Cement & Concrete Composites 33 (2011) 629–636

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Managing trace elements in Portland cement – Part II: Comparison of two methods to incorporate Zn in a cement

N. Gineys *, G. Aouad, D. Damidot

Univ Lille Nord de France, F-59000 Lille, France
EMDouai, MPE-GCE, F-59508 Douai, France

ARTICLE INFO

Article history:
Received 30 September 2010
Received in revised form 10 March 2011
Accepted 14 March 2011
Available online 13 April 2011

Keywords:
Portland cement
Zinc
Clinkerisation
Solidification/stabilisation

ABSTRACT

This study compares two methods to immobilise the same amount of Zn in cement paste. In the first method, Zn is introduced into the raw material before clinkerisation, whereas in the second process, Zn is introduced in the liquid phase used to make the cement paste, which is often referred to as solidification/stabilisation. In laboratory-made clinker, Zn was mainly fixed within a new compound ($Ca_6Zn_3Al_4O_{15}$). Also, Zn was observed in tricalcium silicate (C_3S) and in the interstitial phase (C_3A and C_4AF) with the exception of dicalcium silicate (C_2S). In the present study, the threshold limit value corresponds to the maximum amount of Zn that could be incorporated without the stability of the clinker phases being modified. This threshold was reached when a decrease in C_3A content and/or the presence of $Ca_6Zn_3Al_4O_{15}$ were observed by X-ray diffraction. The threshold limit of Zn in the studied clinker was established at 0.7% by weight. The reactivity of synthesised cement doped with Zn was studied by isothermal calorimetry measurements. These tests revealed that the incorporation of Zn had no effect on calcium silicate hydration (C_3S and C_2S), even if the Zn content exceeded the threshold limit value, i.e., 1%. These results were compared with those obtained through the solidification/stabilisation treatment of Zn in a cement paste. In these experiments, a Zn content of 0.7% induced a significant delay in the cement hydration. This difference in behaviour is due to the slower flow of zinc ions released in solution when it is incorporated in the clinker phases. Thus, the immobilisation during clinkerisation is a good alternative to treat waste with a high Zn content in Ordinary Portland Cement (OPC) without causing the well-known, deleterious effect on cement setting time.

1. Introduction

Each year, industrial activities produce large quantities of waste. Most of the waste contains heavy metals that could be dangerous to human health and cause environmental problems [1]. The growing interest in sustainable development makes the treatment of heavy metals a priority.

The use of Ordinary Portland Cement (OPC) as a binder for heavy metal immobilisation is a common practice and is referred to as solidification/stabilisation [2]. Indeed, this binder has good characteristics, such as a low permeability, high technical properties (strength) and good durability. The immobilisation of heavy metal waste is well documented [3,4]. For the last 50 years [5], the solidification/stabilisation process has been the most widely used process in the final treatment of hazardous waste. It fixes heavy metals by sorption, lattice incorporation and precipitation during the cement hydration [6].

However, this method has its limitations. For many types of waste, such as waste with a high Zn content, the use of OPC as a binder for the solidification/stabilisation process is problematic. Several studies have shown that Zn strongly delays Portland cement hydration and can even stop it entirely [7–9]. Consequently, Zn can affect the early-age compressive strength generated by OPC [10]. This phenomenon has been widely studied, and several hypotheses have been made. The first hypothesis [11] deals with the formation of a heavy metal hydroxide on the surface of the anhydrous cement grains. Recently, Week et al. [12] proposed another mechanism based on the conversion of a metal hydroxide to metal hydroxyl species. This reaction consumes calcium and hydroxide ions and reduces the supersaturation of the solution with respect to C–S–H and $Ca(OH)_2$ and, hence, delays this precipitation.

To solve this problem, some studies have been conducted on new binders, particularly on calcium sulfoaluminate cement (CSA) [13]. This study has shown that adding a high concentration of $ZnCl_2$ (~1% of Zn) in the liquid used to prepare CSA mortars did not induce a strong retardation compared with OPC; the major part of CSA hydration occurred between 4 and 15 h, whereas it

---

* Corresponding author at: EMDouai, MPE-GCE, F-59508 Douai, France. Tel.: +33 (0)327 712 414; fax: +33 (0)327 712 916.

E-mail address: nathalie.gineys@mines-douai.fr (N. Gineys).

0958-9465/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconcomp.2011.03.008

appeared after several days when using OPC. Although CSA cement seems to be a good alternative to Zn solidification/stabilisation despite some possible deleterious volume changes, Zn could be effectively immobilised in OPC by incorporating it during the clinkering process. This alternative method would only be valid if a high Zn content does not alter the stability and reactivity of the clinker phases, namely C_3S, C_2S, C_3A and C_4AF.

Our study is aimed at assessing the validity of this alternative method.

(1) Investigating the localisation of Zn in a laboratory-made clinker using a scanning electron microscope (SEM) and the threshold limit of Zn in the clinker by X-ray diffraction (XRD). The threshold limit corresponds to the maximum amount of Zn that could be incorporated without modifying the stability of the clinker phases.
(2) Comparing the reactivity of the Zn-doped cement paste to a similar Zn concentration directly supplied in the solution during the solidification process. The kinetics of hydration were investigated using isothermal calorimetry and by the measuring the compressive strength of the cement pastes.

One might ask about the originality of this work because the effect of ZnO as a clinker dopant or as a cement additive is well-known. Indeed, many studies deal with this subject. The originality of this work is based on three main points. First, this study showed that the use of Portland cement to immobilise Zn is realistic and thus the use of new binders is not necessary. Secondly, the definition of a Zn threshold limit in clinker is a concept that has never been previously described in the literature. Finally, the comparison, for a same cement composition, between a Zn doped clinker and a cement containing Zn is presented.

2. Materials and methods

2.1. Materials

Clinkers were prepared by mixing analytical grade reagents of $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3, MgO and K_2O. First, a reference clinker with a composition close to that of an average OPC clinker was synthesised in the laboratory. Table 1 shows the chemical and the mineralogical composition (according to Bogue) of the reference clinker after sintering. To prepare the doped clinkers, Zn was introduced into the raw meal in the form of zinc oxide (ZnO). The raw mixes were homogenised and pressed at 5 kN into pellets (height = 23 mm, diameter = 40 mm) to obtain a more regular clinkering process. Pellets were fired up to 1450 °C at a rate of 10 °C/min. After 45 min of burning to the clinkering temperature, the clinker was slowly cooled in the furnace to obtain larger calcium aluminate crystals, which are more easily analysed with SEM. In our experimental conditions, the atmosphere inside the furnace was oxidant whereas it is reductive in the cement industry. The free lime content of the reference clinker was determined according to the standard ethylene glycol method [14] and was equal to 0.35%. The raw mix and burning conditions were unchanged for the reference and the doped clinkers. Cement was produced by mixing pure gypsum with clinkers that were previously ground (<40 μm) in order to reach 3.3% SO_3. The quantities of cement produced in the laboratory are limited. Thus, given the small size of the furnace available in the laboratory, it was only possible to produce about 100 g of the clinker.

Table 1
Chemical and mineral composition (%w/w) of the reference cement.

Chemical composition	
CaO	64.22
SiO_2	21.68
Al_2O_3	4.46
Fe_2O_3	2.57
MgO	0.76
K_2O	0.65
Mineral composition (according to Bogue)	
C_3S	65
C_2S	18
C_3A	8
C_4AF	8

For assays of solidification/stabilisation, Zn was added to the reference cement during mixing in the form of a nitrate salt ($Zn(NO_3)_2{\cdot}6H_2O$). Indeed, results presented previously in Part I [10], showed that nitrates, at the tested concentration, did not affect the reactivity and the compressive strength of cement during mixing. For clarity, all the concentrations are expressed as element weight percentages.

2.2. Methods

The chemical composition of each doped clinker after sintering was verified by X-ray fluorescence. For clarity, all the doping concentrations are expressed as Zn weight percentage present in clinker.

The mineralogy of the clinkers was studied using XRD. A Bruker D8 with Co Kα radiation (1.78 Å) was used. The X-ray patterns were acquired in the 2θ (5–100°) with a step of 0.019 and 3 s per step.

The chemical composition of the clinker phases was investigated on polished sections with a Hitachi S-4300SE/N SEM operating in the backscattered electron mode (20 keV) and equipped with an energy dispersive X-ray spectrometer (EDS). To make the polished section, a piece of clinker was vacuum impregnated in an epoxy resin and then polished with ethanol to avoid reacting with water. Finally, the samples were coated with carbon before observation.

The reactivity of the cements was determined through isothermal calorimetry measurements performed at 20 °C. Five grams of cement and 2.5 g of water previously stored at 20 °C were mixed manually for a few seconds directly outside the calorimeter in measurements cells that were then placed inside the calorimeter. The calorimeter used was a home-made calorimeter using fluxmeters that allowed the calorimeter to equilibrate in less than 5 min. Thus, it was possible to record the heat flux released at the beginning of hydration, even if the mixing of the cement paste was executed outside the calorimeter. The effect of Zn on hydration was studied by determining at what time the heat released due to C_3S hydration begins. An example of the method used to determine the beginning of hydration is described in more detail in Fig. 4.

The microstructures of the cement pastes were also observed through SEM analyses on polished sections after 2 days of curing. The hydration was stopped by immersing the cement pastes into isopropanol and drying them for 24 h at 60 °C.

Due to the limited quantities of the clinker produced in laboratory, the compressive strength was determined on small cylinders (height = 12 mm, diameter = 6 mm) made of cement paste with a water/cement ratio (*w/c*) of 0.45 according to a slightly modified method developed by Perez [15–17]. Cement and water were manually mixed for 3 min. The paste was loaded into polytetrafluoroethylene (PTFE) moulds. The filling of the moulds was performed in two steps on a vibration table. The moulds were kept for 24 h at 100% relative humidity and 20 °C. The paste cylinders were demoulded after 24 h and curing was continued at 100% relative humidity and 20 °C. The compressive strength was measured on 5 samples after 2, 7 and 28 days. The tests were performed at a constant stress of 0.3 MPa/s. using an uniaxial press.

3. Results and discussion

3.1. Incorporation of Zn during the clinkering process

3.1.1. Localisation of Zn in the clinker phases

The SEM analyses (Fig. 1) conducted for clinker doped with 1% Zn, revealed the presence of white areas at the interface of the C_3S and/or C_2S and the interstitial phase. The exact chemical composition of these areas could not be determined accurately by EDS measurements because of their small size. However, these areas had a higher Zn content than the other clinker phases and consequently appeared brighter on the SEM micrograph. Indeed, Zn has a high atomic number and can backscatter electrons more strongly than the other elements present in the clinker phases. In addition, it was noticed that Zn was present in the clinker phases except in C_2S (Table 2).

This result is in accordance with those previously observed. For example, Barbarulo et al. [20] previously observed the formation of white areas in clinker doped with Zn. Bolio-Arceo and Glasser [18,21] have recently identified the exact composition of this phase as $Ca_6Zn_3Al_4O_{15}$. Moreover, several studies [18–20] have reported that Zn is mainly present in the interstitial phase of the clinker (C_3A and C_4AF), and Hornain [22] also showed that it is difficult for Zn to enter into C_2S. Finally, a modification in the stability of the clinker phases (C_3S, C_2S, C_3A and C_4AF), where a decrease in C_3A content occurs, has been previously observed [21].

3.1.2. Threshold limit of Zn in the clinker

The threshold limit corresponds to the maximum Zn content that could be incorporated in a clinker without modifying the stability of the clinker phases. For Zn, the threshold limit is reached when a decrease in C_3A content and/or the presence of $Ca_6Zn_3Al_4O_{15}$ are observed. To determine this maximum, different concentrations of Zn were incorporated into the raw-mix. The resulting clinkers were analysed by XRD (Fig. 2) and compared to the reference.

The XRD analysis conducted on the reference indicated that the major crystalline phases of OPC (C_3S, C_2S (β), C_3A and C_4AF) were present. The comparison with the doped clinkers revealed that the C_3A content decreased when the concentration of Zn incorporated into the clinker was greater than 0.7% by weight. Consequently, this concentration corresponds to the threshold limit of Zn. In addition, $Ca_6Zn_3Al_4O_{15}$ (PDF2 reference code 00-52-1560) was detected by XRD when the concentration was higher than 1% Zn. For clinkers doped with more that 2% Zn, it was observed that C_3A had completely disappeared. The SEM images of a clinker doped with 3% Zn (Fig. 3) confirmed the XRD observations. Indeed, the interstitial phase, surrounding the silicates (C1), was only composed of C_4AF (C2) and $Ca_6Zn_3Al_4O_{15}$ (C3). No C_3A was observed in the SEM image.

Table 2
Zinc localisation in clinker phases measured by EDS. (Assay on clinker doped with 1% Zn).

Clinker phase	Content in Zn (wt.%)
C_3S	0.96
C_2S	0.05
C_3A	0.51
C_4AF	0.68

It is important to note that the current average Zn concentration in OPC is equal to 0.0164% [23]. Thus, the threshold limits are not reached yet.

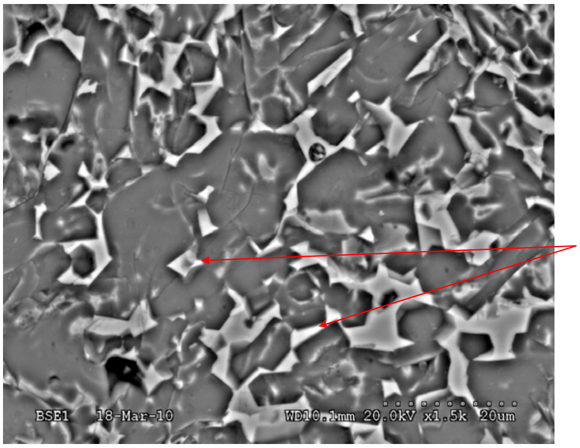
3.2. Comparison of the two methods of Zn immobilisation in a cement paste

3.2.1. Reactivity of cements

Because cement hydration is an exothermic process, the heat released from the process gives information about the kinetics of hydration of the cement constituents. We focused on C_3S hydration because this constituent is primarily responsible for the early compressive strength.

3.2.1.1. Cements pastes doped during the clinkering process. First, the reactivity of the synthesised cement doped with Zn during the clinkering process had to be determined. The first experiment performed was on cement made with a clinker containing 0.7% Zn which corresponds to the threshold limit for this specific cement. Then, the reactivities of cements whose Zn contents exceeded the threshold limits were studied. Cements doped with 1% and 3% Zn were chosen because at 1% a decrease in the C_3A content was observed, and $Ca_6Zn_3Al_4O_{15}$ was present. For cement doped with 3% Zn, C_3A had completely disappeared and was replaced by $Ca_6Zn_3Al_4O_{15}$.

Heat flow curves, presented in Fig. 4, indicate that the presence of Zn in the clinker did not seem to significantly affect hydration. Indeed, for the cements doped with 0.7% or 1% Zn, the major peak of hydration appeared at the same time as the reference cement, i.e., at about 4 h. In contrast, the hydration of the cement doped with 3% Zn was delayed occurring after 20 h. This result is in accordance with Stephan et al. [24], who showed that the hydration of



Zinc-bearing « white areas »

Fig. 1. SEM micrograph of the clinker doped with 1% Zn.

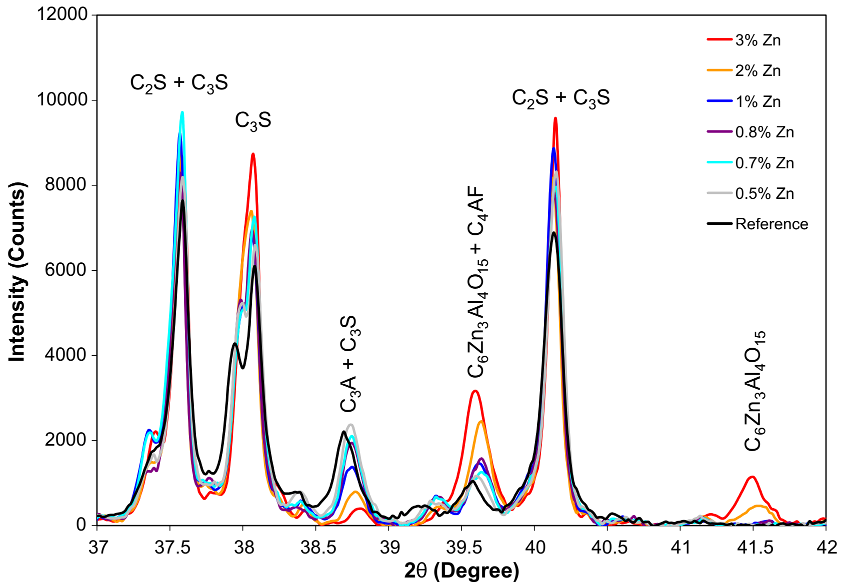


Fig. 2. XRD patterns of clinkers doped with Zn.

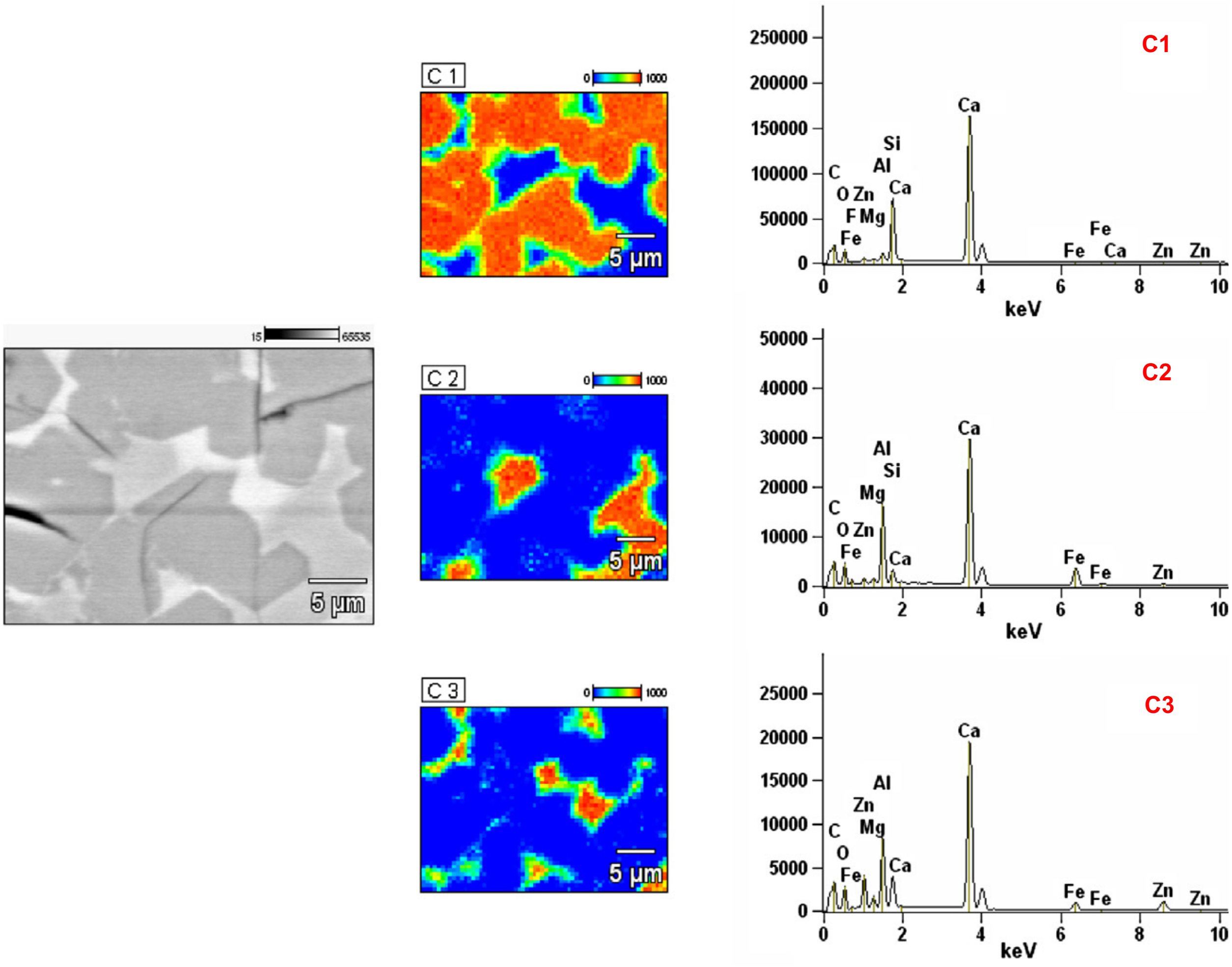


Fig. 3. SEM micrograph (left) and elemental X-ray images (right) of the clinker doped with 3% Zn; C1 = C_3S, C2 = C_4AF and C3 = $Ca_6Zn_3Al_4O_{15}$.

Portland cement doped with 2.5% Zn was delayed, occurring after 15 h.

To explain the difference observed in the cement hydration between the cements doped with 1% and 3% Zn, the concentration of Zn present, in the solution during hydration was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Suspensions of cement were prepared by mixing 2 g of cement with deionised water with a water/cement ratio (*w*/*c*) of

10. The mixes were homogenised mechanically at 20 °C. Leachates were collected and filtered at different times of hydration. The aqueous Zn concentration was measured using a Varian 720-ES ICP-AES. Cement hydration stopping times of 1, 4 and 15 h were chosen following the results of the calorimetry tests presented previously in Fig. 4. The concentrations of Zn in the solution after 1, 4 and 15 h of hydration was less than 0.4 ppm in both cases. This result is in accordance with previous studies. Bolio-Arceo and Glasser [21] showed that Zn incorporated in the clinker phase was very insoluble as the Zn content in the aqueous phase was less than 2 ppm. Consequently, the delay in cement hydration observed between the cement doped during clinkerisation with respectively 1% and 3% Zn, cannot be explained by a high Zn content in solution but by a high Zn flow. In our opinion, Zn precipitates gradually as it dissolves in solution, in a phase that can be designated as X, which acts as a diffusive barrier for anhydrous dissolution. In the case of cement doped with 1% Zn, the content in the X phase was not sufficient to induce a delay in cement hydration.

Another hypothesis can also explain this result. Indeed, in clinker doped with 3% Zn, all C_3A was replaced by $Ca_6Zn_3Al_4O_{15}$. The content of gypsum used in this study to control the reactivity of C_3A was perhaps not optimised in these new conditions and could affect the cement hydration. Although, Bolio-Arceo and Glasser [21], showed that $Ca_6Zn_3Al_4O_{15}$ is a cementitious compound, particularly in combination with gypsum, no studies have shown that C_3A and $Ca_6Zn_3Al_4O_{15}$ have the same reactivity in the presence of gypsum. In addition, it's well known [25] that an overdosage in gypsum could induce a delay in cement hydration.

3.2.1.2. Cements pastes doped with Zn during mixing. Second, the reactivity of cement paste doped with Zn directly supplied to the solution during the solidification process was studied. Similar Zn concentrations to those previously tested in Section 3.2.1.1. were studied.

Heat flow curves (Fig. 5) showed that cement hydration was delayed when 0.7% Zn, which was in the form of a nitrate salt, was introduced during mixing. The main hydration peak occurred after 24 h. The delay was even greater if 1% Zn was added during mixing. In this case, the kinetics of hydration was expected to be very slow because no exothermic peak was observed after 170 h. Given this result, it did not seem necessary to test the highest concentration in Zn, i.e., 3%. This result is in accordance with Nocun-Wczelik

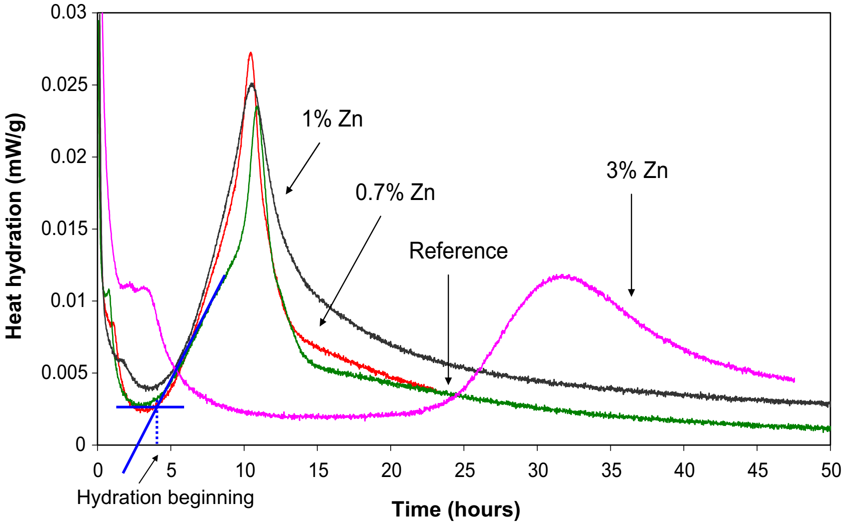


Fig. 4. Heat of hydration versus time of cement pastes doped with Zn during clinkerisation.

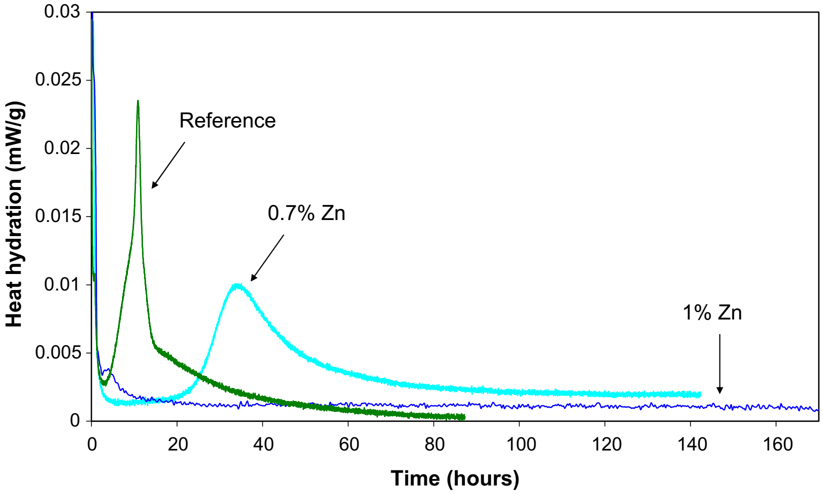


Fig. 5. Heat of hydration versus time of cement pastes doped with Zn during mixing.

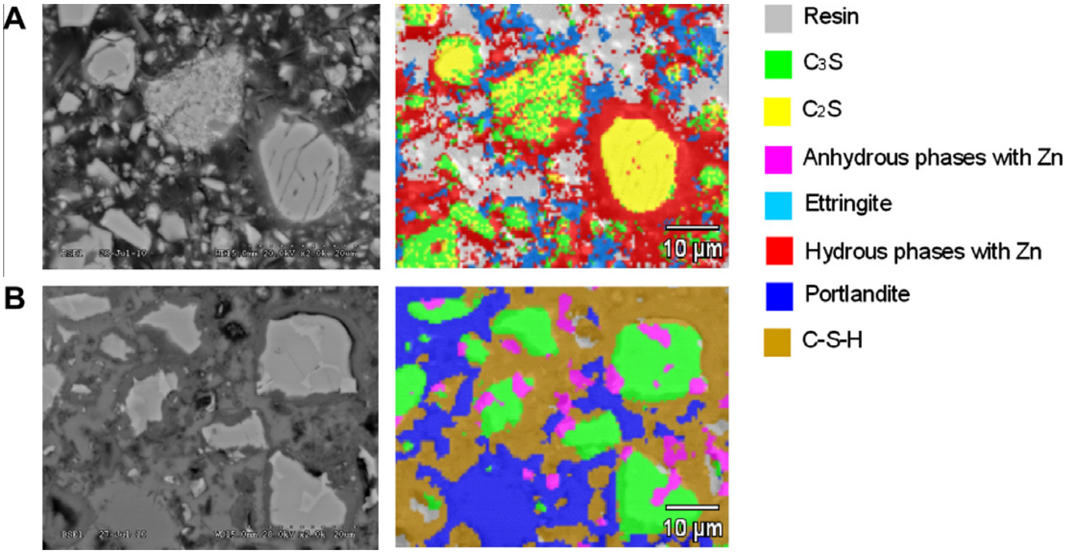


Fig. 6. SEM micrograph (left) and elemental X-ray images (right) of cement pastes doped with 1% Zn introduced during mixing (A) and during the clinkering process (B).

and Malolepszy [26] who had previously studied the effect of 1% Zn introduced as nitrate salt on cement hydration.

As mentioned in Section 3.2.1.1., the addition of 0.7% and 1% Zn during clinkerisation did not delay cement hydration. A delay in cement hydration was observed only for a Zn content of 3%, occurring after 20 h.

Consequently, the incorporation of Zn during the clinkering process is a good alternative to the solidification/stabilisation process that is usually used.

3.2.2. Microstructure

To explain the differences of reactivity between the two methods of Zn immobilisation, the microstructures of the cement paste doped with 1% Zn during either clinkerisation or mixing were studied by SEM coupled with EDS after 2 days of hydration. The objective was to locate Zn in the cement paste and to study the nature of the hydrates.

The analyses revealed that in cement paste doped during mixing (Fig. 6A), Zn was present in hydrates all around the anhydrous grains. In contrast, when Zn was introduced during clinkerisation, Zn was mainly observed in anhydrous grains, particularly in the interstitial phase (Fig. 6B).

Moreover, no $Ca(OH)_2$ and C–S–H were formed in the cement paste doped during mixing (Fig. 6A) whereas they were identified in cement paste doped during clinkerisation (Fig. 6B). The EDS analyses conducted on these two types of hydrates (Table 3) revealed that Zn was primarily fixed in C–S–H.

One might ask about the phenomena responsible for the differences in early hydration microstructure and several explanations can be envisaged. Firstly, such differences could be induced by the flow of Zn^{2+} in solution. During mixing, Zn^{2+} ions are immediately available and can react with the cement phases. Hydrates bearing Zn are formed and grow around the anhydrous grains. These hydrates seem to be responsible for the retardation effect on cement hydration by blocking, either temporarily or permanently, the hydration of anhydrous grains. In contrast, when Zn is incorporated in the clinker phases, the release of Zn^{2+} depends on the rate of dissolution of the Zn-bearing phases. SEM analyses conducted on cement paste obtained with clinker doped by 1% Zn (Fig. 6B) showed that after 2 days of hydration, a part of the interstitial phase containing $Ca_6Zn_3Al_4O_{15}$ was still encapsulated in the silicate grains that had not yet reacted. Consequently, some zinc incorporated in the clinker was not accessible to the mixing water and this could explain why there was no delay in setting time. It is well-known that during hydration of cement, the pH of the solution is very important. Consequently, Zn should precipitate as hydroxides and no important Zn content should be detectable in solution. Tests to measure the aqueous Zn concentration in solution during hydration were conducted for cement doped with 1% Zn during mixing and clinkering process. The same method, as that previously described in Section 3.2.1.1., was used for these tests. Results showed no differences in aqueous Zn content (<0.4 ppm) between the two samples. Therefore, it seems that it is not the instantaneous concentration of Zn in solution but its flow that is responsible for the differences of microstructure observed between the cement pastes doped during mixing and during the clinkering process.

Table 3
Composition of hydrates measured by EDS (Assays on cement pastes doped during the clinkering process with 1% Zn).

Compound	Element (wt.%)								
	O	Mg	Al	Si	S	K	Ca	Fe	Zn
$Ca(OH)_2$	32.37	–	0.16	0.46	0.26	–	66.75	–	–
C–S–H	42.76	0.42	1.26	12.32	0.94	0.14	39.75	1.08	1.34

Finally, it is well-known [27,28], that the rate of hydration in the induction and acceleratory periods is controlled by the nucleation and the growth of hydrates and particularly C–S–H. In our case, the presence and the amount of Zn hydroxides could affect the hydrates growth and consequently delay the early hydration of cement.

3.2.3. Compressive strength

The compressive strengths for the reference and the cement doped with 1% Zn during the clinkering process were determined. These tests were conducted on cement pastes after 2, 7 and 28 days of curing. The results (Fig. 7) indicate that the presence of Zn in the clinker phases does not affect the mechanical compressive strength after either the short (2 days) or the long curing time (28 days). The fact that Zn incorporated during clinkerisation did not affect the early compressive strength is very important to highlight. In a previous study [10], we have shown that Zn added during mixing had, on the contrary, a deleterious effect on mortar compressive strength, particularly after 2 days of curing. This difference in

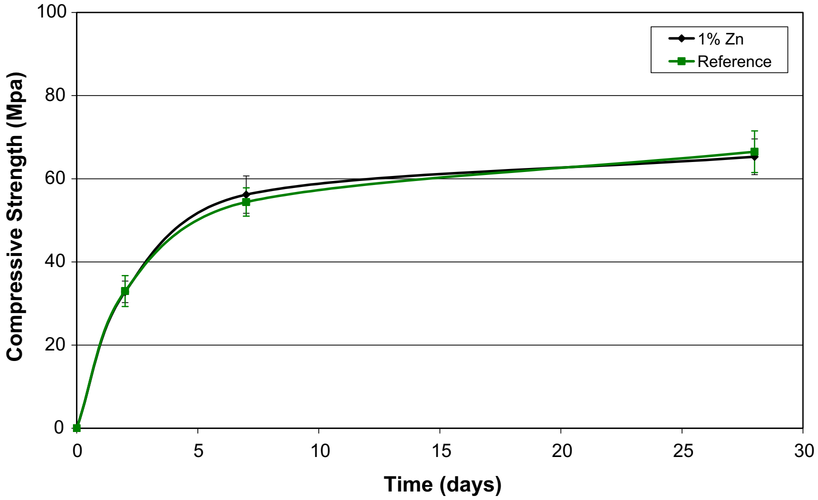


Fig. 7. Compressive strength obtained after 2, 7 and 28 days of cement paste curing.

compressive strength behaviour at the early age is due to the delay in hydration observed when Zn is added during mixing.

4. Conclusions

The purpose of this work was to compare two methods of Zn immobilisation in Portland cement. The main conclusions can be summarised as follows:

(1) In this study, we were able to incorporate 1% Zn in Portland cement without affecting its reactivity and compressive strength.
(2) SEM and XRD analyses revealed that Zn could be incorporated into the clinker (C_3S, C_3A and C_4AF) except in C_2S. If the Zn content in the clinker exceeded 0.7%, the stability of the clinker phases, particularly that of C_3A, was modified. A decrease in C_3A content and the formation of $Ca_6Zn_3Al_4O_{15}$ were observed. Finally, beyond 2% Zn, C_3A disappeared completely and was replaced by $Ca_6Zn_3Al_4O_{15}$.
(3) Calorimetry tests conducted on cement paste doped during clinkerisation revealed that the presence of Zn in the clinker phases did not have an effect on cement hydration. This observation remained true if the Zn content exceeded the threshold limit. Even at high levels of Zn (3%), the cement hydration was not delayed by much as it occurred within the first 24 h.
(4) The delay in hydration observed between cement doped during clinkerisation with respectively 1% and 3% Zn was not due to a higher Zn content in solution during hydration. Analysis of the mixing solution, by ICP-AES, proved that in both case, little Zn was present in the solution.
(5) The reactivity of cement doped during mixing with the same amount of Zn in the form of nitrate salt was studied. A significant delay in cement hydration was observed particularly when 1% Zn was added during mixing. The cement hydration peak was not observed after 170 h.
(6) The difference observed between the two methods of Zn immobilisation could be explained by the flow of Zn^{2+} in solution. During mixing, Zn^{2+} ions are immediately available and can react with the cement. When Zn is incorporated in the clinker phases, the release of Zn^{2+} depends on the rate of dissolution of the Zn-bearing phases. Indeed, some interstitial phase containing $Ca_6Zn_3Al_4O_{15}$ is still encapsulated in the silicate grains that have not yet reacted. In this condition, Zn is not accessible to the mixing water.
(7) Finally, given that Zn is mainly trapped in C–S–H when it is introduced in the cement during clinkerisation, it would be expected to be more slowly released during leaching. In support of this hypothesis, Moudilou [29] showed that Zn is released according to a slow and linear kinetics over time.

References

[1] Bozkurt S, Moreno L, Neretnieks I. Long term processes in waste deposits. Sci Total Environ 2000;250:101–21.
[2] Conner JR. Chemical fixation and solidification of hazardous wastes. Van Nostrand Reinhold, New York; 1990.
[3] Glasser FP. The role of ceramics, cement and glass in the immobilization of radioactive wastes. J Am Ceram Soc 1985;84:1–8.
[4] Glasser FP. Progress in the immobilization of radioactive wastes in cement. Cem Concr Res 1992;22:201–16.
[5] Conner JR, Hoener SL. The history of stabilisation/solidification technology. Crit Rev Environ Sci Technol 1998;28:325–96.
[6] Glasser FP. Fundamental aspects of cement solidification and stabilisation. J Hazard Mater 1997;52:151–70.
[7] Arliguie G, Grandet J. Etude par Calorimétrie de L'Hydratation du Ciment Portland en présence de Zinc. Cem Concr Res 1985;15:825–32.
[8] Arliguie G, Grandet J. Etude de l'hydratation du ciment en présence de zinc. Influence de la teneur en gypse. Cem Concr Res 1990;20:346–54.
[9] Arliguie G, Grandet J. Influence de la composition d'un ciment Portland sur son hydratation en présence de Zinc. Cem Concr Res 1990;20:517–24.
[10] Gineys N, Aouad G, Damidot D. Managing trace elements in Portland cement–Part I: Interactions between cement paste and heavy metals added during mixing as soluble salts. Cem Concr Compos 2010;32:563–70.
[11] 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.
[12] 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.
[13] Berger S, Cau Dit Coumes C, Le Bescop P, Damidot D. Hydration of calcium sulfoaluminate cement by a $ZnCl_2$ solution: investigation at early age. Cem Concr Res 2009;39:1180–7.
[14] Norme PT 207, Dosage de la chaux libre, CERILH, 1970.
[15] Perez J-P. Etude des mécanismes d'action d'additifs organiques lors de l'hydratation des ciments Portland. PhD thesis. Dijon: Université de Bourgogne; 2002.
[16] Perez J-P, Nonat A, Garrault S, Pourchet S, Mosquet M. Influence of triisopropanolamine on the physico-chemical and mechanical properties of pure cement pastes and mortars. Ann Chim Sci Mater 2003;28:S35–42.
[17] Zajac M. Etude des relations entre vitesse d'hydratation, texturation des hydrates et résistance mécaniques finale des pâtes et micro-mortiers de ciments Portland. PhD thesis. Dijon: Université de Bourgogne; 2007.
[18] Bolio-Arcero H, Glasser FP. Zinc oxide in cement clinkering: part 2 hydration, strength gain and hydrate mineralogy. Adv Cem Res 2000;12:173–9.
[19] Kolovos K, Tsivilis S, Kakali G. SEM examination of clinkers containing foreign elements. Cem Concr Compos 2005;27:163–70.
[20] Barbarulo R. Sorrentino F, Sing C. Impact of ZnO on clinker composition and reactivity – coupling with MgO. In: Proceedings of 12th ICCC Montréal 2007.
[21] Bolio-Arcero H, Glasser FP. Zinc oxide in cement clinkering: part 1 systems $CaO–ZnO–Al_2O_3$ and $CaO–ZnO–Fe_2O_3$. Adv Cem Res 1998;10:25–32.

[22] Hornain H. Sur la répartition des éléments de transition et leur influence sur quelques propriétés du clinker. Revue des matériaux de construction 1971;671(/672):203–18.

[23] 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.

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

[25] Frigione G. Gypsum in cement. In: Ghosh SN, editor. Cement technology. New York: Pergamon Press; 1983. p. 485–535.

[26] Nocun-Wczelik W, Malolepszy J. Application of calorimetry in studies of the immobilization of heavy metals in cementious materials. Thermochim Acta 1995;269(/270):613–9.

[27] Fierens P, Verhaegen JP. Hydration of tricalcium silicate in paste–Kinetics of calcium ions dissolution in the aqueous phase. Cem Concr Res 1976;6:337–42.

[28] Older I, Dörr H. Early hydration of tricalcium silicate II. The induction period hydration of tricalcium silicate II. Cem Concr Res 1979;9:277–84.

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