Influence of Zn(II) ions on the Hydration of Calcium Sulfoaluminate Cement – Application to Nuclear Waste Conditioning

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Abstract

Hydration of calcium sulfoaluminate cement ($C\overline{S}A$) was investigated in the presence of Zn(II) ions, a strong retarder of OPC. Calorimetric measurements were combined with mineralogical characterizations using XRD and SEM and showed that the influence of Zn(II) ions on the hydration rate and on the nature of the precipitated products depended both on the gypsum content of cement and on the Zn(II) concentration in the mixing solution. Setting inhibition was never observed even at high Zn concentrations (1 mol/L). Adding a 20% gypsum content to cement was beneficial since it improved the compressive strength of Zn-containing mortars and reduced their expansion under wet-curing. A formulation was then designed to solidify incinerator ashes containing soluble $ZnCl_2$. The waste loading was successfully increased by a factor 2 as compared with current OPC recipes.

Keywords: calcium sulfoaluminate cement, zinc, hydration, incinerator ashes

1. Introduction

Cementitious materials intended for radioactive waste encapsulation usually include substantial amounts of Ordinary Portland Cement (OPC) in their formulation. However, wastes produced by nuclear activities are very diverse and some of their components may chemically react with cement phases or mixing water, thus reducing the quality of the product. For instance, ashes resulting from the incineration of technological wastes including neoprene and polyvinylchloride may contain substantial amounts of soluble zinc chloride [1]. This compound is known to have deleterious effects on OPC hydration. Setting is strongly delayed and can even be inhibited at high Zn loadings [2], while hardening is slowed down [3].
The reactivity of Zn(II) in a cementitious system depends both on pH and concentration. At low Zn(II) concentrations (<1000 µmol/L) and pH within the range 11.7 – 12.8, sorption of Zn (II) to calcium silicate hydrate (C-S-H (I)) is observed [4]. 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. 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 [5]. At high Zn(II) concentrations, the precipitation of β_2-$Zn(OH)_2$ (pH < 12) or calcium zincate $Zn_2Ca(OH)_6.2H_2O$ (pH > 12) is observed. The preferential formation of the former [6-7] or latter phase [8-10] on the

surface of the cement particles has been postulated to explain the delay in cement hydration. Ettringite may also be involved in the retention of Zn(II). By investigating the leaching of cement pastes prepared with a 2 g/L Zn solution, Poon *et al.* [11] noticed that the zinc release and the ettringite destabilization occurred simultaneously.

Two approaches may be considered to reduce adverse waste-cement interactions: *(i)* to perform a chemical pre-treatment of the waste to convert interfering species into compounds stable in cement, or *(ii)* to select a binder which would show a better compatibility with the waste. Different chemical pre-treatments have been investigated, aiming at precipitating Zn(II) as a phosphate, silicate or calcium compound [12]. The pre-treatment step increases however the complexity and cost of the process. This work is thus focused on the second approach.

It has been shown recently that ettringite, and possibly calcium monosulfoaluminate hydrate, provide a good confinement of Zn(II) [13-16]. These phases are known to accommodate many substitutions: a Zn^{2+} / Ca^{2+} substitution in the ettringite structure is postulated to explain the zinc retention. The AF_t and AF_m phases can be formed by hydration of calcium sulfoaluminate ($C\bar{S}A$) cement. This binder is manufactured by mixing $C\bar{S}A$ clinker, which is mainly composed of yeelimite, belite and an Al-rich ferrite [17], with gypsum. By increasing the proportion of gypsum, a series of cements, ranging from rapid-hardening to shrinkage-compensating, and eventually to self-stressing, can be produced [18]. $C\bar{S}A$ cement pastes harden through the formation of an ettringite skeleton, and its subsequent infilling by mixtures of ettringite, calcium monosulfoaluminate hydrate, C-S-H, alumina and ferrite gel [19-20]. The contents of ettringite and calcium monosulfoaluminate hydrate are very sensitive to the amount of added sulphate [21]: the former dominates in a gypsum-rich environment, whereas the latter tends to increase in a gypsum-deficient system.

The objective of this work was to investigate the influence of Zn(II) ions on the hydration kinetics of $C\bar{S}A$ cements with variable gypsum contents, as well as on their strength development and dimensional evolution with time. A formula aiming at stabilizing Zn-rich incinerator ashes by $C\bar{S}A$ cement was then designed.

2. Experimental

2.1 Materials

In the first part of the study, Zn(II) ions were directly introduced in the mixing water at a concentration within the range 10^{-3} – 1 mol/L. Two salts ($ZnCl_2$ or $Zn(NO_3)_2$, analytical grade) were used in order to investigate the effect of the counter-ion on the cement hydration process. Both cement pastes (W/C ratio of 0.45) and standard mortars (W/C ratio of 0.5, S/C ratio of 3 – siliceous sand 0-2mm) were prepared. The binders were either

OPC (control specimens) or $C\bar{S}A$ cements prepared by mixing a $C\bar{S}A$ clinker with the appropriate amount of gypsum (0, 10 or 20% by mass of cement). Their mineralogical compositions are summarized in Tab.1.

Table 1: Chemical and mineralogical compositions of cements.

Cement	Oxides (% weight)										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	TiO_2	SrO	l.i.
OPC[1]	19.9	5.4	2.6	65.0	1.4	0.9	0.1	3.4	-	-	1.0
$C\bar{S}A$ clinker[2]	7.5	30.4	8.6	44.2	0.6	0.17	0.04	6.5	1.1	0.25	0.32
	Minerals (% weight)										
OPC[1]	C_3S 65.6 C_2S 16.0 C_3A 4.0 C_4AF 5.6 Gypsum 4.8 Carbonate 2.8										
$C\bar{S}A$ clinker[2]	$C_4A_3\bar{S}$ 53.5 C_2S 21.2 C_4AF 16.3 Perovskite 9.0										

[1] CEM I 52.5 PM ES CP2 provided by Lafarge Le Teil   [2] TS provided by Belitex

The second part of the study was devoted to the solidification of incinerator ashes mainly composed of amorphous zinc phosphate and chloride (Tab. 2). Their apparent and bulk densities were respectively 0.34 and 3.01, and the grain size distribution was monomodal (d_{10} = 2 μm, d_{50} = 10 μm, d_{90} = 29 μm). To characterize the soluble fraction, a 10 g aliquot was mixed with 25 mL of ultrapure water. The suspension pH was 2.7 and the liquid phase contained Zn^{2+} (22.4 g/L), Cl^- (14.7 g/L), SO_4^{2-} (14.3 g/L) and PO_4^{3-} ions (40.5 g/L); 19% of the zinc fraction was soluble. The cementitious matrix comprised a $C\bar{S}A$ cement with a gypsum content of 20% and a siliceous sand of fine granulometry (0-350 μm).

Table 2: Chemical composition of incinerator ashes (% weight).

Al_2O_3	CaO	Cl	C	Fe_2O_3	K_2O	Na_2O	MgO	P_2O_5	SiO_2	S	Zn
0.29	0.41	3.23	0.15	1.00	3.43	0.84	0.10	36.10	0.1	1.52	29.50

2.2 Methods

Mixing was performed with a standard laboratory mixer (5L-capacity as defined by European standard EN 196-1) according to the following sequence: (1) introduction of the mixing solution (water or Zn(II)-containing solution), (2) in the case of incinerator ashes solidification, addition of the ashes and mixing at low speed for 3 minutes, (3) introduction of cement possibly pre-mixed with sand at low speed, and (4) mixing at high speed for 2 minutes.

Hydration of cement mortars was followed by calorimetry according to the semi-adiabatic method (European standard EN 196-9). This latter consisted in introducing a sample of 1575 ± 1 g of freshly made 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. Supplementary mineralogical analyses of the solidified materials were performed using X-ray diffraction (Siemens D8,

$\lambda_{K\alpha1}$(Cu) = 1.54056 Å, 2 θ range : 5 – 60°, steps of 0.02°, 2 s / step), while microstructure was investigated by scanning electron microscopy (Philips XL PX6631/01, voltage 15 kV, SE imaging, EDS analysis). Hydration was stopped after fixed periods of time by successively immersing the samples (crushed if necessary) into ethanol and acetone, and drying them under vacuum at ambient temperature.

Compressive strengths of 4x4x16 cm^3 specimens cured at 20°C in air, sealed bag or under water were measured according to European standard EN 196-1. Additional experiments were carried out on similar samples placed into cells filled with 700 mL of demineralized water at 19 $\pm$ 0.5 °C. Length changes were measured with displacement gauges consisting of LVDTs (linear variable differential transducers - measurement range $\pm$ 1 mm, resolution 1 µm). Measurements were recorded every 30 minutes on an approximately 140-day period. The experimental set-up allowed to record rapid and unexpected length variations which could have been missed with manual measurements. Water was analyzed for Zn(II) by ICP-AES after 7, 28 and 90 days.

3. Results and discussion

3.1 Investigating the kinetics of hydration

The cumulated heat curves corresponding to mortars prepared with various cements (OPC, or C$\overline{\text{S}}$A cements with a gypsum content of 0, 10 or 20%) and hydrated with a 0.1 M ZnCl$_2$ solution are shown in Fig. 1. Hydration of C$\overline{\text{S}}$A cements was much more rapid than that of OPC. The times for maximum heat output (inflexion point of the sigmoid curves) were respectively 9 h 50 min, 3 h 50 min and 4 h 10 min for C$\overline{\text{S}}$A cements containing 0, 10 or 20% and gypsum, and 4 d 8 h 50 min for OPC. This result justifies the interest taken to C$\overline{\text{S}}$A cements to solidify Zn-rich wastes.
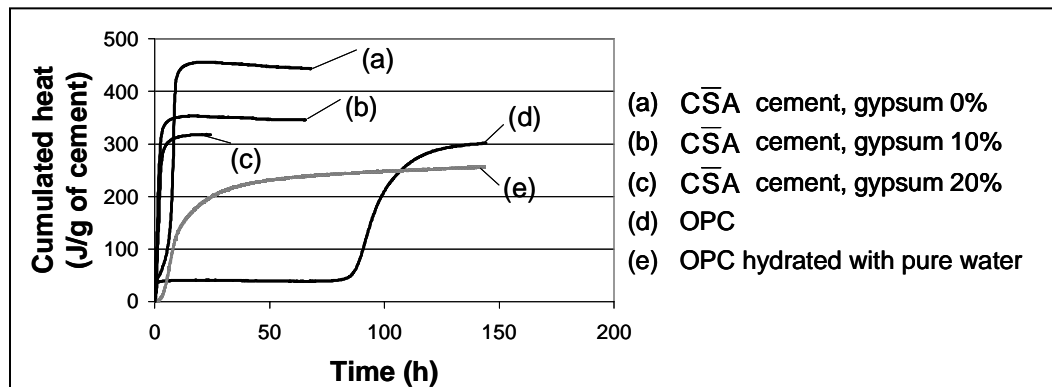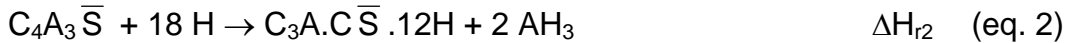

Figure 1: Heat evolution recorded for standard mortars prepared with a 10$^-$^{1} M ZnCl$_2$ solution (Zn/C = 0.33%).

The curve related to OPC mortar showed a rapid heat output just after mixing, which was followed by a long induction period, and a second heat production period, with the same magnitude than that observed without zinc, but translated in time. The pH of the grout was measured 10 minutes after mixing. The value of 10.0 was consistent with the early precipitation of $Zn(OH)_2$ rather than $CaZn_2(OH)_6.2H_2O$, as indicated by zinc speciation calculations carried out with CHESS software, and as postulated by Arliguie *et al.* [2, 6-7]. According to these authors, cement hydration started again through the transformation of amorphous $Zn(OH)_2$ into crystalline $CaZn_2(OH)_6.2H_2O$ when the pH and the calcium concentration were high enough in the mixing solution.

$C\overline{S}A$ cements exhibited different behaviors depending on their gypsum content. The absence of gypsum addition resulted in a delay in the acceleration period, but in a higher heat of hydration. Decreasing the gypsum content should favor the formation of calcium monosulfoaluminate hydrate (eq. 2) instead of ettringite (eq. 1). However, from the enthalpies of reaction, it can be seen that the formation of calcium monosulfoaluminate hydrate is less exothermic than that of ettringite (ΔH_{r1} − ΔH_{r2} = -145.52 kJ/mol):

$$C_4A_3\overline{S} + 2\,C\overline{S}H_2 + 34\,H \rightarrow C_3A.3C\overline{S}.32H + 2\,AH_3 \qquad \Delta H_{r1} \quad \text{(eq. 1)}$$
$$C_4A_3\overline{S} + 18\,H \rightarrow C_3A.C\overline{S}.12H + 2\,AH_3 \qquad \Delta H_{r2} \quad \text{(eq. 2)}$$

The higher heat of hydration of the $C\overline{S}A$ cement without gypsum should then result from the formation of a higher amount of hydrates at the surface of the cement grains before the diffusion-controlled regime.

The influence of the zinc concentration on the hydration of $C\overline{S}A$ cements was then investigated (Tab. 3).

Table 3: Influence of the Zn concentration and type of Zn salt used on the hydration of $C\overline{S}A$ cements.

Gypsum content (%)	[Zn(II)] in the mixing solution (mol/L)	Zn/C (%)	$Zn(Cl)_2$		$Zn(NO_3)_2$	
			Time for maximum heat output	Cumulated heat (J/g)	Time for maximum heat output	Cumulated heat (J/g)
20	0	0	4 h 10 min	307	4 h 10 min	307
	10^{-3}	0.0033	3 h 30 min	296	3 h 50 min	307
	10^{-2}	0.033	4 h 00 min	287	4 h 10 min	297
	10^{-1}	0.33	4 h 10 min	318	4 h 10 min	307
	1	3.3	8 h 30 min	394	5 h 30 min	378
0	0	0	13 h 00 min	402	13h 00 min	402
	10^{-3}	0.0033	13 h 30 min	401	13h 00 min	419
	10^{-2}	0.033	17 h 30 min	403	17h 40 min	420
	10^{-1}	0.33	9 h 50 min	443	11h 00 min	445
	1	3.3	9 h 50 min	453	5 h 50 min	459

Up to a $ZnCl_2$ concentration of 0.1 mol/L in the mixing solution, the kinetics of hydration of the $C\overline{S}A$ cement containing 20% of gypsum remained almost unchanged. A retardation was observed when the concentration

reached 1 mol/L but it remained largely acceptable within the framework of waste conditioning (setting times below 24 h being required). It resulted from a decrease in the hydration rate rather than from an increase in the induction period (Fig. 2-A).
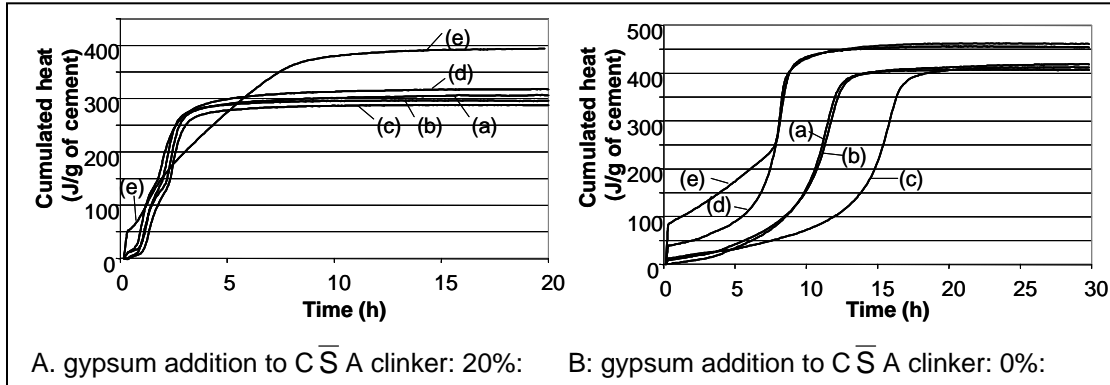

A. gypsum addition to C$\overline{\text{S}}$A clinker: 20%: B: gypsum addition to C$\overline{\text{S}}$A clinker: 0%:

Figure 2: Heat evolution recorded for standard mortars prepared with a C$\overline{\text{S}}$A cement and a $ZnCl_2$ solution.
(a) [Zn(II)] = 0 mol/L, (b) [Zn(II)] = 10^{-3} mol/L, (c) [Zn(II)] = 10^{-2} mol/L, (d) [Zn(II)] = 10^{-1} mol/L, (e) [Zn(II)] = 1 mol/L

More complex results were obtained in the absence of gypsum. Hydration was delayed for a Zn concentration of 10^{-2} mol/L, which was mainly due to an increase in the induction period. It was however accelerated for concentrations of 10^{-1} and 1 mol/L; in particular, the maximum rates of hydration (the slopes at the inflexion point on the cumulated heat curves) were increased (Fig. 2-B).
Similar trends were observed when zinc chloride was replaced by zinc nitrate, which shows that the observed phenomena were mainly due to zinc rather than to its counter-ion (Tab. 3).
When the zinc concentration in the mixing solution was high ($\geq$ 0.1 mol/L for a C$\overline{\text{S}}$A cement with no addition of gypsum, 1 mol/L for a C$\overline{\text{S}}$A cement with 20% of gypsum), a rapid heat output was detected just after mixing, especially when the C$\overline{\text{S}}$A cement contained no additional gypsum (Fig. 2). In that case, the heat evolved increased with the zinc concentration. Attempts to identify the precipitated species by XRD gave no results. The heat production might have resulted from the precipitation of an amorphous compound such as $Zn(OH)_2$ (with the possible transitory formation of simonkoleite ($Zn_5(OH)_8Cl_2$) which is thermodynamically stable within the pH range 6 – 8.5).

3.2 Investigating the mineralogy

Crystallized phases were investigated by XRD in C$\overline{\text{S}}$A cement pastes hydrated with a 1 M $ZnCl_2$ solution or with pure water (control samples). The diffraction patterns are shown in Fig. 3 and 4.
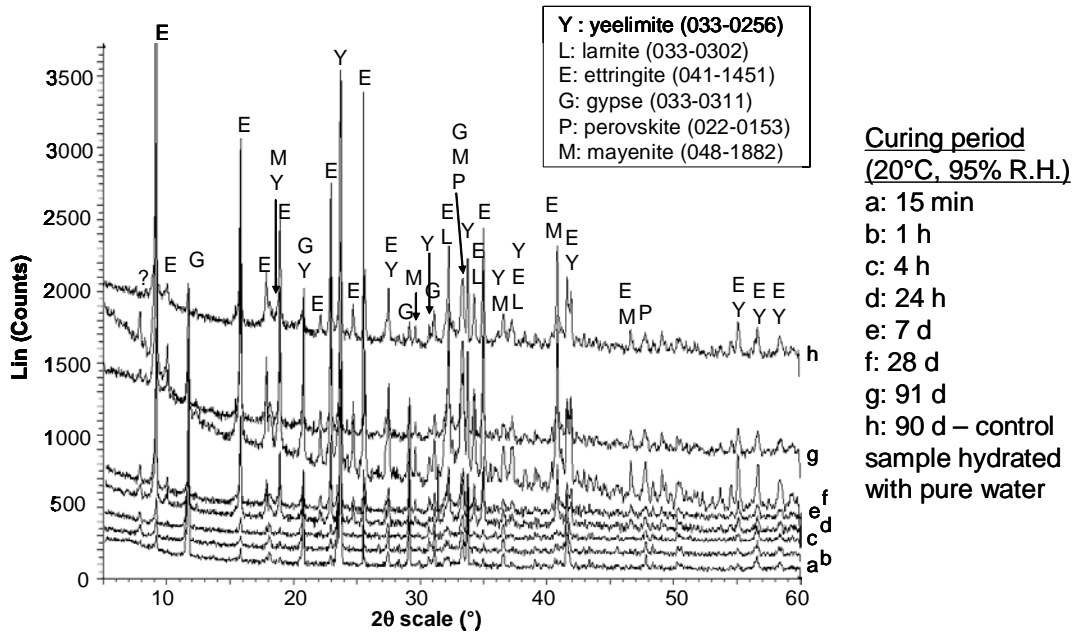
Figure 3: XRD powder diffraction patterns of a C S̄ A cement paste (gypsum addition in cement: 20%) hydrated with a 1 M $ZnCl_2$ solution.
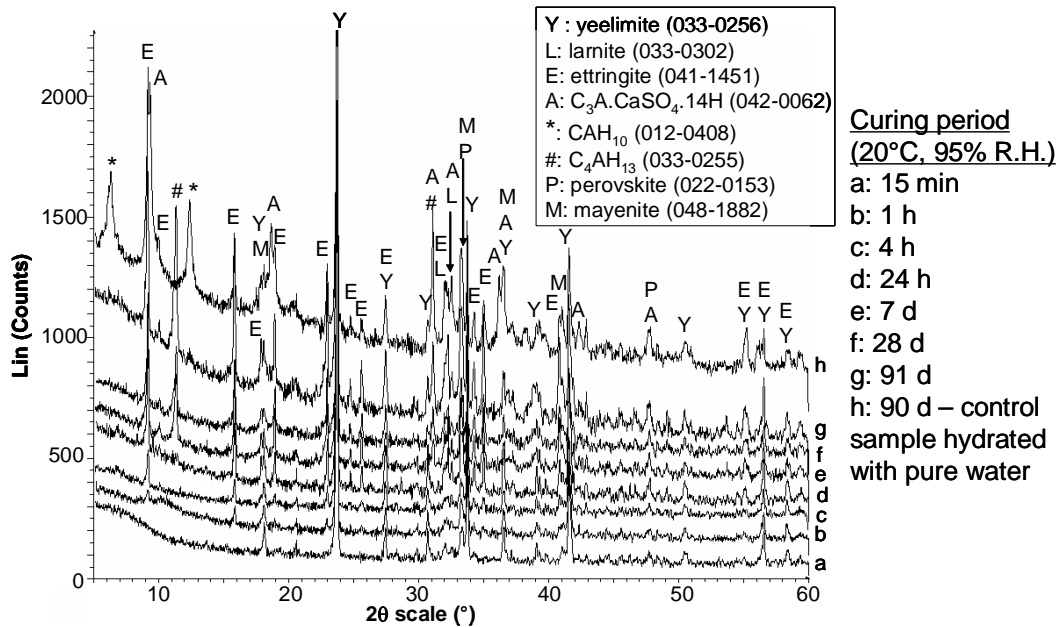

Figure 4: XRD powder diffraction patterns of a C S̄ A cement paste (gypsum addition in cement: 0%) hydrated with a 1 M $ZnCl_2$ solution.

When the C S̄ A cement contained 20% of gypsum, ettringite was the only clearly identified hydrate from the first characterization date (15 min). Its diffraction peaks were not shifted as compared to the JCPDS reference. After 90 d of curing, hydration was not complete since yeelimite, larnite,

gypsum, perovskite and mayenite were still present. The diagrams were very similar to those of the control sample hydrated with water. The only difference was, for the Zn-containing samples, the occurrence, after 1 h of hydration, of a small peak at $2\theta = 7.7°$ which could not be attributed with certainty. One possibility might be the precipitation of a Zn-compound ($5ZnO.Al_2O_3.ZnSO_4.15H_2O$), the peaks at d = 5.6 Å and 3.71 Å being respectively confounded with those of ettringite and gypsum.

When no gypsum was added to the $C\overline{S}A$ cement, the detected hydrates were ettringite and C_4AH_{13} from respectively 15 min and 7 d of hydration. Anhydrous cement phases (yeelimite, larnite, mayenite, perovskite) were still observed after 90 d. The most striking feature was the change in the diffraction patterns as compared to the probe samples: calcium monosulfoaluminate hydrate ($C_3A.CaSO_4.14H_2O$, JCPDS n° 042-0062) was not detected anymore in the presence of zinc, and C_4AH_{13} was observed instead of CAH_{10}.

3.3 Investigating the location of Zn(II) in the cement paste

Some mortars prepared with a 0.9 M $ZnCl_2$ solution were submitted to wet-curing in order to investigate their dimensional stability (see section 3.5). The curing solution was analyzed for Zn(II) after 7 d, 28 d and 90 d. In each case, the Zn(II) concentration was below the detection limit (7.6×10^{-6} mol/L), which meant that the leached fraction of Zn(II) did not exceed 0.02%. This result shows that Zn(II) was precipitated into very-low solubility phases.

Fractures of cement pastes prepared with a 1 M $ZnCl_2$ solution were observed by SEM after increasing periods of hydration (from 15 min to 28 d at 20°C and 95% R.H.). The gypsum addition in the $C\overline{S}A$ cement was 0 or 20%. At early age (<24 h), all the samples contained a large number of acicular crystals of ettringite which, according to EDS analyses, was partially substituted by Zn and Cl (Fig. 5). At later age, formation of massive space-filling ettringite occurred, possibly mixed with other phases (AF_m, C-S-H, AH_3), and observation of individual crystals was much more difficult.

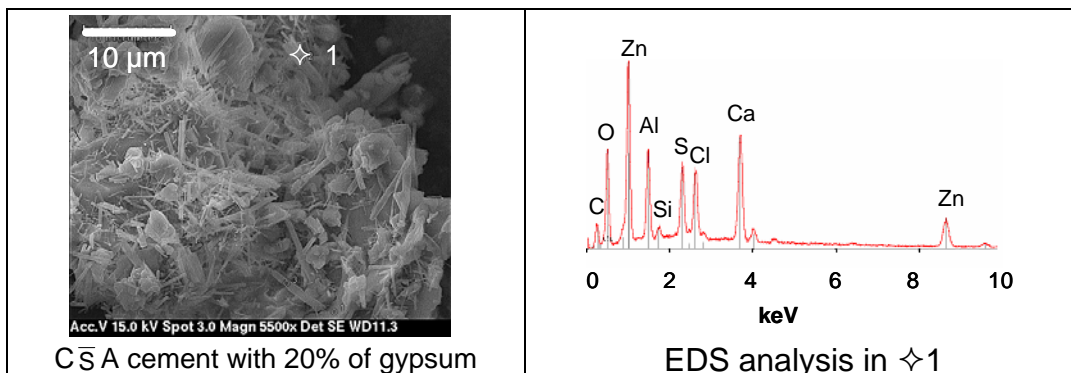| $C\overline{S}A$ cement with 20% of gypsum | EDS analysis in ✧1 |

Figure 5: SEM analysis of cement pastes. Duration of hydration: 1 h.

Some Zn(II)-containing phases could thus be inferred from this work: ettringite, $Zn(OH)_2$ (with a possible transitory formation of simonkoleite) under the assumption that the formation of this compound is responsible for the rapid heat output observed at high zinc concentration, and possibly $5ZnO.Al_2O_3.ZnSO_4.15H_2O$ in a sulphate-rich environment (cement with 20% of gypsum). However, no conclusion could be drawn on the possibility to incorporate Zn(II) in an AF_m structure.

3.4 Investigating the compressive strength

Fig.6-a shows the evolution with time of the compressive strength of mortars prepared with a 0.5 M $ZnCl_2$ solution. Adding gypsum to $C\overline{S}A$ clinker improved the compressive strength. When the cement contained 20% of gypsum, hardening was very rapid: the strength of the specimen reached 37 MPa at demoulding, 24 h after mixing. It went on increasing at later age, but more slowly, and exceeded 50 MPa at 90 d.

The influence of the Zn(II) concentration depended on the gypsum addition to $C\overline{S}A$ clinker (Fig 6-b and 6-c). For a 20% addition, the compressive strength at 28 d remained almost constant, whatever the Zn(II) concentration in the mixing solution and the curing conditions. However, for a 0% addition, the strength strongly decreased when the Zn concentration increased, especially when the samples were cured in air.

(a) $ZnCl_2$ concentration in the mixing solution : 0.5 M Conservation in sealed bag

(b) Gypsum addition in cement: 0% Curing period: 28 d

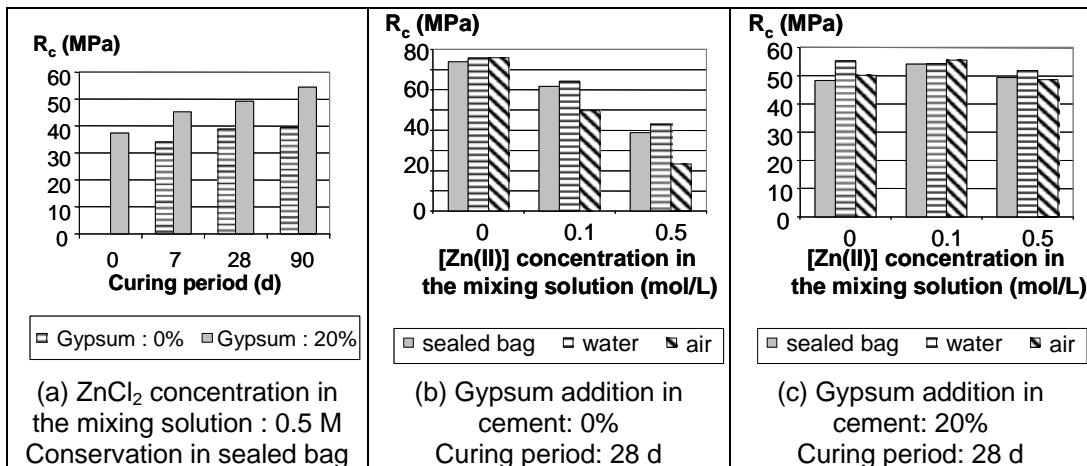(c) Gypsum addition in cement: 20% Curing period: 28 d

Figure 6: Compressive strength (MPa) of mortars. (a) Influence of the gypsum addition on the evolution with time, (b) and (c): influence of the $ZnCl_2$ concentration in the mixing solution on the compressive strength at 28 d

3.5 Investigating the dimensional stability under wet-curing

Under wet-curing, most mortars exhibited a rapid expansion in the first month, which then slowed down and tended towards equilibrium (Fig. 7). However, samples prepared with a 0.5 M $ZnCl_2$ solution and a low gypsum content seemed to behave differently. A transitory shrinkage at early age was

observed in the absence of gypsum, and possibly for a 10% gypsum addition (it might follow in that case a rapid expansion during the first 2 hours of immersion). Complementary experiments are under way to confirm these observations, and to look for a possible correlation between this shrinkage and the important heat output recorded just after mixing for these samples (see Fig.2-B, curve (e)). A transitory Zn-containing product might indeed precipitate into the cement paste at very early age. Its further conversion, which would occur with a much slower kinetics and would be promoted by the presence of water, might then generate chemical shrinkage.

Adding $ZnCl_2$ to the mixing solution had little effect on final swelling when the $C\overline{S}A$ cement contained 10 or 20% of gypsum, but strongly increased expansion when the cement contained no additional gypsum.
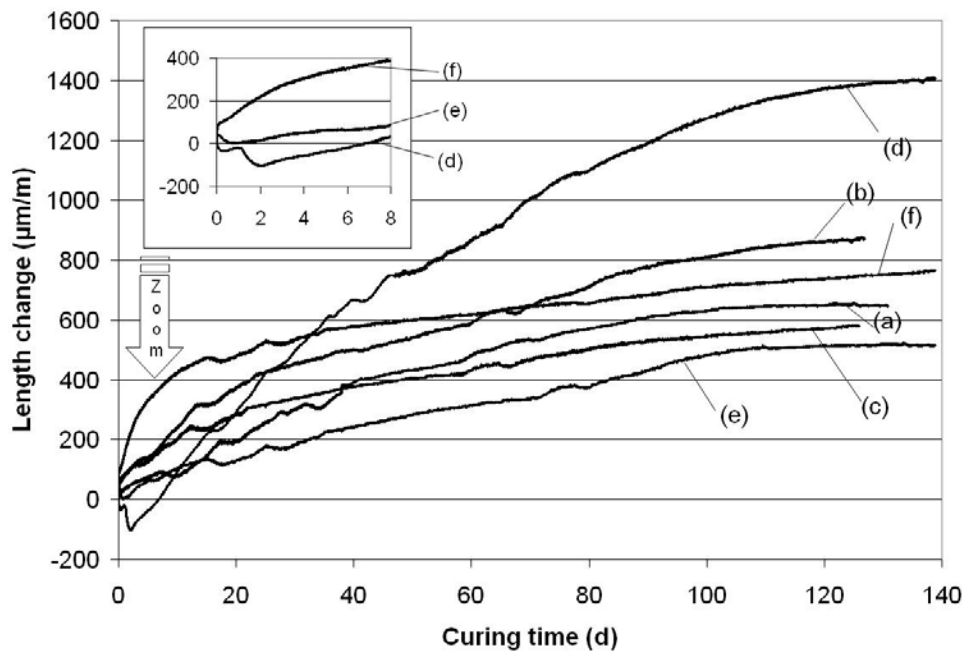

Figure 7 : Length change of mortars under wet-curing at room temperature. (a) gypsum addition = 0%, $[ZnCl_2]$ = 0 mol/L, (b) gypsum addition = 10%, $[ZnCl_2]$ = 0 mol/L, (c) gypsum addition = 20%, $[ZnCl_2]$ = 0 mol/L, (d) gypsum addition = 0%, $[ZnCl_2]$ = 0.5 mol/L, (e) gypsum addition = 10%, $[ZnCl_2]$ = 0.5 mol/L, (f) gypsum addition = 20%, $[ZnCl_2]$ = 0.5 mol/L.

3.6 Designing a cementitious matrix to encapsulate Zn-rich incinerator ashes

A cement containing 20% of gypsum was selected to encapsulate Zn-rich incinerator ashes. Because of the strong acidity of the waste, a neutralization step had to be carried out. The ashes were mixed with water and pH was raised to 7 by adding concentrated sodium hydroxide, before introducing pre-mixed cement and sand. The formulation is given in Tab. 4, as well as the properties of the solidified waste forms. Because of the very fine particles of ashes, the W/C ratio was raised to 0.85 to get a workable

grout. The waste loading could be doubled as compared to an encapsulation with OPC: it was increased up to 20% (which corresponded to a Zn/C ratio of 17.4%, or by taking into account soluble zinc only, of 3.44%) while keeping acceptable properties at the laboratory scale. In particular, setting occurred 12 to 15 h after mixing, and the compressive strength largely exceeded the minimum required value (8 MPa) after 7 d only. The weak point was an important shrinkage, which should be however reduced by increasing the sand to cement ratio.

Table 4: Cement-waste formula and properties of the resulting material.

Cement-waste formula	W/C	0.85
	S/C	0.5
	Gypsum content in cement	20%
	Waste loading	20% (by mass)
Properties of the solidified waste forms	Vicat setting time:	12 h – 15 h
	Bleeding at 1 h, 3 h, 24 h	0%
	Compressive strength (wet curing):	7 d: 19 MPa
		28 d: 23.3 MPa
	Expansion (wet curing)	7 d : + 597 µm/m
		28 d : + 828 µm/m
	Shrinkage (sealed bag):	7 d : -1352 µm/m
		28 d : -1782 µm/m

4. Conclusion

$C\bar{S}A$ cements showed a much better compatibility with Zn(II) ions than OPC. In particular, setting inhibition was never observed, even when the Zn(II) concentration reached 1 mol/L in the mixing solution. Adding a 20% gypsum content to cement was recommended since it improved the compressive strength of mortars prepared with a 0.5 M $ZnCl_2$ solution and reduced their expansion under wet-curing.

Zn(II) ions were rapidly precipitated into low-solubility phases. SEM observations showed the presence of Zn-substituted ettringite in all samples, whatever the gypsum content of cement. The possible formation of $5ZnOAl_2O_3.ZnSO_4.15H_2O$ in a sulphate-rich environment was inferred from XRD diffraction patterns. Furthermore, calorimetric investigations revealed a rapid heat output just after mixing at high Zn concentrations, which might indicate the precipitation of an amorphous compound such as $Zn(OH)_2$.

The influence of Zn(II) ions on the hydration rate of $C\bar{S}A$ cement depended both on the gypsum content of cement and on the Zn(II) concentration. Complementary investigations are under way to elucidate the mechanisms involved, as well as to determine the location of Zn in ettringite (Ca^{2+} / Zn^{2+} or SO_4^{2-} / $Zn(OH)_4^{2-}$ substitution).

From a more practical point of view, a formulation was designed to encapsulate Zn-rich incinerator ashes. By using a $C\bar{S}A$ cement instead of OPC, the waste loading could be increased by a factor 2 without any setting problems.

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