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Managing trace elements in Portland cement – Part I: Interactions between cement paste and heavy metals added during mixing as soluble salts

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ABSTRACT

The aim of this work is to investigate the effect of the addition of Cu, Cd, Ni, Pb and Zn nitrate salts on the compressive strength of a CEM I Portland cement. Concentrations of 0.018 or 0.18 mol/kg of cement of each trace element were tested. After 2 days age, the compressive strength was reduced by various extents by addition of heavy metals, with the exception of Ni. This difference is due to a delay in tricalcium silicate hydration (C_3S) as shown by an isothermal calorimetry test. Trace elements also influence the 28-days compressive strength, whereas the measured degree of hydration of these cement pastes is the same. As shown by scanning electron microscopy and X-ray diffraction, Cu and Pb are predominantly absorbed in the calcium silicate hydrate gel (C–S–H) while Cd, Ni and Zn are mainly precipitated as hydroxides within the intergranular porosity. Thus, trace elements precipitated as hydroxides have only a slight effect on the compressive strength. In contrast, Cu and Pb cause an increase in mechanical resistance by changing the C–S–H nanometric assembly and its density.

1. Introduction

Portland cement clinker is manufactured by burning at high temperature a raw meal consisting mainly of limestone and clay. In recent years, an increase in the content of trace elements such as heavy metals in cement has been observed [1,2]. Trace elements may be derived from raw materials or fuels. Among raw materials, a distinction is made between primary (limestone, clay,...) and secondary (sediments, sludge) raw materials. Fuels are of two types: fossil fuels (coal, oil coke,...) and secondary fuels (tires, waste oils,...) [2]. The presence of trace elements in clinker and thereafter in Portland cement can have significant consequences. First, during the clinkerization, trace elements can induce changes in phase stability. Indeed, several studies [3–11] have shown that trace elements can be incorporated into clinker phases. Second, during the hydration of cement, trace elements are released into the pore solution having a basic pH and can thereafter react. They are likely to be absorbed on some hydrates such as the calcium silicate hydrate gel (C–S–H) or form new compounds such as hydroxides [3–11]. Several consequences can arise with respect to technical properties of the cement such as its setting times and compressive strengths [12–18]. Also, the environmental impact of such cement pastes containing trace elements has to be considered. Indeed, according to the immobilization nature of trace elements in the cement paste, the kinetics of their leaching will be very different [4,19–25]. As a consequence, numerous studies have dealt with one or several of the points mentioned above. Two main types of studies have been carried out. On the one hand, trace elements are added during the clinkering process mainly to study phase stability and their subsequent consequences on technical properties and on the other hand, trace elements are introduced during mixing as soluble salts to study their impact on the hydration and also on the environment.

The results presented in literature highlight several contradictions concerning the effect of trace elements added during mixing. Most studies compare the effect of various trace elements on mixing, as they worked in weight percentage [4,9,11,18,26–28] and without taking into account the effect of the counter ion, which in our opinion can lead to two types of inaccuracies in the interpretation of the results: (a) working with weight percentages induces different molar concentrations of trace elements as a function of their molar weight. Indeed, at equal weight percentage, a trace element with a higher molar weight will be less concentrated. (b) It is well established that chlorides have an accelerating effect on hydration [31] while nitrates cause a delay [29,32], therefore, in our opinion it is difficult to compare trace elements effects without considering their corresponding counter ion as for example in comparing the results obtained by Rossetti and Medici [29] who worked on trace elements as chloride salts with results by Díez

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et al. [30] who used nitrate salts. Thus, to better understand the effect of trace elements and to compare them, it is necessary to use the same counter ion and an equal number of moles of trace element per unit mass of cement.

The results presented here are part of a larger study on the impact of trace elements on the technical and environmental properties of Portland cement. The aim of this paper is to assess the effect of Cu, Cd, Ni, Pb and Zn added during mixing, by using the same counter ion (nitrates) and an equal number of moles, on the mechanical strength of mortars.

First, the compressive strengths at 2 and 28 days were monitored, and then its evolution has been correlated to modifications of the microstructure. Finally, to confirm the previously observed trends, the effects of the addition of Cd and Zn as chloride salts were also studied.

2. Materials and methods

The compressive strength was determined on standard mortars made according to the French standard (NF-EN-196–13 [33]). The mercury intrusion porosimetry, isothermal calorimetry, thermogravimetry, X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements described below were performed on cement pastes with a water/cement ratio (w/c) by mass equal to 0.5. The cement used in this study is an Ordinary Portland Cement (OPC) (CEM I 52.5 N) produced by Lafarge. Its chemical composition is given in Table 1.

Three controls were made: Control 1, without admixture, Control 2 adding $Ca(NO_3)_2{\cdot}4H_2O$,and Control 3 with $CaCl_2{\cdot}2H_2O$. For assays, added trace elements during mixing were in the form of nitrate or chloride (hydrated) salts: $Ni(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Pb(NO_3)_2$, $CdCl_2{\cdot}5H_2O$ and $ZnCl_2$. The tested concentrations in trace elements were 0.018 and 0.18 mol of element per kilogram of cement. Table 2 compares the highest concentrations to those of OPC [2]. For clarity, the concentrations are expressed in weight percentage.

After 2 and 28 days of curing at 100% relative humidity, the compressive strength was measured on six samples following the NF-EN-196–13 standard [33] with an Instron 4206 press.

The heat of hydration of cement pastes was measured by means of an isothermal calorimeter. A sample of 5 g of cement and 2.5 g of water previously stored at 20 °C were mixed manually for a few seconds before placing the cells inside the calorimeter. The measurements were processed at 20 °C. The effect of trace elements on hydration was studied by determining at what time the heat released due to C_3S hydration begins.

The experimental methods described below were applied on 28-days-old cement pastes, whose hydration was stopped by vacuum drying.

Total porosity and pore size diameter were measured by mercury intrusion porosimetry (MIP). Measurements were performed by using a Micrometrics-Autopore IV system at low and high pressure (31,000 psi or 231.2 MPa).

The calcium hydroxide (portlandite) content of the pastes was determined by thermogravimetric analysis (TGA) using a Netzsch STA 409 system. One gram of sample was placed in an alumina crucible and heated from 20 to 105 °C at a rate of 2 °C/min. The temperature was stabilized at 105 °C for 30 min. The sample was finally heated from 105 to 1100 °C at a rate of 3 °C/min. Throughout the analysis, the sample was maintained under an argon atmosphere, flowing at a rate of 75 ml/min. XRD analyses were performed on cement paste powders. A Bruker D8 with Co Kα radiation ($K\alpha$ = 1.78 Å) is used. The X-ray patterns were acquired in the 2θ (10–100°) interval with a step of 0.0197° and 3 s per step.

Table 2
Comparison of average trace element concentrations in OPC and those introduced in the present study.

Trace element	Average concentration in OPC [2], wt.%	The 0.18 mol/kg converted to wt.%
Ni	0.0045	1.05
Cu	0.0038	1.14
Zn	0.0164	1.18
Cd	0.00006	2.02
Pb	0.0027	3.73

The microstructure was observed on polished sections with a Hitachi S-4300SE/N SEM operating in backscattered electron mode (20 KeV and 2 KA) and also equipped with an energy dispersive X-ray spectrometer (EDS). To make the polished sections, a piece of cement paste was vacuum impregnated in epoxy resin and then polished with ethanol to avoid reaction with water. Finally, the samples were carbon coated before observation.

3. Results and discussion

3.1. Compressive strengths

The compressive strength of cement is an important technical property; therefore, it is essential to determine the impact of trace elements. The results of the mortars' compressive strengths after 2 and 28 days of curing are summarized in Table 3.

At 2 days, the measurements of compressive strength reveal two trends. First, the addition of Cu, Zn, Cd and Pb lead to a decrease in compressive strength compared to Controls 1 and 2. However, large differences exist between these four trace elements. Indeed, it is noted that the compressive strength of mortars doped with Cd and Pb are lower than controls. In contrast, for mortars doped with Cu and Zn, the compressive strength is close to zero. Finally, the addition of Ni has no significant effect.

To explain the differences observed between the early compressive strengths of mortars, calorimetric measurements were per-

Table 3
Compressive strengths obtained after 2 and 28 days of mortar curing.

	Compressive strength (MPa)		
	2 days	28 days	
Control 1 (CEM I)	45.1 ± 1.5	69.6 ± 2.2	
Samples	0.18 mol/kg	0.018 mol/kg	0.18 mol/kg
Control 2 ($Ca(NO_3)_2$)	42.2 ± 0.5	64.5 ± 1.9	70.4 ± 2.7
$Ni(NO_3)_2$	40.4 ± 1.1	64.4 ± 1.2	69.2 ± 2.4
$Cu(NO_3)_2$	1.2 ± 0.0	71.9 ± 1.4	72.8 ± 2.3
$Zn(NO_3)_2$	1.0 ± 0.0	71.1 ± 1.9	62.9 ± 1.0
$Cd(NO_3)_2$	36.4 ± 0.4	65.3 ± 0.8	68.4 ± 1.6
$Pb(NO_3)_2$	22.5 ± 1.1	69.0 ± 2.3	81.2 ± 2.1

Table 1
Chemical composition of cement.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MgO	SO_3	Mn_2O_3	TiO_2	P_2O_5	SnO	LOI	Total	Free lime
Dry, wt.%	20.76	4.54	2.70	65.38	0.07	0.88	1.38	3.30	0.02	0.28	0.21	0.02	0.83	100.37	0.31

formed on cement paste containing 0.18 mol of trace element/kg of cement. Given that cement hydration is an exothermic process, the observation of heat released provides information about the kinetics of hydration of each cement constituent. Here, focus was on C_3S hydration because this constituent is mainly responsible for the early-age compressive strength. Curves presented in Fig. 1 indicate that the peak due to C_3S hydration for Controls 1 and 2 appears at about 2 h. Moreover, the trace elements seem to have different effects on hydration. Except Ni, which has a small influence on C_3S hydration, the four other trace elements lead to a delayed hydration reaction compared to the controls. Indeed, for cement paste doped with Cd and Pb, the hydration occurs respectively at about 5 h and 25 h. Finally the most important delay is observed for cement pastes doped with Cu or Zn. Their hydration occurs after a longer time, respectively at about 100 and beyond 360 h.

Thus, the decrease in early-age compressive strength seems to be caused by a delay of the C_3S hydration. Indeed, the more the C_3S hydration is delayed, the more the compressive strength at early ages is low. Díez et al. [30] have previously observed that 5 wt.% of Cd as a nitrate salt retards the cement hydration and decreases the early compressive strength.

At 28-days, the mortar compressive strength has been monitored for 0.018 and 0.18 mol of trace element/kg of cement (Table 3). The results reveal that the highest effect is observed for the higher concentration in each trace element. Moreover, three main trends have been highlighted. First, the addition of Cu and Pb lead to an increase in compressive strength compared to the controls, which is in accordance, for example, with Cullinane et al. [14], who have previously shown that the addition of 5 wt.% of Pb as a nitrate salt in cement strongly enhances the compressive strength. However, a distinction must be made between these two trace elements. Indeed, the addition of Pb causes a greater increase in compressive strength than Cu. Then, the values obtained for Ni and Cd are close to those of the controls. Therefore, Ni and Cd have no significant effect on the compressive strength. Finally, the addition of Zn leads to a slight decrease in the compressive strength compared to the controls. This last result is less in accordance with those observed in the literature. For example, a decrease in the compressive strength was observed, only for up to 7 days, when 15 wt.% of Zn are added to cement [18]. The disagreement between our results and those of Olmo et al. [18] is probably due to different experimental conditions such as the concentration and the nature of the counter ion. In the previous example [18], zinc is introduced in the form of an oxide. Our study is the first, where similar experimental conditions are used for all the studied trace elements. In fact, all trace elements were added at equal molar concentration and having a single counter ion.

In order to correlate the evolution of the 28-days mechanical strength to the modifications of microstructure, TGA, total porosity, pore size diameter, SEM and XRD measurements were carried out. The results are presented in the following sections. Given that trace elements added at 0.018 mol/kg of cement induce no significant effect on the 28-days compressive strengths, further discussion will be exclusively focussed on the results obtained with the higher concentration in trace elements (0.18 mol/kg).

3.2. Calcium hydroxide (portlandite) content

To compare the effect of trace elements on the degree of cement hydration, the content of calcium hydroxide was determined by TGA. The results are presented in Table 4 as a weight percentage. The dehydration of calcium hydroxide occurs between 400 and 500 °C as described by the following equation:

$$Ca(OH)_2 \rightarrow CaO + H_2O$$

The TGA shows that, after 28 days, the difference of portlandite content between cement pastes made with each trace element is not significant. Therefore, the degree of hydration of cement pastes

Table 4
Portlandite content, total porosity and pore size diameter (nm) of 28-days-old cement pastes with 0.18 mol of trace element/kg of cement.

Samples	$Ca(OH)_2$ (wt.%)	Total porosity (%)	Pore size diameter (nm)
Control 1 (CEM I)	20.8	25.0	24.8
$Ni(NO_3)_2$	20.7	24.7	23.1
$Cu(NO_3)_2$	20.3	19.3	15.1
$Zn(NO_3)_2$	19.7	21.7	26.7
$Cd(NO_3)_2$	19.6	27.1	25.6
$Pb(NO_3)_2$	20.8	20.9	16.9

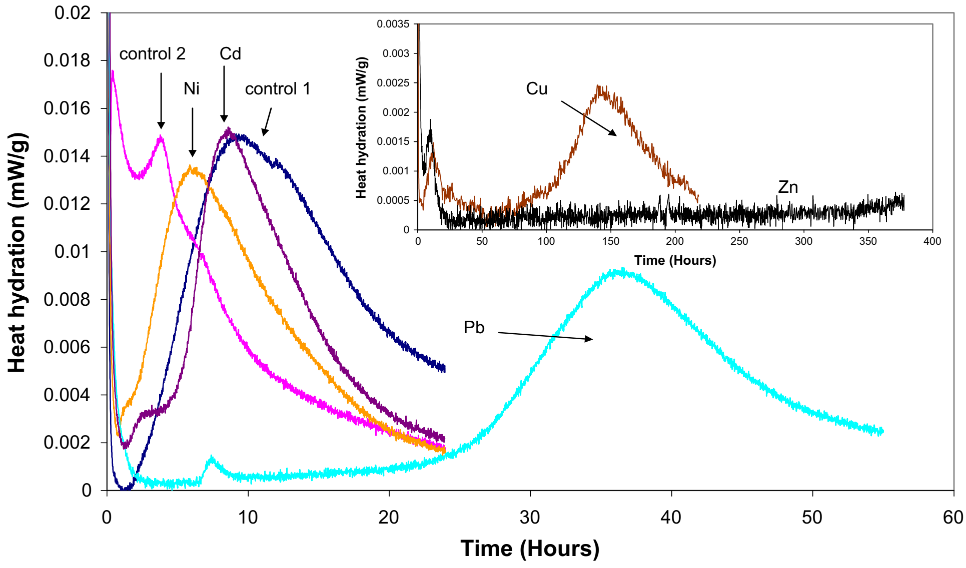

Fig. 1. Heat of hydration versus time of different cement pastes doped with 0.18 mol of trace elements/kg of cement as nitrate salt.

is very close and can not be the cause of differences encountered in terms of mechanical strength. This result implies that this difference can be caused by the microstructure and the density of C–S–H. Several studies [34–39] have shown that temperature can modify the density of C–S–H and by that the compressive strength. One might suppose that trace elements could have the same consequences as temperature. Indeed, in equal molar amount, if the C–S–H is less dense, it will occupy a larger volume resulting in a lower total porosity and an increased compressive strength.

To validate this hypothesis, total porosity, pore size diameter, SEM and XRD measurements were carried out.

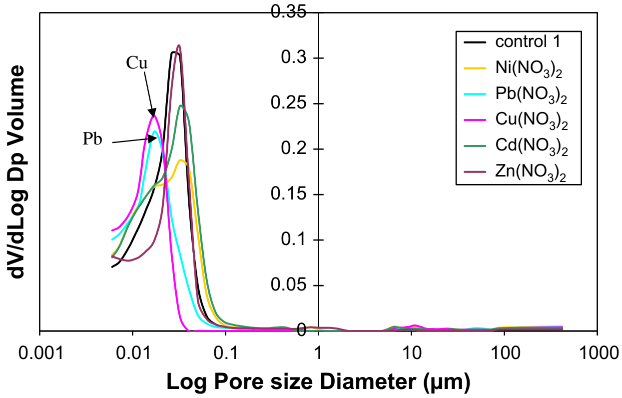

Fig. 2. Pore size diameter distribution for cement paste 28 days aging and doped with 0.18 mol of trace element/kg of cement.

3.3. Total porosity and pore size diameter

Total porosity and pore size diameter (Table 4) reveal a wide disparity of behaviours depending on the trace element. Three main trends have been highlighted. We noted, in particular, that cement pastes doped with Cu and Pb lead to different values from the other compounds. Indeed their porosity and pore size diameter are the lowest. Nickel has no effect on porosity and pore size diameter. Finally, Zn and Cd did not significantly affect the pore size diameter, although the highest porosity is obtained in the presence of Cd.

The pore size diameter distribution (Fig. 2) indicates that the samples doped with Cu and Pb have once again different behaviours from the other trace elements. They have indeed the lowest pore size diameter. For the three other trace elements, the results are close to those of the control.

The results for cement pastes with high contents of Cu and Pb are consistent with the high values of 28-days compressive strength obtained previously. For the three other compounds, no correlation between total porosity and compressive strength could be established.

3.4. SEM analyses

SEM coupled with EDS was used to determine the distribution of trace elements in cement pastes. Knowing that trace elements have been introduced during mixing, they would be present in hydrated phases like portlandite, ettringite or C–S–H. For example, the C–S–H, which is a product of the calcium silicate hydration, grows mainly around the anhydrous grains of cement.

The analyses reveal that Cu and Pb (Fig. 3) seem to be mainly fixed, in the periphery of anhydrous cement grains. They are there-

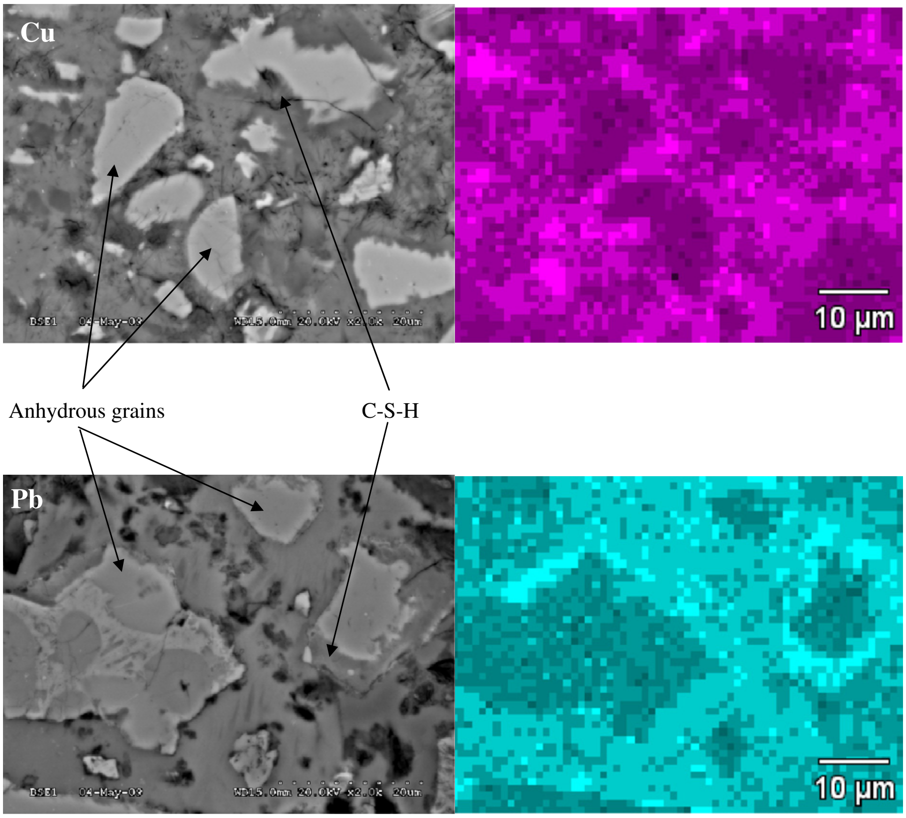

Fig. 3. SEM photos (left) and elemental X-ray images (right) of cement pastes doped with Cu and Pb.

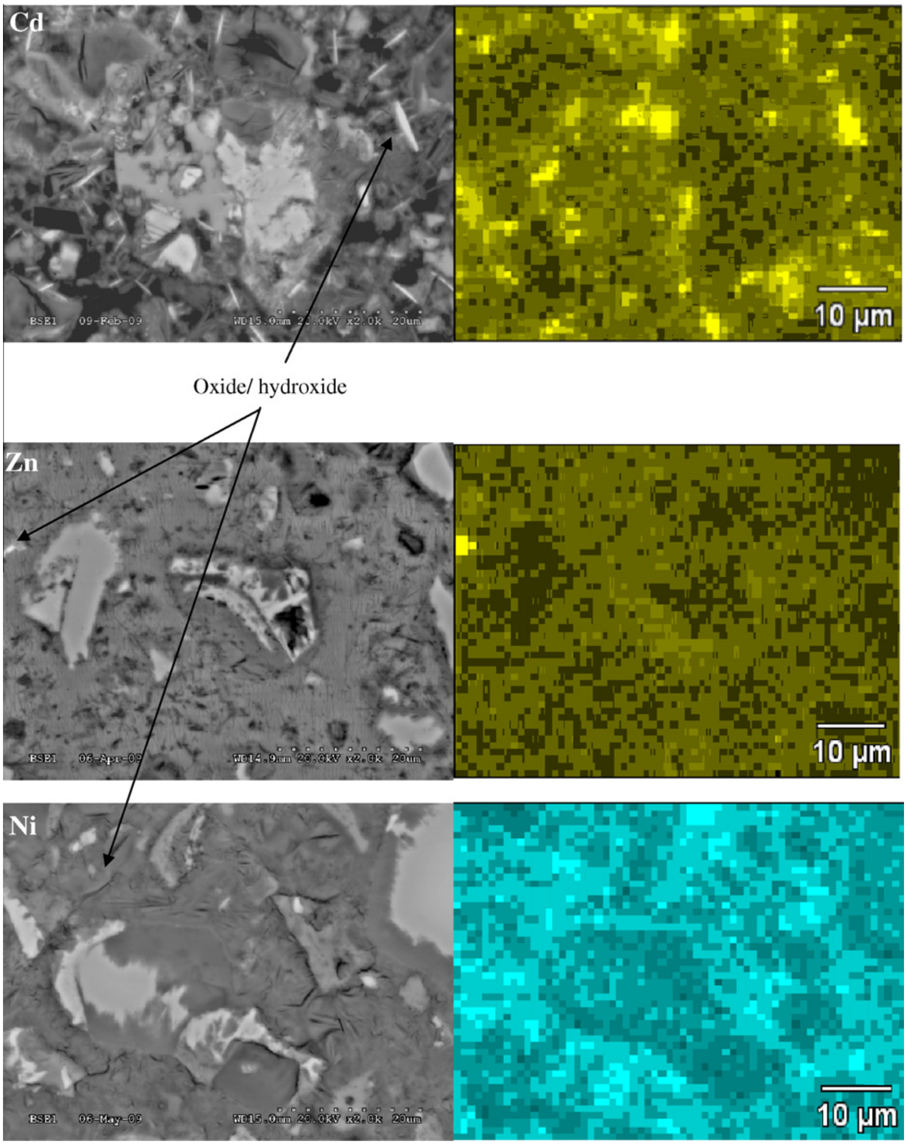

Fig. 4. SEM photos (left) and elemental X-ray images (right) of cement pastes doped with Cd, Zn and Ni.

fore mainly concentrated in the C–S–H. Also, Cd and Zn enriched areas have been detected. These two trace elements could be present in cement paste in oxide or hydroxide forms (Fig. 4). Finally, Ni seems to behave as Cd and Zn. Indeed, it does not appear to be fixed in the C–S–H (Fig. 4).

All these results should be taken with caution because the trace elements are difficult to detect by SEM. Further analyses would be necessary to study in more detail the results obtained. Recall that the aim of this paper is to assess the impact of trace elements added during mixing by using the same counter ion and an equal molar concentration.

3.5. XRD analyses

XRD patterns show that cement pastes contain crystalline hydrates (ettringite, portlandite) and anhydrous grains (C_3S and C_2S) which have not totally reacted. Thus, the complete hydration of cement is not achieved at 28 days. Moreover, in the case of Cd and Zn, the results reveal that new compounds have been formed during hydration compared to the control. Indeed, after 28 days, the analysis of cement paste with a high content of Cd indicates the presence of $CaCd(OH)_4$ (labelled X in Fig. 5). In our conditions, the well-known calcium hydroxo-zincate ($CaZn_2(OH)_6 \cdot 2H_2O$) is not detected at 28 days. However, additional tests conducted at early ages (2 days of curing) confirm the presence of this compound (labelled Y in Fig. 6). Regarding cement pastes doped with Cu, Ni and Pb, no new compounds were identified.

3.6. Complementary tests

In order to validate the trace element effect on technical properties, we studied the evolution of compressive strength when Cd and Zn are added as chloride salts to cement during mixing. These trace elements were chosen because, when they are introduced as nitrate salts, their effects on the 28 days compressive strength were significantly different.

The results (Table 5) reveal that the early compressive strength measured for Cd is lower than that of Control 3. At 28 days aging, their values are very close to each other. In the case of Zn, the compressive strengths measured after 2 days are close to zero. Then

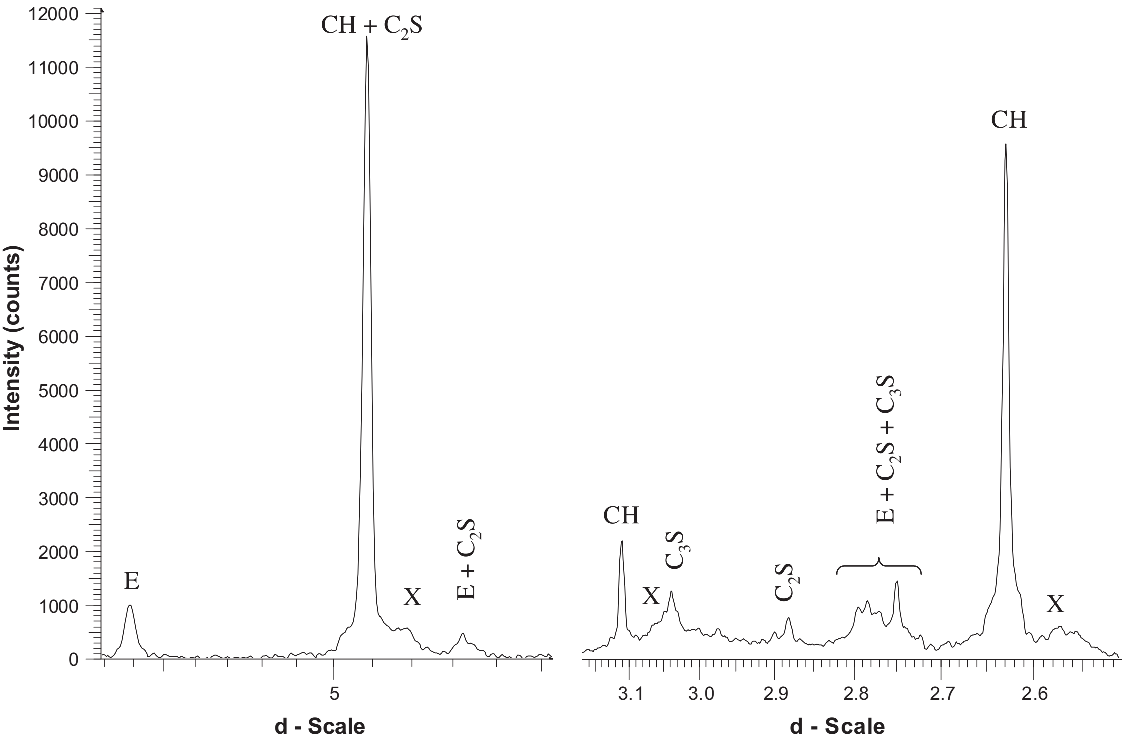

Fig. 5. XRD patterns of cement paste doped with Cd hydrated for 28 days; C_3S, C_2S, E = ettringite, CH = portlandite, X = $CaCd(OH)_4$.

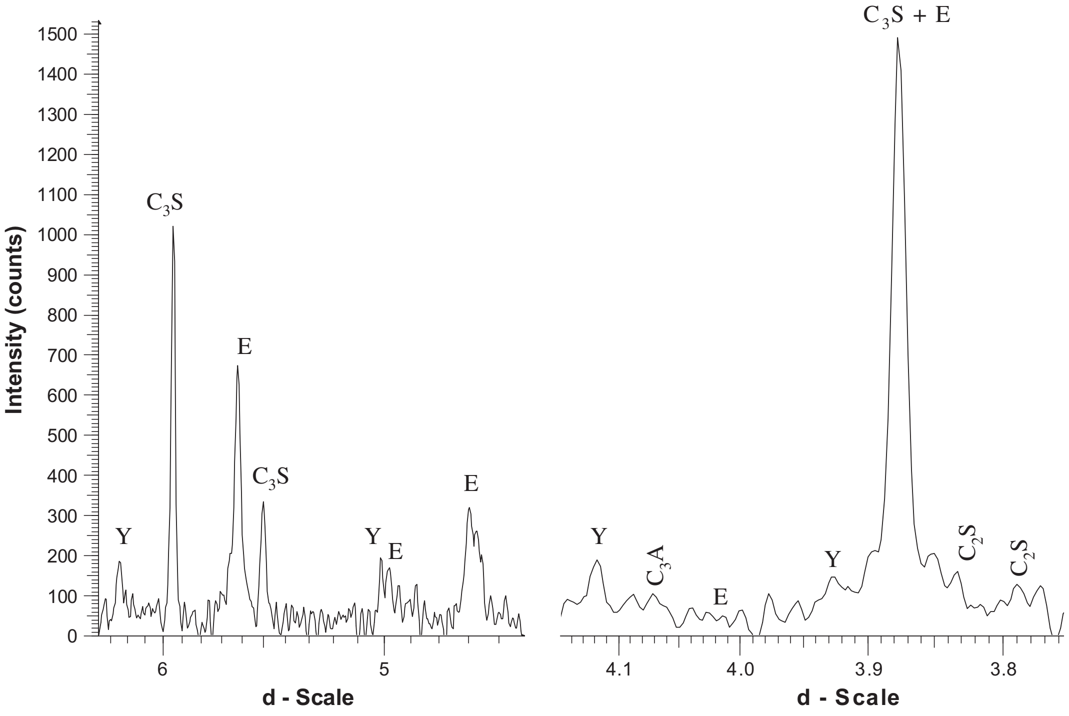

Fig. 6. XRD patterns of cement paste doped with Zn hydrated for 2 days; C_3S, C_2S, C_3A, E = ettringite, CH = portlandite, Y = $CaZn_2(OH)_6.2H_2O$.

after 28 days, this value is lower than that of Control 3. All these results seem to be in accordance with the previous observations made for these two trace elements added as nitrate salts.

The effects of the considered trace elements were confirmed by calorimetric measurements (Fig. 7). We note that C_3S hydration is delayed compared to Control 3. Indeed in the case of cement paste doped with Cd, the main peak appears at 5 h. The delay observed for Zn is longer as C_3S hydration occurs only after 360 h. These results are in accordance with the values of compressive strength.

Finally, as mentioned in Section 1, these last experiments confirm that chlorides have an accelerating effect on hydration com-

Table 5
Compressive strengths obtained after 2 and 28 days of mortar curing for a concentration of 0.18 mol in trace element/kg of cement.

Samples	Compressive strength (MPa)	
	2 days	28 days
Control 1 (CEM I)	45.1 ± 1.5	69.6 ± 2.2
Control 2 ($Ca(NO_3)_2$)	42.2 ± 0.5	70.4 ± 2.7
Control 3 ($CaCl_2$)	46.6 ± 1.5	74.6 ± 1.7
$CdCl_2$	41.1 ± 0.9	75.8 ± 1.3
$ZnCl_2$	0.5 ± 0.0	58.2 ± 2.6

pared to nitrate salts. Consequently it is always necessary to take into account the effect of the counter ion in these experiments.

4. Conclusions

(1) Considered trace elements can be classified according to two distinct groups. Similarities in behaviour have been observed for Cu and Pb. Cd, Ni and Zn, have no significant effect at the examined concentrations.

(2) SEM and XRD analyses reveal that Cd, Ni and Zn are mainly present in the hydroxide form whereas Cu and Pb are possibly fixed in the C–S–H. These differences could generate modifications in term of the microstructure that affect the mechanical properties and the material's resistance to transport.

(3) Trace element addition modifies the compressive strength in various ways. The early compressive strength (2 days) is correlated to C_3S hydration. The more C_3S hydration is delayed, the lower is the compressive strength. At 28 days of curing, the degree of hydration is the same for each sample doped with trace elements, whereas their total porosity and pore distribution are different. Thus, it implies that the microstructure and the density of C–S–H are responsible for the differences observed in compressive strength.

(4) Literature concerning the accelerating and/or retarding effect of trace elements on setting time and compressive strength development of Portland cement is large but contradictory. The mechanism of retardation has long been thought to be due to a coating formed on the surface of the cement grains by heavy metal hydroxides [40]. However this hypothesis has been recently disputed. Indeed, Weeks et al. [41] proposed that the retardation of setting was induced by the conversion of a metal hydroxide to a metal hydroxyl-species. This reaction consumes calcium and hydroxide ions and delays the supersaturation of the solution and hence the precipitation of C–S–H and $Ca(OH)_2$. The results, that were obtained in XRD, show the presence of $CaCd(OH)_4$ and $CaZn2(OH)_6{\cdot}2H_2O$. However, at this stage of the study, we are not able to validate one of hypotheses over the others described above.

(5) Given the observed effects on compressive strength and microstructure, trace elements can lead to different phenomena of diffusivity and dissolution as indicated below. Cu and Pb being trapped in C–S–H, would be expected to be more slowly mobilized during leaching. In support of this, Moudilou [21] has shown that this was true in the case of Pb, since it was never detected in the leaching solution. Regarding Cu, his comments indicate that it is released according to a slow and linear kinetics over time. In addition, the measured levels are correlated with the increase in the silicon from the C–S–H silicate sheets in the altered zone. Despite this different leaching behaviour, Moudilou [21] still suggests that the Pb and Cu are trapped in an identical manner in the silica tetrahedra of C–S–H. However, Labhasetwar and Shrivastava [42] propose an alternative model of retention of Pb in C–S–H, which consists of little or no reversible chemisorption phenomenon due to a substitution for calcium in C–S–H. Knowing that the atomic radii of Pb and Ca are close, this could explain the differences observed by Moudilou [21] for Pb and Cu leaching.

The purpose of this work was to investigate the impact of trace elements added during mixing on CEM I hydration as for example when they are immobilized in a cement matrix. However, incorporating trace elements during mixing does not fully reflect their effect when they are contained in the clinker. Indeed, in industrial cement, trace elements are present before hydration in the mineralogical clinker phases. Thus, trace elements' concentration in solution depends on the dissolution kinetics of these phases. Future work will be to study the impact of the content of trace elements from the clinkering process on the technical and environmental properties of cement.

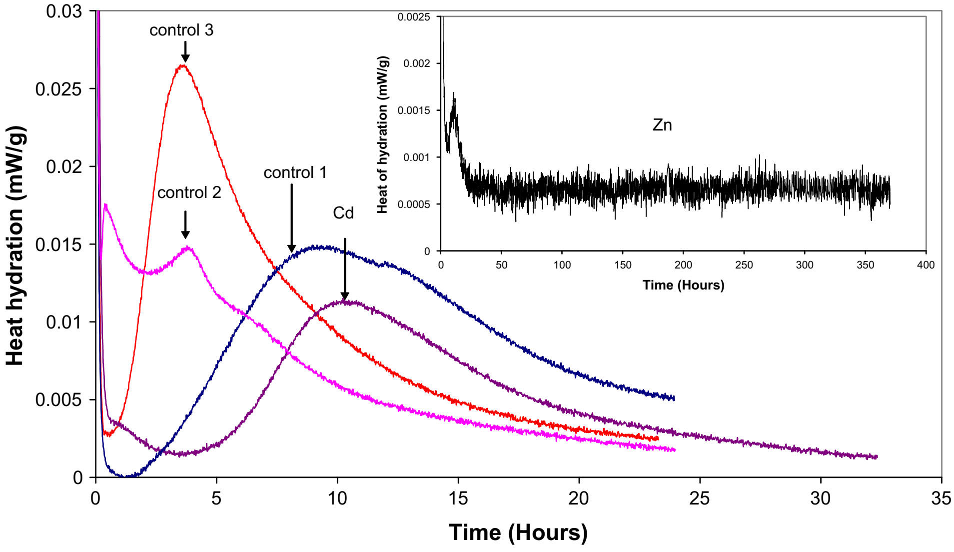

Fig. 7. Heat evolution versus time of different cement pastes doped with 0.18 mol of trace elements/kg of cement as chloride salt.

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References

[1] Zhang J, Liu J, Li C, Nie Y, Jin Y. Comparison of the fixation of heavy metals in raw material, clinker and mortar using a BCR sequential extraction procedure and NEN7341 test. Cem Concr Res 2008;38:675–80.

[2] Achternbosch M, Bräutigam KR, Hartlieb N, Kupsch C, Richers U, Stemmermann P. Impact of the use of waste on trace element concentrations in cement and concrete. Waste Manage Res 2005;23:328–37.

[3] Kakali G. Investigation of the effect of Zn oxide on the formation of Portland cement clinker. Cem Concr Res 1995;25:79–85.

[4] Murat M, Sorrentino F. Effect of large additions of Cd, Pb, Cr, Zn to cement raw meal on the composition and properties of the clinker and the cement. Cem Concr Res 1996;26(3):377–85.

[5] Katyal NK, Parkash R, Ahluwalia SC, Samuel G. Influence of titania on the formation of tricalcium silicate. Cem Concr Res 1999;29:355–9.

[6] Katyal NK, Ahluwalia SC, Parkash R. Effect of barium on the formation of tricalcium silicate. Cem Concr Res 1999;29:1857–62.

[7] Stephan D, Maleki H, Knöfel D, Eber B, Härdtl R. Influence of Cr, Ni and Zn on the properties of pure clinker phases. Part 1: C3S. Cem Concr Res 1999;29:545–52.

[8] Stephan D, Maleki H, Knöfel D, Eber B, Härdtl R. Influence of Cr, Ni and Zn on the properties of pure clinker phases. Part 2: C3A and C4AF. Cem Concr Res 1999;29:651–7.

[9] Andrade FRD, Maringolo V, Kihara Y. Incorporation of V Zn and Pb into the crystalline phases of Portland clinker. Cem Concr Res 2003;33:63–71.

[10] Katyal NK, Ahluwalia SC, Parkash R. Effect of Cr2O3 on the formation of C3S in 3CaO:1SiO2:xCr2O3 system. Cem Concr Res 2000;30:1361–5.

[11] Kolovos K, Tsivilis S, Kakali G. SEM examination of clinkers containing foreign elements. Cem Concr Compos 2005;27:163–70.

[12] Tashiro C, Oba J, Akama K. The effects of several heavy metal oxides on the formation of ettringite and the microstructure oh hardened ettringite. Cem Concr Res 1979;9:303–8.

[13] Poon CS, Clark AI, Perry R. Permeability study on the cement based solidification process for the disposal of hazardous wastes. Cem Concr Compos 1986;16:161–72.

[14] Cullinane MJ, Bricka RM, Francingues NR. An assessment of materials that interfere with stabilization/solidification processes. Report EPA/600/9/87/015. WA: Environmental Protection Agency; 1987.

[15] Ortego JD, Jackson S, Yu GS, McWhinney H, Cocke DL. Solidification of hazardous substances. A TGA and FTIR study of Portland cement containing metals nitrates. J Environ Sci Health Part A 1989;24(6):589–602.

[16] Bhatty JJ, West PB. Stabilization of heavy metals in Portland cement matrix: effects on paste properties. In: Gilliam TM, Wiles CC, editors. Stabilization and solidification of hazardous, radioactive and mixed wastes, ASTM STP 1240, vol. 33. West Conshohoken, (PA USA): American Society for Testing Materials; 1996.

[17] Stephan D, Mallmann R, Knöfel D, Härdtl R. High intakes of Cr, Ni and Zn in clinker. Part 2: Influence on the hydration properties. Cem Concr Res 1999;29:1959–67.

[18] Olmo IF, Chacon E, Irabien A. Influence of lead, zinc, iron (III) and chromium (III) oxides on the setting time and strength development of Portland cement. Cem Concr Res 2001;31:1213–9.

[19] Serclérat I. Les métaux trace dans le clinker de ciment Portland: rétention dans les mortiers et intégration dans les hydrates du ciment. PhD thesis. Lyon: INSA Lyon; 1996.

[20] Hillier SR, Sangha CM, Plunkett BA, Walden PJ. Long-term leaching of toxic trace metals from Portland cement concrete. Cem Concr Res 1999;29:515–21.

[21] Moudilou E. Cinétiques et mécanismes de relargage des métaux lourds présents en traces dans les matrices cimentaires. PhD thesis. Orléans: Université d'Orléans; 2000.

[22] Benard A. Le plomb et le chrome dans les ciments: spéciation et modélisation du transfert au cours de la lixiviation. PhD thesis. Aix-Marseille: Université Aix-Marseille III; 2003.

[23] Marion AM, Laneve MD, Grauw AD. Study of the leaching behaviour of paving concretes: quantification of heavy metal content in leachates issued from tank test using demineralized water. Cem Concr Res 2005;35:951–7.

[24] Poon CS, Clark AI, Perry R, Barker AP, Barnes P. The cement-based solidification process for the disposal of hazardous wastes. Cem Concr Res 1986;16:161–72.

[25] Dimitru G, Vazquez T, Puertas F, Blanco-Varela MT. Influence of BaCO3 on hydration of Portland cement. Mater Constr 2000;49(254):43–8.

[26] Akhter H, Cartledge FK, Roy A, Tittlebaum ME. A study of the effects of nickel chloride on hydration of Portland cement. Cem Concr Res 1993;23:833–42.

[27] Stephan D, Mallmann R, Knöfel D, Härdtl R. High intakes of Cr, Ni and Zn in clinker. Part 1: Influence on burning process and formation of phases. Cem Concr Res 1999;29:1949–57.

[28] Tsivilis S, Kakali G. A study on the grindability of Portland cement clinker containing transition metal oxides. Cem Concr Res 1997;27:673–8.

[29] Rossetti VA, Medici F. Inertization of toxic metals in cement matrices: effects on hydration, setting and hardening. Cem Concr Res 1995;25:1147–52.

[30] Díez JM, Madrid J, Macías A. Characterization of cement-stabilized Cd wastes. Cem Concr Res 1997;27:337–43.

[31] Taylor HFW. Cement chemistry. London: Academic Press; 1990.

[32] Medela M. Etude des interactions entre les phases minérales constituant le ciment Portland et des solutions salines concentrées. PhD thesis. Dijon. Université de Bourgogne; 2005.

[33] Norme NF-EN-196-13, Méthodes d'essais des ciments – Partie 1: détermination des résistances mécaniques. AFNOR; 2006.

[34] Kjellsen KO, Detwiler RJ, Glorv OF. Pore structure of plain cement pastes hydrated at different temperatures. Cem Concr Res 1990;20:927–33.

[35] Kjellsen KO, Detwiler RJ. Reaction kinetics of Portland cement mortars hydrated at different temperatures. Cem Concr Res 1992;22:112–20.

[36] Kjellsen KO, Detwiler RJ, Glorv OF. Development of microstructures in plain cement pastes hydrated at different temperatures. Cem Concr Res 1991;21:179–89.

[37] Escalante-García JI, Sharp JH. Effect of temperature on the hydration of the main clinker phases in Portland cements: part I, neat cements. Cem Concr Res 1998;28:1245–57.

[38] Escalante-García JI, Sharp JH. The chemical composition and microstructure of hydration products in blended cements. Cem Concr Compos 2004;26:967–76.

[39] Bentur A, Berger RL, Kung JH, Milestone NB, Young JF. Structural properties of calcium silicate pastes: II, effect of curing temperature. J Am Ceram Soc 1979;62(7–8):362–6.

[40] Thomas NL, Jameson DA, Double DD. The effect of lead nitrate on the early hydration of Portland cement. Cem Concr Res 1981;11:143–53.

[41] Weeks C, Hand RJ, Sharp JH. Retardation of cement hydration caused by heavy metals present in ISF slag used as aggregate. Cem Concr Compos 2008;30:970–8.

[42] Labhasetwar N, Shrivastava OP. Ca_2^+/Pb_2^+ exchange reaction of calcium silicate hydrate. J Mater Sci 1989;24:4359–62.