



## Hydration kinetics of tricalcium silicate by calorimetric methods

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### ABSTRACT

The kinetics of the cement hydration reaction is a relevant issue in the cement research field, particularly in the presence of additional inorganic and organic components that consistently increase the complexity of the cement paste. In the present study, the hydration reaction of pure tricalcium silicate has been monitored by different calorimetric approaches: the conventional Isothermal Conduction Calorimetry (IC) and a novel Differential Scanning Calorimetry (DSC) protocol. The measured hydration curves have been modeled by using the *Boundary Nucleation and Growth Model* (BNGM) to extract thermodynamic parameters of the early stages of the hydration reaction. IC and DSC methods provide similar results in terms of rate constants, linear growth, and nucleation rates even though the IC accesses the total evolved heat while DSC discloses the fraction of unreacted water. The validation of the DSC approach as a reliable analytical method to the study of cement hydration kinetic is of particular importance because it allows following very long hydration processes, such as those of pastes containing organic retarders or superplasticizers. The thermodynamic and kinetic parameters for the tricalcium silicate setting has been also evaluated and discussed as a function of the surface area of the powder.

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### 1. Introduction

The hydration reaction of a cement powder is a complex process in which dissolution of ions, interfacial phenomena, and solid-state reactions combine together and contribute to the transformation of the initial anhydrous phases in the final hydrated phases. In particular, a well-known scheme [1–4] identifies five stages for the reaction of a dry cement powder with water:

- (1) initial hydration processes,
- (2) induction period,
- (3) acceleration and set,
- (4) deceleration,
- (5) hardening.

The first stage is a short ( $\leq 15$  min) strongly exothermic time interval in which the wetting of highly hydrophobic cement particles occurs, with congruent dissolution of the soluble salts in the aqueous phase and incongruent dissolution of other chemical species, leading to the precipitation of the first hydrated products. The second part of the process is a quiescence period, called *induction*. At the end of the induction period, the rate of the reaction increases rapidly, because of the beginning of the nucleation and

the growth of the hydrated phases. The formation of the majority of the hydrated colloidal products occurs during the *acceleration* and *deceleration* steps, with a significant heat evolution. In these phases, colloidal hydrated calcium silicate and the by-product crystalline calcium hydroxide form, where the first is the main responsible for the development of mechanical properties of the cured product. The final part of the reaction proceeds at a slower rate and the associated, evolved heat diminishes progressively. During the hardening period, the rate-limiting process is the diffusion of the water through the dense hydrated products toward the anhydrous grains. For this reason, the last part of the hydration is often called *diffusional period*.

Because of the exothermic nature of the reactions occurring in the first stages of the cement hydration, the process is usually monitored by means of calorimetry. In general, three different methods can be used for the investigation of the cement hydration kinetics: (a) *Heat of Solution Calorimetry* [5]; (b) *Semi-Adiabatic/Adiabatic Calorimetry* [6]; (c) *Isothermal Conduction Calorimetry* [7]. Each technique has its own advantages and disadvantages. *Heat Solution Calorimetry* measures the heat of dissolution of the cement pastes in a mixture of nitric and hydrofluoric acid. The difference between the solution heats of anhydrous and hydrated cement corresponds to the heat evolved during the hydration process. This method is laborious, destructive, and gives no indication on the hydration rate. On the other hand, it allows the analysis of aged samples. In the *Semi-Adiabatic/Adiabatic Calorimetry*, the system is maintained in adiabatic conditions by increasing the temperature of the bath

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accordingly with the temperature rise of the sample. In an ideal adiabatic calorimeter there is no heat exchange between the calorimetric vessel and its surroundings. Calorimeters used for the study of cement hydration reactions are often semi-adiabatic (i.e., quasi-adiabatic) or isoperibolic. In these systems, a correction must be applied to account for the heat exchange with the surroundings. The hydration rate is progressively accelerated by the temperature increase. The whole hydration heat can be thus determined in a few days. Obviously, this technique does not provide information about the reaction rate nor about the activation energy of the process. Nowadays, the most used technique to access the hydration kinetics in the cement research field is the *Isothermal Conduction Calorimetry* (IC). This technique allows the investigation of the hydration rate and the calculation of the activation energy in the early stage of the reactions, when the most part of the heat is evolved [8]. It is worth to mention that, after a few days of hydration, the rate of the evolved heat becomes too low to be distinguished from the instrumental noise. This is the main drawback of the application of the IC technique to the cement hydration, considering that nowadays organic retarders and superplasticizers have become of outstanding importance to tailor the rheological and mechanical characteristics of the pastes [9–11]. The investigation of their kinetic and thermodynamic parameters, unfortunately, is not easily achievable because the traditional IC technique can hardly follow, until completeness, very long processes such those produced by addition of some superplasticizers.

In the last years, our group proposed an innovative method to monitor the hydration process of cement, which is based on the use of the Differential Scanning Calorimetry (DSC) [12]. Shortly, this approach relies on the fact that the cement hydration strictly depends on the water phase, which is consumed in the reaction. The unreacted water is quantified, after different hydration times, through the integration of its melting peak, which allows the determination of the Free Water Index (FWI) [12–14]. This is an indirect method, because it allows the *post*-evaluation of the kinetic process through the disappearance of one of the reactants. The two main advantages of the DSC approach are as follows: (1) the hydration reaction can be monitored until completeness (i.e., until any water is no more present in the sample), because it is a “discontinuous” method and (2) it is not limited by the evolved heat, enabling the acquisition of data also for the diffusional stage.

In this work, we compare the hydration kinetics of the same tricalcium silicate powder ( $\text{Ca}_3\text{SiO}_5$  or shortly  $\text{C}_3\text{S}$ ) as obtained by means of the two complementary methods: IC and DSC. The results obtained with the two techniques show a good agreement, throughout the first part of the kinetics. We then fitted the curves according to a recently proposed kinetic model, the Boundary Nucleation and Growth Model (BNGM) [15], further demonstrating that the IC and the DSC methods provide consistent results for the analysis of the tricalcium silicate nucleation and growth process. The BNGM has been implemented to directly model the FWI avoiding any assumption on the hydration reaction stoichiometry.

Two  $\text{C}_3\text{S}$  batches with different specific surface area have been compared by means of DSC only: the effect of the surface area on the rate constants has been discussed and is in agreement with the BNGM.

## 2. Material and methods

Two different batches of chemically pure tricalcium silicate were obtained from CTG-Italcementi (Bergamo, Italy) as a gift. Hereinafter, they will be indicated as  $\text{C}_3\text{S}$ -A and  $\text{C}_3\text{S}$ -B. The properties of these powders are described in Table 1.

Samples for DSC measurements have been prepared with 0.4 water/solid ratio by mass. With 20 mg of water (purified by a

**Table 1**

Specific surface area detected by  $\text{N}_2$  sorption isotherms and mean radius of the investigated  $\text{C}_3\text{S}$  bathes.

	Specific surface (BET) ( $\text{cm}^2/\text{g}$ )	Mean radius of the grains ( $\mu\text{m}$ )
$\text{C}_3\text{S}$ -A	0.65	4.66
$\text{C}_3\text{S}$ -B	0.40	5.75

Millipore Organex system;  $R \geq 18 \text{ Mw cm}$ ), 50 mg of  $\text{C}_3\text{S}$  was manually mixed. In the case of  $\text{C}_3\text{S}$  pastes, it is very common to manually mix the sample without adopting any mechanical mixing which is usually strongly required for mortar or concrete samples, where the heterogeneity of the solid phases requires a rigorous standardization of the mixing methodology [13,15,27]. About 40 mg of this paste was transferred in a steel pan (diameter 7.4 mm, capacity 60  $\mu\text{l}$ ) and sealed with the appropriate cover, equipped with an O-ring, to avoid water leaking. The steel pans containing the samples were maintained in thermostatic baths at constant temperatures (10, 20, 30, and 40  $^\circ\text{C}$ ,  $\pm 1$   $^\circ\text{C}$ ). Periodically, the samples were removed from the thermostatic baths and analyzed by the DSC calorimeter. Differential Scanning Calorimetry measurements were performed using a DSC Q2000 from TA Instruments; data were elaborated with the Q Series software, version 5.2.4. The measurements were carried out with the following temperature program: equilibrate to  $-30$   $^\circ\text{C}$ , isothermal for 1 min, from  $-30$   $^\circ\text{C}$  to  $-12$   $^\circ\text{C}$  at 20  $^\circ\text{C}/\text{min}$ , from  $-12$   $^\circ\text{C}$  to  $+25$   $^\circ\text{C}$  at 4  $^\circ\text{C}/\text{min}$ . Two different samples have been monitored throughout the curing period for each temperature. In this work, we equilibrate the paste at  $-30$   $^\circ\text{C}$  to freeze the bulk and capillary water. In a pure tricalcium silicate sample, with  $w/c = 0.4$ , during the first week after the mixing, only a few percentage ( $\sim 5\%$ ) of the water is already confined in the smallest porosity (freezing at temperature lower than  $-30$   $^\circ\text{C}$ ), as evident from a Low-Temperature DSC (LT-DSC) analysis (the Supporting information reports two LT-DSC thermograms showing the freezing of water confined in the smallest porosity of a  $\text{C}_3\text{S}/\text{water}$  paste. The complete analysis of the paste microstructure during the hydration process by means of LT-DSC is in progress and will be the subject of a future paper). The consumption of this confined water takes place only during the diffusional period, when the capillary water is completely consumed. For this reason, following the early stages of the hydration through the disappearance of the bulk water peak does not introduce any further uncertainty.

An eight channel TAM Air Isothermal Calorimeter (Thermometric AB, Sweden) was applied for measuring the hydration heat flow of pure  $\text{C}_3\text{S}$  at a temperature of 20  $^\circ\text{C}$  [16]. To 12 g  $\text{C}_3\text{S}$ , 4.8 g of water was added (water/solid ratio 0.4 by mass), which had been placed inside a plastic container. The paste was mixed by hand for 2 min, using a spatula. The paste was distributed (about 7 g each) in two glass ampoules, which were then capped and placed inside the calorimeter. Due to the external mixing, the heat flow evolved directly after the addition of water could not be recorded. In a pilot study, it was found that the use of the TAM Air 20 ml Admix ampoule, allowing the injection of water and the stirring of the fresh paste inside the calorimeter, was not possible, as the paste with  $w/c = 0.4$  was too sticky to be properly mixed inside the calorimeter. The heat flow of the two separate runs was recorded for 92 h. The measured heat flow was normalized to 1 g of  $\text{C}_3\text{S}$ . The total heat was obtained by integration of the heat flow curve, omitting the first 30 min of hydration time. The degree of hydration of  $\text{C}_3\text{S}$  can be eventually calculated using the value of  $(517 \pm 13) \text{ J/g}$  for complete  $\text{C}_3\text{S}$  hydration given by Taylor [3].

The software used for the implementation of the BNGM was Igor Pro, version 6.2.

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