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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.

Table 2
Shorthand notations of the investigated compositions.

Gypsum content (% by weight of cement)	Paste		Mortar	
	Curing at 20 °C	Thermal cycle at early age	Curing at 20 °C	Thermal cycle at early age
0	CE0	CE0t	ME0	ME0t
1	–	–	–	ME0.1t
2	–	–	–	ME0.2t
3	–	–	–	ME0.3t
5	–	–	–	ME0.5t
7	–	–	–	ME0.7t
10	CE1	CE1t	ME1	ME1t
20	CE2	CE2t	ME2	ME2t
35	CE3.5	CE3.5 t	ME3.5	ME3.5t

Hydration was stopped after fixed periods of time (from 5 min to 1 year) by successively immersing the crushed pastes into isopropanol and drying them in a controlled humidity chamber (with a 20% relative humidity at 22 ± 2 °C).

Crystallized phases were identified by X-ray diffraction (Siemens D8 – Copper anode $\lambda_{K\alpha1} = 1.54056$ Å generated at 40 mA and 40 kV) on pastes ground to a particle size of less than 100 μm. The acquisition range was from 5° to 60° 2θ in 0.02° 2θ steps with integration at the rate of 50 s per step. The evolution of the amounts of ye'elimite over time was assessed from XRD patterns by measuring the areas of corresponding reflections using the EVA analysis software (© 2005 Bruker AXS). The uncertainty of the method was estimated around 5% by analysing mixes of gypsum and anhydrous clinkers of known compositions. Thermogravimetric analyses were carried out under N_2 atmosphere on 50 ± 2 mg of sample using a TGA/DSC Netzsch STA 409 PC instrument at 10 °C/min up to 1000 °C.

The compressive strength of mortar prisms cured in sealed bag or under water was measured after 1 d, 7 d, 28 d, 90 d, 180 d and 360 d. Triplicate specimens were used at each testing age.

Expansion and mass gain under water were assessed on 4 × 4 × 16 cm mortar bars placed into cells filled with 700 mL of demineralized water (one sample per cell, no renewal of solution) after 7 d, 28 d, 90 d, 180 d and 360 d.

Total water porosity ϕ_w was estimated by measuring the total water amount removed from water-saturated mortar samples after drying at 60 °C (to limit ettringite degradation) until stable mass loss (Eq. (1)).

$$\Phi_w(\%) = \frac{m_a - m_d}{m_a - m_w} \times 100 \qquad (1)$$

where m_a and m_w are the water-saturated sample mass values measured in air and under water respectively, and m_d the mass of the dried sample measured in air.

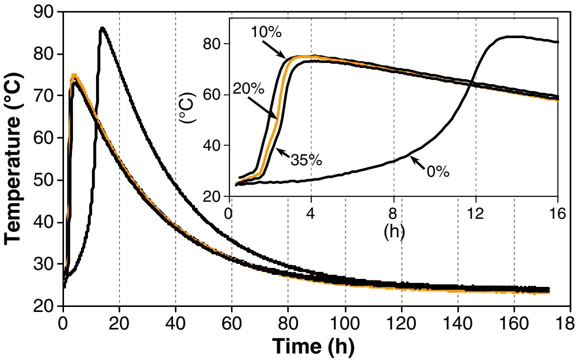

Fig. 1. Thermal cycles applied to pastes and mortars as a function of the initial gypsum content of the cement.

Thermodynamic calculations were carried out using the CHESS software [29]. The solubility constants of the selected cement phases in the database are given in Table 3.

3. Results and discussion

3.1. Hydration of cement pastes cured at 20 °C

3.1.1. Gypsum-free cement

The mineralogical changes of the cement pastes cured at 20 °C with ongoing hydration were determined by XRD and TGA (Figs. 2 and 3). At the end of the mixing step (5 min after the addition of water), small amounts of ettringite and X-ray amorphous aluminum hydroxide were already detected. Between 5 min and 5 h, hydration progressed very slowly, as can be seen from ye'elimite consumption (Fig. 4) and weight loss by TGA (Fig. 3). Similar results were obtained by Peysson [18], who reported the absence of significant amounts of hydrates 6 h after mixing of a ye'elimite-rich clinker with water at a w/c ratio of 0.25.

The main peak of temperature occurred after 14 h, and resulted from the rapid dissolution of the clinker. After 24 h, the residual ye'elimite content was reduced to 17% and the content of bound water had strongly increased (up to 26%). Besides ettringite and aluminum hydroxide, other hydrates were detected: CAH_{10}, $C_3A.C\bar{S}.H_{12}$ and $C_3A.1/2C\bar{C}.1/2CH.H_{11}$, and possibly $C_3A.1/2C\bar{S}.1/2CH.H_{12}$. The accurate identification of the AFm phases was difficult because these minerals can form solid solutions and may have variable water contents [30,31].

In order to assess the contributions of the minor phases of the clinker to the hydrates assemblage (mainly mayenite, which is known to have a high reactivity in water), an additional paste was prepared with pure ye'elimite at a w/c ratio of 0.55 (Fig. 5). It exhibited the same solid phase composition, excepting CAH_{10} which was not precipitated. Formation of CAH_{10} in paste CE0 at 20 °C, which was also observed by Peysson [18], was rather unexpected. For instance, hydration of mayenite by pure water yields a mix of CAH_{10} and C_2AH_8 at 4 °C, but C_2AH_8 only at 20 °C [32]. However, in this study, competition between ettringite and C_2AH_8 should be taken into account. The maximum oversaturation domain of ettringite being reached before that of C_2AH_8 [33], formation of ettringite would be favoured at early age against that of C_2AH_8 which would not precipitate under these conditions. Nevertheless, CAH_{10} is a metastable phase at room temperature and is expected to be transformed at later age.

In both pastes prepared with clinker or pure ye'elimite, hydration produced a mix of AFm phases, ettringite and amorphous aluminum hydroxide, which disagreed with mass balance equation (Eq. (2)) and the results of Okushima et al. [34].

$$C_4A_3\bar{S} + 18H \rightarrow C_3A.C\bar{S}.H_{12} + 2AH_3 \qquad (2)$$

These authors reported indeed that, after 12 to 24 h of hydration of a fine powder (particle size between 5 and 10 μm), ye'elimite was fully hydrated and the anhydrous grains were replaced by a complex network of calcium monosulphoaluminate hydrate and aluminum hydroxide. Lan and Glasser [35] reported however ettringite as the main hydration product of ye'elimite after two days of hydration at 20 °C. Precipitation of ettringite was also observed by hydrating a ye'elimite-rich clinker in the absence of gypsum [13,18]. It is expected from a thermodynamic point of view. According to Damidot et al. [26,27], calcium monosulphoaluminate hydrate is unstable with respect to a mixture of ettringite and C_3AH_6 at temperatures below 50 °C. The depletion of sulphates from the aqueous phase by the precipitation of ettringite may explain the simultaneous formation of AFm phases with low sulphate content.

Beyond 14 h, hydration progressed much more slowly. The bound water content only increased from 26 to 30% between 1 and 7 days,

Table 3
Solubility data ($T = 25$ °C, 1 bar) of the cement phases considered for thermodynamic modelling.

Mineral	Formation reaction	Log *K*
Anhydrite	$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4$	4.3064
C_2AH_8	$2\ Ca^{2+} + 2\ AlO_2^- + 9\ H_2O \rightarrow C_2AH_8 + 2\ H^+$	−14.198
C_4AH_{13}	$4\ Ca^{2+} + 2\ AlO_2^- + 16\ H_2O \rightarrow C_4AH_{13} + 6\ H^+$	−58.528
CAH_{10}	$Ca^{2+} + 2\ AlO_2^- + 10\ H_2O \rightarrow CAH_{10}$	7.662
C_3AH_6	$3\ Ca^{2+} + 2\ AlO_2^- + 8\ H_2O \rightarrow C_3AH_6 + 4\ H^+$	−33.389
Siliceous hydrogarnet	$3\ Ca^{2+} + 2\ AlO_2^- + 0.8\ SiO_2(aq) + 6.4\ H_2O \rightarrow HgSiHigh + 4\ H^+$	−27.456
C–S–H (I)	$1.1\ Ca^{2+} + SiO_2(aq) + 5\ H_2O \rightarrow C\text{–}S\text{–}H\ (I) + 2.2\ H^+$	−17.91
C–S–H (II)	$1.8\ Ca^{2+} + SiO_2(aq) + 7\ H_2O \rightarrow C\text{–}S\text{–}H\ (II) + 3.6\ H^+$	−33.85
$SiO_2(am)$	$SiO_2(aq) \rightarrow SiO_2(am)$	2.78
Ettringite	$6\ Ca^{2+} + 2\ AlO_2^- + 3\ SO_4^{2-} + 34\ H_2O \rightarrow Ettringite + 4\ H^+$	−10.052
C_2ASH_8	$2\ Ca^{2+} + 2\ AlO_2^- + SiO_2(aq) + 9\ H_2O \rightarrow C_2ASH_8 + 2\ H^+$	−3.9
Gibbsite[a]	$AlO_2^- + H^+ + H_2O \rightarrow Gibbsite$	14.3
Gypsum	$Ca^{2+} + SO_4^{2-} + 2\ H_2O \rightarrow Gypsum$	4.526
Monosulpho[b]	$4\ Ca^{2+} + 2\ AlO_2^- + SO_4^{2-} + 14\ H_2O \rightarrow Monosulpho + 4\ H^+$	−25.55
Portlandite	$Ca^{2+} + 2\ H_2O \rightarrow Portlandite + 2\ H^+$	−22.922

Solubility data from [40].

[a] Log *K* of gibbsite (a crystallized phase which was not observed in our samples) was decreased from 15.5 to 14.3, which corresponded to an amorphous phase and was in better agreement with our experimental findings.

[b] For calcium monosulphoaluminate hydrate, Log *K* was increased from −26.15 to −25.55 to get a small stability domain at 25 °C.

and the residual ye'elimite content was still 9% after 7 d. Increased amounts of CAH_{10} and $C_3A.1/2C\,\bar{C}.1/2CH.H_{11}$ were precipitated between 1 and 7 days (Fig. 2). Their contents decreased however at later age, while those of calcium monosulphoaluminate hydrate and ettringite increased. Siliceous hydrogarnet was detected in one-year old samples, and resulted from the partial conversion of CAH_{10}, with belite as the silicon source. It is well known that hydrogarnet, usually defined as the silicon-free composition C_3AH_6, can form a solid solution with grossularite C_3AS_3 [36].

After one year, ye'elimite was not fully depleted (residual content of 2%, maybe corresponding to the grains with the largest particle size). The hydrated phase assemblage, which comprised calcium monosulphoaluminate hydrate, ettringite, siliceous hydrogarnet, calcium hemicarbonate and CAH_{10}, was still unstable from a thermodynamical point of view. To assess the long term evolution of cement paste CE0, fully hydrated cement was prepared by stirring a suspension ($w/c = 10$) for one week. The reactive anhydrous phases of the clinker (ye'elimite, mayenite, and belite) were totally depleted (Fig. 6). The water loss determined by TGA reached 33%, which corresponded to a w/c ratio of 0.49. The chemical water demand of the clinker was thus lower than the investigated w/c ratio (0.55). The hydrates were calcium monosulphoaluminate hydrate (main component), strätlingite, aluminum hydroxide, and ettringite (traces). Siliceous hydrogarnet was not detected anymore. Formation of C–S–H could not be clearly evidenced, which agreed with the observations of Winnefeld et al. [14]. A thermodynamic calculation was performed to simulate the increasing addition of belite to a phase assemblage resulting from the hydration of ye'elimite ($C_3A.C\,\bar{S}.H_{12}$, AH_3 and traces of $C_3A.C\,\bar{S}.H_{32}$) (Fig. 7-a). It showed that, as long as AH_3 was present in the system, or, in another way, as long as the belite content was lower than twice the initial content of ye'elimite, strätlingite precipitated, consuming AH_3 according to balance equation (Eq. (3)).

$$C_2S + AH_3 + 5\,H \rightarrow C_2ASH_8 \tag{3}$$

Precipitation of C–S–H required an excess of C_2S over $C_4A_3\,\bar{S}$, which did not correspond to the investigated experimental conditions. The predicted equilibrium pH was in excellent agreement with that of the suspension measured after 7 days (pH 11.95).

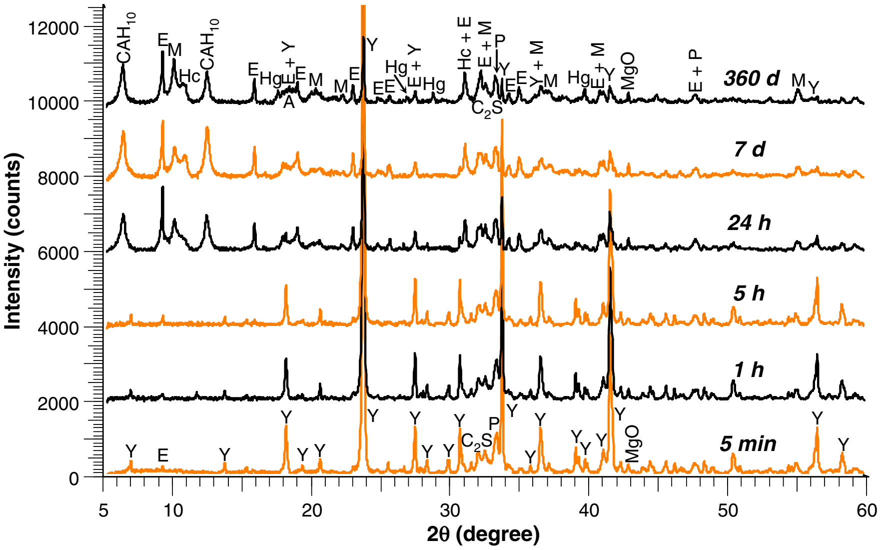

Fig. 2. X-ray diffraction analysis of cement paste CE0 cured at 20 °C after 5 min, 1 h, 5 h, 24 h, 7 d, and one year of hydration (E = ettringite, Hc = calcium hemicarboaluminate hydrate, M = calcium monosulphoaluminate hydrate, A = aluminum hydroxide, Hg = siliceous hydrogarnet, P = CaO.TiO₂).

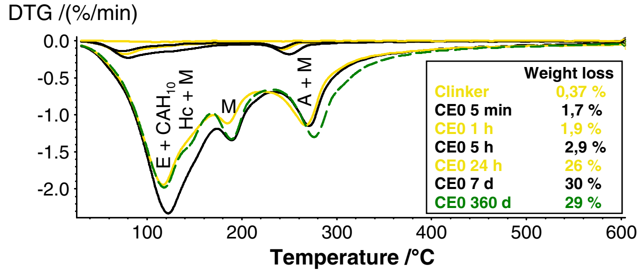

Fig. 3. Thermogravimetric analysis of clinker and cement paste CE0 cured at 20 °C after 5 min, 1 h, 5 h, 24 h, 7 d, and one year of hydration (E = ettringite, Hc = calcium hemicarboaluminate hydrate, M = calcium monosulphoaluminate hydrate, A = aluminum hydroxide).

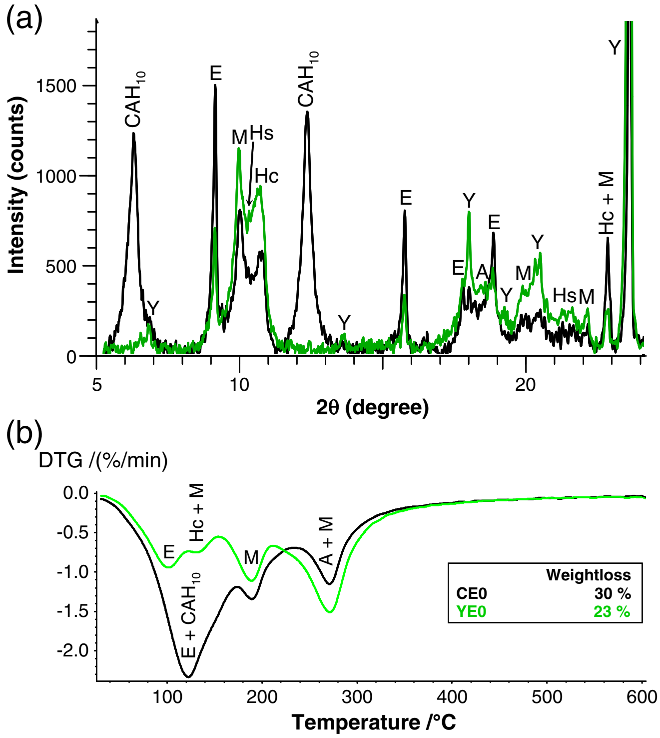

Fig. 5. Solid phase composition of pastes prepared with clinker (CE0) and pure ye'elimite (YE0) (*w*/*c* ratio of 0.55) after 7 d of hydration. Investigation by X-ray diffraction (a) and thermogravimetry analysis (b) (Y = ye'elimite, E = ettringite, Hc = calcium hemicarboaluminate hydrate, Hs = calcium hemisulphoaluminate hydrate, M = calcium monosulphoaluminate hydrate, A = aluminum hydroxide).

3.1.2. Gypsum-containing cements

The mineralogical evolutions of the cement pastes prepared with increasing amounts of gypsum were characterized by X-ray diffraction and TGA (Figs. 8 and 9 for a gypsum content of 20%). During the first 2 h after mixing, hydration proceeded very slowly. Both ettringite and amorphous aluminum hydroxide were detected, in slightly higher amounts than for a gypsum-free cement paste, but the depleted fractions of ye'elimite and gypsum remained very small (less than 5% after 2 h if the clinker was initially blended with 20% gypsum). A strong acceleration occurred after 2 h, as shown by the evolution of the core temperature of the samples and their residual ye'elimite content (Fig. 4). At 5 h, the precipitated amounts of ettringite and aluminum hydroxide had strongly increased and about 40% ye'elimite was depleted, whereas, at the same time, hydration of a gypsum-free cement was just beginning (1.5% ye'elimite consumed only) (Table 4). The residual fraction of gypsum depended on its initial content (0%, 40 ± 10% and 70 ± 10% for clinkers respectively blended with 10%, 20% and 35% gypsum). Some AFm phases ($C_3A.C\bar{S}.H_{12}$, and possibly $C_3A.1/2C\bar{C}.1/2CH.H_{12}$ and $C_3A.1/2C\bar{S}.1/2CH.H_{12}$ or their solid solution in cement paste CE1) were detected from 24 h in the cement pastes with low gypsum contents only (10% and 20%). In agreement with the literature, increasing the initial gypsum content of cement promoted the precipitation of ettringite against that of AFm phases. After 7 days, some residual gypsum was still detected in pastes CE2 (≈4% of its initial content) and CE3.5 (≈15%). The amount of depleted ye'elimite decreased when the initial gypsum content of the cement increased (Table 4). Moreover, the bound water contents of the samples were rather similar, whatever their initial gypsum concentration, even though the pastes prepared with gypsum mainly contained water-richer hydrates. It should be noted that the bound water contents were always lower than the theoretical water contents assuming full consumption of the mixing water, which means that, unless heterogeneities in the samples, hydration was not stopped by lack of water. Adding gypsum to the clinker thus accelerated the beginning of hydration (reduction of the induction period), but limited the hydration degree at later age (7 d). A similar result was also suspected for higher gypsum content (40%) by Peysson [18]. To explain the deceleration of hydration of an alite-sulphoaluminate cement, Liu et al. [37] assumed the rapid formation of a dense layer of ettringite over the clinker grains, leading to a diffusive regime in which hydration is limited by the rate of transport of water through the early-formed hydrate layer. Hydrating a gypsum-free cement produced a mix of AFm phases, ettringite and aluminum hydroxide which might form a more heterogeneous and porous shell around the clinker grains, leading to delay the diffusive regime.

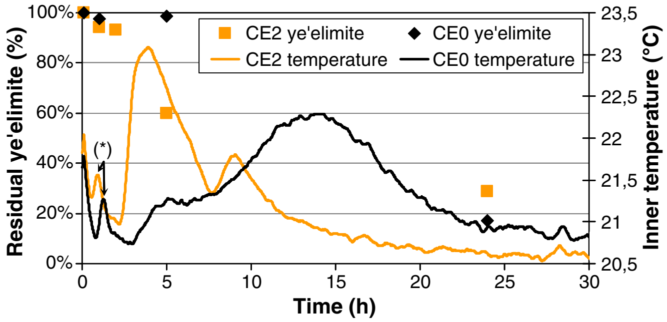

Fig. 4. Evolution of the ye'elimite content and core temperature of cement pastes CE0 and CE2 over the first 30 h of hydration. * Artefacts caused by a defect in temperature regulation of the climatic chamber.

At later age, from 7 d to 1 year, the pastes prepared with gypsum exhibited only minor mineralogical evolutions. Their residual fraction of ye'elimite decreased slightly but remained higher than that of paste CE0. Hydration mainly produced calcium monosulphoaluminate hydrate and AH_3 in pastes CE1 and CE2, and ettringite and AH_3 in paste CE3.5. No siliceous phase could be detected. To assess the long term evolution of the cement pastes, a suspension was prepared with cement CE2 ($w/c = 10$). This latter was fully hydrated after one week of mixing. The precipitated hydrates were ettringite, calcium monosulphoaluminate hydrate, strätlingite, and amorphous aluminum hydroxide (Fig. 6). The bound water content was measured to be 37%, which corresponded to a *w*/*c* ratio of 0.54 (by taking into account the water brought by gypsum). Precipitation of strätlingite was well predicted by thermodynamical calculations simulating the hydration of C_2S in a system containing gibbsite, calcium monosulphoaluminate hydrate and ettringite (formed by hydrating a mix of ye'elimite and gypsum in pure water) (Fig. 7-b). It was accompanied by a consumption of AH_3, which was experimentally confirmed by the

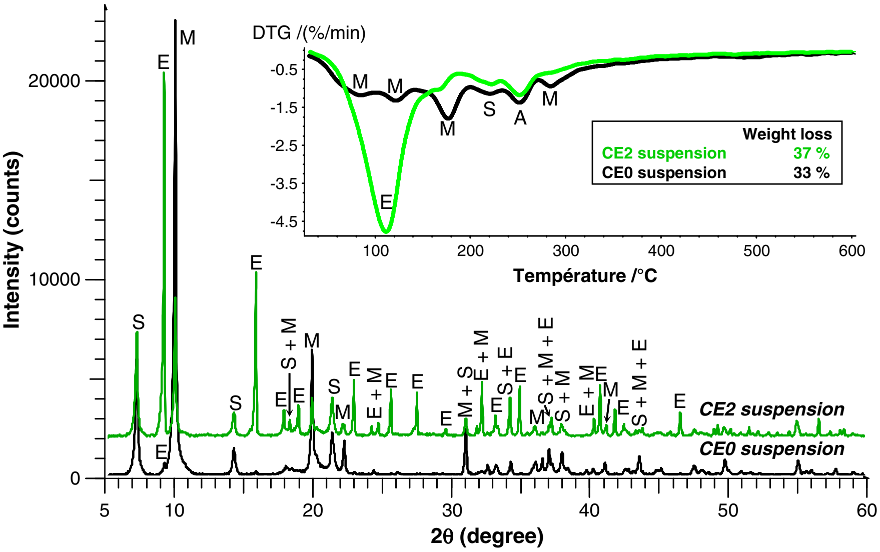

Fig. 6. X-ray and TGA analysis of the solid fraction of suspensions ($w/c = 10$) prepared with cements CE0 and CE2 after 7 days of stirring at 25 °C (S = strätlingite, E = ettringite, M = calcium monosulphoaluminate hydrate, A = aluminum hydroxide).

very low AH_3 content of the suspension, as compared to that of paste CE2. With excess gypsum ($C\bar{S}H_2/C_4A_3\bar{S}$ molar ratio >2), the calculations showed that C–S–H would precipitate before C_2ASH_8.

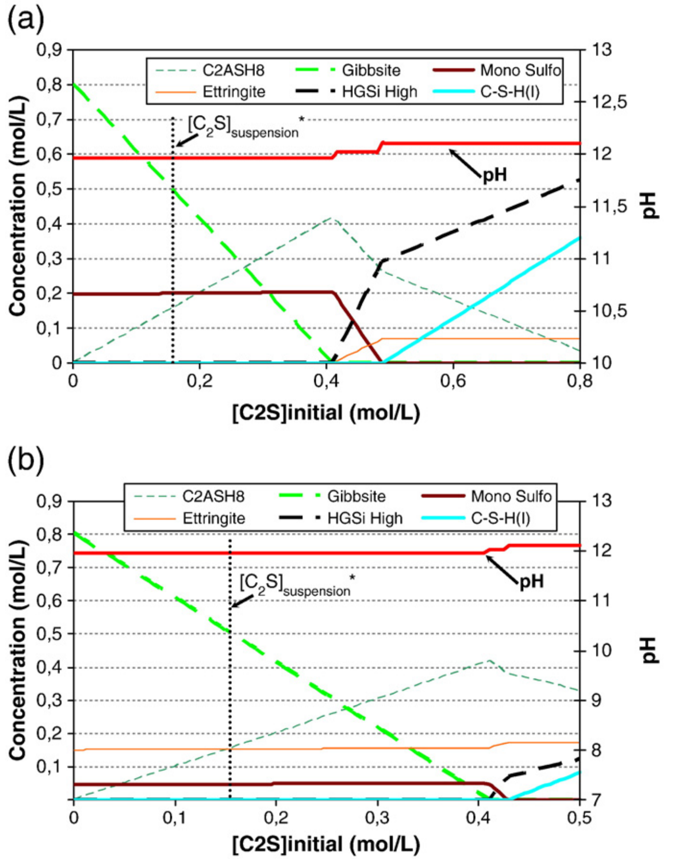

Fig. 7. Thermodynamic modelling. (a) Simulation of the addition of belite to a mixture of $C_3A.C\ S.H_{12}$, AH_3 and $C_3A.C\ S.H_{32}$ (traces) produced by hydrating ye'elimite (0.2 mol/L). (b) Simulation of the addition of belite to a mixture of $C_3A.C\ \bar{S}.H_{12}$, AH_3 and $C_3A.3C\ \bar{S}.H_{32}$ produced by hydrating ye'elimite (0.2 mol/L) and gypsum (0.1 mol/L).

3.2. Hydration of cement pastes submitted to a thermal cycle

3.2.1. Gypsum-free cement

During the first 5 h, hydration of paste $CE0_t$ undergoing the thermal cycle proceeded in the same way as that of CE0, yielding very small amounts of ettringite and amorphous aluminum hydroxide (Figs. 10 and 11). This was explained by the small temperature gap between the two materials until 5 h (maximum of 5 °C at 5 h).

However, after one day, paste CE0t had a much higher hydration degree: ye'elimite was almost fully depleted (residual of 3% instead of 17% for CE0). The difference was reduced, but still noticeable after 7 days (residual ye'elimite of 2% instead of 9% for CE0). However, the bound water content was not increased by the thermal cycle. This could be explained by the lower water content of the precipitated hydrates. After 7 days, the main products were AH_3, $C_3A.C\ \bar{S}.H_{12}$, C_2ASH_8 and siliceous hydrogarnet, while CE0 contained significant amounts of $C_3A.3C\ \bar{S}.H_{32}$, CAH_{10}, AH_3 and a mix of AFm phases ($C_3A.C\ \bar{S}.H_{12}$, $C_3A.1/2C\ \bar{C}.1/2CH.H_{11}$ and $C_3A.1/2C\ \bar{S}.1/2CH.H_{12}$). The thermal cycle destabilized ettringite formed during the early stage of hydration. It is well known that increasing the temperature above 50 °C causes the decomposition of ettringite into calcium monosulphoaluminate hydrate in a sulphate-poor medium [27]. Hemicarbonate is also predicted to be unstable above 50 °C [38]. The thermal excursion thus promoted hydration of ye'elimite into a mixture of AH_3 and $C_3A.C\ \bar{S}.H_{12}$ according to (Eq. (2)). Moreover, it did not allow CAH_{10} to be formed as a transitory phase. Hydration of belite was accelerated and silicate phases were detected from one day (siliceous hydrogarnet after one day, combined with strätlingite after 7 days).

From 7 days to one year, only minor mineralogical changes were detected. Ye'elimite had already almost totally reacted and the bound water content remained constant. The main evolution was due to the advanced hydration of belite: increased amounts of strätlingite were precipitated, which consumed some AH_3, as shown by thermogravimetry. According to the thermodynamic simulation from Fig. 7, siliceous hydrogarnet can only form after total depletion of AH_3. These two phases were simultaneously observed in one-year old cement paste CE0t. This may indicate some heterogeneities in the material, with local equilibria (for instance $C_3A.C\ \bar{S}.H_{12} + AH_3 +$ traces of $C_3A.3C\ \bar{S}.H_{32}$ in the vicinity of ye'elimite, and $C_2ASH_8 +$ siliceous hydrogarnet + C–(A)–S–H + $C_3A.C\ \bar{S}.H_{12}$ or $C_3A.3C\ \bar{S}.H_{32}$, or $C_2ASH_8 + C_3A.C\ \bar{S}.H_{12} + AH_3 +$ C–(A)–S–H in the vicinity of belite), and/or the precipitation of hydrogarnet with a lower silica content not taken into account in the calculation.

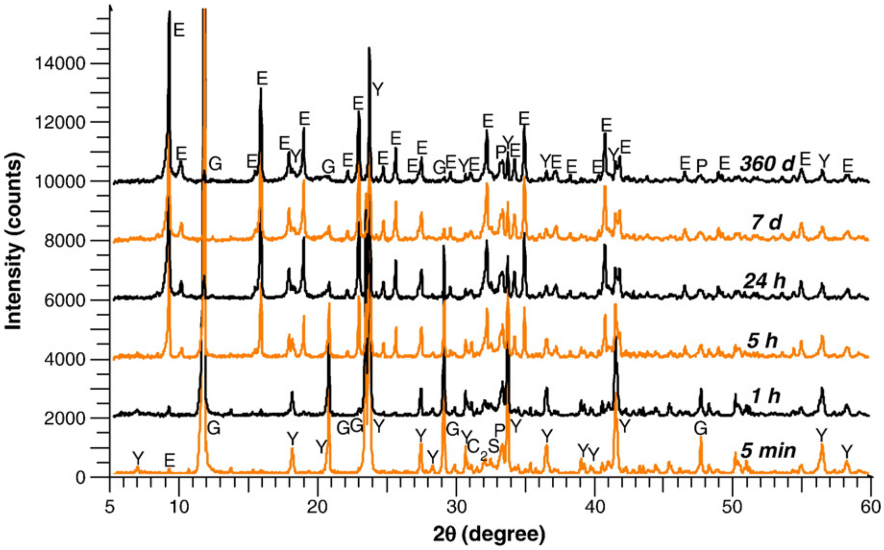

Fig. 8. X-ray diffraction analysis of cement paste CE2 cured at 20 °C after 5 min, 1 h, 5 h, 24 h, 7 d, and one year of hydration (Y = ye'elimite, E = ettringite, G = gypsum, P = $CaO.TiO_2$).

3.2.2. Gypsum-containing cements

Applying a thermal cycle accelerated the early stages of hydration. For initial gypsum contents of 10, 20 or 35%, the induction period was reduced by 1 h as compared with samples cured at 20 °C, and dissolution of ye'elimite was accelerated: the fractions of ye'elimite depleted after 5 h, 24 h and 7 d always exceeded those obtained under curing at 20 °C (Table 4). The influence of the initial gypsum content on the rate of hydration was similar to that already observed for the samples cured at 20 °C. Increasing the gypsum content from 0 to 10% strongly reduced the delay before the acceleration period (Table 5). This latter then increased slightly for higher gypsum dosages. From 5 to 35%, increasing the gypsum content also reduced the total cumulated heat of hydration. It was checked, by performing complementary experiments in which gypsum was replaced by the same weight of sand, that this reduction could not be explained by the sole dilution of clinker. The heat output mainly resulted from the dissolution of ye'elimite (the dissolution enthalpy of gypsum being +0.75 kJ/mol), which means that the gypsum-rich binders had a lower hydration degree at the end of the acceleration period. This was confirmed by their higher ye'elimite content, as assessed from XRD patterns.

The thermal cycle also modified the proportion of AFt versus AFm phases in pastes CE1t and CE2t. AFm phases (mainly calcium monosulphoaluminate hydrate, and traces of mixed AFm phases such as $C_3A.1/2C\ \overline{S}.1/2CH.H_{12}$) were detected from 5 h (instead of 24 h in the samples cured at 20 °C), and were present in larger amounts at 24 h and 7 d (Fig. 12). On the contrary, pastes CE3.5 and CE3.5 t exhibited the same hydrates assemblage. The increased precipitation of AFm phases in the pastes with low gypsum contents submitted to the thermal cycle resulted from two factors. (i) They had higher hydration degrees (ettringite forms during the early stages of reaction with water, while further hydration yields AFm phases). (ii) Increasing the temperature improved the stability of calcium monosulphoaluminate hydrate against ettringite which required more gypsum to be stabilized. The mineralogical changes caused by the thermal cycle thus decreased when the initial gypsum content of the cement increased.

Beyond 24 h, hydration progressed very slowly, yielding aluminum hydroxide and ettringite (paste CE3.5 t) or calcium monosuloaluminate hydrate (paste CE1t and CE2t). In these two latter samples, mixed AFm phases disappeared. After one year, 8 to 10% of ye'elimite were still unreacted.

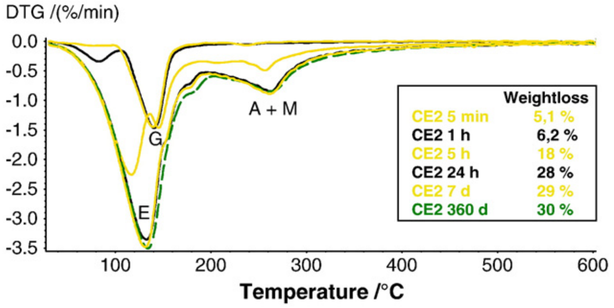

Fig. 9. Thermogravimetric analysis of cement paste CE2 cured at 20 °C after 5 min, 1 h, 5 h, 24 h, 7 d, and one year of hydration (E = ettringite, M = calcium monosulphoaluminate hydrate, A = aluminum hydroxide, G = gypsum).

3.3. Properties of hardened mortars

3.3.1. Compressive strength

The compressive strength of mortars cured in sealed bag at ambient temperature (21 ± 2 °C) was measured over one year (Fig. 13). Initially, during their first week, the specimens were either kept at 20 °C or submitted to a thermal cycle. Whatever the history of the samples, the compressive strength increased very rapidly. It already reached 79 ± 9% of the one-year strength after 1 day, and 87 ± 6% after 7 days. This result was consistent with the rapid hydration of the investigated binders, which only presented small mineralogical evolutions beyond 7 d. Among the different samples, the mortars containing gypsum and

Table 4
Influence of the gypsum content on the amounts of depleted ye'elimite (XRD) and bound water (TGA) as a function of time.

	Depleted ye'elimite (g/100 g of cement)				Bound water (%) weight loss between 30 and 600 °C			
	5 h	24 h	7 d	Max[a]	5 h	24 h	7 d	Max[b]
CE0	≤1	57	63	68.5	2.9	26	30	35.5
CE0t	≤1	67	67	68.5	2.1	26	29	35.5
CE1	24	42	47	61.6	18	25	27	36.9
CE1t	46	49	51	61.6	25	26	26	36.9
CE2	22	39	41	54.8	18	28	29	38.2
CE2t	43	46	47	54.8	28	26	30	38.2
CE3.5	18	36	37	44.5	20	30	31	40.2
CE3.5 t	39	40	41	44.5	31	32	33	40.2

[a] Initial ye'elimite content in 100 g of cement.

[b] Maximum weight loss assuming total consumption of water (provided by gypsum and mixing solution).

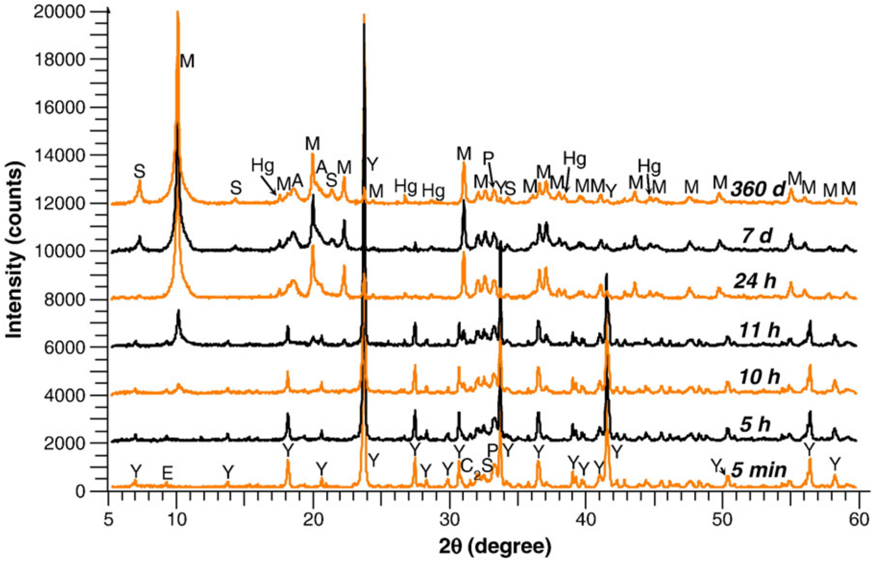

Fig. 10. X-ray diffraction analysis of cement paste CE0t submitted to a thermal cycle after 5 min, 5 h, 10 h, 11 h, 24 h, 7 d, and one year of hydration (Y = ye'elimite, S = strätlingite, E = ettringite, M = calcium monosulphoaluminate hydrate, A = aluminum hydroxide, Hg = siliceous hydrogarnet, P = CaO.TiO$_2$).

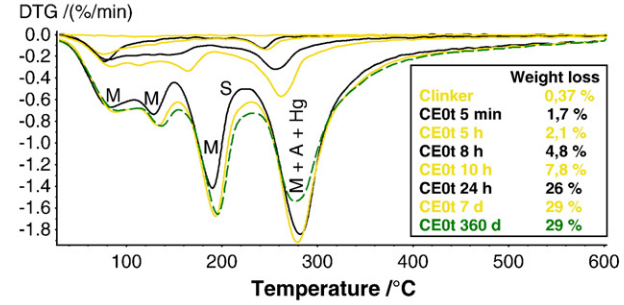

Fig. 11. Thermogravimetry analysis of clinker and cement paste CE0t submitted to a thermal cycle after 5 min, 5 h, 8 h, 10 h, 24 h, 7 d, and one year of hydration (S = strätlingite, M = calcium monosulphoaluminate hydrate, A = aluminum hydroxide, Hg = siliceous hydrogarnet).

submitted to the thermal cycle exhibited the fastest hardening. As previously shown, the early stages of hydration were accelerated under these conditions.

The one-year compressive strength of the mortars depended on their initial gypsum content. Whatever the curing conditions, the strength went through a minimum at 10% gypsum, and increased for higher contents. With 35% gypsum, the strength went on increasing after 28 d, which was consistent with the results of Peysson [18] showing that the strength reached its maximum only when gypsum was totally depleted.

When cured at 20 °C, the mortars prepared with a gypsum-free cement exhibited the highest strength. However, this strength was

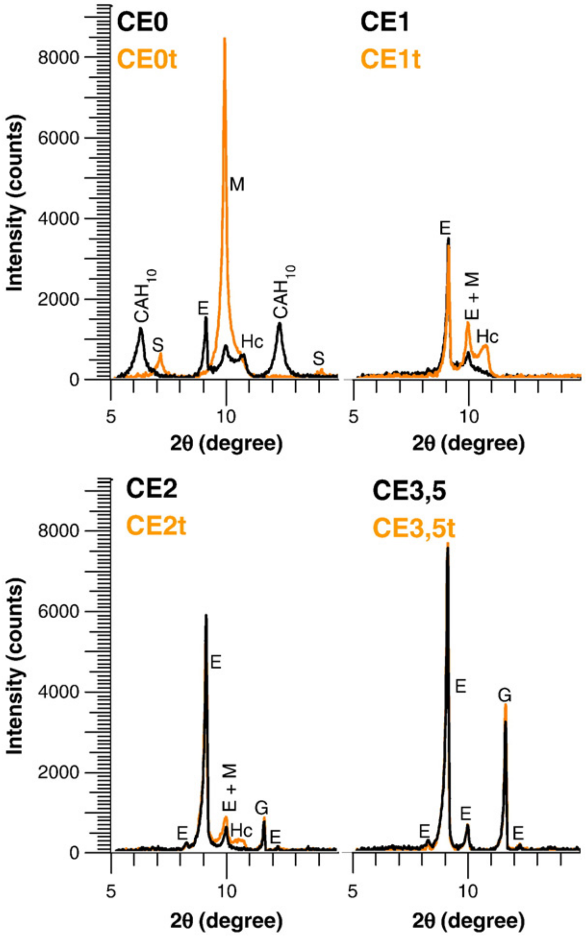

Fig. 12. Influence of the initial gypsum content and curing conditions on the XRD patterns of 7 d-old samples (S = strätlingite, E = ettringite, Hc = calcium hemicarboaluminate hydrate, M = calcium monosulphoaluminate hydrate, G = gypsum).

Table 5
Influence of the initial gypsum content on the thermal evolution of mortars under semi-adiabatic conditions (T_{max} = maximum temperature achieved during hydration, Q_{max} = total cumulated heat of hydration/gram of cement, t_{Tmax} = time for maximum temperature, t_{infl} = time for maximum heat flux, t_{acc} = time corresponding to the beginning of the acceleration period).

	T_{max} (°C)	Q_{max} (J/g)	t_{Tmax} (h)	t_{infl} (h)	t_{acc} (h)
ME0t	82.8	453	13.8	11.8	9.5
ME0.1t	83.6	446	11.8	10.3	7.6
ME0.2t	82.7	450	9.5	8.0	5.3
ME0.3t	82.7	455	6.8	5.3	3.2
ME0.5t	82.9	441	5.3	3.8	2.3
ME0.7t	79.0	408	4.7	3.0	1.7
ME1t	75.1	365	3.5	2.0	1.3
ME2t	74.9	361	3.5	2.5	1.8
ME3.5t	73.1	361	4.0	2.8	2.1

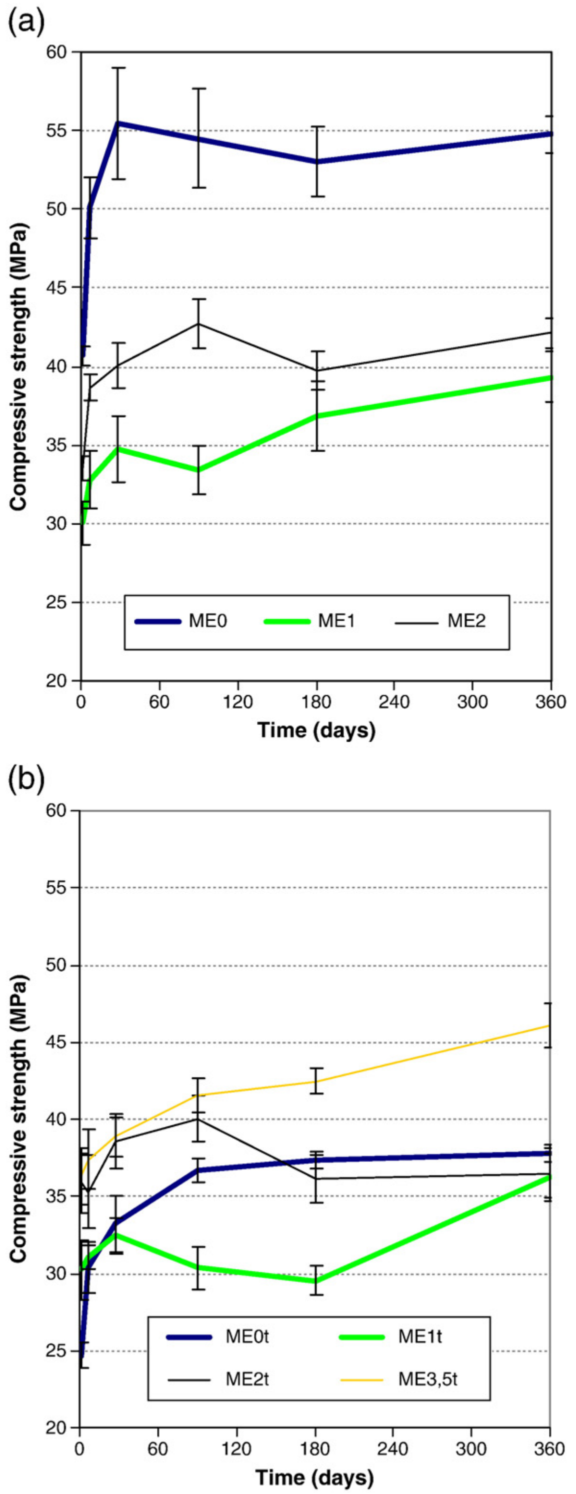

Fig. 13. Influence of the initial gypsum content and thermal cycle on the compressive strength of 4×4×16 cm mortar specimens cured in sealed bag; (a) mortars without thermal cycle; (b) mortars with thermal cycle.

strongly reduced (by 35±4%) by the thermal cycle at early age. Blending the clinker with gypsum allowed reducing the strength loss to 8–10%. This could be explained as follows: increasing the gypsum content stabilized ettringite at high temperature and thus limited the subsequent mineralogical changes induced by the thermal cycle.

The compressive strength of the samples was not simply correlated to their total water porosity, as shown in Table 6. The mortars submitted to the thermal cycle were usually less porous, but also less resistant.

Table 6
Compressive strength and total water porosity of one-year old mortar samples (4×4×16 cm specimens) depending on their thermal history at early age and curing conditions (water or sealed bag).

Sample	Wet curing		Curing in sealed bag	
	Total porosity (%)	Compressive strength (MPa)	Total porosity (%)	Compressive strength (MPa)
ME0	15.2±0.4	46.6	18.1±0.6	55.0
ME0t	16.9±0.5	21.0	16.2±0.1	38.0
ME2	19.4±0.6	42.1	22.7±0.4	43.0
ME2t	14.8±0.5	30.0	14.1±0.1	37.0

Complementary investigations on the pore distribution in each sample would be required to explain these results. Preliminary attempts using mercury intrusion porosimetry were not successful because the high vacuum required by the preparation of the samples in this method damaged ettringite.

3.3.2. Volume stability under water

The length change and mass gain of the mortars cured under water are summarized in Fig. 14. The samples were immerged after 7 days and exhibited a rapid mass increase which may have had different origins:

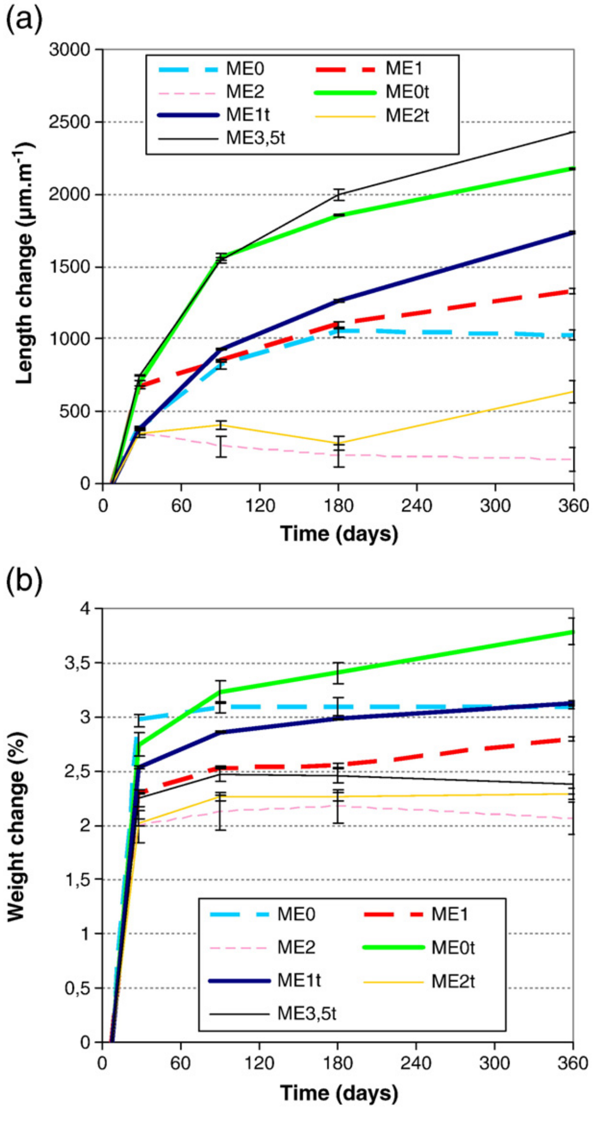

Fig. 14. Influence of the initial gypsum content and thermal cycle on the length change and mass gain of 4×4×16 cm mortar specimens cured under water.

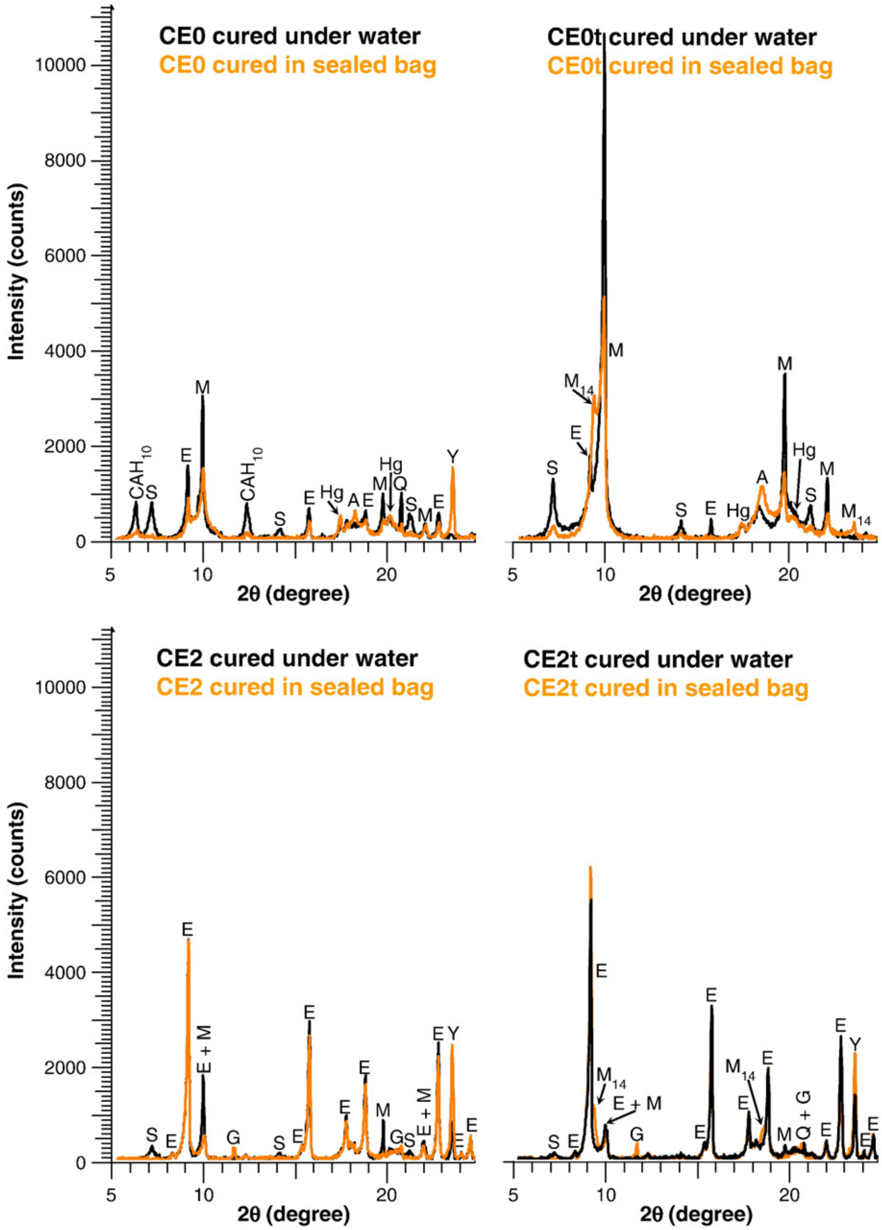

Fig. 15. X-ray diffraction patterns of one-year old mortars cured under water or in sealed bag (S = strätlingite, E = ettringite, Y = ye'elimite, M = $C_3A.C\overline{S}.H_{12}$, M_{14} = $C_3A.C\overline{S}.H_{14}$, A = aluminum hydroxide, Hg = siliceous hydrogarnet, Q = quartz).

water uptake due to capillary suction to compensate for water depleted by hydration, water penetration due to osmosis (the interstitial solution being more concentrated than the curing solution), and continuation of hydration. The mass gain was rapid during the first 28 days and, excepting sample ME0t, tended to stabilize after 90 d. It was slightly higher (by 7 to 12%) for the mortars submitted to the thermal cycle, which could result from their advanced hydration at 7 d as compared with the same samples cured at 20 °C. The water uptake also increased when the initial gypsum content decreased. The corresponding samples at 7 d (ME0, ME1, ME0t, ME1t) contained reduced amounts of ettringite and had higher hydration degrees.

Swelling under water was also highly dependent on the initial gypsum content of the binder. Mortars ME2 and ME2t (20% gypsum) exhibited the smallest length change (less than 1000 μm/m after one year). The thermal excursion at early age promoted expansion of gypsum-free mortars only: the length change of sample ME0t was almost twice that of sample ME0. Cracking was however never observed. It is well known that CSA cements with high gypsum contents can be expansive [9,39], which is explained by the prolonged precipitation of ettringite once hardening has occurred [20]. Expansion of materials with low gypsum contents has been reported by Alaoui et al. [21], but is still not well understood. One-year old mortars were thus characterized by X-ray diffraction after their curing under water, and their mineralogy was compared to similar samples cured in sealed bag (Fig. 15). Gypsum-free mortars exhibited significant mineralogical changes: under wet curing, ye'elimite was fully depleted in both samples ME0 and ME0t. Sample ME0 contained higher amounts of calcium monosulphoaluminate hydrate and ettringite, as well as CAH_{10} and strätlingite which were not formed in sealed bag. As for sample ME0t, the wet curing caused the precipitation of a small amount of ettringite, and strongly increased the precipitated amounts of calcium monosulphoaluminate hydrate ($C_3A.C\overline{S}.H_{12}$) and strätlingite, while

$C_3A.C\,\overline{S}.H_{14}$ was not observed anymore. The mineralogies of samples ME2 and ME2t were less dependent on the curing conditions. In particular, their ettringite contents remained almost constant. The wet curing led to higher hydration degrees, ye'elimite and gypsum being respectively partly and fully depleted, and increased the amount of calcium monosulphoaluminate hydrate. Strätlingite was also detected in sample ME2. The stronger expansion of the gypsum-free mortars may thus result from their mineralogical assemblage which is far from thermodynamical equilibrium before the wet curing, and which thus undergoes significant evolutions with possible volume increase, such as retarded ettringite formation due to a restart of hydration and/or to a reprecipitation of primary ettringite decomposed by the thermal cycle (sample ME0t), and precipitation of strätlingite from C_2S and AH_3 ($\Delta V/V = +3.5\%$).

4. Conclusion

The purpose of this article was to investigate the consequences of a thermal cycle at early age on the hydration of pastes and mortars prepared with CSA cements containing variable gypsum contents (from 0 to 35 wt.%). In a general way, at ambient temperature, hydration progressed very slowly during the first 1 to 10 h, yielding only small amounts of ettringite and amorphous aluminum hydroxide. Then, a strong acceleration occurred: mayenite, ye'elimite and gypsum (if present) were rapidly depleted and a mixture mainly composed of aluminum hydroxide, ettringite and/or AFm phases (calcium monosulphoaluminate hydrate and possibly mixed AFm phases such as $C_3A.1/2C\,\overline{C}.1/2CH.H_{11}$ or $C_3A.1/2C\,\overline{S}.1/2CH.H_{12}$) was precipitated. Hydration then slowed down. After one day, the hydration degree was high: 69 to 90% of ye'elimite were already consumed, and the compressive strength of mortars reached 70 to 90% of its value at one year. Hydration of belite occurred later and mainly produced strätlingite. Formation of C–S–H could not be evidenced. Only small mineralogical evolutions were noticed beyond 7 d.

Applying a thermal cycle, which lasted one week and reproduced the temperature rise (up to 85 °C) and fall occurring in a massive block, accelerated the early stages of hydration. Significant mineralogical changes occurred in the absence of gypsum: CAH_{10} and mixed AFm phases were no longer observed. Instead, calcium monosulphoaluminate hydrate coexisted with ettringite, aluminum hydroxide and siliceous phases (strätlingite and siliceous hydrogarnet). When the CSA clinker was blended with low gypsum contents ($\leq 20\%$), precipitation of AFm phases was increased. The thermal excursion degraded the properties of the gypsum-free hardened materials: the compressive strength of specimens cured in sealed bag was reduced by 35% after one year, and their expansion under water was almost doubled. This strong dimensional instability resulted from the mineralogical evolutions towards a more stable phase assemblage.

Blending the CSA clinker with gypsum had several positive effects. Increasing the gypsum content improved the stability of ettringite at high temperature, and the influence of the thermal cycle was limited when the initial gypsum content exceeded 10%. The induction period was reduced from a dosage of 1% and the hydration rate in the acceleration period increased. However, hydration was less advanced at 7 d when the gypsum content exceeded 5%. The compressive strength also went through a minimum for a dosage of 10%, but was significantly improved with 20% gypsum. Such a dosage also limited the swelling of specimens cured under water and was thus a good compromise. By contrast, gypsum-free cements should be used very cautiously for practical application.

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