



Influence of a thermal cycle at early age on the hydration of calcium sulphoaluminate cements with variable gypsum contents

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ABSTRACT

Hydration of a belite calcium sulphoaluminate cement was investigated over one year as a function of its initial gypsum content (variable from 0 to 35%). Particular attention was paid to the influence of the thermal history of the material at early age on its subsequent evolution. Pastes and mortars (w/c 0.55) were either cured at 20 °C or submitted for one week to a thermal treatment simulating the temperature rise (up to 85 °C) and fall occurring in drums of cemented radwastes. The thermal cycle accelerated the early stages of hydration and mainly decreased the proportion of AFt versus AFm hydrates, especially at low initial gypsum contents ($\leq 20\%$ by weight of cement). It also strongly reduced the compressive strength of gypsum-free specimens (by 35% after one year), and doubled their expansion under water. These results were explained by mineralogical evolutions towards a more stable phase assemblage which included retarded ettringite formation.

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1. Introduction

Calcium sulphoaluminate (CSA) cements are receiving increasing attention nowadays since their manufacture may produce less CO₂ than ordinary Portland cement (OPC) [1–4]. These binders may have very variable compositions [5], but all of them contain ye'elinite, also called Klein's compound or tetracalcium trialuminate sulphate $C_4A_3\bar{S}$ [6,7], in their clinker. This article is focussed on sulphoaluminate-belite cements in which ye'elinite predominates over belite. Depending on the composition of the raw meal, their clinker may also contain other minor phases such as calcium aluminates (CA, $C_{12}A_7$), ferrite, gehlenite, excess anhydrite or calcium oxide [8]. Whereas OPC clinker is normally interground with a few weight percents of calcium sulphate (including gypsum, hemihydrate or anhydrite), CSA clinkers can be blended with much higher contents (typically 16 to 25 wt.% [9]).

Hydration of calcium sulphoaluminate cements strongly depends on the amount and reactivity of the added calcium sulphate. The main crystallized hydrates are calcium monosulphoaluminate hydrate and ettringite, the former being progressively replaced by the latter with increasing gypsum content [10]. Both of them are precipitated together with amorphous aluminum hydroxide. Depending on the composition of the minor phases, other hydration products may also be observed, such as C–S–H [11,12], strätlingite [13,14], siliceous hydrogarnet [14] and/or

hemi- or monocarboaluminate [15]. The hydration progress of CSA cement pastes occurs by the initial precipitation of ettringite and aluminum hydroxide, followed by the precipitation of calcium monosulphoaluminate hydrate once calcium sulphate has been depleted [12,14]. Belite has a slower hydration rate [16]. Bernardo et al. [17] investigated the hydration of a CSA cement containing mainly ye'elinite (53% by weight) and reported that this phase was almost fully depleted within the first 24 h whereas belite was still unreacted after 28 d. Depending on its initial content, residual gypsum may be observed in hardened cement pastes. Peysson characterized one-year old cement pastes prepared with increasing amounts of gypsum (from 10 to 40% by weight of cement) [18]. This phase was still observed for initial contents $\geq 20\%$. The selected w/c ratio (0.25) was however very low and hydration probably stopped due to lack of water.

The initial gypsum content not only influences the distribution of hydrated products, but also the rate of hydration. Sulphates exert an accelerating effect on the rate of hydration at early age [18–22]. The particle size of the calcium sulphate source must be adapted to that of the clinker grains. Palou and Majling [23] reported that this parameter significantly influences the rate of ettringite formation. When too coarse particles are used, precipitation of calcium monosulphoaluminate hydrate or hydrogarnet can even be observed [24].

The properties of hardened CSA cement-based materials are highly dependent on the gypsum content of the binder. By increasing this parameter, a wide series of materials can be designed, ranging from rapid-hardening to shrinkage-compensating, and eventually to self-stressing [9]. Wang et al. [20] characterized cement pastes ($w/c = 0.3$)

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