STABILIZATION OF ZnCl₂-CONTAINING WASTE USING CALCIUM SULFOALUMINATE CEMENT

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Abstract

The potential of calcium sulfoaluminate (CSA) cement was investigated to solidify and stabilize radwastes containing large amounts of soluble zinc chloride (a strong inhibitor of Portland cement hydration). Hydration of pastes and mortars prepared with a 0.5 mol/L ZnCl₂ mixing solution was characterized over one year as a function of the gypsum content of the binder and the thermal history of the material. Blending the CSA clinker with 20% gypsum enabled rapid hydration, with only very small delay compared with a reference prepared with pure water. It also improved the compressive strength of the hardened material and significantly reduced its expansion under wet curing. Moreover, the hydrate assemblage was less affected by a thermal treatment at early age simulating the temperature rise and fall occurring in a large-volume drum of cemented waste. Fully hydrated materials contained ettringite, amorphous aluminum hydroxide, strätlingite, together with AFm phases (Kuzel’s salt associated with monosulfoaluminate or Friedel’s salt depending on the gypsum content of the binder), and possibly C-(A)-S-H. Zinc was readily insolubilized and could not be detected in the pore solution extracted from cement pastes, or in their leachates after 3 months of leaching by pure water at pH 7. The good retention of zinc by the cement matrix was mainly attributed to the precipitation of a hydrated and well crystallized phase with platelet morphology (which may belong to the layered double hydroxides family) at early age (< 1 day), and to chemisorption onto aluminum hydroxide at later age.

Keywords: waste management, calcium sulfoaluminate cement, zinc chloride, hydration, leaching

1. INTRODUCTION

Cementitious materials intended for radioactive waste solidification and stabilization 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 with 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 zinc loadings [2], while hardening is slowed down [3]. Moreover, zinc in its ionic form is an environmental pollutant. Acute and chronic effects of zinc have been widely described for different aquatic organisms and exposure routes [4]. In humans, although zinc is an essential trace element which takes part in many enzymatic reactions, its prolonged and excessive intake may lead to toxic effects, such as carcinogenesis, mutagenesis and teratogenesis, as a result of its accumulation [5].
The reactivity of Zn(II) in a cementitious system depends both on pH and concentration. At low Zn(II) concentrations (<1 mmol/L), and pH within the range 11.7–12.8, sorption of Zn(II) to calcium silicate hydrate (C-S-H) is observed [6]. The most probable mechanism is incorporation of Zn(II) in the interlayer of C-S-H [7], rather than exchange for Ca\(^{2+}\). It has been confirmed recently that nanocrystalline C-S-H with a C/S ratio of 2/3 can incorporate zinc up to a Zn/(Zn+Ca) limit of 1/6 [8]. At high Zn(II) concentrations, the precipitation of \(\beta\)-Zn(OH)\(_2\) (pH < 12) or calcium zincate \(Zn_2Ca(OH)_{6.2H_2O}\) (pH > 12) is observed. The preferential formation of the former [9], or latter phase [10] on 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(II) solution, Poon et al. [11] noted that zinc release and ettringite destabilization occurred simultaneously.

Two approaches may be considered to reduce adverse waste/cement interactions. The first is to perform chemical pretreatment of the waste to convert interfering species to compounds that are stable in cement. Various treatments have been investigated, aiming at precipitating Zn(II) as a phosphate, silicate or calcium compound. The reactions with phosphates and silicates are slow at ambient temperature, and only calcium precipitation would meet industrial requirements [12]. However, the pretreatment step increases the complexity and cost of the process. The second approach, which is investigated in this article, aims at selecting a binder having improved compatibility with the waste.

Calcium sulfoaluminate (CSA) cements can have highly variable compositions, but all of them contain ye’elimite, also called Klein’s compound or tetracalcium tri aluminate sulfate, in the clinker [13]. In this article, we will consider only sulfoaluminate belite cements in which ye’elimite \((C_4A_3S)\) predominates over belite \((C_2S)\) [14]. A wide range of gypsum contents (typically from 10 to 25\%) can be ground with CSA clinker to produce different CSA cements, ranging from rapid-hardening (at low gypsum content) to shrinkage-compensating, and eventually to self-stressing (at high gypsum content) [15]. The hydration progress of CSA cement pastes occurs by the initial precipitation of ettringite and aluminum hydroxide, followed by the precipitation of calcium monosulfoaluminate hydrate once calcium sulfate has been depleted [16]. The ettringite and calcium monosulfoaluminate hydrate are very sensitive to the amount of added sulfate: the former dominates in a gypsum-rich environment, whereas the latter tends to increase in a gypsum-deficient system [18]. Depending on the composition of the minor phases, other hydration products may also be observed, such as C-S-H [16], strätlingite [19], siliceous hydrogarnet [19] and / or hemi- or monocarboaluminate [20].

CSA cements may present at least two advantages to stabilize ZnCl\(_2\)-rich wastes. It has been shown recently that their hydration is much less retarded by zinc chloride than that of OPC [21]. Moreover, their two main hydrates, ettringite and calcium monosulfoaluminate hydrate are expected to provide good Zn\(^{2+}\) confinement due to their flexible structure [22][23][24][25][26]. Auer et al. [27] performed TEM-EDX analyses of ettringite crystals formed in mixtures of calcium aluminate cement with fly ash arising from municipal solid waste incineration and concluded indeed that zinc was partially incorporated in the crystal lattice of ettringite (Zn\(^{2+}\) / Ca\(^{2+}\) substitution).

This work aimed at assessing the potential of CSA cement for stabilizing wastes with high soluble zinc chloride content. A cement matrix material intended for immobilization has to meet a number of requirements. The cemented waste form should set within a reasonable period of time and remain a stable monolith thereafter. Excessive heat generation during hydration should be avoided, as well as segregation of water. Moreover, the pollutants from the waste should be confined, at least to some extent, under leaching conditions. This work had thus four main objectives:

- supplement the data concerning hydration at early age of CSA cements by a ZnCl\(_2\) solution by following their mineralogical evolution over a one-year period,
- assess the influence on hydration of a brief temperature rise and fall at early age, as it may occur in a 200 L drum filled with a cemented waste,
• investigate the strength development and volume change of ZnCl₂-rich mortars as a function of their gypsum content,

• characterize the mineralogical evolution and zinc release of a hydrated CSA cement paste under leaching conditions.

2. EXPERIMENTAL

2.1. Materials and specimen preparation

CSA cements were prepared by mixing a ground industrial CSA clinker (the composition of which is summarized in TABLE 1; \( d_{10} = 2.67 \mu m, d_{50} = 17.6 \mu m, d_{90} = 50.8 \mu m \), BET specific surface area = 1.3 m²/g) with the appropriate amount of analytical grade gypsum (from 0 to 20% by weight of cement; \( d_{10} = 5.4 \mu m, d_{50} = 19.6 \mu m, d_{90} = 50.3 \mu m \), BET specific surface area = 0.4 m²/g) for 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.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>( C_4A_S )</th>
<th>( C_2S )</th>
<th>( C_{12}A_7 )</th>
<th>CT</th>
<th>Periclase</th>
<th>CS</th>
<th>Quartz</th>
<th>Others*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>68.5</td>
<td>15.9</td>
<td>9.5</td>
<td>2.9</td>
<td>1.5</td>
<td>0.5</td>
<td>0.5</td>
<td>2.4</td>
</tr>
</tbody>
</table>

* include 1.2% of iron oxide
Shorthand cement notations: \( C = CaO, A = Al_2O_3, S = SiO_2, S = SO_3, T = TiO_2, H = H_2O \)

Both cement pastes and mortars were made with the same w/c ratio of 0.55. A blend of two siliceous sands (0.1–1.2 mm) with a sand to cement weight ratio of 3 was used to optimize the workability and limit the heat release of fresh mortars during hydration. The mixing solution was prepared by dissolving the appropriate amount of analytical grade salt in distilled water (ZnCl₂ 0 or 0.5 mol/L, which was representative of the concentration released in mixing water by actual radioactive incinerator ashes). 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 treatment in an oven (Memmert UFP 500) for 7 days before being cured at 20°C. Mortars were cast into 4×4×16 cm molds and cured for 7 days at 20 ± 1°C and 95 ± 5% R.H, or submitted to thermal treatment. 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.
TABLE 2. SHORTHAND NOTATIONS OF THE INVESTIGATED COMPOSITIONS.

<table>
<thead>
<tr>
<th>gypsum content (% by weight of cement)</th>
<th>([\text{ZnCl}_2]) in mixing water (mol/L)</th>
<th>Paste Curing at 20°C</th>
<th>Mortar Curing at 20°C</th>
<th>Thermal treatment at early age</th>
<th>Thermal treatment at early age</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>CE0</td>
<td>ME0</td>
<td>CE0t</td>
<td>ME0t</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>CZ0</td>
<td>MZ0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>CZ0t</td>
<td>MZ0t</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>CE2</td>
<td>ME2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>CZ2</td>
<td>MZ2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CZ2t</td>
<td></td>
<td>ME2t</td>
<td></td>
</tr>
</tbody>
</table>

Complementary experiments were performed on cement suspensions (w/c ratio = 10) stirred under nitrogen atmosphere at room temperature for 7 days. The objective was to reach higher degrees of hydration than in cement pastes.

2.2. Thermal cycles

Thermal cycles were applied on pastes and mortars to reproduce the temperature rise and fall that may occur in a massive mortar block (such as waste encapsulated in mortar with typical w/c and s/c ratios of 0.55 and 3, and placed in a 200 L drum). 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 consisted in introducing 1575 g ± 1 g of fresh mortar into a cylindrical container, which was then placed into a calibrated Langavant calorimeter to determine the quantity of heat emitted versus the temperature.

The core temperature of pastes and mortars was measured with waterproof penetration probes (type K TC) and recorded with a Testo 735-2 thermometer.
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 20% relative humidity at 22 ± 2°C). Crystallized phases were identified by X-ray diffraction (Siemens D8 – copper anode λ_Kα₁ = 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 reactants and products over time was qualitatively assessed from XRD patterns by measuring the areas of corresponding reflections using EVA analysis software (© 2005 Bruker AXS). Thermogravimetric analyses were carried out under N₂ 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 following European standard EN 196-1 after 1, 7, 28, 90, 180 and 360 days. Triplicate specimens were used at each testing age. Expansion under water was assessed on mortar bars placed in cells filled with 700 mL of demineralized water (one sample per cell). Their length change was measured with displacement gauges consisting of linear variable differential transducers (LVDT, measurement range ± 1 mm; resolution 1 µm). External signal conditioning was performed using a modular multichannel 600 system from RDP with a data logger and computer interface. Data collection was controlled using the Labview software. A sketch of the device is given in [28]. Measurements were recorded every hour over approximately one year, which allowed an accurate monitoring of the sample evolution. Mass gain was assessed on additional specimens kept under water at room temperature after 7, 28, 90, 180 and 360 days.

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

\[
\phi_w(\%) = \frac{m_a - m_d}{m_a - m_w} \times 100
\]  

\( m_a \) is the mass of the saturated sample, \( m_d \) is the mass of the dry sample, and \( m_w \) is the mass of the water.

\[\text{FIG. 1. Thermal cycles applied to pastes and mortars as a function of the initial gypsum content of the cement (0: 0% gypsum; 2: 20% gypsum) and zinc concentration (E: 0 mol/L; Z: 0.5 mol/L) in the mixing solution.}\]
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.

The microstructure and chemical composition of the cement pastes were investigated using SEM (JEOL JSM-5910 LV with a tungsten filament, or ESEM XL30-FEI microscope equipped with a thermal field emission gun). X-ray microanalyses were performed using an energy dispersive X-ray system (EDX EDAX type). In the STEM-in-SEM mode (FEI ESEM XL-30), a 3 mm diameter TEM copper grid with the sample was placed on the head of a TEM sample holder fixed on a vertical axis set to the stage of the SEM. The incident electron beam passed through the sample. The signal was then collected by an annular semiconductor detector classically used for the collection of backscattered electrons. In our experiments, the detector was located below the sample to collect electrons that were scattered by the sample, transmitted electrons passing through the hole at the center of the STEM detector. Using this method, a large fraction of the scattered electrons was available to form an image and high contrast dark field images could be obtained.

Additional observations were performed with a 200 kV field emission gun Transmission Electron Microscope (JEOL 2010F) equipped with an energy-dispersive spectrometry system (INCA-OXFORD EDX) with a detector dedicated to light element detection.

All samples observed by STEM-in-SEM or TEM were prepared using the following procedure: hydrated cement particles were dispersed in methanol using an ultrasonic bath. Several dilutions were performed to obtain a very low material concentration. A drop of suspension was then laid down on a 200 mesh copper grid, covered on the back with a holey carbon film. The excess methanol was soaked away using filter paper.

Thermodynamic calculations were carried out using the CHESS software [29]. The solubility constants of CSA cement hydrates were previously given in [30], those of the Kuzel’s salt and Friedel’s salt were taken from [31]. Data relative to zinc-containing phases were found in [46] and [47].

2.4. Leaching test

After 3 months of curing (20°C, 95% RH), some cylinders (5 cm in diameter, 3 cm high, protected against lateral degradation by a polymer coating) of CZ2t paste were leached in deionized and decarbonated water thermo-regulated at 20 ± 1°C and kept under N₂ atmosphere to avoid carbonation. The ratio between the sample surface area and the solution volume was maintained at 0.46 dm²/L. The composition of the leaching solution remained constant during the tests, with a pH fixed at 7.0 by adding nitric acid (0.25 mol/L) in the reactor. The leaching solution was renewed when the volume of added nitric acid reached 1% of the solution volume. After each renewal, the solution was sampled and analyzed by ion chromatography and AES-ICP. The mineralogy of the leached zone was assessed by progressively scraping the samples from the external surface to the sound core using a micromilling machine. With the help of XRD, TGA, and SEM/EDS, it was possible by this way to determine the phases within slices approximately 100 µm thick, parallel to the leached surface.

3. RESULTS

3.1. Rate of hydration

The rate of hydration of the cement pastes prepared with a 0.5 mol/L ZnCl₂ solution was investigated as a function of their gypsum content. The core temperature of the materials cured at 20°C or in a semi-adiabatic Langavant calorimeter was recorded as a function of time, and the residual ye’elimite content of the pastes was assessed from their XRD patterns acquired after increased periods of time (
(a) Gypsum = 0%; curing at 20°C; mixing solution = water or ZnCl₂ 0.5 mol/L
(b) Gypsum = 0%; curing at 20°C or thermal treatment; mixing solution = ZnCl₂ 0.5 mol/L
(c) Gypsum = 20%; curing at 20°C; mixing solution = water or ZnCl₂ 0.5 mol/L
(d) Gypsum = 0% or 20%; thermal treatment; mixing solution = ZnCl₂ 0.5 mol/L

FIG. 2).
Hydration of the gypsum-free cement at room temperature was retarded by almost 70 hours compared with a reference prepared with pure water (a) Gypsum = 0%; curing at 20°C; mixing solution = water or ZnCl₂ 0.5 mol/L (b) Gypsum = 0%; curing at 20°C or thermal treatment; mixing solution = ZnCl₂ 0.5 mol/L (c) Gypsum = 20%; curing at 20°C; mixing solution = water or ZnCl₂ 0.5 mol/L (d) Gypsum = 0% or 20%; thermal treatment; mixing solution = ZnCl₂ 0.5 mol/L FIG. 2-a). After one day, only 18% of ye’elimite were depleted, versus 83% for the reference. Simulating a temperature rise up to 85°C strongly reduced the hydration delay. The heat flux reached its maximum after 14.3 h, instead of 12.1 h for the reference with pure water cured under the same conditions, and ye’elimite was almost fully consumed after 24 h (residual of 2%) (f) Gypsum = 20%; curing at 20°C; mixing solution = water or ZnCl₂ 0.5 mol/L (g) Gypsum = 0% or 20%; thermal treatment; mixing solution = ZnCl₂ 0.5 mol/L FIG. 2. Influence of the composition of the mixing water, gypsum content of the binder and curing conditions on the hydration rate of CSA cements (dots: ye’elimite content, curves: T).
(a) Gypsum = 0%; curing at 20°C; mixing solution = water or ZnCl₂ 0.5 mol/L

(b) Gypsum = 0%; curing at 20°C or thermal treatment; mixing solution = ZnCl₂ 0.5 mol/L

(c) Gypsum = 20%; curing at 20°C; mixing solution = water or ZnCl₂ 0.5 mol/L

(d) Gypsum = 0% or 20%; thermal treatment; mixing solution = ZnCl₂ 0.5 mol/L

FIG. 2-b). Raising the gypsum content of the binder to 20% was another way to increase the rate of hydration. The maximum temperature was reached after 8.3 h in sample CZ2, instead of 79 h for sample CZ0.
(c) Gypsum = 20%; curing at 20°C; mixing solution = water or ZnCl₂ 0.5 mol/L

(d) Gypsum = 0% or 20%; thermal treatment; mixing solution = ZnCl₂ 0.5 mol/L

FIG. 2-c). Similarly, with a thermal cycle, the heat flux reached its maximum after 3.2 h in sample CZ2t instead of 14.3 h in sample CZ0 (a) Gypsum = 0%; curing at 20°C; mixing solution = water or ZnCl₂ 0.5 mol/L

(b) Gypsum = 0%; curing at 20°C or thermal treatment; mixing solution = ZnCl₂ 0.5 mol/L

(c) Gypsum = 20%; curing at 20°C; mixing solution = water or ZnCl₂ 0.5 mol/L

(d) Gypsum = 0% or 20%; thermal treatment; mixing solution = ZnCl₂ 0.5 mol/L

FIG. 2-d). With 20% gypsum, the retardation induced by zinc chloride was almost suppressed: pastes CE2 and CZ2 exhibited rather similar ye’elimite depletion rates (c)
(a) Gypsum = 0%; curing at 20°C; mixing solution = water or ZnCl₂ 0.5 mol/L
(b) Gypsum = 0%; curing at 20°C or thermal treatment; mixing solution = ZnCl₂ 0.5 mol/L
(c) Gypsum = 20%; curing at 20°C; mixing solution = water or ZnCl₂ 0.5 mol/L
(d) Gypsum = 0% or 20%; thermal treatment; mixing solution = ZnCl₂ 0.5 mol/L

FIG. 2-c). The origin of the retardation induced by ZnCl₂ on a gypsum-free CSA cement was discussed in a previous work [21]. Unlike what would be expected for OPC, the delay results from the strong retardation caused by chloride anions, which is partly balanced by an accelerating effect due to zinc cations. Sulfate anions also strongly accelerate hydration and, when 20% gypsum is added to the binder, the delay is almost compensated.

3.2. Mineralogical evolution over one year

The mineralogical changes of the cement pastes with ongoing hydration were determined by XRD and TGA. FIG. 3 shows an example of the results obtained for paste CZ0 while FIG. 4 summarizes the evolution over time of the hydrate assemblage in the four investigated materials (CZ0, CZ0t, CZ2, CZ2t).
FIG. 3. X-Ray diffraction (a) and thermogravimetry (b) analysis of cement paste CZ0 cured at 20°C after 5 min, 1 h, 5 h, 24 h, 7 d, and one year of hydration.

(a) E = ettringite, F = Friedel’s salt, K = Kuzel’s salt, Y = ye’elimite, P = perovskite, G = gypsum, M = monosulfoaluminate.

3.2.1. Paste CZ0

During the first 5 minutes of hydration, a rapid stiffening of the paste occurred simultaneously with the precipitation of gypsum and an unidentified compound, subsequently referred to as “phase λ”, which was responsible for two diffraction peaks at 2θ = 7.8° and 15.7°, and for a weight loss at 95°C by TGA (FIG. 5).
Up to 24 h, only small amounts of hydrates were precipitated, mainly ettringite, which replaced gypsum, phase \( \lambda \), amorphous aluminum hydroxide, and Friedel’s salt, an AFm phase in which the positively-charged main layers are balanced by the insertion of chloride anions in the interlayer (\( \text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10 \text{H}_2\text{O} \)). After 7 days, phase \( \lambda \) was no longer detected and the phase assemblage had significantly evolved. The main hydrates were ettringite and Kuzel’s salt, an AFm-structured compound containing ordered chloride and sulfate anions (\( \text{C}_3\text{A} \cdot 0.5\text{CaSO}_4 \cdot 0.5\text{CaCl}_2 \cdot 10\text{H}_2\text{O} \)). Smaller amounts of CAH\(_{10}\), monosulfoaluminate and Friedel’s salt were also observed. At later age, from 7 d to 1 year, the paste exhibited only minor mineralogical evolutions. The residual amount of ye’elimite slightly decreased (from 13\% to 7\%) while the amount of Kuzel’s salt tended to increase at the expense of Friedel’s salt. CAH\(_{10}\) is known to be formed mainly at low temperature (below 15°C) during the hydration of calcium aluminate cement. However, its formation has already been reported at 20–25°C during the hydration of CSA clinker [21]. Nevertheless, CAH\(_{10}\) is a metastable phase at ambient temperature and is expected to be transformed at later age. To assess the long-term evolution of cement paste CZ0, fully hydrated cement was prepared using the suspension technique (w/c = 10) with the same \([\text{ZnCl}_2]/\text{cement}\) ratio as in the cement paste (the \(\text{ZnCl}_2\) concentration in solution was thus decreased to 0.0275 mol/L to take into account the dilution factor of the suspension). After one week of mixing, the reactive anhydrous phases of the clinker (ye’elimite and mayenite) were totally depleted. The water loss determined by TGA reached 32\%, which corresponded to a w/c ratio of 0.47. The chemical water demand of the clinker was thus lower than the investigated w/c ratio (0.55). The phase assemblage comprised monosulfoaluminate and Kuzel’s salt, ettringite, amorphous aluminum hydroxide and strätlingite (FIG. 4). Crystallized Zn-containing phases were not detected. In addition to the precipitation of Cl-AFm phases, the CSA clinker hydrated with a \(\text{ZnCl}_2\) solution differed from a reference prepared with pure water by its higher ettringite content and lower strätlingite content. As chloride ions partly replaced sulfates in the structure of the AFm phases, more sulfates were available for ettringite precipitation in CZ0 than in CE0. Precipitation of strätlingite is well predicted by thermodynamic calculations simulating the addition of belite to a phase assemblage resulting from the hydration of ye’elimite [30]. Strätlingite is formed according to the balance equation \(\text{C}_2\text{S} + \text{AH}_3 + 5\text{H} \rightarrow \text{C}_2\text{ASH}_8\) as long as \(\text{AH}_3\) is present in the system. Precipitation of C-S-H requires an excess of belite over ye’elimite. Two assumptions may be considered to explain the low strätlingite content in suspension CZ0:

- local precipitation of C-S-H near C\(_2\)S grains could not be excluded,
- or, more likely, belite was not fully reacted, its hydration being strongly delayed by zinc chloride.

3.2.2. Paste CZ0t

The temperature in paste CZ0t exceeded 70°C from 14 to 26 h. As already observed for CSA cement pastes prepared with pure water [21], high temperatures promoted the precipitation of monosulfoaluminate instead of ettringite, which had a smaller stability domain under these conditions [33]. After 1 day, the amount of monosulfoaluminate tended to decrease, together with that of...
Friedel’s salt, to form Kuzel’s salt. This evolution was consistent with the results of Glasser [34] and Balonis [31], showing that the binary monosulfoaluminate / Friedel’s salt system is unstable and either leads to the formation of Kuzel’s salt and monosulfoaluminate if the \([\text{SO}_4^{2-}] / 2[\text{Cl}^-]\) ratio is above 1, or to the formation of Kuzel’s salt and Friedel’s salt if the ratio is below 1. The temperature rise also induced a faster consumption of phase \(\lambda\), which could no longer be detected beyond 5 h (instead of 24 h for the paste cured at room temperature), and \(\text{CAH}_{10}\) was never observed (whereas it persisted from 7 d to 1 year in paste CZ0).

3.2.3. Paste CZ2

When the CSA clinker was blended with 20% gypsum, precipitation of phase \(\lambda\) at early age increased. However, this compound could not be detected beyond one day. The main hydrates were then ettringite and amorphous aluminum hydroxide. The gypsum addition clearly promoted the precipitation of AFt instead of AFm phases as already observed for pastes prepared with pure water. Only small amounts of Friedel’s salt were detected after 7 d, and increased slightly over one year, meaning that a significant fraction of chlorides should remain insolubilized. The pore solutions of 1 d, 7 d, and 28 d-old cement pastes (w/c raised to 0.75 to collect enough solution) were extracted using pressure (Walter Bai 102/3000 – HK4, applied force within the range 0–1700 kN) and analyzed (TABLE 3).

TABLE 3. COMPOSITION OF THE PORE SOLUTIONS EXTRACTED FROM PASTES CE2 AND CZ2 (W/C = 0.75) CURED FOR 1 D, 7 D AND 28 D AT 20°C AND 95% R.H. (CONCENTRATIONS IN MMOL/L, CONDUCTIVITY IN MS)

<table>
<thead>
<tr>
<th></th>
<th>CE2</th>
<th>CZ2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 d</td>
<td>7 d</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K(^+)</td>
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<td>55</td>
</tr>
<tr>
<td>Na(^+)</td>
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<td>15</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
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<td>0.25</td>
</tr>
<tr>
<td>Sr(^{2+}) (*)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td>12</td>
<td>7.6</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
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<td>0.82</td>
</tr>
<tr>
<td>pH</td>
<td>12.3</td>
<td>12.4</td>
</tr>
<tr>
<td>Conductivity</td>
<td>8.2</td>
<td>11</td>
</tr>
</tbody>
</table>

(*) Strontium was initially contained by the clinker (0.09 weight %)

As expected, their chloride concentrations were high, ranging from 150 to 250 mmol/L, and offset by high concentrations of calcium, sodium and potassium. Conversely, their zinc concentration always remained below the detection limit (< 2 µmol/L). The long-term evolution of cement paste CZ2 was assessed from the analysis of a cement suspension (w/c = 10, [ZnCl\(_2\)] = 0.0275 mol/L in the solution to maintain a constant [ZnCl\(_2\)] to [cement] ratio). After one week of stirring at room temperature, ye’elimite and mayeneite were totally consumed. The precipitated hydrates were mainly ettringite and
amorphous aluminum hydroxide, with smaller amounts of strätlingite, Friedel’s and Kuzel’s salts (FIG. 4). For comparison, the hydrate assemblage of a reference prepared with pure water contained ettringite, amorphous aluminum hydroxide, strätlingite and monosulfoaluminate, which formed once gypsum was depleted. In the presence of ZnCl$_2$, monosulfoaluminate was replaced by Kuzel’s salt given the instability of the monosulfoaluminate / Friedel’s salt system.

3.2.4. Paste CZ2t

Paste CZ2t exhibited very rapid hydration. After only 5 hours, gypsum was almost totally consumed and the residual ye’elimite content reached 7%. Phase $\lambda$ briefly precipitated at early age, but was rapidly depleted: it was no longer detected after 2 hours. The hydrate assemblage observed from 5 hours to one year comprised ettringite, Friedel’s salt and amorphous aluminum hydroxide. Friedel’s salt was precipitated in much higher amounts than in the paste cured at 20°C, while the ettringite content was slightly lower. With rising temperature, there was a drop in the thermodynamic stability of ettringite in favor of Friedel’s salt. However, with the subsequent decrease in temperature, ettringite could form again at the expense of Friedel’s salt: between 7 d and one year, the X-Ray diffraction patterns showed a slight increase in the ettringite peaks and a decrease in those corresponding to Friedel’s salt.

3.2.5. Modeling of the mineralogical evolution

The chronological evolutions of the phases precipitated during hydration in pastes CZ0 and CZ2 were in fairly good agreement (excepting the Zn-containing phases) with thermodynamic calculations simulating the hydration of ye’elimite, or ye’elimite + gypsum, in a ZnCl$_2$ solution. FIG. 6 shows the successive precipitation of gypsum and AH$_3$ (pH < 9.6), ettringite (pH > 9.6) with consumption of gypsum, Friedel’s salt (pH > 10.2), Kuzel’s salt (pH > 10.8) with consumption of Friedel’s salt, and finally monosulfoaluminate. The calculation overestimated the amount of AH$_3$ precipitated at the beginning of hydration. In the cement pastes, the latter may have been limited by the incorporation of aluminum in transient phase $\lambda$.

FIG. 6. Thermodynamic modeling of the hydrates precipitation with ongoing hydration (dissolution of ye’elimite in a solution containing initially 0.1 mol/L of Zn$^{2+}$ and 0.2 mol/L of Cl). The zinc-containing phases were omitted for better clarity. The model predicted the successive precipitation Zn$_5$(OH)$_2$Cl$_2$ (pH $\leq$ 9), Zn(OH)$_2$ (9 $\leq$ pH $\leq$ 11.7), and CaZn$_2$(OH)$_6$ (pH $\geq$ 11.7). ZnO is more stable than zinc hydroxide, but is known to precipitate with a slower rate. It was thus excluded from the database.
3.3. Compressive strength

The properties of hardened materials were investigated on heat-treated mortars MZ0t and MZ2t to take into account the significant temperature rise occurring in actual cemented waste drums as a result of the heat generated by hydration. FIG. 7 shows the evolution with time of their compressive strength, which increased very rapidly. It already reached 89 ± 5% of the final (one-year) strength after one day, compared with 79 ± 9% for mortars ME0t and ME2t prepared with pure water. Hardening was thus accelerated by zinc chloride. The compressive strength continued to increase at later age, but much more slowly. This result is consistent with the rapid hydration of the binders which exhibited only small mineralogical evolutions beyond 1 day. Zinc chloride also improved the final strength of the mortars, especially when the cement contained gypsum (increase of 31 ± 7% for MZ2t compared to ME2t, and 13 ± 5% for MZ0t compared to ME0t). These results could not be simply explained by differences in the total water porosity of the samples. Complementary investigations on the pore distribution in each mortar would be required. However, preliminary attempts using mercury intrusion porosimetry were not successful because the high vacuum required by the method damaged ettringite, and thus modified the microstructure.

![Compressive strength and water porosity of 4 × 4 × 16 cm mortar specimens submitted to a thermal treatment at early age, and subsequently cured in sealed bag at room temperature.](attachment:image)

3.4. Volume stability under water

The length change and mass gain of the mortars cured under water are summarized in FIG. 8. The samples were immersed after 7 days and exhibited a rapid mass increase which may have had different origins: 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 continued hydration. The mass gain was rapid during the first 28 days and tended to stabilize after 90 d for samples ME2t and MZ2t, but not for the gypsum-free mortars which also exhibited higher water uptake.
Swelling under water was also highly dependent on the initial gypsum content of the binder and on the ZnCl₂ concentration in the mixing solution. Mortar MZ2t exhibited the same behavior as reference ME2t, with a small length change which remained below 400 µm/m after one year. On the contrary, the expansion of mortar MZ0t (+ 4100 µm/m at 1 year) was almost twice that of mortar ME0t (+ 2000 µm/m), which was itself characterized by high swelling compared with gypsum-containing materials. This significant expansion did not induce any cracking of the samples at macroscopic scale. However, wet curing decreased the compressive strength of mortar MZ0t (24 MPa) by 42% and increased its water porosity (15.8 ± 0.2%) by 12%, compared with curing in a sealed bag.

In order to understand the origin of the volume instability of gypsum-free materials, one-year old mortars MZ0t and MZ2t were characterized by X-ray diffraction after curing under water, and their mineralogy was compared to similar samples cured in sealed bags (FIG. 9).

Mortar MZ0t exhibited significant mineralogical changes: under wet curing, precipitation of strätlingite, ettringite and monosulfoaluminate was observed, whereas the amount of chloro-AFm phases (Friedel’s and Kuzel’s salt) tended to decrease. This could result from the continuation of hydration, but also from the leaching of chlorides. Their concentration in the curing solution (750 mL for a 4 × 4 × 16 cm specimen) after one year reached 19 mmol/L. Three main processes could contribute to the volume change:

- the retarded ettringite formation, due to the restart of hydration and/or to the reprecipitation of primary ettringite decomposed by the thermal excursion,
- the precipitation of strätlingite from C₃S and AH₃ (ΔV/V = -3.5%),
- the transformation of chloro-AFm phases into monosulfoaluminate, Friedel’s salt (268 mL/mol) and Kuzel’s salt (289 mL/mol) having a smaller molar volume than monosulfoaluminate (309 mL/mol).

By contrast, the mineralogy of sample MZ2t was less dependent on the curing conditions. The ongoing hydration induced by wet curing led to the precipitation of small amounts of strätlingite and Kuzel’s salt, while Friedel’s salt was partly depleted. The amount of ettringite did not exhibit noticeable variations. The leaching of chlorides was reduced (11 mmol/L in the curing solution). Under wet curing, the porosity of mortar MZ2t (12.2 ± 0.2%) decreased by 10%, and its compressive strength (53 MPa) slightly increased (by 8%) compared with curing in a sealed bag.
3.5. Durability under leaching by pure water

The previous results showed that blending the CSA clinker with 20% gypsum was interesting to stabilize a 0.5 mol/L ZnCl₂ solution: hydration was almost not delayed, the temperature rise during hydration was reduced, the mineralogy of the hydrated phases was less dependent on the thermal history, the compressive strength of mortars was improved and their length change under wet curing was limited. Complementary investigations thus focused on sample CZ2t, which was submitted to leaching by pure water using a standard test developed by the CEA in order to understand and model the degradation processes of the cement hydrates [35].

3.5.1. Characterization of the leaching solution

The cumulative quantities of OH⁻, Ca²⁺, SO₄²⁻ and Cl⁻ released in the leaching solution increased linearly as a function of the square root of time. Leaching was controlled by diffusion. The corresponding fluxes were respectively 9.03 ± 0.04 mmol/dm²/day¹/₂ (OH⁻), 7.63 ± 0.03 mmol/dm²/day¹/₂ (Ca²⁺), 1.82 ± 0.01 mmol/dm²/day¹/₂ (SO₄²⁻), and 1.59 ± 0.01 mmol/dm²/day¹/₂ (Cl⁻). Silicates and aluminates were not detected in the solution. However, an amorphous white compound, identified as aluminum hydroxide by EDX microanalysis, precipitated in the leachate. The zinc concentration always remained below the detection limit of the ICP method (2 µmol/L), meaning that, for the whole test (18 renewals), the leached fraction of zinc was less than 0.1%. The cement matrix thus provided good confinement of zinc.

3.5.2. Characterization of the degraded solid

We tried to estimate the position of the degradation front in sample CZ2t after 3 months of leaching. Portlandite is usually a good indicator for the location of the degradation front for common OPC-based materials [36]. However, the tracer for the degradation of CSA-based materials was unknown. Different techniques were thus combined: SEM observations and X-ray microanalysis, as well as X-ray diffraction.
The first approach was to use chemical contrast from SEM/BSE images, the density of the degraded zone being lower than that of the sound core due to decalcification. A sharp transition was effectively observed between a bright zone (sound core) and a dark one (degraded material) (FIG. 10). The degradation depth was around 700 µm. Ca- and S-mapping clearly showed the decalcification and sulfur loss from the cement paste near the surface exposed to leaching, in a zone with a thickness of 700 µm, which was in good agreement with the estimation derived from the BSE image. The silicate density in this zone appeared to increase slightly. The Cl-mapping revealed however that chlorides were leached within a larger domain, to a depth of 1600 µm from the surface. The alumina and zinc content appeared to remain relatively constant whatever the considered depth.

In a second approach, XRD analyses were carried out on the samples surface which was scraped off step by step (thickness ≈ 100 µm for each step) to obtain XRD profiles (FIG. 11). The first signs of alteration were noticed from a depth of 2500 µm. Several processes were observed:

- dissolution of Friedel’s salt (from 2 500 µm to 1 900 µm) and Kuzel’s salt (from 1900 to 1500 µm) which released chlorides,
- transient precipitation of monosulfoaluminate (from 2 100 to 1 300 µm),
- dissolution of monosulfoaluminate (from 1 500 to 1 300 µm) and of residual ye’elimite (from 1 300 to 1 100 µm),
- dissolution of ettringite (from 1500 to 700 µm).

The surface layer, with a depth of 700 µm (consistent with the SEM observations), was mainly composed of perovskite, poorly crystallized aluminum hydroxide, and probably C-A-S-H. The latter were not identified with certainty, but the leached silicate flux was below the detection limit and STEM analyses performed on the surface layer showed the presence of small amounts of calcium and silicon, together with aluminum. In addition, TGA curves exhibited a weight loss at 98°C which could correspond to C-A-S-H. This surface layer was highly porous and friable.
FIG. 11. XRD pattern of the degraded zone of paste CZ2t (from the surface (bottom) to the sound core (top)) after 3 months of leaching (pure water, pH 7, 20°C)

S = strätlingite, E = ettringite, M = monosulfoaluminate, K = Kuzel’s salt, F = Friedel’s salt, G = gypsum, A = aluminum hydroxide, Y = ye’elimite, P = perovskite.

To summarize, examination of paste CZ2t after three months revealed three zones:

- the surface layer, with very low mechanical strength, composed of aluminum hydroxide, perovskite and C-A-S-H, which could be easily detected from BSE images, Ca- and S-mapping (EDS analysis), and X-ray diffraction (disappearance of the ettringite signal);

- a less porous intermediate zone in which several precipitation and dissolution fronts occurred, as shown by X-Ray diffraction and Cl-mapping (EDS analysis);

- the sound core.

Zinc was homogeneously distributed in all the three zones, which rules out the assumption of dissolution in the intermediate zone, followed by reprecipitation in the surface layer.
4. DISCUSSION

Zinc was efficiently immobilized by the CSA cement matrix, as shown by the pore solution analysis of paste CZ2, and by the leaching test performed on sample CZ2t. This raised the question of its speciation in the solid phase.

4.1. Zinc speciation in the CSA matrix at early age

In the cement pastes prepared with a ZnCl$_2$ solution, transient precipitation of phase $\lambda$ was observed during the first hours of hydration, and was responsible for rapid stiffening of the grout. This phase was not detected in the absence of zinc (cement mixed with pure water, or with a CaCl$_2$ solution). Moreover, its formation was promoted by the addition of gypsum to the binder, and strongly limited the precipitation of aluminum hydroxide at early age, as compared to reference materials prepared with pure water. These results suggest that phase $\lambda$ may contain zinc, aluminum and possibly sulfates. It was characterized by two X-ray diffraction peaks at $d_1 = 11.26$ Å (main intensity) and $d_2 \approx d_1/2 = 5.64$ Å. It also exhibited water loss around 95°C, and possibly 195°C, indicating that it was a hydrated phase. SEM observations of the CSA cement paste just after stiffening showed the precipitation of hexagonal platelets at the surface of the clinker grains (FIG. 5). The crystals were too fine to be accurately analyzed by EDS. Their morphology is typical of layered double hydroxides (LDH). [Zn-Al-Cl] LDHs or Zn/Al hydrotalcite (Zn$_6$Al$_2$(OH)$_{16}$CO$_3$·4H$_2$O) were excluded because of their very different diffraction patterns [37], [38]. A possible candidate might be zinc aluminum sulfate hydrate 5ZnO·Al$_2$O$_3$·ZnSO$_4$·15H$_2$O, which, according to JCPDS file number 44-0600, has a hexagonal lattice, and gives by X-ray diffraction a strong line at $d = 11.13$ Å (diffraction plane (0, 0, 6)), and two less intense lines at $d = 5.57$ Å (diffraction plane (0, 0, 12)) and $d = 3.72$ Å (diffraction plane (12, 0, 0)).

We synthesized this compound by dissolving aluminum in 1 mol/L NaOH, and mixing it with aqueous ZnSO$_4$·7H$_2$O in stoichiometric ratio with excess water at 25°C. Precipitation occurred almost instantaneously. The solid crystallized as small hexagonal platelets and exhibited the expected diffraction pattern (strong line at $d = 11.13$ Å, and two secondary lines at $d = 5.59$ Å and $d = 3.72$ Å). Three weight losses were recorded by thermogravimetry at 79°C (main variation), and 176 and 277°C. These characteristics differed slightly from those of phase $\lambda$, and it could not be concluded with certainty that phase $\lambda$ was a zinc aluminum sulfate hydrate.

4.2. Zinc speciation in the CSA matrix at later age

Although zinc was efficiently insolubilized, crystallized Zn-containing phases could not be detected beyond 1 day. Several uptake mechanisms could be considered, including incorporation in mineral structures through coprecipitation or lattice diffusion, precipitation, and adsorption on mineral surfaces.

4.2.1. Incorporation in the structure of AFm or AFt phases

As mentioned in the introduction, Zn$^{2+}$ / Ca$^{2+}$ substitution in the structure of ettringite is often postulated to account for the good retention of zinc by cement pastes containing this hydrate. However, two of our experimental results contradict this assumption.

Some particles of hydrated cement were observed using the STEM-in-SEM (scanning transmission electron microscopy in the scanning electron microscope) technique and analyzed by EDX. The much lower electron energy (30 kV) in the STEM-in-SEM versus TEM presented two main advantages for this study. First, the degradation of fragile phases such as ettringite under the electron beam was limited. Second, the contrast enhancement was improved, which limited the excited volume and increased the electron scattering cross-section. Numerous particles of ettringite from paste CZ2 and CZt were characterized (FIG. 12), but none of them contained zinc. Similar results were obtained for AFm phases.
FIG. 12. STEM-in-SEM/EDX microanalysis of ettringite (carbon comes from the sample holder, Cu from the copper grid, and Cr from the detector).

Elemental mapping was performed using SEM/EDX on polished sections of hydrated pastes CZ2 and CZ2t. For some experiments, the zinc concentration was increased from 0.5 to 2 mol/L to make its detection easier. Zinc was absent from the zones rich in sulfur (ettringite and calcium monosulfoaluminate) or chloride (Kuzel’s or Friedel’s salt).

4.2.2. Precipitation as an amorphous compound or as nanocrystals undetectable by X-ray diffraction

Precipitation of zinc hydroxide or calcium zincate has already been reported in a Portland cement paste. Other phases should also be considered in our systems.

- Simonkolleite $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ has been observed in zinc rusts formed under marine atmosphere [39] and is stable in a slightly alkaline medium. It was transiently detected by X-ray diffraction instead of phase $\lambda$ at early age in a cement paste (20% gypsum) prepared with a 2 mol/L $\text{ZnCl}_2$ solution. Its TGA diagram showed significant weight loss around 500°C, but such a variation was never observed in the pastes prepared with a 0.5 mol/L $\text{ZnCl}_2$ solution. Precipitation of simonkolleite in those materials thus seemed rather unlikely.

- Basic zinc sulfates $\text{ZnSO}_4\cdot\text{Zn(OH)}_2\cdot\text{nH}_2\text{O}$ have been identified during the cementation process of lead metal from lead sulfate slurries, zinc being used as the precipitant [40].

- LDHs are made of a stacking of positively charged octahedral sheets with $[\text{M}^{II}_{1-x}\text{M}^{III}_x(\text{OH})_2]^{x+}$ composition. They can be prepared with $\text{Zn}^{2+}$ and $\text{Al}^{3+}$ as the divalent $\text{M}^{II}$ and trivalent $\text{M}^{III}$ metal ions [41]. The net positive charge, due to substitution of divalent by trivalent metal ions, is balanced by an equal negative charge of the interlayer solvated anions $[\text{X}_{x/m}\cdot\text{nH}_2\text{O}]^{-}$ $[\text{Zn-Al-Cl}]$. LDHs have been synthesized by coprecipitation in aqueous solution with a pH ideally comprised between 9 and 12, $\text{ZnO}$ becoming predominant at higher pH [37], [38]. These compounds seem however to be unstable in the presence of sulfates: their layered structure is damaged by ion exchange with $\text{SO}_4^{2-}$ and precipitation of basic zinc sulfates is observed [48].

The relatively low zinc content (1.2 weight% Zn) of paste CZ2t and its large number of phases made the detection of zinc precipitates difficult. However, after 3 months of leaching by pure water, this sample exhibited a simplified mineralogy in its degraded zone which still contained zinc, as shown by EDX elemental mapping. Particular attention was thus paid to the surface layer. None of its X-ray diffraction peaks or weight losses by TGA could be ascribed to one of the above-mentioned zinc species. In particular, the absence of any weight loss at 155°C or 290°C excluded the occurrence of zinc hydroxide [42] or basic zinc sulfates [40].

Zinc did not precipitate as a crystalline phase and its occurrence as a specific amorphous or nanocrystalline product did not seem very likely.
4.2.3. Adsorption on mineral surfaces

The hypothesis of zinc adsorption on anhydrous cement phases can be ruled out since most of them were rapidly consumed in paste CZ2t. Moreover, perovskite was the only anhydrous phase remaining in the surface zone of sample CZ2t after leaching, but elemental mapping did not show any correlation between the distributions of zinc and titanium.

Sorption of zinc onto C-S-H has already been described at low zinc concentrations [6], [7]. Precipitation of C-S-H in sound pastes CZ2 and CZ2t was not clearly evidenced, the Si-bearing phase being rather strätlingite. However, the formation of C-A-S-H was suspected in the degraded materials after leaching. EDX analyses performed on the surface layer showed the simultaneous presence of Ca, Al, Si and Zn. If we assume complete hydration of belite into C-S-H with a Ca/Si ratio of 2/3, and if we suppose, as shown by Stumm et al. [8], that the maximum zinc incorporation rate in such hydrates is 1/6, the fraction of zinc sorbed onto C-S-H in pastes CZ2 and CZ2t could not exceed 36%, which is insufficient to explain the excellent retention of zinc by these materials.

The other candidate for zinc sorption is aluminum hydroxide which is formed in significant amounts by hydration of CSA cements. 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 sediment environments. According to Micera et al. [43], the threshold pH for zinc adsorption on aluminum hydroxide is about 5, and adsorption increases abruptly above this pH. Chlorides promote the sorption of chloro-complexes (such as ZnCl$^-$), while sulfates enhance 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 the formation of a mixed-metal Zn(II) – Al(III) coprecipitate occurs with a layered double hydroxide structure [44], [45].

STEM-in-SEM and TEM were used to characterize cement particles from the sound core and leached surface of sample CZ2t. X-ray microanalyses confirmed that zinc was always associated with a significant amount of aluminum attributed to aluminum hydroxide. It was shown by TEM that the Zn-rich zones did not exhibit any clear organization (FIG. 13). The aluminum hydroxide content (around 30 molar%) was much higher than that of zinc (less than 1 molar%) in hydrated cement pastes, which suggested a low Zn(II) sorption density and a sorption mechanism involving the binding of Zn(II) to AlO$_6$ in an edge-sharing bidentate geometry. Besides, a parallel may be drawn between the precipitation of phase $\lambda$ occurring in our materials at early age, when the zinc/hydrates ratio is high, and the situation described by Trainor et al. [44] at high Zn(II) sorption densities, leading to the dissolution of the aluminum substrate and the reprecipitation of a mixed Zn-Al hydroxide coprecipitate with LDH structure.
5. CONCLUSION

The purpose of this work was to assess the potential of CSA cements for ZnCl₂ stabilization and solidification. The main conclusions can be summarized as follows.

1. CSA cements were found to be interesting candidates. Their setting was never inhibited, even at high ZnCl₂ (0.5 mol/L) in the mixing water, and zinc was readily insolubilized. Blending the CSA clinker with 20% gypsum was recommended for several reasons. (i) The hydration delay observed for a gypsum-free binder was suppressed. The strong retardation caused by chloride anions was indeed offset by the cumulative accelerating effects of zinc and sulfate ions. (ii) The temperature rise and cumulative heat produced during hydration were reduced. (iii) The compressive strength of the hardened materials was improved and their expansion under wet curing strongly limited. (iv) Their mineralogy was less dependent on the thermal history at early age.

2. When the CSA cements were hydrated with a ZnCl₂ solution, chloro-AFm was precipitated. Fully hydrated materials contained ettringite, amorphous aluminum hydroxide, strätlingite and Kuzel’s salt irrespective of the gypsum content. In addition, monosulfoaluminate was detected when a gypsum-free cement was used, while Friedel’s salt precipitated when the cement initially contained 20% gypsum. Transient phases also formed with ongoing hydration: an unidentified compound named phase λ and gypsum (binders with 0% or 20% gypsum), together with Friedel’s salt and CAH₁₀ (binder with 0% gypsum). The latter was however only observed when hydration occurred at ambient temperature.
3. Hydration of CSA cement is more exothermic than that of OPC, and resembles that of calcium aluminate cement in that respect. Since a significant amount of heat is at early age, large-volume drums of cemented waste forms may exhibit a substantial temperature rise. With CSA cements, it is most important, for laboratory studies on small scale samples, to take into account this thermal evolution at early age in order to understand how actual cemented waste forms will perform. Applying a cycle which reproduced the temperature rise and fall in a massive mortar block accelerated the rate of hydration of the cement-waste grout, especially in the absence of gypsum. Moreover, the hydrate assemblage was modified. When a gypsum-free cement was used, high temperatures promoted the precipitation of monosulfoaluminate instead of ettringite, and CAH₁₀ was no longer formed. When the cement contained 20% gypsum, the mineralogy was less dependent on the curing conditions and only minor evolutions were observed (increased precipitation of Friedel’s salt, slight decrease in the ettringite content).

4. A simulated cemented waste form (cement paste prepared with a binder containing 20% gypsum and a 0.5 mol/L ZnCl₂ mixing solution, and submitted to a thermal cycle at early age) was submitted to leaching by pure water (fixed pH of 7) for three months. The cumulative quantities of Ca²⁺, OH⁻, Cl⁻ and SO₄²⁻ ions in the leachates increased linearly versus the square root of time, showing that leaching was controlled by diffusion. Zinc was never detected, showing the excellent confining properties of the cement matrix. Examination of the solid sample at the end of the experiment revealed three zones: (i) the highly porous and friable surface layer, composed of aluminum hydroxide, perovskite and probably C-(A)-S-H (thickness: 700 µm), (ii) a less porous intermediate zone in which several precipitation and dissolution fronts occurred (thickness: 1800 µm), and (iii) the sound core. Ettringite was a good tracer for the degradation of CSA-cement based materials.

5. The confinement of zinc by the cement matrix was attributed at early age (< 1 day) to the precipitation of phase λ, a hydrated and well crystallized compound with platelet morphology, the stoichiometry of which remains unidentified. At later age, the most probable mechanism was sorption of Zn²⁺ onto aluminum hydroxide (which involved the binding of Zn²⁺ to AlO₆ in an edge-sharing bidentate geometry), rather than Zn²⁺ ↔ Ca²⁺ substitution in the structure of ettringite or AFm phases, as previously postulated. Sorption of Zn²⁺ onto C-(A)-S-H could also occur, but could not by itself explain the good retention of zinc.

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