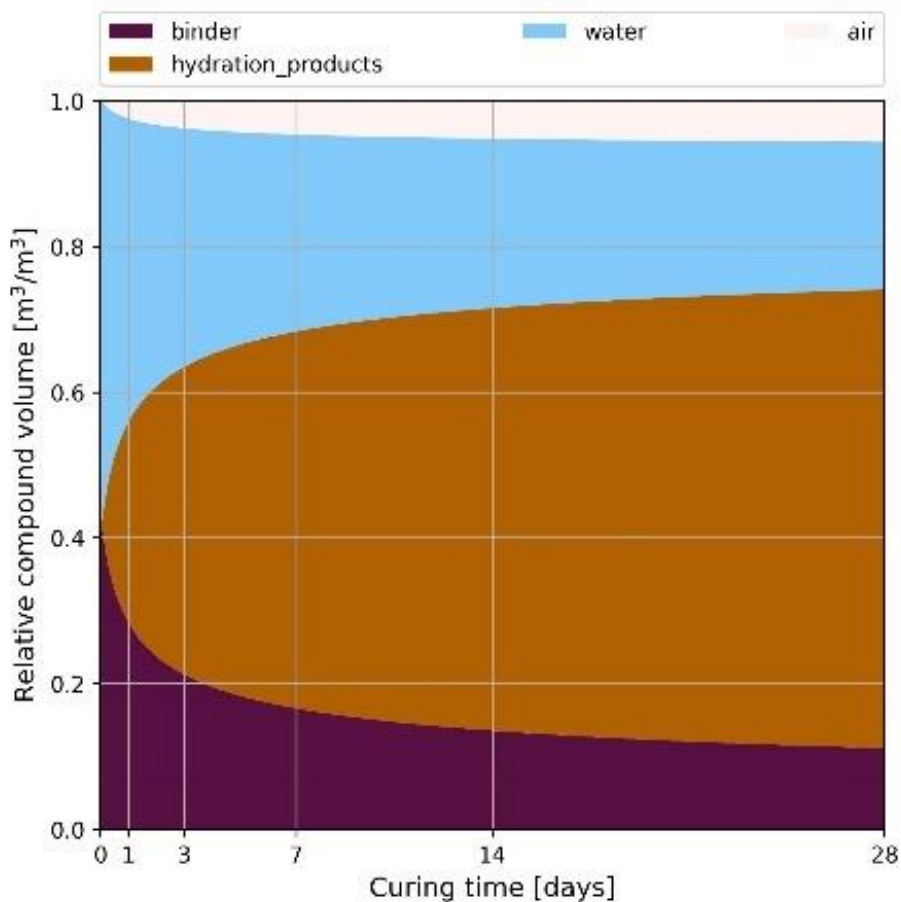


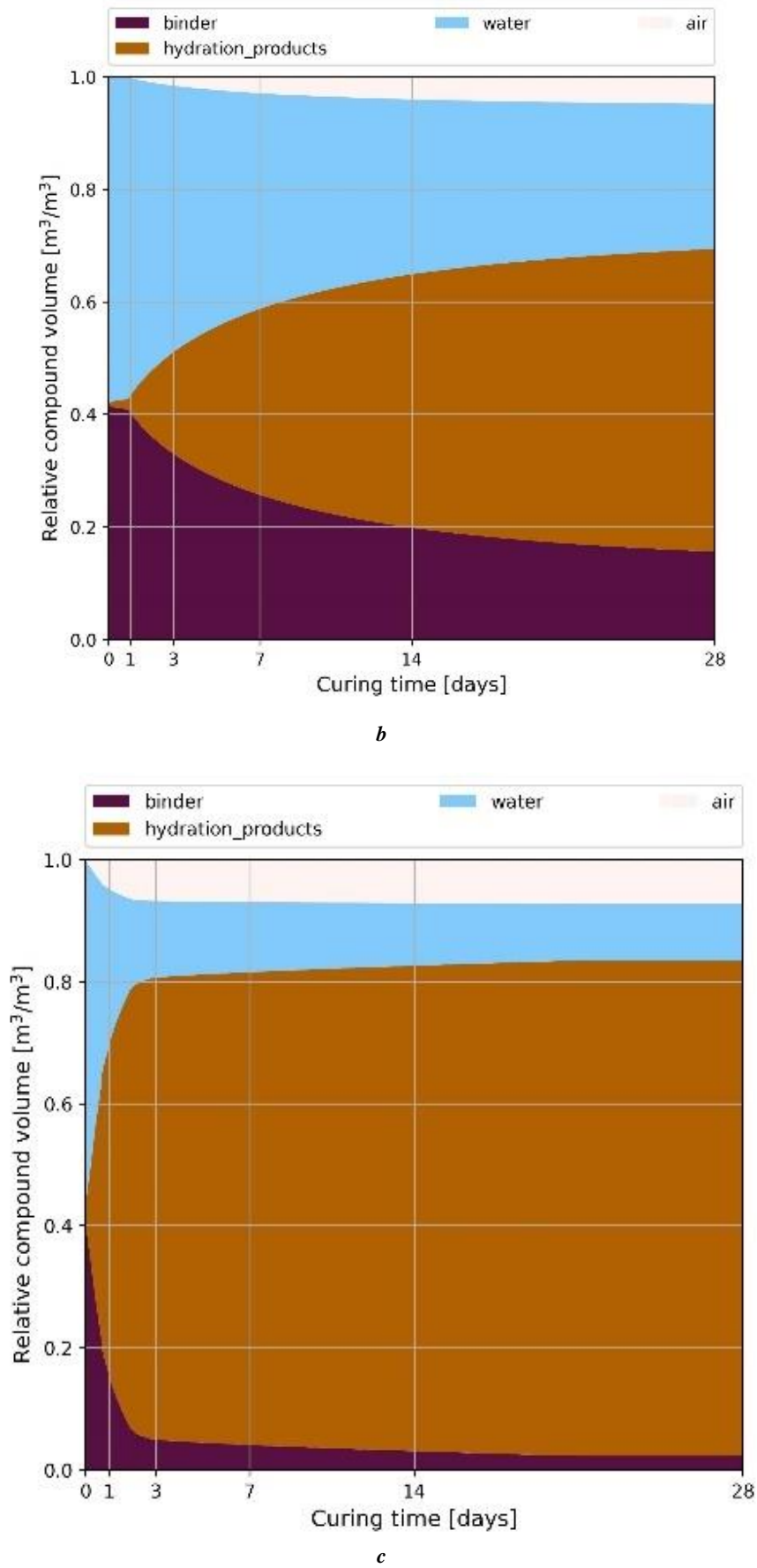
Figure 1. – The comparison of the hydration degree over time in the overall kinetics models



a

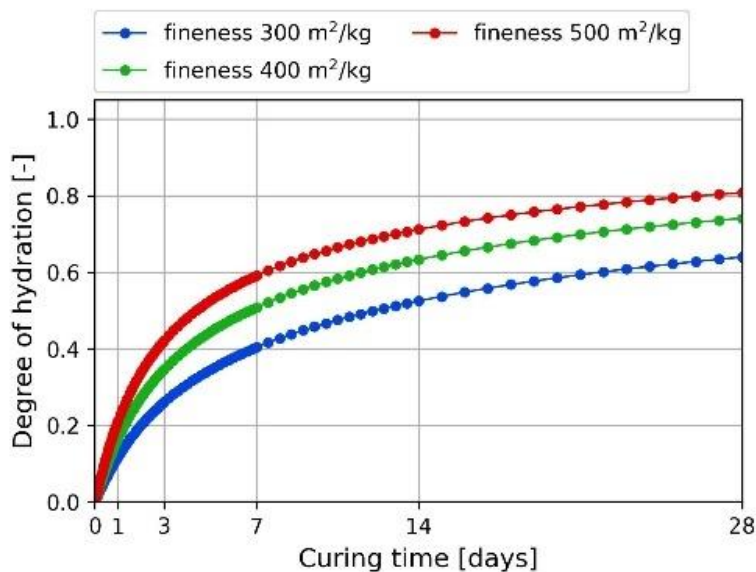
a – Parrot and Killoh model

Figure 2. – The comparison of the volumetric composition of the cement paste in the overall kinetics models (beginning)

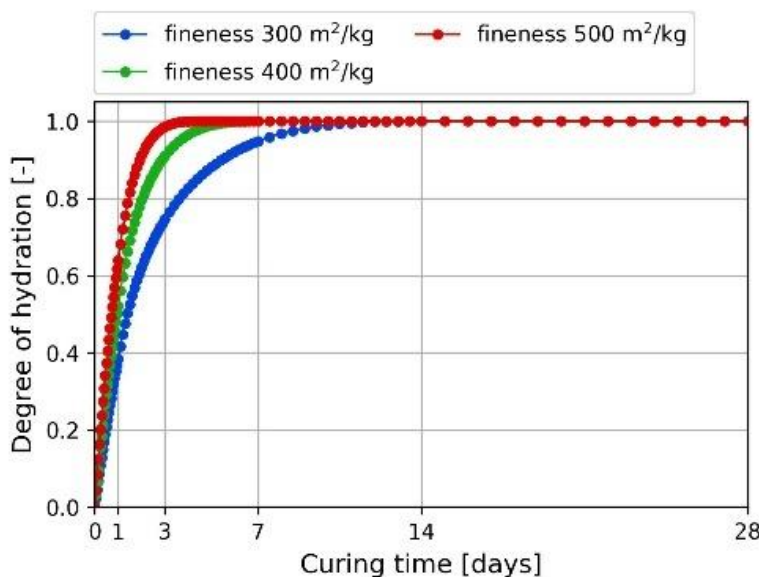


b – Avrami model; *c* – Bernard at al. model

Figure 2. – The comparison of the volumetric composition of the cement paste in the overall kinetics models (ending)



a



b

a – Tomosawa model; b – Navi-Pignat model

Figure 3. – The comparison of the hydration degree over time in the particle kinetics models

Conclusion. We can make such conclusions.

1. Cement hydration is an extremely complex process, so there is no generally accepted model for predicting it.
2. The existing hydration kinetics models are phenomenological and include a sufficient number of coefficients depending on experimental results. It should be attentive to their values, since changing even one value can significantly affect the final result.
3. The overall hydration kinetics models are computational simple and the most suitable for determining the volumetric composition of the cement paste. The particle kinetic hydration kinetics models are computational complexity and based on a significant assumption about a spherical shape of cement particles. They are most suitable for determining the pore size distribution of the cement paste.
4. The use of overall hydration kinetics models is highly recommended by co-modelling with models of microstructure development of the cement paste. This makes it possible to take into account the parameters of the porous space, producing more accurate values of the hydration degree. Moreover, it is a very flexible approach making the modelling of cement hydration more realistic by using not only spherical models of microstructure development, but also discrete ones with random morphologies.

REFERENCES

1. Van Breugel, K. (1997). *Simulation of hydration and formation of structure in hardening cement-based materials. Second edition.* Delft: Delft University Press.
2. Pichler, C., Lackner, R. & Mang, H.A. (2007). A multiscale micromechanics model for the autogenous-shrinkage deformation of early-age cement-based materials. *Engineering Fracture Mechanics*, 74(1–2), 34–58. DOI: 10.1016/j.engfracmech.2006.01.034.
3. Tennis, P.D. & Jennings, H.M. (2000). A model for two types of calcium silicate hydrate in the microstructure of Portland cement pastes. *Cement and Concrete Research*, 30(6), 855–863. DOI: 10.1016/S0008-8846(00)00257-X.
4. Jensen, O.M. & Hansen, P.F. (2001). Water-entrained cement-based materials: I. Principles and theoretical background. *Cement and Concrete Research*, 31(4), 221–233. DOI: 10.1016/S0008-8846(01)00463-X.
5. Park, K.B., Noguchi, T. & Plawsky, J. (2005). Modelling of hydration reactions using neural networks to predict the average properties of cement paste. *Cement and Concrete Research*, 35(9), 1676–1684. DOI: 10.1016/j.cemconres.2004.08.004.
6. Bernard, O., Ulm, F.J. & Lemarchand, E. (2003). A multiscale micromechanics-hydration model for the early-age elastic properties of cement-based materials. *Cement and Concrete Research*, 33(9), 1293–1309. DOI: 10.1016/S0008-8846(03)00039-5.
7. Lothenbach, B., Matschei, T., Möschner, G. & Glasser, F.P. (2008). Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement. *Cement and Concrete Research*, 38(1), 1–18. DOI: 10.1016/j.cemconres.2007.08.017.
8. Navi, P. & Pignat, C. (1996). Simulation of cement hydration and the connectivity of the capillary pore space. *Advanced Cement Based Materials*, 4(2), 58–67. DOI: 10.1016/S1065-7355(96)90052-8.
9. Lavergne, F., Ben Fraj, A., Bayane, I. & Barthélémy, J.F. (2018). Estimating the mechanical properties of hydrating blended cementitious materials: An investigation based on micromechanics. *Cement and Concrete Research*, 104, 37–60. DOI: 10.1016/j.cemconres.2017.10.018.

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ОСНОВНЫЕ ПРИНЦИПЫ МОДЕЛИРОВАНИЯ ГИДРАТАЦИИ ПОРТЛАНДЦЕМЕНТА

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Моделирование процесса гидратации портландцемента является ключевым этапом прогнозирования механических свойств материалов на основе цемента, поскольку результаты моделирования фактически являются исходными данными для моделей прогнозирования. Некорректное моделирование на этом этапе с высокой вероятностью приведет к неадекватным значениям механических свойств. Основная трудность моделирования состоит в том, что гидратация цемента представляет собой чрезвычайно сложный процесс, который до сих пор до конца не изучен. Это обуславливает тот факт, что моделирование гидратации в настоящее время базируется на феноменологическом подходе, зависящем от коэффициентов, определяемых из экспериментальных данных.

В данной статье представлены основные принципы моделирования гидратации портландцемента и проанализированы наиболее широко используемые модели для оценки степени гидратации цемента, чтобы установить их допущения и ограничения.

Ключевые слова: портландцемент, кинетика гидратации, объемный состав, моделирование.