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Accelerated growth of calcium silicate hydrates: Experiments and simulations

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ABSTRACT

Despite the usefulness of isothermal calorimetry in cement analytics, without any further computations this brings only little information on the nucleation and growth of hydrates. A model originally developed by Garrault et al. is used in this study in order to simulate hydration curves of cement obtained by calorimetry with different known hardening accelerators. The limited basis set of parameters used in this model, having a physical or chemical significance, is valuable for a better understanding of mechanisms underlying in the acceleration of C–S–H precipitation. Alite hydration in presence of four different types of hardening accelerators was investigated. It is evidenced that each accelerator type plays a specific role on one or several growth parameters and that the model may support the development of new accelerators. Those simulations supported by experimental observations enable us to follow the formation of the C–S–H layer around grains and to extract interesting information on its apparent permeability.

1. Introduction

Due to necessities to minimize the energy consumption and to have faster construction processes worldwide, the cement portion of next generation concretes must be significantly reduced and has to react more rapidly. For this reason, the concrete producer requires efficient hardening accelerators. Working mechanisms of known accelerators on silicate hydration are still badly understood. As an example, accelerating early hydration very often results in poor mechanical properties at later ages. This phenomenon is not understood and hence it incites compounders of concrete or developers of new accelerator formulations to find the best compromise in terms of acceleration at the early age and acceptable strength at the mature age. The important mechanisms occurring during the first hours of cement hydration control the whole life of concrete and how it will further evolve after many years.

As a first simplification, it is generally considered that the strength development in cement is obtained by the precipitation of C–S–H. Understanding the C–S–H precipitation, in other words its nucleation and growth, is the key point in order to follow and potentially modify the strength evolution of concrete. Many modeling and experimental works are dedicated to the C–S–H nucleation and growth [1–3]. A model proposed by Garrault et al. [4] was developed to describe C–S–H growth in alite or belite pastes, alite and belite being the principal silicate phases of anhydrous cement. This model allows one to make numerical simulations in order to fit the evolution of alite hydration with time with a small number of fitting parameters. Yet, the fit is possible during the accelerating part of the hydration i.e. only during the very first hours of hydration. These parameters have a clear physical or chemical significance and can be readily varied experimentally. This growth model and the various related numerical simulations on controlled systems have shown good accordance with experimental data, thereby comforting the model validity [5,6]. Such numerical simulations can be helpful in the development of new types of accelerators or to find synergetic combinations between existing accelerator chemistries.

In this study, the aforementioned model was further developed and used to assess the role of various accelerators on the nucleation and growth of calcium silicate hydrate during the hydration of alite. The first step is the validation of simulations, namely it is attempted to correlate simulated output data with experimental data. For this purpose, observations by cryogenic microscopy are carried out in order to estimate C–S–H layer thicknesses formed on alite grains. The measured thicknesses are then compared with the simulated ones. A correlation was also found between the computed permeability of the dense C–S–H layer and the surface density of nuclei.

2. Growth model

Alite hydration is parallel process of dissolution of alite and precipitation of C–S–H with calcium hydroxide:

$$Ca_3SiO_5 + 3H_2O \rightarrow 3Ca^{2+} + 4OH^- + H_2SiO_4^{2-} \qquad \text{(alite dissolution)}$$

$$1,7Ca^{2+} + 1,4OH^- + H_2SiO_4^{2-} \rightarrow (CaO)_{1,7}-(SiO_2)-(H_2O)_y \qquad (C-S-H\ \text{precipitation})$$

$$1,3Ca^{2+} + 2,6OH^- \rightarrow 1,3Ca(OH)_2 \qquad (Ca(OH)_2\ \text{precipitation})$$

The focus of this article is the C–S–H growth. Our study is then limited to alite dissolution and C–S–H precipitation. Recently, it was highlighted that alite dissolution occurs by formation of etch pits [7] as in many other silicate systems already investigated in depth [8–10].

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