Multi-phase hydration model for prediction of hydration-heat release of blended cements

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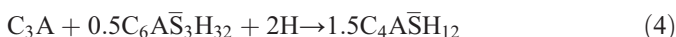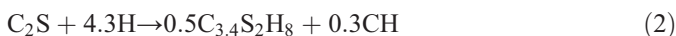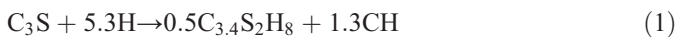
Abstract

Recently, the heat release during cement hydration and the so-caused temperature rise was exploited for (i) identification of material properties of early-age cement-based materials (stiffness, strength), and (ii) determination of the diameter and the cement content of jet-grouted structures. In this paper, the underlying hydration model for determination of the heat release and its rate is refined for Ordinary Portland Cements (OPC) and extended towards blended cements. Hereby, the overall degree of hydration with one kinetic law is replaced by a multi-phase hydration model, taking the hydration kinetics of the main clinker phases into account. As regards blended cements, which are commonly used in engineering practice, the effect of slag hydration is incorporated into the presented multi-phase model. The developed hydration model for both plain and blended cement is validated by means of differential-calorimetry (DC) experiments.
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1. Introduction

The chemical reactions taking place during the hydration process are described by the stoichiometric reactions of the four main clinker phases of Portland cement[1] [Tricalciumsilicate (C_3S), Dicalciumsilicate (C_2S), Tricalciumaluminate (C_3A), and Tetracalciumaluminateferrite (C_4AF)] [1]:

$$C_3S + 5.3H \rightarrow 0.5C_{3.4}S_2H_8 + 1.3CH \tag{1}$$

$$C_2S + 4.3H \rightarrow 0.5C_{3.4}S_2H_8 + 0.3CH \tag{2}$$

$$C_3A + 3C\overline{S}H_2 + 26H \rightarrow C_6A\overline{S}_3H_{32} \tag{3}$$

$$C_3A + 0.5C_6A\overline{S}_3H_{32} + 2H \rightarrow 1.5C_4A\overline{S}H_{12} \tag{4}$$

$$C_3A + CH + 12H \rightarrow C_4AH_{13} \tag{5}$$

$$C_4AF + 2CH + 10H \rightarrow 2C_3(A, F)H_6 \tag{6}$$

Eqs. (3)–(5) describe the formation of calcium aluminate hydrates (C–A–H) from C_3A in the presence of gypsum. In general, the latter is added in order to delay setting of C_3A. Initially, C_3A reacts with gypsum to form ettringite, see Eq. (3). After all gypsum is consumed, C_3A reacts with the previously formed ettringite to form monosulfoaluminates, see Eq. (4). Following depletion of the ettringite supply, C_3A reacts with portlandite (CH), which is one of the products of C_3S and C_2S hydration, see Eqs. (1) and (2).

Already in the mid-1990s an overall degree of hydration ξ was introduced in order to compute the hydration extent, representing the entire set of chemical reactions, with $\xi=0$ at the start of hydration and 1 at complete hydration. More recently, four degrees of hydration, referring to the main clinker phases (ξ_{C_3S}, ξ_{C_2S}, ξ_{C_3A}, and ξ_{C_4AF}, with $0 \leq \xi_x \leq 1$), were introduced [2]. The hydration kinetics of each clinker phase x is given by nucleation and growth laws that link the reaction rate

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[1] Throughout this paper standard cement chemistry abbreviations were used, with C=CaO, S=SiO$_2$, A=Al$_2$O$_3$, F=Fe$_2$O$_3$, $\overline{S}$=SO$_3$, H=H$_2$O, M=MgO, Na=NaO and F=Fe$_2$O$_3$.

change from dissolution to nucleation-
and growth-controlled hydration (e.g. C$_4$AF)

ξ^*=0.6

change from nucleation- and growth-
controlled to diffusion-limited
hydration

dissolution | diffusion-limited C$_3$S-hydration

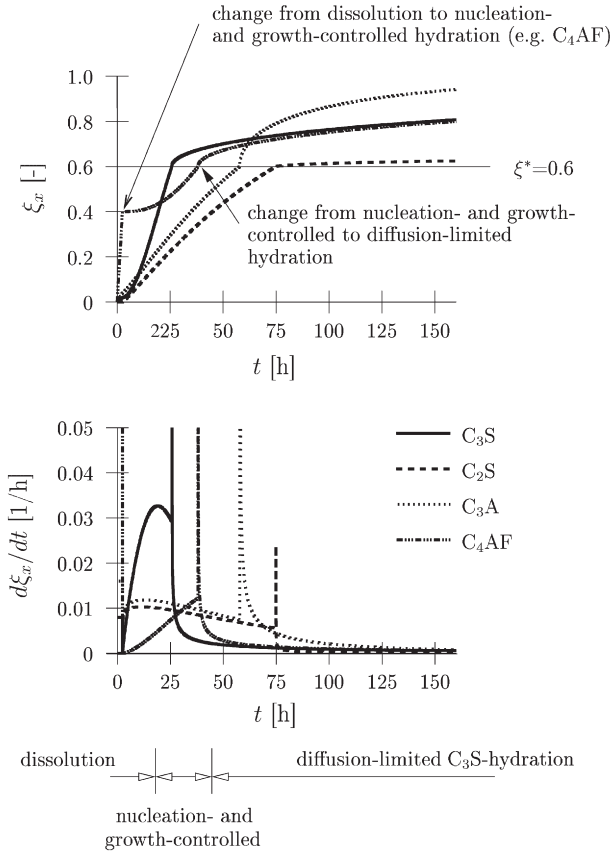nucleation- and
growth-controlled

Fig. 1. ξ_x and dξ_x/dt for the four main clinker phases for ξ^*=0.6 (water/cement-ratio=0.3; temperature=293 K; average particle size r_p=7 μm).

dξ_x/dt to the respective driving force of the chemical reaction (chemical affinity $\tilde{A}(\xi_x)$), reading in dimensionless form

$$\tau_x \frac{d\xi_x}{dt} = \tilde{A}(\xi_x), \qquad (7)$$

where τ_x is the characteristic time associated with the reaction. For the three stages of the hydration process [(a) induction, (b) nucleation/growth, and (c) diffusion], the following kinetic laws were proposed in [2]:

(a) Induction (dissolution of the clinker phases until $t=t_{x,0}$ and $\xi=\xi_{x,0}$): Given the relatively short period, the process is simulated by a constant reaction rate, i.e. $\tilde{A}=1$ and $\tau_x = \tau_{x,0} = t_{x,0}/\xi_{x,0}$, where $t_{x,0}$ is the duration of the induction period and $\xi_{x,0}$ is the hydration threshold of clinker phase x at the end of the induction period.

(b) Nucleation/growth (nucleation- and growth-controlled hydration of clinker phases until the critical hydration degree $\xi=\xi_x^*$): this process is simulated by the Avrami model, commonly employed in cement chemistry, with

$$\xi_x = 1 + \xi_{x,0} - \exp[-a^\kappa] \qquad (8)$$

and

$$\frac{d\xi_x}{dt} = \exp[-a^\kappa]\kappa a^{\kappa-1}\frac{1}{\kappa\tau_0\mathrm{Arr}}, \qquad (9)$$
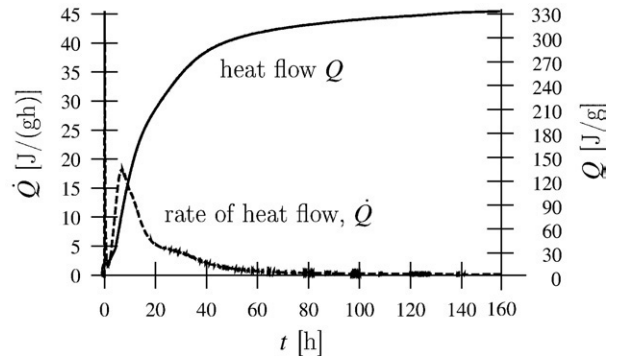

Fig. 2. Output of DC test: history of heat-flow rate $\dot{Q}$ and heat flow Q.

where $a=(t-t_0)/(\kappa\tau_0\mathrm{Arr})$ and $\mathrm{Arr}=\exp[E_{ax}/R(1/T-1/T_0)]$, where E_{ax} is the activation energy parameter for the x-th clinker phase and R is the universal gas constant (8.314 J/(mol K)). In Eqs. (8) and (9), κ is the Avrami parameter [2] and τ_0 is the characteristic time of the nucleation/growth process at reference temperature T_0, with T_0=293 K. According to [2], $E_{a,C_3S}/R$, $E_{a,C_2S}/R$, $E_{a,C_3A}/R$, $E_{a,C_4AF}/R$ were set equal to 4500, 2500, 5500, and 4200.

(c) Diffusion (diffusion-controlled hydration beyond $\xi=\xi_x^*$): beyond ξ_x^*, the kinetics of the hydration reactions is limited by diffusion of dissolved ions through the layers of hydrates formed around the clinker. According to [3],

$$\xi_x = 1 - \left(-\frac{\sqrt{2D(t-t_x^*)}}{r_p\sqrt{\mathrm{Arr}}\sqrt{\Phi_0/\Phi}} + \sqrt[3]{1-\xi_x^*}\right)^3 \qquad (10)$$

and

$$\frac{d\xi_x}{dt} = -3\left(-\frac{\sqrt{2D(t-t_x^*)}}{r_p\sqrt{\mathrm{Arr}}\sqrt{\Phi_0/\Phi}} + \sqrt[3]{1-\xi_x^*}\right)^2 \left(\frac{-\sqrt{2D}(t-t_x^*)^{-1/2}}{2r_p\sqrt{\mathrm{Arr}}\sqrt{\Phi_0/\Phi}}\right), \qquad (11)$$

where D is a diffusion coefficient (values given in [2] for each clinker phase, depending on w/c-ratio), r_p is the average particle size, Φ_0 is the specific surface area of the cement used for determination of the parameters of the kinetic model of the four clinker phases [2], with Φ_0=3602 cm^2/g, and Φ is the specific surface area of the investigated type of cement.

Table 1
Composition (in [mass%]) and properties of investigated types of cement (r_p [μm]: average particle size, Q_∞ [J/g]: total heat release at the end of hydration, W_n [1]: maximum amount of bound water present in fully-hydrated cement)

Component	m_x [mass%]
C$_3$S	62.2
C$_2$S	10.9
C$_3$A	8.1
C$_4$AF	6.7
Gypsum	7.4
Q_∞[J/g]	475
W_n [−] according to Eq. (14)	0.22