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# Speciation of cadmium in cement
# Part II. $C_3S$ hydration with $Cd^{2+}$ solution

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**Abstract**

$C_3S$ was hydrated with Cd-containing solutions to prepare suspensions [water/solid (w/s) ratio = 100] and pastes (w/s = 0.45). XRD, EXAFS, and $^{113}$Cd-NMR experiments show that the immobilization of Cd depends on Cd concentration and water/cement ratio. For pastes, there is formation of a mixed Ca/Cd hydroxide, but a fraction of Cd ions is probably sorbed on the C–S–H. In suspensions with large Cd content, there is precipitation of $Cd(OH)_2$; in suspensions with low Cd contents, $Cd(OH)_2$ is not detected, which supports the hypothesis that Cd is sorbed on C–S–H. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* C–S–H; EXAFS; Adsorption; Cadmium; Waste management

## 1. Introduction

To understand the retention of pollutants in cements, one needs to understand immobilization mechanisms, phase solubility and leaching, and transport properties in porous media. The main immobilization mechanisms of inorganic pollutants are (1) hydroxide precipitation due to high pH, (2) silicates precipitation, (3) incorporation into calcium-containing hydrated phases, and (4) sorption onto high surface area C–S–H [1].

Many studies have been devoted to the immobilization of cadmium in Portland cement. TCLP tests indicate that retention is effective (at contents less than 0.1 mg $l^{-1}$, i.e. $9 \times 10^{-6}$ mol $l^{-1}$) when cadmium is introduced as insoluble cadmium hydroxide or soluble cadmium nitrate [2,3]. The mechanisms of Cd immobilization and the influence of Cd on cement hydration are not well understood so far. Cartledge et al. [2] have found that cadmium (Cd/cement mass ratio = 0.1) introduced as hydroxide is a source of nucleation sites for the precipitation of C–S–H and portlandite [$Ca(OH)_2$]. When cadmium is introduced as a soluble salt (nitrate of chloride), precipitation of $Cd(OH)_2$ occurs immediately as the pH increases due to clinker dissolution. This suggests that the main immobilization mechanism is physical entrapment. Many authors [3–5] agree with this result, but Herrera et al. [3] have noted that the substitution of $Ca^{2+}$ by $Cd^{2+}$ can involve diffusion or dissolution to form mixed hydroxides or calcium hydroxycadmiates, $CaCd(OH)_4$. Rossetti and Medici [6], using XRD, have not observed the precipitation of any calcium hydroxide in materials made with white cement mixed with cadmium chloride solution (Cd/cement = 0.02). Calorimetric tests have shown setting acceleration. On the contrary, Mollah et al. [7] have found that cadmium delays Portland cement hydration, which can be explained by the solubilization of $Cd(OH)_2$ to form $Cd(OH)_4^{2-}$ in highly alkaline environment (pH = 11–13). The retardant effect is due to the formation of calcium hydroxycadmiate by reaction between cadmium hydroxyl ions and the calcium ions that coat the C–S–H surfaces [8]. Recently, Park and Batchelor [9] have deduced from the concentration of residual cadmium in cement pore water that the main mechanism of immobilization is sorption of $Cd(OH)_4^{2-}$ on C–S–H surfaces.

In a companion paper [10], we have considered the exchange capacity of cadmium salts with already formed C–S–H. The present text deals with the case where cadmium is in the solution that is used for the cement hydration.

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## 2. Experimental

Due to the complexity of real Portland cement, the study has been conducted using the main "pure" phase, which is $C_3S$. Both very diluted systems (suspensions with water/solid (w/s) = 100) and pastes (w/s = 0.45) have been studied.

Triclinic-T1 $C_3S$ was prepared by repeated heating at 1550°C of a mixture of silica (Aerosil, Prolabo) and calcium carbonate. The residual content of CaO was determined by selective dissolution and found to be $\approx 1.7\%$. $C_3S$ was dry-milled to a Blaine surface area of $\approx 4000$ $cm^2$ $g^{-1}$.

The Cd-containing aqueous solution was prepared by dissolution of cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$] to yield $Cd/C_3S$ weight ratios of 0.05, 0.1, and 0.2.

Suspensions were prepared with 1.5 g of $C_3S$ ($T$ = 20°C, atmosphere of $CO_2$-free nitrogen). The pH was monitored during reaction. After times varying from 1 min to 7 days, the suspensions were filtered, and the filtrates were immediately dried with acetone then ether. Titration of Cd, Ca, and Si was done by ICP-AES.

Pastes were prepared by hand mixing 20 g of $C_3S$ and Cd-containing solutions during 1 min. Then, they were cured for 28 days at 20°C in sealed polyethylene bottles. Hydration was stopped by acetone/ether filtration of crushed samples.

Solid phases were characterized by XRD (Cu $K_\alpha$, Philips PW1710, with Si as an internal standard), $^{113}Cd$ CPMAS-NMR, and Cd-EXAFS. Ca/Cd hydroxide solid solutions were used as references for spectroscopic and XRD investigations. Details about NMR and EXAFS and about synthesis of mixed hydroxides are given in the companion paper [10].

## 3. Results

### 3.1. Suspensions

As shown in Table 1, cadmium retention is very fast, since the Cd concentration in the liquid falls from $4.4 \times 10^{-3}$ (initial value when $Cd/C_3S$ = 0.1) to $2.4 \times 10^{-3}$ mol $l^{-1}$ in 1 min only, to $5 \times 10^{-6}$ mol $l^{-1}$ in 10 min, and to less than $10^{-6}$ mol $l^{-1}$ in 3 days and longer. The residual concentration ($< 10^{-6}$ mol $l^{-1}$) is in good agreement with the values that were found in pore water of OPC with initial cadmium/cement ratios of 0.003 and 0.025 [4]. As far as the silicon concentration is concerned, the behavior is similar to that observed in diluted hydration of pure $C_3S$ [11]. The Si concentration is maximum after $\approx 10$ min, then decreases to $\approx 50 \times 10^{-6}$ mol $l^{-1}$. The maximum corresponds to the maximum of supersaturation with respect to C–S–H [12]. At the same time, the calcium concentration and pH increase. As seen later on, portlandite precipitates at times between 1 h and 3 days, and the final concentration of calcium stabilizes at a value slightly higher than the solubility of portlandite ($22 \times 10^{-3}$ mol $l^{-1}$) [13].

Table 1
Chemical analyses of solutions

| Sample | | | | Comparison of solution | | | |
|---|---|---|---|---|---|---|---|
| Water/ $C_3S$ | $Cd/C_3S$ | Cd ($10^{-3}$ mol $l^{-1}$) | Time | Si ($10^{-6}$ mol $l^{-1}$) | Ca ($10^{-3}$ mol $l^{-1}$) | Cd ($10^{-6}$ mol $l^{-1}$) | pH |
| 100 | 0.05 | 4440 | 7 days | 7 | 25 | < 1 | 12.3 |
| 100 | 0.1 | 8880 | 1 min | 260 | 8 | 2360 | 8.7 |
| | | | 10 min | 535 | 12 | 4.7 | 12.1 |
| | | | 1 h | 48 | 18 | 1.2 | 12.4 |
| | | | 3 days | 6 | 30 | < 1 | 12.5 |

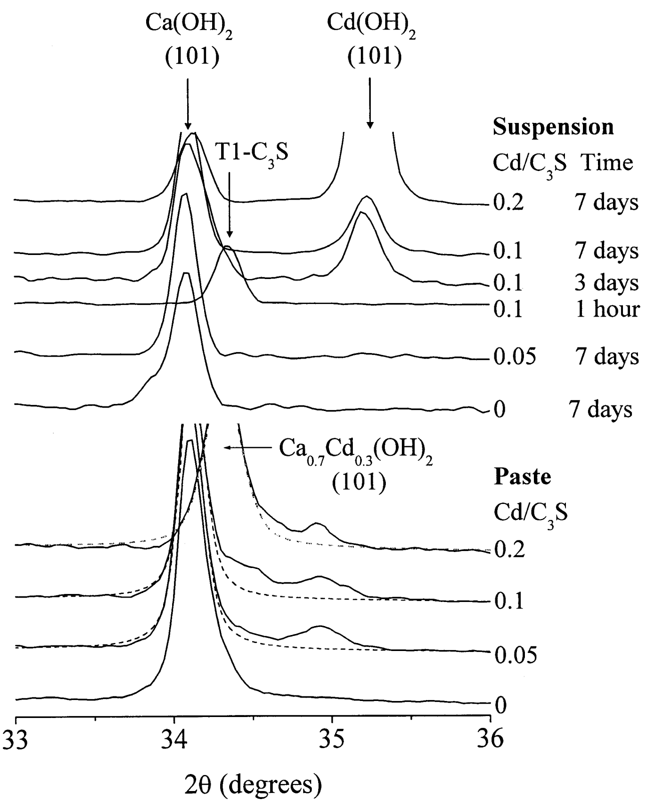

Fig. 1. XRD patterns between 33° and 36° (2θ) of $C_3S$ suspensions (water/$C_3S$ = 100) and pastes (water/$C_3S$ = 0.45) mixed with cadmium solution. Dashed lines are the fit of the (101) reflection.

For all suspensions, XRD patterns of products hydrated for 7 days show the formation of poorly crystallized C–S–H, $Ca(OH)_2$, and residues of $C_3S$. $Cd(OH)_2$ is only observed in solids with $Cd/C_3S \geq 0.1$. For the suspension with $Cd/C_3S$ = 0.1, the precipitation of $Cd(OH)_2$ occurs between 1 h and 3 days, then the quantity of precipitate is stable from 3 to 7 days (Fig. 1).

For the material with $Cd/C_3S$ = 0.05 hydrated for 7 days, the radial distribution function obtained by Fourier transform of Cd-EXAFS spectra shows one peak only, attributed to the Cd–O shell at 2.25 Å with a coordination number of 5 (Fig. 2 and Table 2). The absence of any peak beyond this shell is characteristic of disordered materials. For the material with $Cd/C_3S$ = 0.1 hydrated for 7 days, EXAFS confirms the presence of $Cd(OH)_2$. The first shell (Cd–O) is at the same distance as in $Cd(OH)_2$, with a

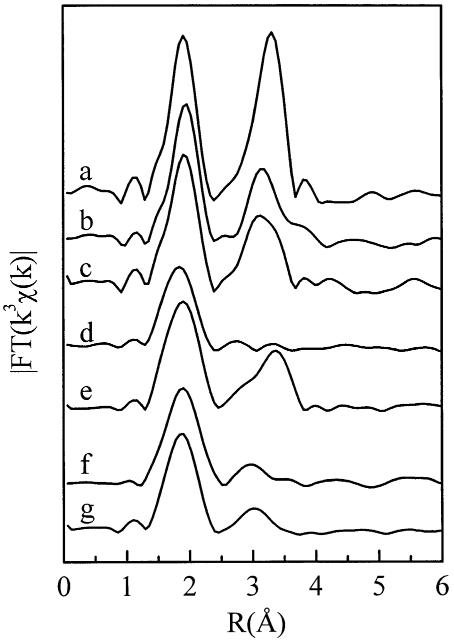

Fig. 2. Cd-EXAFS Fourier transform amplitude (radial distribution function) of (a) $Cd(OH)_2$, (b) $Cd_{0.1}Ca_{0.9}(OH)_2$, (c) $Cd_{0.5}Ca_{0.5}(OH)_2$, (d) suspension (water/$C_3S$ = 100) with Cd/$C_3S$ = 0.05, (e) suspension (water/$C_3S$ = 100) with Cd/$C_3S$ = 0.1, (f) paste (water/$C_3S$ = 0.45) with Cd/$C_3S$ = 0.05, and (g) paste (water/$C_3S$ = 0.45) with Cd/$C_3S$ = 0.10.

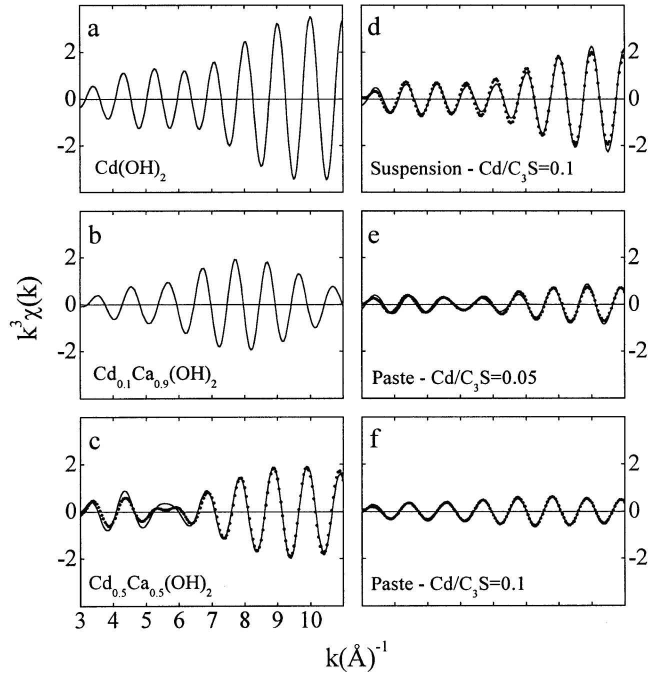

Fig. 3. Filtered EXAFS function of the second shell of the radial distribution function (from 2.4 to 4 Å) of Cd-containing samples. Dots are the fitted curves. Results of the fitting procedures are given in Table 2.

coordination number of ≈6. The Debye–Waller parameters, which characterize thermal and static disorder, are similar in both materials. The second peak of the Fourier transform of the EXAFS function is well fitted by a unique Cd–Cd shell at 3.49 Å as in $Cd(OH)_2$ (Fig. 3), but with two differences, namely, (1) the peak is smaller and (2) the coordination number is ≈3.5 [instead of ≈6 in $Cd(OH)_2$]. Since EXAFS probes the mean environment of all atoms of a given type, this result means that the partition of Cd atoms is ≈60% in $Cd(OH)_2$ and ≈40% in the other solid phases, whose EXAFS contribution is small in this radius range. This Cd amount corresponds approximately to the total amount of Cd in the material with Cd/$C_3S$ = 0.05. So, it may be assumed that the environment of this cadmium fraction is the same in both cases.

Cd-CPMAS-NMR spectra of materials with Cd/$C_3S$ superior to 0.1 are shown in Fig. 4 (the materials with smaller Cd contents yield noisy spectra). The results con-

Table 2
Structural parameters as determined by fitting the EXAFS function

| | | | First shell Cd–O | | | Second shell Cd–Cd/Ca | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | *d* (Å) | Δσ (Å)[a] | *N* | Shell | *d* (Å) | Δσ (Å)[a] | *N* |
| *Phases of reference* | | | | | | | | | |
| $Cd(OH)_2$ | | | 2.27[b] | – | 6[b] | Cd–Cd | 3.50[b] | – | 6[b] |
| $Cd_{0.1}Ca_{0.9}(OH)_2$ | | | 2.29 | 0.025 | 5.7 | Cd–Ca | 3.50[b] | – | 6[b] |
| $Cd_{0.5}Ca_{0.5}(OH)_2$ | | | 2.28 | 0.037 | 6.0 | Cd–Ca | 3.50 | 0.008 | 2.9 |
| | | | | | | Cd–Ca | 3.50 | 0.001 | 3.1 |
| *Cd-containing $C_3S$ pastes and suspensions* | | | | | | | | | |
| Water/$C_3S$ | Cd/$C_3S$ | Time | | | | | | | |
| 0.45 | 0.05 | 1 month | 2.27 | 0.061 | 5.9 | Cd–Cd | 3.48 | 0.024 | 1.3 |
| | | | | | | Cd–Ca | 3.52 | 0.034 | 2.6 |
| 0.45 | 0.10 | 7 days | 2.27 | 0.057 | 5.7 | Cd–Cd | 3.48 | 0.015 | 1.1 |
| | | | | | | Cd–Ca | 3.52 | 0.022 | 2.9 |
| 100 | 0.05 | 7 days | 2.25 | 0.060 | 5.0 | | | | |
| 100 | 0.10 | 7 days | 2.28 | 0.008 | 6.0 | Cd–Cd | 3.49 | 0.005 | 3.5 |

*d* = mean distance between neighbors and Cd atoms, σ = Debye–Waller parameter, and *N* = number of neighbors.

[a] Difference between fitted and references values of σ for each Cd–*X* shell.

[b] Fixed values during refinement.

firm the presence of $Cd(OH)_2$ in materials hydrated for times superior to 3 days. After 1 h hydration (no $Cd(OH)_2$ detected by XRD), there is a broad peak at ≈ 175 ppm, a chemical shift that is not in the range of chemical shifts observed in Cd/Ca hydroxide solid solutions or Cd/Ca silicate hydrates [10].

### *3.2. Pastes*

The XRD patterns of paste materials differ from that of suspension materials (Fig. 1). In pastes, $Cd(OH)_2$ is never observed, but there is precipitation of Ca/Cd hydroxide solid solution. In the companion paper (Part I), we have reported that a Ca/Cd solid solution (portlandite type) forms from a mixture of Cd and Ca salts treated in alkaline media. In the present case, the material with $Cd/C_3S = 0.2$ leads to a significant shift of the $Ca(OH)_2$ Bragg peaks, which suggests that portlandite is enriched with cadmium. Using the cell parameter vs. Cd content relationship, one finds $Ca_{0.7}Cd_{0.3}(OH)_2$ as hydroxide formula. For the materials less concentrated in cadmium, there is no significant shift of the $Ca(OH)_2$ peaks, but the pattern decomposition shows the presence of a broad peak located between the $Ca(OH)_2$ and $Cd(OH)_2$ peaks for a given hkl reflection. This indicates a continuous Ca/Cd hydroxide solid solution.

Cd-EXAFS analysis of the second radial distribution shell confirms that the Cd atoms are mainly located in the Cd/Ca hydroxide (Fig. 3 and Table 2). The shell contains ≈ 3 Ca atoms and 1 Cd atom at about the same distance of the central atom. The sum is ≈ 4 instead of 6, which would be the value if all the cadmium atoms were located in the hydroxide. The presence of the hydroxide is corroborated by NMR (Fig. 4).

The chemical shifts of the main line in materials with $Cd/C_3S = 0.1$ and 0.2, respectively are in the range of what is observed for $Ca_{0.5}Cd_{0.5}(OH)_2$ and $Ca_{0.9}Cd_{0.1}(OH)_2$.

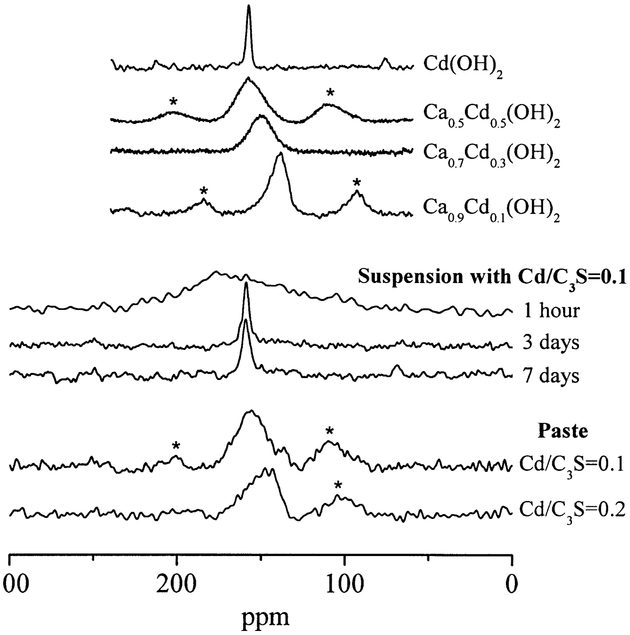

Fig. 4. Cd-CPMAS-NMR of Cd-containing samples. * = spinning side bands.

## 4. Discussion

All these results show that the Cd speciation in $C_3S$ systems is not a simple precipitation of $Cd(OH)_2$, as expected by many authors when the pH increases during the $C_3S$ dissolution [2–5]. $Cd(OH)_2$ has a low solubility ($K_{sp} = 10^{-13.7}$; [14]) even in alkaline media at pH = 13, where solubility is inferior to $10^{-6}$ mol $l^{-1}$ [9,14]. In $C_3S$ suspensions, our results show that there is no Cd hydroxide precipitation even after long times for Cd concentrations of $\leq \approx 4 \times 10^{-3}$ mol $l^{-1}$ ($Cd/C_3S = 0.05$), and no precipitation after 1 h for a Cd concentration of $8 \times 10^{-3}$ mol $l^{-1}$ ($Cd/C_3S = 0.1$). In all cases, the pH is superior to 12. Barret and Bertrandie [15] and Barret et al. [16] have suggested that in $LaCl_3$ salt solution mixed with $C_3S$ (water/$C_3S = 20$), immobilization is due partly to the formation of a silicate hydrate and partly to an insoluble hydroxide ($K_{sp} = 2 \times 10^{-19}$). Precipitation of lanthanum silicate hydrate is possible during the short period of maximum supersaturation with respect to C–S–H where a maximum concentration of $SiO_2$ of 1 mmol/l is observed. Subsequently, the silicate concentration becomes negligible with respect to $OH^-$, so La precipitates as hydroxide. Whereas we have shown in the first part of this series of articles that cadmium silicate or cadmium/calcium silicate hydrates may be formed in special conditions, we do not think that this mechanism occurs significantly in the present case. First, Cd-NMR and EXAFS studies do not agree on the formation of such silicates. Second, in the case of the suspension with an initial cadmium concentration of $8.8 \times 10^{-3}$ mol $l^{-1}$, after 1 h reaction, all the cadmium is fixed as a solid phase. If all cadmium atoms would precipitate as silicate hydrates, a further formation of $Cd(OH)_2$, which is observed after 1 day, should not occur, because the solubility of metal silicate hydrate is generally lower than that of the corresponding metal hydroxide [17].

### *4.1. Suspensions*

Interpretation of our results implies sorption of cadmium on C–S–H as an important immobilization mechanism during hydration of $C_3S$. To support this hypothesis, a suspension of $C_3S$ (water/$C_3S = 100$) has been filtrated after 10 min reaction. The pH of the solution was measured to be about 12.0. Then, a concentrated cadmium nitrate solution was added drop by drop to this solution until the total Cd concentration reached $4 \times 10^{-3}$ mol $l^{-1}$. In this case, immediate precipitation of cadmium hydroxide occurred as confirmed by XRD.

The radial distribution function of Cd (calculated from EXAFS data) in the $Cd/C_3S = 0.05$ sample is characteristic of an outer shell aqueous complex for which only a unique ligand shell may be distinguished and supports the mechanism of nonspecific sorption. Mollah et al. [8] and Park and Batchelor [9] have suggested that the sorption of metals onto C–S–H implies metallic anionic species like $CrO_4^{2-}$, $Cd(OH)_4^{2-}$, and $Pb(OH)_4^{2-}$, which are the dominant aqueous species in very alkaline media. The negatively charged metal ions would not be expected to adsorb on the negatively charged silica surface of C–S–H. However, a positive charge of the Stern layer due to absorption of calcium (or sodium in the case of Portland cement) can exceed the negative charge of the surface and explain the electrostatic interaction of metal anions with C–S–H. These triple layer models can not easily explain the delayed precipitation of $Cd(OH)_2$ after a time that depends on the initial Cd concentration. Analysis results show that immobilization is a very fast step and occurs probably at a pH much lower than 12. Then, the sorption mechanism probably implies cations like $Cd^{2+}$ and $Cd(OH)^+$ rather than anions. Due to the chemical similarity between calcium and cadmium cations, $Cd^{2+}$ may be mixed with $Ca^{2+}$ and form a counterion layer around negative C–S–H surface. The subsequent precipitation of $Cd(OH)_2$, which appears after a substantial time when the initial cadmium concentration is important, is probably the consequence of the slow increase of $OH^-$ ions in solution during the dissolution of $C_3S$ before the supersaturation maximum with respect to portlandite.

### *4.2. Pastes*

Differences between the fixation mechanism of cadmium in suspensions and in pastes have been pointed out in this study. In the case of pastes, it is likely that a part of the calcium/cadmium hydroxide solid solution is formed immediately when $C_3S$ is mixed with cadmium nitrate solution, because residual lime, present in the raw material, is quickly dissolved before $C_3S$ dissolution starts. The rapid increase of pH and $Ca^{2+}$ concentration promotes the precipitation of the mixed hydroxide until all the $OH^-$ released by the dissolution of CaO are consumed. These hypotheses are supported by the fact that the quantities of Cd-containing hydroxides in pastes do not seem to depend on initial cadmium content for $Cd/C_3S < 0.20$. In these cases, the large range of hydroxide solid solution composition probably reflects a chemical composition heterogeneity of the system.

For diluted Cd samples, ($Cd/C_3S \leq 0.1$), EXAFS analysis shows that a fraction of the cadmium atoms are not immobilized in hydroxides. It supports the hypothesis of the sorption of that fraction of cadmium atoms on C–S–H as in suspension samples. However, for the concentrated Cd sample ($Cd/C_3S = 0.2$), Cd fixation is strongly influenced by the w/s ratio. Whereas, in suspension, Ca and Cd precipitate as separate hydroxides $Ca(OH)_2$ and $Cd(OH)_2$, in paste, they form a unique solid solution hydroxide $Ca_{1-x}Cd_x(OH)_2$ with $x = 0.3$. With the present data, it is not possible to give a simple explanation of these differences and complementary experiments, in particular with intermediate w/s ratio, are in progress.

## 5. Conclusion

Spectroscopic investigation of $C_3S$ hydrated in cadmium nitrate solutions has revealed different mechanisms of cadmium immobilization depending on w/s and cadmium/tricalcium silicate ratios. In Cd-containing samples hydrated in a large quantity of water, $Cd(OH)_2$ does not precipitate after 1 week for low Cd contents. As initial cadmium concentration increases, precipitation of $Cd(OH)_2$ occurs but is delayed with respect to the increase of pH, which is normally propitious to the hydroxide precipitation. These results support the assumption that the sorption of $Cd^{2+}$ on hydrated products is an important mechanism of retention.

In the case of low w/s ratio (0.45), for the Cd-diluted samples, one part of the cadmium is found in continuous calcium–cadmium mixed hydroxides, and the other part is probably sorbed on C–S–H. For the Cd-concentrated samples, the excess of cadmium is mixed with portlandite. It may be noticed that the present results can not be extrapolated to real cement for which the concentrations of ionic species in interstitial solution are very different but may serve as a starting point for an ulterior study.

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