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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 (≤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.

1. Introduction

Calcium sulphoaluminate (CSA) cements are receiving increasing attention nowadays since their manufacture may produce less CO_2 than ordinary Portland cement (OPC) [1–4]. These binders may have very variable compositions [5], but all of them contain ye'elimite, also called Klein's compound or tetracalcium trialuminate sulphate $C_4A_3\overline{S}$ [6,7], in their clinker. This article is focussed on sulphoaluminate-belite cements in which ye'elimite 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'elimite (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 ≥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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prepared with a clinker containing 60.4% ye'elimite and 29.8% belite. For initial gypsum contents below 15–20%, ettringite mostly precipitated during the first 24 h while, for contents above 25%, precipitation occurred on a longer period of time and specimens cured in sealed bag exhibited expansion. Sudoh et al. [25] noticed that the compressive strength of mortars ($w/c=0.65$, $s/c=2$) reached a maximum for gypsum contents comprised between 20% and 25%. Higher contents led to swelling and microcracking, which weakened the strength of the materials. Peysson [18] reported however that the highest strengths were achieved with a ye'elimite-rich cement without gypsum.

Hydration of CSA cement is more exothermic than that of OPC. Since a significant heat amount is released within the first 12 h, large cross-sections may undergo considerable self-heating. While excessive temperature rise is not a problem affecting small-scale laboratory samples, it is necessary to understand how real massive structures will perform. The question is all the more important since the hydrates assemblage in these materials strongly depends on temperature: increasing the temperature decreases the stability domain of ettringite, but increases that of calcium monosulphoaluminate hydrate [26,27]. Literature on the influence of temperature on the physico-chemical evolution of CSA cements is very limited and only devoted to hydration at early age (<7 d).

- Zhang and Glasser [12] investigated the hydration of cement pastes (w/c 0.44, 17% gypsum by weight of cement) during their first 24 h under isothermal conditions (25 °C, 50 °C and 80 °C). Elevated temperatures increased the rate of formation of ettringite as well the hydration degree of clinker minerals (given sufficient water), and coarsened the pore structure.
- Berger et al. [28] applied on cement pastes and mortars a thermal cycle reproducing the temperature rise and decrease occurring in a massive mortar block such as a 200 L drum of stabilized waste. They characterized the samples during their first seven days and concluded that the thermal excursion accelerated hydration and modified the proportion of AFt versus AFm phases when the binder had a gypsum content below 20%.

This article has two main objectives: (i) to supplement these data by following hydration of CSA cements submitted to an initial thermal cycle on a much longer period of time (1 year), and (ii) to assess the influence of this thermal cycle on the properties of the hardened materials (mechanical strength and volume change). It is focussed on cements containing variable gypsum contents (between 0 and 35 wt.%).

2. Experimental

2.1. Materials and preparation of the specimens

CSA cements were prepared by mixing a ground industrial CSA clinker (the composition of which is summarized in Table 1; $d_{10}=2.67$ µm, $d_{50}=17.6$ µm, $d_{90}=50.8$ µm, BET specific surface area $=1.3$ m^2/g) with the appropriate amount of analytical grade gypsum (from 1 to 35% by weight of cement; $d_{10}=5.4$ µm, $d_{50}=19.6$ µm, $d_{90}=50.3$ µm, BET specific surface area $=0.4$ m^2/g) during 15 min. In the clinker, ye'elimite predominated over belite and mayenite. The other minor constituents, mainly phases containing titanium and iron, could be regarded as hydraulically inactive. Both cement pastes and mortars were made with the same w/c ratio of 0.55. Siliceous sand (0.1–1.2 mm) was used with a sand to cement weight ratio of 3 to optimize the workability and limit the heat release of fresh mortars during hydration. The mixing solution was demineralized water at a temperature comprised between 19 and 22 °C. Mixing was performed in a standardized laboratory mixer (following European standard EN 196-1) at low speed for 3 min and at high speed for 2 min. Cement pastes were cast into airtight polypropylene boxes (7 mL of paste per box), and cured at 20 °C for one year, or submitted to a thermal cycle in an oven (Memmert UFP 500) for 7 days before being cured at 20 °C. Mortars were cast into 4 × 4 × 16 cm moulds and cured for 7 days at 20 ± 1 °C and 95 ± 5% R.H, or submitted to a thermal cycle in an oven. The specimens were then demoulded, weighed, measured, and kept at room temperature in sealed bag or immersed under water at 20 ± 1 °C. Mortars were also used for semi-adiabatic calorimetry investigation.

Shorthand notations were used to refer to the different investigated compositions, as summarized in Table 2.

Complementary experiments were performed on cement suspensions (w/c ratio $=10$) stirred under nitrogen atmosphere at room temperature for 7 d. The objective was to obtain an advanced hydration degree and thus to describe the mineralogical phase assemblage reached after long-term evolution.

To determine the influence of minor anhydrous phases on cement hydration, some paste samples ($w/c=0.55$) were prepared with pure ye'elimite (BET specific surface area $=0.6$ m^2/g, provided by M.R. Pro, Meyzieu, France) and cured in air-tight boxes at room temperature for 90 d.

2.2. Thermal cycles

Thermal cycles were applied on pastes and mortars with the objective to reproduce the temperature rise and fall that may occur in a massive mortar block (such as a waste encapsulated in a mortar with typical w/c and s/c ratios of 0.55 and 3, and placed in a 200 L canister). This evolution was estimated for each investigated cement composition by recording the temperature during hydration of 800 mL mortar samples placed in semi-adiabatic Langavant calorimeters (Fig. 1). Temperature profiles were then defined in each case by interpolating the recorded curves as closely as possible using 40 segments. Since cement pastes produced more heat than mortars, some corrections were implemented when necessary to keep similar temperature evolutions in the heart of mortars and their corresponding pastes with the same gypsum content.

2.3. Characterization methods

Hydration of mortars was followed by calorimetry according to the semi-adiabatic method (European standard EN 196-9). This latter consisted in introducing 1575 g ± 1 g of fresh mortar into a cylindrical container which was then placed into a Langavant calibrated calorimeter in order to determine the quantity of heat emitted versus the temperature evolution.

The core temperature of pastes and mortars cured at 20 °C was measured with waterproof penetration probes (type K TC) and recorded with a Testo 735-2 thermometer.

Table 1
Mineralogical composition of the investigated CSA clinker (KTS 100 provided by Belitex).

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	MnO	P_2O_5	Cr_2O_3	SrO	Na_2O	K_2O	SO_3	ZnO	Cl^-	LOI
wt.%	5.54	39.23	1.21	42.75	1.5	1.67	0.01	0.17	0.03	0.09	0.03	0.14	8.99	0.01	0.03	0.42

Minerals	$C_4A_3\overline{S}$	C_2S	$C_{12}A_7$	CT	Periclase	$C\overline{S}$	Quartz	Others[a]
wt.%	68.5	15.9	9.5	2.9	1.5	0.5	0.5	2.4

LOI = loss on ignition.
[a] Include 1.2% of iron oxide.