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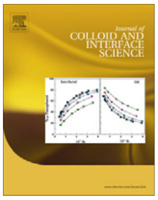

Influence of acrylic superplasticizer and cellulose-ether on the kinetics of tricalcium silicate hydration reaction

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ABSTRACT

This paper reports on the analysis of the hydration kinetics of a tricalcium silicate paste cured in presence of polymers industrially used in the extrusion process of mortars. In particular, we investigated the effect of a rheology-modifying additive (a methyl hydroxy ethyl cellulose) and a superplasticizer (a polyacrylic polymer). These polymers have been added to tricalcium silicate paste, both separately and together, to understand their distinct influence on the tricalcium silicate hydration and their possible synergies. The kinetic curves have been monitored from 10 to 40 °C by means of Differential Scanning Calorimetry and fitted using the generalized Boundary Nucleation and Growth Model combined to a diffusion-limited model, to extract: induction times, reaction rates, activation energies and diffusion coefficients. As a main result, this paper contributes to the advancement of the knowledge in the field of the extrusion process of cementitious materials, providing a thermodynamic support to the empirical evaluations of the additives performances.

1. Introduction

Concrete is the most widely used construction material. It is basically a mixture of Ordinary Portland Cement (OPC), sand, and aggregates [1]. OPC is the most important binder phase, even though nowadays an increasing number of cement products contains supplementary cementitious materials, also acting as binders. OPC is mainly constituted by tricalcium silicate (or shortly C_3S). The cement industry constantly develops new formulations to meet an increasing number of requests for innovative applications. During the past few decades, new highly performing cements have been developed and applied. Several of these formulations have been specifically designed for extrusion; among these, as an example, fiber-reinforced cement composites (FRCCs) deserve a special mention because of their remarkable mechanical performances [2–4]. In this advanced processing technique, a dough-like fresh cement mixture is forced through a die of desired cross-section. In the FRCC case, the paste is reinforced by short fibers (usually made of cellulose, PET, PVA or other). The high compression and shear densify the cement matrix and facilitate the alignment of the fibers in the extrusion direction, improving also the fiber–matrix bond [5]. For these reasons, the durability and the mechanical resistance of extruded FRCC are greatly enhanced compared to conventionally casted pastes with the same composition. Extrusion, moreover, shows other characteristics with increasing industrial interest. In particular, this production technique: (i) is “environmental friendly” (low consumption of energy and water), (ii) has a lower net cost than conventional approaches, (iii) can easily produce laminar and tubular structures, and (iv) allows the complete automation of the production [6].

The formulation must contain a rheology-modifier to render the paste viscous enough to be suitable for an extrusion process. Cellulose-ethers are one of the most common classes of additives used for this purpose. In addition, superplasticizers are included to maintain a low water content without decreasing the workability. In the past decades, numerous studies have been published on the mechanical properties of extrudates and on the relation of these properties with the composition [7–9] while, to the best of our knowledge, only one paper deals with the hydration kinetics of pastes formulated for extrusion [10].

Since the beginning of the so-called cement chemistry, thermal analysis has been of primary importance in unraveling the reaction degree of the cement hydration. In particular, the foremost technique used to monitor the hydration kinetics is the Isothermal Calorimetry (IC). IC monitors the heat evolved in the early stages of the process and enables to correlate it to the degree of reaction of the cement, giving a direct tool to follow the hydration [11,12]. In the past years, our group proposed a valid alternative to IC for the evaluation of the hydration kinetics of cementitious materials: this method is based on the Differential Scanning

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Calorimetry (DSC) and relies on the fact that the water phase is progressively consumed during the reaction. The unreacted water is quantified, after different hydration times, through the integration of its melting peak, which allows for the determination of the Free Water Index (FWI) [13–15], monitoring directly the "state" of the sample throughout the reaction. IC measures the "rate" which the sample state evolves at. In particular, IC measures thermal power that can be integrated to give the heat, which is proportional to the amount of reacted water: to perform such a conversion, the enthalpy of the process must be known and constant. Dealing with cement samples, this condition may not be met when several reacting phases with different reaction enthalpies are present. For these reasons in many cases, the DSC method can be advantageous compared to IC.

In a recent publication [16], the good accordance of the DSC results with those of the well-established IC approach has been demonstrated. The advantage of the DSC method is the intrinsic possibility to monitor the kinetics of whatever cement formulation, including those containing retarders or superplasticizer, whose hydration is often very long, until completeness, that is, throughout all the final diffusional period [17].

The most recent kinetic model developed to specifically describe the first stages of hydration kinetics in cementitious systems is the Boundary Nucleation and Growth Model (BNGM) [18]. The BNGM implements and generalizes the previous Avrami-Erove'ev model [13–15,19,20], considering that the nucleation of new phases mainly occurs at the boundary interface of the C_3S grains. The BNGM provides a good physicochemical description of the tricalcium silicate early hydration as followed by IC [18,21], quasi-elastic neutron scattering (QENS) [22] and DSC [1].

Due to the heterogeneity of cement pastes in terms of both constituting materials and formation of hydrated phases, the fundamental studies on the hydration kinetics are often presented on simplified systems rather than on real mixes. C_3S is commonly used as a model of the entire cement, because it is the most important phase in determining the hydration times and the mechanical properties of the cured specimen. The recent literature presents some papers whose scope is the investigation into the effect of inorganic [23] and organic additives [17] on such model phase. In this framework, we present here a calorimetric study on the effect of the co-presence of a cellulose-ether polymer and a superplasticizer on the thermodynamics of the tricalcium silicate hydration, being these two additives essential for the achievement of cement based extrudable formulations.

2. Experimental section

2.1. Materials

Synthetic tricalcium silicate (C_3S) with BET specific surface area of 0.40 ± 0.05 m^2/g and particles median radius of 5.75 μm was obtained from CTG-Italcementi Group. Methyl hydroxy ethyl cellulose (MHEC) has an average degree of substitution (DS) of 1.76, and the molar degree of substitution is 0.28. A 2% aqueous solution of MHEC at 20 °C has a viscosity of approximately 40,000 mPa s. The superplasticizer (SP) is classified as a polyacrylic polymer for applications requiring low slump loss, high mechanical resistance, and high durability.

Samples for both calorimetric and electron microscopy measurements have been prepared with 0.4 water/solid ratio by mass. Samples containing cellulose-ether were prepared by mixing the dry C_3S powder with the MHEC powder (2.5% on C_3S weight) and the proper amount of water to produce a paste with a 0.4 water/C_3S ratio. To prepare the C_3S/water/SP and the C_3S/water/SP/MHEC pastes, 10 g/l solution of the SP was used instead of pure water, resulting in a 0.4% w/w SP/C_3S ratio. Water was purified by a Millipore Organex system ($R \geqslant 18$ MΩ cm).

2.2. Calorimetric method

DSC measurements were performed using a DSC Q2000 from TA Instruments (Philadelphia, USA). The paste (roughly 40 mg) was placed in a steel pan (diameter 7.4 mm, capacity 60 μl) and sealed with the cover equipped with a neoprene O-ring to avoid water leaking. Each sample was maintained in a thermostatic bath at constant temperature (10, 20, 30, or 40 °C). The measurements were carried out with the following temperature program: equilibrate to −30 °C, isothermal for 1 min, from −30 °C to −12 °C at 20 °C/min, from −12 °C to +25 °C at 4 °C/min. From the enthalpy variation of the water melting, we calculated the Free Water Index (FWI) according to the procedure reported in previous works [13,14].

The melting peak of the unreacted water present inside a C_3S paste decreases over time as the water is consumed by the hydration reaction. As an example, Fig. 1 shows the time evolution of the melting peak for sample C_3S/MHEC at 20 °C. This melting peak is measured and integrated periodically during the hydration process to extract the fusion enthalpy, ΔH_{exp}. The *FWI* parameter is then calculated for each time by knowing the original weight fraction of water in the paste, ϕ_w and the theoretical value of melting enthalpy of water, ΔH_{theor} (333.4 J/g) [13]:

$$FWI = \Delta H_{exp}/\phi_w \Delta H_{theor} \tag{1}$$

When model systems are used, as in the present case where pure synthetic C_3S is hydrated, the stoichiometry of the calcium silicate hydrate, C–S–H, and portlandite, $Ca(OH)_2$, formation is known [24]:

$$C_3S + 3.1H_2O \rightarrow C_{1.7}SH_{1.8} + 1.3Ca(OH)_2 \tag{2}$$

and the FWI can be directly linked to the amount of products [16].

2.3. Scanning electron microscopy

SEM observations were carried out on fracture surfaces by means of a Cambridge Stereoscan 360S, working at 20 kV of acceleration potential, with a working distance of 20 mm. Each paste was fractured and deposited onto the stub, exposing the internal surfaces to the electron beam. The samples were coated with a gold film (Agar automatic sputter coater) to make them conductive.

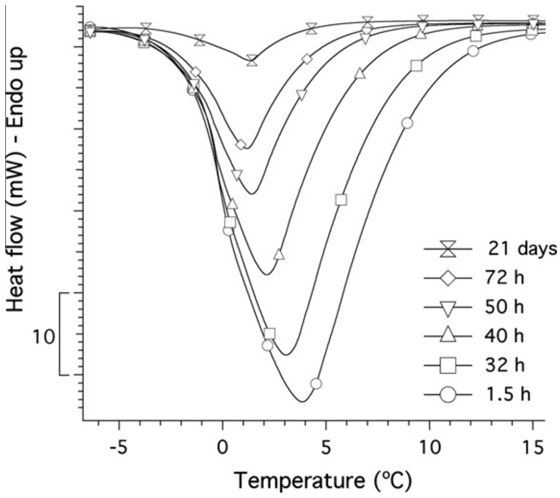

Fig. 1. Heat flow for sample C_3S/MHEC hydrating at 20 °C obtained by DSC at different times during the hydration reaction.