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Hydration of calcium sulfoaluminate cement by a $ZnCl_2$ solution: Investigation at early age

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ABSTRACT

Hydration of calcium sulfoaluminate cement at early age was investigated as a function of the gypsum content of the binder, the thermal history of the material, and the $ZnCl_2$ concentration in the mixing solution. Early hydration was strongly accelerated by the presence of gypsum, but lower percentages of reaction were reached after 24 h. The slowing down effect induced by $ZnCl_2$, even at a concentration as high as 0.5 mol/L, was moderated compared to OPC but had a greater intensity in the absence of gypsum. Unlike what would have been expected for Portland cement, it was shown that the delay of a gypsum-free calcium sulfoaluminate cement resulted from the strong retardation caused by chloride anions, which was partly compensated by the accelerating effect of Zn^{2+} cations. The mineralogical observations revealed the precipitation of chloro–AFm phases such as Friedel's and Kuzel's salts, but no crystallized zinc-containing phases could be identified by XRD. The thermal history of the samples proved to be a key parameter. Applying a thermal cycle which reproduced the temperature rise and decrease occurring in a massive mortar block accelerated the rate of hydration and mainly modified the proportion of AFt versus AFm hydrates, especially when the binder had a gypsum content below 20%.

1. Introduction

Calcium sulfoaluminate (CSA) cements have been manufactured and successfully used on an industrial scale in China for about 20 years [1]. Furthermore, they arouse the interest of western countries since they may be regarded as low-energy cements: their production requires less energy than Portland cement, and the CO_2 emissions are reduced [2,3]. Several factors are involved [4,5]. *(i)* The lower lime content of the raw meal reduces the energy demand for limestone decarbonation as well as the CO_2 emission. *(ii)* The clinker is prepared by burning mixtures of limestone, bauxite and gypsum of appropriate compositions, ultimately to moderate temperatures (1300–1350 °C, which is 100 to 150 °C lower than that required for OPC). *(iii)* The fired CSA clinker is easier to grind. *(iv)* Industrial wastes or by-products such as fly ash, blast-furnace slag, "red mud" (a largely unwanted product of the Bayer process for alumina purification) or phosphogypsum can also be used as raw components which provide additional environmental advantages [6–9].

CSA cements can have highly variable compositions but all of them contain yeelimite, also called Klein's compound or tetracalcium trialuminate sulphate, in their clinker [10–13]. This article is focussed on a sulfoaluminate belite cement, the clinker of which is mainly composed of yeelimite ($C_4A_3\bar{S}$), belite (C_2S) and mayenite ($C_{12}A_7$) [14]. A wide range of gypsum contents can be ground with CSA clinker to produce different CSA cements. A series of cements, ranging from rapid-hardening to shrinkage-compensating, and eventually to self-stressing, can be produced by increasing the proportion of gypsum (typically from 10 to 25%) [3]. CSA cement pastes harden through the formation of an initial ettringite network, and its subsequent infilling by mixtures of ettringite, calcium monosulfoaluminate hydrate, C–S–H, alumina and ferrite gels [15,16]. Strätlingite has also been observed by Andac et Glasser after 7 days of hydration of a CSA clinker [14]. A possible hydration scheme has been proposed, but it does not include strätlingite as a hydration product [17]. The contents of ettringite and calcium monosulfoaluminate hydrate are very sensitive to the amount of added sulphate: the former dominates in a gypsum-rich environment, whereas the latter tends to increase in a gypsum-deficient system. Water requirement for rheology is broadly similar for OPC and CSA cement [18]. However, while a W/C ratio of 0.4 is theoretically adequate to ensure complete hydration of OPC, this ratio might exceed 0.55 for CSA clinker blended with sufficient gypsum. It has been shown

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that the chemical water demand increases with the gypsum content up to a maximum which corresponds to the maximum of ettringite precipitation [3]. If properly formulated, CSA cements give high early strength: Pera *and al.* [19] reported the development of a concrete with 40 MPa compressive strength after 6 h, and 55 MPa strength after 1 day. Good durability is reported, especially in sulphate environments [20,21], and expansion can be controlled by adjusting the amount of gypsum added [22]. Recently, CSA cements have been used to stabilize wastes containing heavy metal salts [23–26]: ettringite and calcium monosulfoaluminate hydrate, the two main phases formed, can accommodate substitutions [27–31]: Ca^{2+}, Al^{3+}, SO_4^{2-} and OH^- are suitable to be replaced by many cations or oxyanions of heavy metals, such as Cd^{2+}, Cr^{3+} or CrO_4^{2-}. In this article, the focus is placed on the stabilization of zinc chloride, which is present in large amounts in ashes resulting from the incineration of technological wastes including neoprene and polyvinylchloride. According to previous studies, Zn^{2+}/Ca^{2+} and $2Cl^-/SO_4^{2-}$ substitutions in the structure of AFt and AFm might be involved [32]. During leaching of Zn-containing cement pastes by acidic solutions, it was observed that the zinc release and the ettringite destabilization occurred simultaneously [33]. In other studies [25,26], CSA cement pastes were prepared with $ZnCl_2$, $ZnSO_4$ $7H_2O$ and $Zn(NO_3)_2$ solutions. Hydrated samples were ground and mixed with de-ionized water from 24 to 72 h. Analysis of the solutions did not show the presence of zinc. The authors thus concluded that CSA hydrated cements have a good capacity to retain zinc. At low Zn(II) concentrations (<1000 µmol/l), sorption of Zn(II) to C–S–H has also been observed [34]. Furthermore, the $2Cl^-/SO_4^{2-}$ substitution in AFm and AFt phases is well known. A chloro–ettringite was precipitated at low temperature (<20 °C) and studied by Schwiete *et al.* [35]. A chloro–AFm termed Friedel's salt ($3CaO–Al_2O_3–CaCl_2–10H_2O$) and a mixed compound containing chloride and sulphate referred as Kuzel's salt ($3CaO–Al_2O_3–0.5CaCl_2–0.5CaSO4–10H_2O$) were also synthesized and described [29,36]. Little is known however on the influence of $ZnCl_2$ on the hydration rate of a CSA cement.

The aim of this work was thus to gain understanding in the hydration at early age of CSA cement by pure water or a zinc chloride solution. Particular attention was paid to the influence of the gypsum content in the binder and to the thermal history of the cementitious materials.

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 area = 1.3 m^2/g) with the appropriate amount of analytical grade gypsum (from 0 to 35% by mass of cement; $d_{10}=5.4$ µm, $d_{50}=19.6$ µm, $d_{90}=50.3$ µm, BET specific area = 0.4 m^2/g) during 15 min. The higher specific area of CSA clinker resulted from its higher fraction of fine particles (the first decile of the distribution was twice as low as that of gypsum). Both cement pastes and mortars were made with the same water to cement (W/C) weight ratio of 0.55. A blend of two siliceous sands (0.1–1.2 mm) was used with a sand to cement (S/C) weight ratio of 3 to optimize the workability and limit the heat release of fresh mortars during hydration.

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

Minerals (% weight)							
$C_4A_3\bar{S}$	C_2S	$C_{12}A_7$	CT	Periclase	$C\bar{S}$	Quartz	Others[a]
68.5	15.9	9.5	2.9	1.5	0.5	0.5	2.4

[a] Include 1.2% of iron oxide.

The mixing solution was prepared by dissolving the appropriate amount of analytical grade salt ($ZnCl_2$ 0, 0.01 or 0.5 mol/L, $ZnSO_4$, $7H_2O$ 0 or 0.5 mol/L, $Zn(NO_3)_2$, $6H_2O$ 0 or 0.5 mol/L, $CaCl_2$, $2H_2O$ 0 or 0.5 mol/L, $Ca(NO_3)_2$, $4H_2O$ 0 or 0.5 mol/L) into distilled water. Water brought by the salts was taken into account for the calculation of the W/C ratio. The solution (with a temperature comprised between 19 and 22 °C) was introduced in a standardized laboratory mixer (European standard EN 196-1) with the cement, pre-mixed with sands for mortars preparation. Mixing was performed at low speed for 3 min and at high speed for 2 min. Cement pastes were cast into polystyrene airtight boxes (7 ml of paste per box), and cured for 7 days at 20 °C or submitted to a thermal cycle in an oven (Memmert UFP 500) for 7 days. Mortars were used for semi-adiabatic calorimetry investigation.

2.2. Thermal cycle

Thermal cycles were temperature profiles applied on pastes in a programmable oven. The objective was to reproduce the temperature rise and decrease which may occur in a massive mortar block (such as a 200 L drum containing a stabilized waste using a mortar formulation with typical S/C and W/C ratios of respectively 3 and 0.55) during hydration. This temperature evolution was estimated by recording, for every investigated compositions of cement and mixing solution, the temperature of 800 ml mortar samples placed in semi-adiabatic Langavant calorimeters as a function of time. Temperature profiles were then defined in each case by interpolating the recording temperature evolution as best as possible using 40 segments. Some corrections were brought when required to keep the same temperature evolution in the heart of mortars and pastes. Fig. 1 gives an example of the differences between the thermal evolutions of two cement pastes (10% gypsum in the binder, mixing with pure water) respectively cured at 20 °C and submitted to the thermal cycle recorded on the corresponding mortar with the same binder and mixing solution compositions.

2.3. Analytical 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 calibrated calorimeter in order to determine the quantity of heat emitted in accordance with the development of temperature.

Inner temperature of pastes and mortars was measured with waterproof penetration probes (TC type K) and recorded with a Testo 735-2 thermometer.

Hydration was stopped after fixed periods of time (from 5 min to 7 days) by successively immersing the crushed pastes into isopropanol

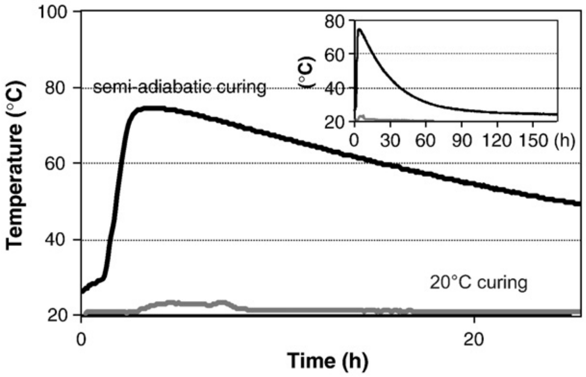

Fig. 1. Influence of the curing conditions on temperature evolution in cement pastes prepared with 10% gypsum and pure water.

and drying them into a controlled humidity chamber (with a relative humidity of 20% at 22 ± 2 °C).

Crystallized phases were identified using 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 less than 100 µm. The acquisition range was from 5° to 60° 2θ at 0.02° 2θ steps with integration at the rate of 50 s per step. Evolution of the amounts of reactants and products with time was qualitatively assessed from XRD patterns by measuring the areas of characteristic peaks using the EVA analysis software (© 2005 Bruker AXS).

3. Results and Discussion

3.1. Hydration of CSA cement by pure water

3.1.1. Influence of the gypsum content in the binder

The cumulated heat evolution versus hydration time is shown in Fig. 2 for mortars prepared with increasing amounts of gypsum (from 0 to 35%). The heat output which mainly resulted from cement dissolution (yeelimite giving the major contribution) decreased when the gypsum content increased whereas the induction period was reduced.

- From 0 to 3% of gypsum, the total cumulated heat did not change significantly but the induction period and the times for maximum heat fluxes (inflexion point of the curves in Fig. 3) were strongly reduced.
- From 3 to 7%, the delays before the acceleration period were approximately the same; however, the times for maximum heat fluxes decreased when the gypsum content increased, but more slightly. The total cumulated heat distinctly decreased.
- From 7 to 10%, the induction period, the time for maximum heat flux and the total cumulated heat reached a minimum.

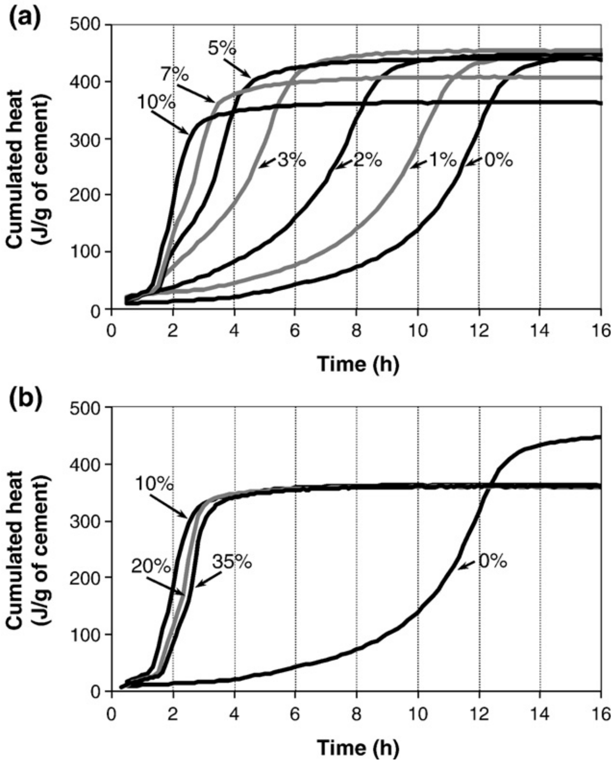

Fig. 2. Influence of the gypsum content on the heat produced by CSA mortars during hydration by pure water (initial gypsum content in the binder: (a) 0–10%, (b) 10–35%).

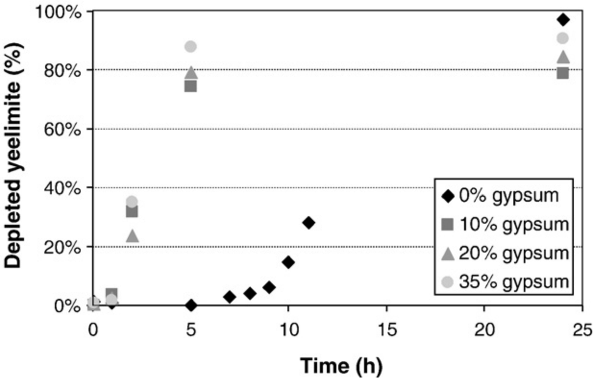

Fig. 3. Influence of the initial gypsum content on the yeelimite consumption over the first 24 h.

- From 10 to 35%, increasing the gypsum content resulted in a slight increase in the induction period, whereas the total cumulated heat did not vary anymore.

The higher cumulated heat produced without or with a low gypsum content may have resulted from a higher hydration degree. Indeed, the mineralogical changes of CSA cement pastes were investigated over the first 24 h by XRD (Fig. 3). The samples followed the same thermal evolution than the corresponding mortars used in the calorimetry experiments. Yeelimite started to react much later in the absence of gypsum than in its presence, which was in agreement with the longer induction period observed by calorimetry on mortar. However, yeelimite was almost totally depleted after 24 h while 10 to 20% were still unreacted in the presence of gypsum. In that case, it was checked that hydration was not stopped due to a lack of water. If all the mixing water had been used up for hydration, the fractions of bound water should have respectively reached 36.9%, 38.2% and 40.2% for gypsum contents of 10, 20 and 30% (desiccation of the samples was checked to be negligible during the thermal cycle). The experimental fractions of bound water, estimated using TGA from the weight loss of the samples between 30 °C and 600 °C, were always lower (respectively 26%, 30% and 33% for gypsum contents of 10, 20 and 30%), which means that free water was still present. Gypsum-rich binders had thus a lower hydration degree at the end of the acceleration period.

Gypsum dissolution always occurred before that of yeelimite and was almost complete after 5 h for initial contents of 10 or 20% in the blend (Table 2).

The products formed at 24 h were mainly ettringite, calcium monosulfoaluminate hydrate and AH_3, which was poorly crystallized (Fig. 4) and better evidenced by thermogravimetry analysis from its weight loss between 240 and 280 °C. Increasing the gypsum content promoted the precipitation of ettringite against calcium monosulfoaluminate hydrate. This latter phase was not observed anymore when the binder contained 35% gypsum.

3.1.2. Influence of the thermal cycle

The mineralogies of cement pastes cured at 20 °C or undergoing a thermal cycle were compared. Table 3 shows that, as expected, the

Table 2
Influence of the initial gypsum content on the fractions of depleted gypsum and yeelimite (% based on relative peak areas) over the 5 first hours of hydration.

	10% gypsum		20% gypsum		35% gypsum	
	gypsum	yeelimite	gypsum	yeelimite	gypsum	yeelimite
5 min	0	0	0	0	0	0
1 h	34	4	32	3	34	2
2 h	100	32	52	24	44	35
5 h	100	74	97	79	82	88

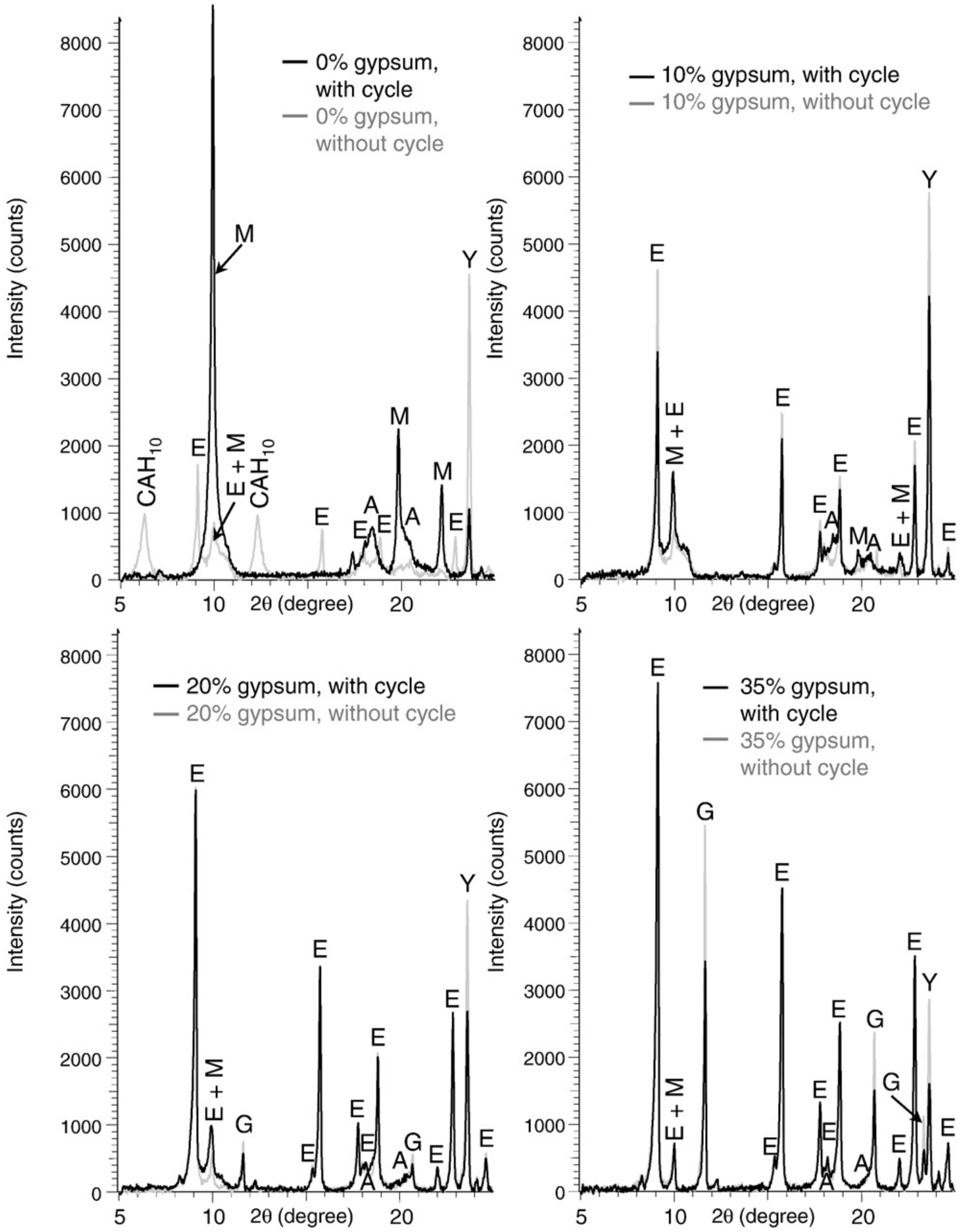

Fig. 4. XRD patterns of 24 h-old cement pastes prepared with pure water : influences of initial gypsum content and curing conditions (conservation at 20 °C or application of a thermal cycle); E = ettringite, M = calcium monosulfoaluminate hydrate, A = AH_3, Y = yeelimite.

thermal cycle promoted the dissolution of yeelimite: in most cases the fraction of depleted yeelimite after 24 h exceeded that obtained after 7 days under curing at 20 °C. Some changes in the hydration products were observed at low gypsum contents (≤20%, Fig. 4). When curing was performed at 20 °C, CAH_{10} precipitated in gypsum-free samples, which could seem quite surprising at first sight since this phase is usually known to be mainly formed at low temperature (below 15 °C) during the hydration of calcium aluminate cements. However, it has also been reported to precipitate at higher temperature (from 15 to 35 °C), together with C_2AH_8 and AH_3 [37]. According to Scrivener, CAH_{10} would even be the first phase to be formed at 40 °C [38]. Moreover, Guirado *et al.* [39] reported that its conversion could take several years at ambient temperature, and Jensen *et al.* [40] observed that CAH_{10}, when heated at 100% relative humidity, was fully depleted above 88 °C only. Nevertheless CAH_{10} is a metastable phase at room temperature and is expected to be transformed at later ages. Moreover the addition of gypsum in the binder, and/or the application of the thermal cycle, did not allow CAH_{10} to be formed as a transitory phase.

Table 3
Influence of the thermal cycle on the fraction of depleted yeelimite in cement pastes over a 7 day-period.

Initial gypsum content	0% gypsum	10% gypsum	20% gypsum	35% gypsum
After 1 day, with cycle	97	79	85	91
After 1 day, without cycle	83	69	71	81
After 7 days, with cycle	98	79	87	91
After 7 days, without cycle	91	76	76	83

Ettringite always precipitated, even without any gypsum addition to the binder. Calcium monosulfoaluminate hydrate was only observed at low gypsum content (0 and 10%).

With a thermal cycle, calcium monosulfoaluminate hydrate was favoured against ettringite which had a smaller stability domain when the temperature increased and thus required more gypsum to be

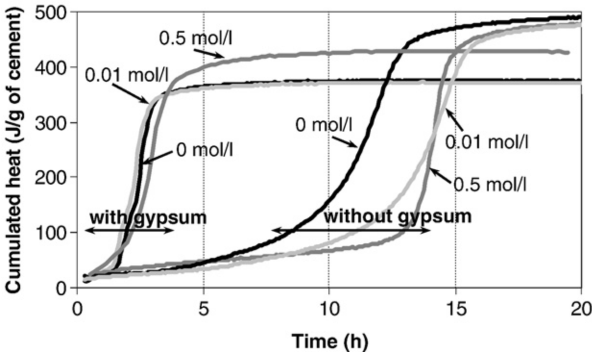

Fig. 5. Influence of the $ZnCl_2$ concentration in the mixing solution on the cumulated heat produced by mortars during hydration.

stabilized [41] (Fig. 4). As a consequence this effect decreased when the gypsum content in the binder increased, and, for a 35% content, the same XRD patterns were observed whatever the curing conditions: ettringite remained stable despite the temperature increase.

3.2. Hydration of CSA cement by a $ZnCl_2$ solution

3.2.1. Rate of hydration

Influence of zinc chloride on CSA cement hydration was investigated by semi-adiabatic calorimetry on mortars prepared with a solution containing $ZnCl_2$ (0.01 mol/L or 0.5 mol/L) (Fig. 5). This salt tended to retard the hydration process, especially when the binder did not contain any gypsum. In that case, the delay was observed even at the lowest $ZnCl_2$ concentration, but did not seem to increase significantly with more concentrated solutions. When the gypsum content reached 20%, the retardation was only noticeable for a 0.5 mol/L $ZnCl_2$ concentration. It should be noticed however that the delays observed with CSA cements remained much lower than with a Portland cement (OPC). With a 0.5 mol/L $ZnCl_2$ concentration, the maximum heat fluxes were respectively recorded within 15 h and 4 h for gypsum contents of 0 and 20% while, under similar conditions, they would be of several days for OPC-based materials [42–44].

Complementary experiments were performed in order to assess the respective effects of zinc cations and chloride anions on the rate of hydration. Mortars were prepared with mixing solutions containing either a zinc salt ($ZnCl_2$, $ZnSO_4$, $Zn(NO_3)_2$) or its corresponding calcium salt ($CaCl_2$, $CaSO_4$, $Ca(NO_3)_2$) at a fixed concentration of 0.5 mol/L. Their cumulated heats of hydration as a function of time are given in Fig. 6.

Whatever the anion ($2Cl^-$, $2NO_3^-$, SO_4^{2-}), mortars prepared with a gypsum-free cement hydrated more rapidly when the mixing solution contained zinc cations instead of calcium cations. Whatever the cation (Zn^{2+} or Ca^{2+}), chlorides strongly retarded hydration while sulphates accelerated it. The influence of nitrates depended on the counter-ion (acceleration for $Zn(NO_3)_2$, but retardation for $Ca(NO_3)_2$). The delay induced by the $ZnCl_2$ mixing solution in our experiments thus mainly resulted from the retarding effect of chloride anions which was partly counteracted by the acceleration effect of zinc cations. It should be emphasized that an opposite behaviour would have been obtained with Portland cement since in that case, it is well known that zinc salts are strong retarders while calcium chloride is an efficient accelerator [45,46]. The unexpected retarding effect of $CaCl_2$ on the hydration of a gypsum-free calcium sulfoaluminate cement has already been described [47]. Although the mechanism of retardation is not known with certainty, rapid precipitation of Friedel's salt has been observed in that case, at the expense of ettringite and other AFm phases during the retardation period.

Different results were obtained when the cement contained 20% gypsum: the strong accelerating effect of gypsum was predominant and mortars prepared with $ZnCl_2$ or $CaCl_2$ were only slightly retarded as compared to the reference prepared with pure water (Fig. 7).

3.2.2. Products formed at 7 days

Mineralogical evolutions induced by zinc chloride were assessed on cement pastes at early age using X-Ray diffraction (Fig. 8). Without any gypsum addition, the products formed under curing at 20 °C were CAH_{10}, ettringite, calcium monosulfoaluminate hydrate and gibbsite, as well as Friedel's and Kuzel's salts. A fraction of calcium monosulfoaluminate hydrate observed in the reference prepared with pure water was thus replaced by partly and fully chloride-substituted AFm phases. When a thermal cycle was applied, the formation of calcium monosulfoaluminate hydrate was favoured instead of ettringite. CAH_{10} was not observed anymore, as already noticed for the reference, while the Kuzel's and Friedel's salts remained stable.

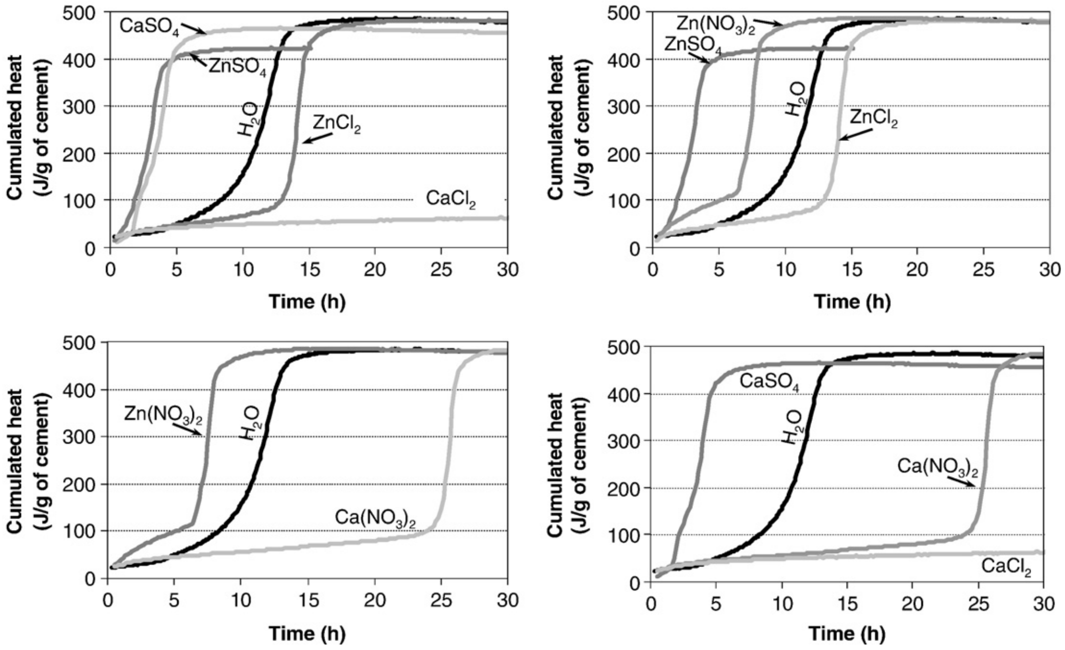

Fig. 6. Influence of the mixing solution composition on the cumulated heat produced by mortars under semi-adiabatic curing (all salts introduced at a concentration of 0.5 mol/L).

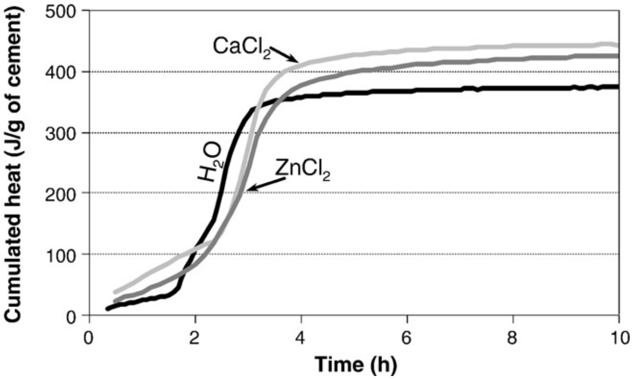

Fig. 7. Comparative influence of $CaCl_2$ and $ZnCl_2$ (at a concentration of 0.5 mol/L in the mixing solution) on the cumulated heat produced by mortars with 20% of gypsum under semi-adiabatic curing.

With a 20% gypsum addition, ettringite was the main hydrate formed in the samples cured at 20 °C. Small amounts of gibbsite also precipitated. There was no clear evidence of a crystallized phase containing chlorides. The thermal cycle induced the formation of the Friedel's salt and had almost no influence on the stability of ettringite, as already observed with pure water and high gypsum contents.

Crystallized Zn-containing phases were never identified by XRD, whatever the sample and the curing conditions. The pore solution of a 24 h-old cement paste cured at 20 °C (w/c raised to 0.75 to collect enough solution) was extracted using pressure (WALTER BAI 102/3000 — HK4, applied strength within the range 0–1700 KN). It was characterized by a pH of 9.8 and a zinc concentration below the detection limit of the selected ICP method (0.1 mg/L). This shows that zinc was efficiently insolubilized. Several assumptions might then be considered.

(i) *Sorption onto anhydrous or hydrated phases*. Two candidate phases might be C–S–H and AH_3. Sorption of Zn(II) onto type I–C–S–H (C/S ratio = 1) has been described at low Zn(II) concentrations (<1000 µmol/L) and pH within the range 11.7–12.8 [34]. The most probable mechanism would be an incorporation of Zn(II) in the interlayer of C–S–H (I) rather than an exchange for Ca [34,48,49]. It has been confirmed recently that nanocrystalline C–S–H with a C/S ratio of 2/3 can incorporate zinc up to a limit of Zn/(Zn + Ca) of 1/6 [50]. Sorption of zinc onto metal oxyhydroxides has been thoroughly investigated since the process is of importance to understand the migration of potentially toxic metal ions in soil and sediments environments. According to Micera *et al.* [51], the threshold pH for zinc adsorption on aluminium hydroxide is about 5 and, above this pH, adsorption increases abruptly. Chloride promotes the sorption of chloro-complexes (such as $ZnCl^+$), while sulphate enhances the cationic adsorption by making the surface potential more negative. Extended X-Ray absorption fine structure spectroscopy has been used to probe the Zn atomic environment at the metal/gibbsite interface, showing that at low sorption densities, Zn(II) forms predominantly inner-sphere bidentate surface complexes with AlO_6 polyhedra, whereas at higher sorption densities formation of a mixed-metal Zn(II)–Al(III) hydroxide coprecipitate occurrs with a layered double hydroxide structure [52,53].

(ii) *Partial substitution in AFm or AFt phases*. As mentioned in introduction, Zn^{2+}/Ca^{2+} substitutions in the structure of ettringite or calcium monosulfoaluminate hydrate might be involved [23–28,33], although such Zn-containing phases have never clearly been identified.

(iii) *Precipitation as amorphous compounds or as very fine crystals undetectable by X-ray diffraction*. At high Zn(II) concentrations (>1000 µmol/L), the precipitation of β_2-$Zn(OH)_2$ (pH<12) or calcium zincate $Zn_2Ca(OH)_6\ 2H_2O$ (pH>12) has been reported. The preferential formation of the former [42,44] or latter phase [54–56] on the surface of the cement particles has been postulated to explain the delay in ordinary Portland cement hydration. Other minerals should also be considered. Simonkolleite $Zn_5(OH)_8Cl_2$ has been observed in zinc rusts formed under marine atmosphere [57] and is stable in slightly alkaline medium: it could thus transitorily precipitate at the beginning of cement hydration. Basic zinc sulphates $ZnSO_4\ 3Zn(OH)_2.nH_2O$ have been identified during the cementation process of lead metal from lead sulphate slurries, zinc being used as the precipitant [58]. Layered double hydroxides, also called anionic clays, are layered compounds that have a stacking of positively

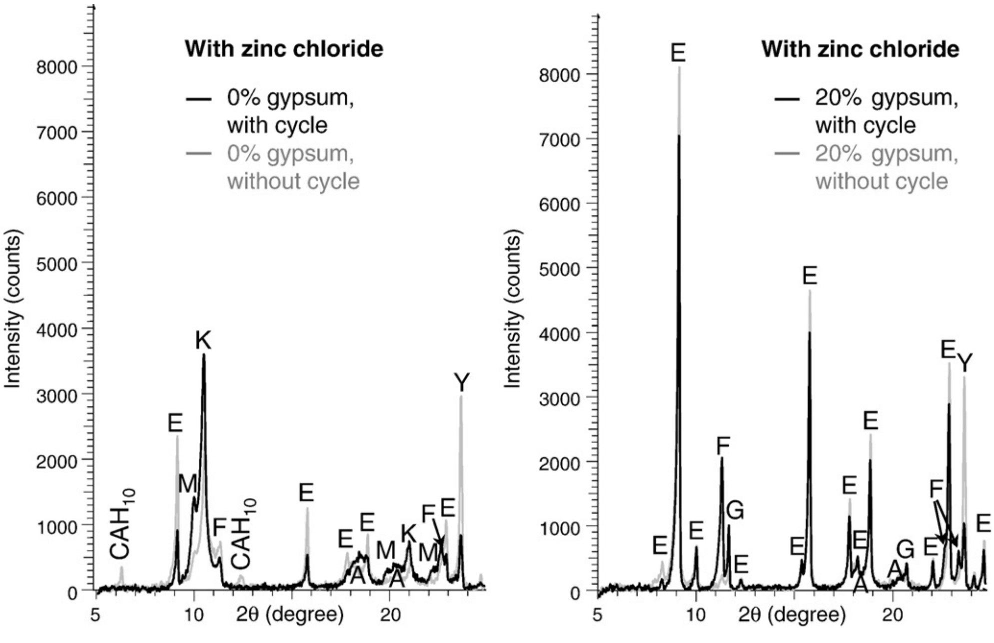

Fig. 8. XRD patterns of 7 day-old cements pastes prepared with a 0.5 mol/L $ZnCl_2$ solution: influences of initial gypsum content and curing conditions (conservation at 20 °C or application of a thermal cycle); E = ettringite, M = calcium monosulfoaluminate hydrate, A = AH_3, Y = yeelimite, G = gypsum, F = Friedel's salt, K = Kuzel's salt.

charged octahedral sheets with $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}$ composition. They can be prepared with Zn^{2+} and Al^{3+} as the divalent M^{II} and M^{III} metal ions [59]. The net positive charge, due to substitution of trivalent by divalent metal ions, is balanced by an equal negative charge of the interlayer solvated anions $[X_{x/m}{}^{m-}.nH_2O]^{x-}$. Zn/Al hydrotalcites ($Zn_6Al_2(OH)_{16}$ CO_3 $4H_2O$) and [Zn–Al–Cl] LDHs have been synthesized by coprecipitation in aqueous solution with a pH ideally comprised between 9 and 12, ZnO becoming predominant at higher pH [60,61]. The layered structure of [Zn–Al–Cl] LDHs seems however to be damaged by the ion exchange with SO_4^{2-}, LDH crystals being converted into basic zinc sulphates [62].

Complementary investigations are required to specify the location of zinc in the CSA cement pastes, and will be reported in a future paper.

4. Conclusion

The purpose of this article was to investigate hydration of CSA cement at early age as a function of the gypsum content in the binder, thermal history of the material, and $ZnCl_2$ concentration in the mixing solution. The main conclusions can be summarized as follows.

1. Hydration of CSA cements was much less retarded by zinc chloride than that of OPC. The slowing down for CSA binders had a greater intensity in the absence of gypsum.
2. Chloride anions induced a strong retardation of gypsum-free CSA cements, but this effect was balanced by an accelerating effect due to zinc cations and sulphate anions.
3. When the mixing solution contained zinc chloride, the mineralogy observations revealed the precipitation of chloro–AFm such as Kuzel's salt and Friedel's salt in most cement pastes whatever the gypsum content or the thermal history. Complementary investigations are under way to determine the zinc location in these materials.
4. The thermal history of the samples proved to be a key parameter. Applying a thermal cycle which reproduced the temperature rise and decrease occurring in a massive mortar block accelerated the rate of hydration and mainly modified the proportion of AFt versus AFm, especially when the binder had a low gypsum content. Increasing the gypsum content above 20% allowed stabilizing ettringite whatever the temperature histories investigated in the present work.
5. CSA cements seemed interesting candidates for $ZnCl_2$ stabilization/solidification. Setting inhibition of the binder was never observed, even at a $ZnCl_2$ concentration as high as 0.5 mol/L in the mixing solution, and Zn^{2+} ions were readily insolubilized. Adding a 20% gypsum content to cement was beneficial since the temperature rise during hydration was reduced and the mineralogy of the hydrated phases was less dependent on the thermal history. Furthermore, it was shown in a previous work that it also improved the compressive strength of mortars prepared with a 0.5 mol/L $ZnCl_2$ solution and reduced their expansion under wet-curing [63]. These results should however be supplemented by an investigation of the long-term evolution of the solidified waste forms.

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