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Modeling hydration kinetics based on boundary nucleation and space-filling growth in a fixed confined zone

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ABSTRACT

A semi-analytical model of hydration kinetics based on the boundary nucleation and space-filling growth for early hydration and a diffusion-controlled kinetics for late hydration is proposed. The objective is to develop a simple model that can be coupled with more complex approaches required for the estimation of properties at early-age, but without neglecting some key mechanisms driving the kinetics. The particle size distribution (PSD) of cement is explicitly accounted for. The impingements are modeled by means of an exponential boundary condition in which a limited reaction zone is defined. Numerical solutions for the model are obtained and compared to experimental data. The model can reproduce some relevant features regarding hydration kinetics such as calorimetric data and the influence of the w/c ratio on late kinetics.

1. Introduction

A relevant description of hydration kinetics is necessary in the study of cement-based materials at early-age. Heat release as well as transfer and mechanical properties evolve as a function of the degree of hydration. Also, the viscoelastic behaviour is dependent on the aging processes imposed by the evolution of the material due to hydration reactions. Therefore, the determination of the thermo-hygro-mechanical behaviour of concrete structures at early-age demands such a precise description of the kinetics.

Microstructure-based models have been developed to study cement hydration [1–5] and have the advantage of providing a more precise representation of the microstructure at the level of the cement grain as well as a more precise assessment of the influence of the particle size distribution on the kinetics. However, these models may be computationally expensive to be coupled with multiscale and multiphysics approaches necessary to determine the behaviour of a concrete structure at early-age.

Empirical or simplified analytical laws have often been used instead [6–8], but generally these laws do not completely and accurately capture some important mechanisms driving cement hydration, such as the influence of the PSD and additional materials on kinetics. Moreover, since the main mechanisms are not explicitly taken into account, such kinds of models cannot in general be directly extrapolated to other scenarios of interest with, for example, different compositions, w/c or PSD. This motivates the development of an analytical model that would be able to capture the main driving mechanisms underlying the kinetics of cement hydration but remaining sufficiently simple to be easily coupled with more complex analyses.

The identification of the relevant mechanisms to be taken into account may be complicated because some key phenomena concerning the mechanisms of cement hydration remain not completely understood. Regarding the hydration of alite, which is the main constituent of Portland cement [9], five periods are generally identified [1]: (1) initial dissolution controlled, (2) latent, (3) acceleration, (4) deceleration and (5) slow reaction periods. Nucleation and growth are deemed to be the driving mechanisms of latent, acceleration and at least the initial part of the deceleration periods [1]. Diffusion controlled reaction is deemed to drive the slow reaction phase [1]. The transition from deceleration to slow reaction is still a controversial subject [2,5]. The decrease of available surface for reaction, local variations of concentration on the grain surface and space filling have been pointed out as factors affecting the deceleration [10].

The behaviour at late ages, especially within the first 28 days, is of practical interest for constructions in concrete, since the most important properties for the structural design such as the Young modulus and strength develops in this stage. These properties have often been described as a function of the degree of hydration [11]. However, most of the studies on cement hydration kinetics focus on the early hydration (up to the deceleration period); the description of hydration in the long term has been much less studied [10]. For common Portland cements with no additions, the deceleration period starts within the first day and after 28 days only about 20% remains non-hydrated (mostly belite phase) [10]. This highlights the importance of a kinetic

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description accounting for the potential progress in hydration reactions within the slow reaction period.

The PSD of cement grains, as generally occurs in heterogeneous solid-state kinetics, is reported to affect the description of cement hydration [12]. Since the range of grain sizes is very large in cements [10], the influence of the PSD on the kinetics of hydration should be explicitly taken into account in a relevant model [10]. Some works intend to reproduce this influence by accounting for the surface area of the reactive powder in question [13], but according to the mechanisms considered, this property does not seemto be sufficient to accurately describe the actual influence of the PSD on kinetics. Among the different approaches proposed so far in the literature, we highlight reference [14], in which the PSD of cement and supplementary cementitious materials (SCM) are taken into account explicitly by means of a discrete approach; although no mechanistic approach is used to determine the rate at which the particles are consumed. Nonat and coworkers propose a model in which the PSD is considered in order to determine the surface of the growth; the model parameters, namely, the number of initial nuclei, the parallel growth rate, the perpendicular growth rate and a coefficient describing the permeability of the C-S-H layer formed around the grain, are fixed by the physical chemistry aspects [15]. This approach requires, however, a more fundamental understanding of the thermodynamic aspects related to the different species present in the reacting system, which is beyond the scope of an early-age concrete structure analysis.

Hydration often occurs in a confined zone [16], so the availability of space for product growth potentially affects the kinetics. A microstructure-based model developed by Bishnoi and Scrivener [2,17] describes, from the geometry of cement particles, the hydration following different kinetics mechanisms. These authors propose a space-filling process coupled with boundary nucleation and growth to explain the deceleration period rather than a transition of a diffusion-controlled reaction. Since the geometry is explicitly represented, the space available for product growth and the impingements can be accounted for directly. To account for the space availability in an analytical way, an exponential box can be used as proposed by Biernaki and Xie [5]. These authors employ the boundary nucleation and space-filling growth and propose an exponential box in order to account for the interaction with the neighbouring particles in a one-particle-based model. The size of this zone is a function of the w/c ratio and the particle size. Additionally, the idea of a reaction zone has been investigated by Masoero et al. [4] within a microstructure-based model. These authors define the confined zone based on a fixed distance from the dissolving surface. In this case, differently from Biernaki and Xie [5], the confined zone is not a function of the w/c, but is rather used as a fitting parameter. The confined zone as defined by Biernaki and Xie [5] represents the overall space available for products to grow according to space left by water in the system. On the other hand, the confined zone as defined by Masoero et al. [4] restricts the available space to a zone near the particle reacting, independently, *a priori*, of the particle size and w/c. In this latter sense, a characteristic length defining this confined zone would be related to hydration. Mechanisms related to diffusion of the species resulting from the dissolution of clinker minerals could explain the existence of such a zone, which is coherent with the idea of boundary nucleation and growth.

Diffusion-controlled growth is deemed to drive a slow reaction period. Different diffusion-controlled kinetics were used to describe the hydration of cement and clinker minerals [6–8,18–22]. Fujii and Kondo's [18] equation, which is derived for a specific particle size and accounts for a transition time from which diffusion becomes the rate-limiting process, is extensively used to describe late hydration [21].

We propose to model (semi)-analytically the kinetics of hydration by means of a mechanistic approach. Simple analytical tools are useful in studies in which other complex aspects, besides hydration, are also considered such as the multiscale estimation of the physical properties of cement-based materials or the coupled analysis of concrete at early-age. On the other hand, a 'mechanistic' approach, compared to a phenomenological one, allows generalizing the response for different cement compositions. In this work, we provide a simple analytical formulation comprising early and late hydration, in which key mechanisms are explicitly accounted for. These mechanisms are boundary nucleation and space-filling growth in a fixed confined zone for early hydration and diffusion-controlled kinetics for late hydration combined in a formulation in which the PSD is explicitly considered. Differently from previous works, to account for the confined zone effect, we combine two different but complementary approaches: the exponential box and the fixed length defining the reaction zone as proposed by Biernaki and Xie [5] and Masoero et al. [4], respectively. Also, the developed formulation allows keeping the same set of parameters for different w/c and PSD configurations, which seems more physically founded.

We focus on the acceleration and deceleration periods of alite hydration, at first. The influence of the PSD of cement grains is highlighted. The model is fitted to experimental data from calorimetry tests [12]. Then, we propose an extension of the model to a multiphasic system in order to study cement hydration. Early and late hydration are considered. Late hydration is driven by diffusion-controlled kinetics. Finally, the model is validated against calorimetric data for the cement hydration (data for the same cement as obtained by [23] and in specific tests done for this paper). Because many aspects are involved in cement hydration, some simplifying hypotheses are adopted and will be detailed along the paper. Other aspects which may affect kinetics, such as flocculation and shear effects [24], are not considered.

2. Mechanisms driving the kinetics

In this section, the formulations of the different mechanisms are presented. The strategy to model the interaction with the neighbouring particles, the influence of the PSD and of the temperature is described. The model is developed for C_3S hydration based on the formation of C-S-H, the main reaction product. The extension is straightforward for C_2S hydration, for which some rate constants may take into account the more limited reactivity of belite compared to alite.

2.1. Boundary nucleation and growth

In boundary nucleation and growth models, the nucleation and growth is favoured on a specific site near the boundary of the untransformed phase rather than homogeneously in the reacting domain [25] (p. 477). Heterogeneous nucleation occurs in competition with homogeneous nucleation; the mechanism with the faster kinetics dominates [25] (p. 477). The presence of special sites in the material that are capable of lowering the critical energy needed to form a nuclei favours the heterogeneous nucleation rather than the homogenous one [25] (p. 478). A hypothesis generally adopted in heterogeneous kinetics models, in which concurrent nucleation and growth occur, is the stochastic independence of the nucleation events, i.e. any particular nucleation event in the untransformed material is not influenced by any other nucleation event [25] (p. 478). This means that the likely impingement between hydrates growing in neighbouring particles is generally not taken into account [26].

Different authors applied Cahn's [27] BNG model to cement hydration [1–4,26,28]. Good fit with experimental data has been observed for the acceleration and early deceleration periods. The formulation accounts for the superposition of hydrates growing near each other but does not account for impingements with growing products of neighbouring particles [26]. The model remains analytical and may account for anisotropic and symmetrical growth (see [26] for more details).

Bishnoi and Scrivener [2] proposed a formulation in which the nuclei can form due to homogeneous nucleation in a specific volume between the initial radius R_0 of the reacting particle and R_0+g_2t, where g_2 is the rate of growth in the normal direction with respect to the surface of the