

Hydration Study of Ordinary Portland Cement in the Presence of Zinc Ions

Monica Adriana Trezza*

Facultad de Ingeniería, Universidad Nacional del Centro de la Pcia. de Bs. As.,
Av. del Valle, 5737 Olavarría - Buenos Aires, Argentina

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Hydration products of Portland cement pastes, hydrated in water and in the presence of zinc ions were studied comparatively at different ages. Hydration products were studied by X ray diffractions (XRD) and infrared spectroscopy (IR). Although IR is not frequently used in cement chemistry, it evidenced a new phase $\text{Ca}(\text{Zn}(\text{OH})_3)_2 \cdot 2\text{H}_2\text{O}$ formed during cement hydration in the presence of zinc. The significant retardation of early cement hydration in the presence of zinc is assessed in detail by differential calorimetry as a complement to the study carried out by IR and XRD, providing evidence that permits to evaluate the kinetic of the early hydration.

Keywords: Portland cement, infrared spectroscopy, X ray diffraction, zinc

1. Introduction

The industry of the production of Portland cement and concrete plays an important role in the management of hazardous wastes by using those with residual calorific power as alternative fuel or by replacing the hydration water with non-treated industrial water. However, both processes imply the incorporation of heavy metals in the system which represents a serious risk for people's health and the environment.

The efficiency of the heavy metals immobilization in Portland cement pastes and concretes is strongly related to the microstructure and porosity. The pH paste also plays an important role in the solidification/stabilization (S/S) process¹. One of the best methods of elimination is transforming these wastes into water-insoluble materials, reducing the damage by leaching.

Zinc is one of the heavy metals being added by the utilization of used tires as alternative fuel, profiting from of its high residual calorific power. There has been an increasing interest in the chemical reactions of Zn with cement minerals because Zn is known to interact with the cement clinker grains during hydration and to retard setting.

It has been reported that $\text{Ca}(\text{OH})_2$ was the main phase involved in the fixation reaction of Zn and that C-S-H was unlikely to be involved in the fixation mechanism².

Other authors have reported that Zinc incorporation to cement systems implies the formation of calcium hydroxy-zincate, $\text{CaZn}(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ during hydration³⁻⁸. Recent research works emphasize the outstanding role of C-S-H as the most likely way for the metal fixation, particularly Zn^{2+} incorporation in the inter-layer C-S-H^{9,10}. However, these studies have not been completed yet.

The present research work contributes to evaluate the effect of zinc ions on the early hydration of Portland cement with a low content of C_3A (less than 0.3%). Zinc ions were incorporated in different concentrations through the hydration water.

Hydration products are studied by the technique of X rays diffraction (XRD) and infrared spectroscopy (IR).

Also, IR spectroscopy and differential calorimetry make it possible to corroborate the formation of the phase $\text{CaZn}(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ and to determine the zinc stabilization, thus contributing to the quantification of the known retarding effect of zinc^{11,12} with respect to the hydration ages.

2. Experimental

2.1. Materials and test techniques

Ordinary Portland cement (OPC) was used in this study. Chemical and potential compositions are summarized in Table 1.

Adequate amounts of cement were hydrated with a w/c ratio 0.4 in the reference sample. In the study samples, the water was substituted for zinc solution (as ZnNO_3). Table 2 shows the variable concentration of zinc used in this study. The denomination given to each sample is also mentioned. The pastes were kept in sealed recipients until the trial age. Hydration was stopped by grinding with acetone and the powders were dried at 40 °C.

All the pastes hydrated at different ages were analyzed by X ray techniques using a Philips PW 3710 diffractometer with copper anode. The infrared measurements were recorded with a NICOLET spectrophotometer, FTIR - Magna 500 using KBr pellets technique. The study was completed following the early hydration (first 48 hours) using a differential calorimeter. The calorimetric determinations were carried out with two Dewar jars and a differential thermopair. The system was insulated and temperature was kept at 20 °C during the trial.

3. Results

3.1. X ray analysis

Figure 1 shows, as an example, the XRD patterns of C0 hydrated for 28 days and the assignments of the main peaks.

The semi-quantitative following of the hydration was carried out through the appearance age and the relative intensity of the main peaks of CH ($2\theta = 34.2^\circ$), ettringite ($2\theta = 15.7^\circ$) and C_3S ($2\theta = 32.32^\circ$). Table 3 shows the species present at each age by order of importance for each study sample.

This XRD study clearly shows the retarding effect of zinc in hydration of Portland cement with respect to the reference. When the percentage of incorporated Zn increases, the retardation also does. To 28-hydration days C3 and C5 haven't set yet and the main present phase is non-hydrated C_3S .

In C3 to 28 days the relative intensity of the peaks are C_3S (100), CH (70.8) and ettringite (35) respectively. From the structural point of view, neither new compound nor shift that may indicate any alteration

*e-mail: mtrezza@fio.unicen.edu.ar

Table 1. Chemical and potential composition of cement (in % w.w⁻¹).

| SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | K ₂ O | Na ₂ O | SO ₃ | PPC | C ₃ S | C ₂ S | C ₃ A | C ₄ AF |
|------------------|--------------------------------|--------------------------------|-------|------|------------------|-------------------|-----------------|------|------------------|------------------|------------------|-------------------|
| 21.44 | 3.40 | 4.20 | 63.45 | 0.57 | 1.18 | 0.04 | 2.91 | 1.82 | 58 | 18 | 2 | 13 |

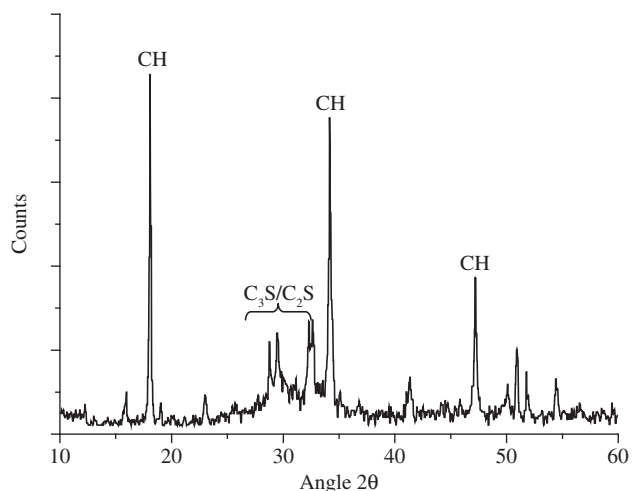
Table 2. Percentages of Zn²⁺ incorporated and samples denomination.

| [Zn ²⁺] (% w.w ⁻¹) | 0 | 0.1 | 0.2 | 0.5 | 1.0 | 3.0 | 5.0 |
|--|----|-----|-----|-----|-----|-----|-----|
| Identification | C0 | C01 | C02 | C05 | C1 | C3 | C5 |

Table 3. Hydration products present at each hydration age.

| | 3 days | 7 days | 28 days |
|----|--------|--------|---------|
| C0 | Δ * X | Δ * X | Δ |
| C1 | * Δ X | Δ * X | Δ X |
| C3 | * | * X | * Δ X |
| C5 | * | * | * X |

Δ: CH; X: Ettringite; *: C₃S.

**Figure 1.** XRD pattern of C0 hydrated for 28 days C₃S/C₂S: calcium silicates, CH = Ca(OH)₂.

in the phases by presence of Zn were identified. Only inversions of the relative intensities of the main peaks of CH can be observed in this case. The XRD technique permit to identify the main crystalline hydration phases and to evaluate the PC hydration velocity in the presence of Zn²⁺ ions.

3.2. IR- analysis

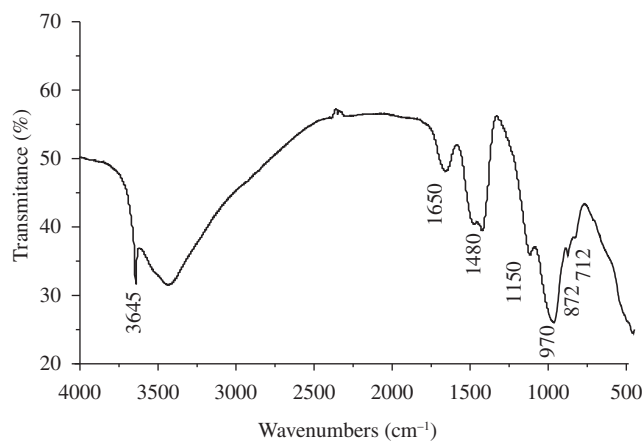
Table 4 shows the identification of the main IR bands of hydrated portland cement.

In Figure 2a the IR spectrum of C0 hydrated during 28 days is shown. In the high zone, the C0 spectrum presents a very acute peak at 3645 cm⁻¹, whose intensity increases with the hydration time. This is assigned to the O-H stretching of Ca(OH)₂ formed¹³⁻¹⁶.

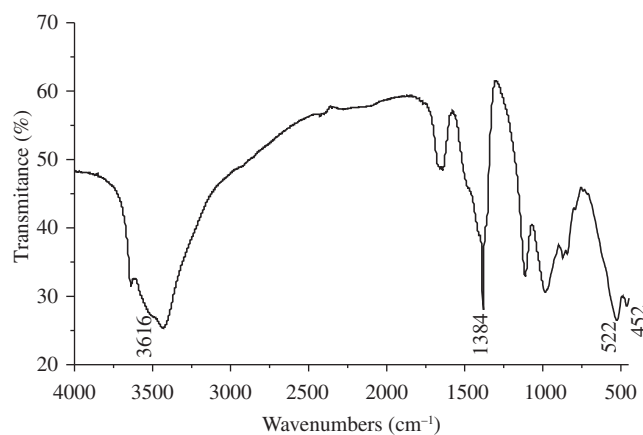
The wide band that is observed in the region 3100 – 3400 cm⁻¹ is caused by the symmetric and asymmetric stretching (ν1 and ν3) of the O-H vibrator of the water molecules. The band at approximately

Table 4. IR frequencies of the principal bands of the hydrated Portland cement.

| Frequencies (cm ⁻¹) | Assignment |
|---------------------------------|---|
| 3645 | Stretching O-H of Ca(OH) ₂ |
| Zone 3100- 3400 | Symmetric and asymmetric stretching (ν1 and ν3) of O-H |
| 1650 | Deformation (ν2) H-O-H |
| 1480 | ν3, CO ₃ ²⁻ |
| 872 | ν2, CO ₃ ²⁻ |
| 712 | ν4, CO ₃ ²⁻ |
| 970 | Stretching Si-O (ν3) (in polymeric unit of SiO ₄ ⁴⁻) |
| 925 | Stretching Si-O (ν3) (in non-hydrated cement) |
| 522 | ν4, Si-O |
| 452 | ν2, Si-O |
| 1115 | ν3, SO ₄ ²⁻ |



(a)



(b)

Figure 2. IR- spectra of C0 and C3 at 28 hydration days. a) C0; and b) C3.

1650 cm^{-1} is the deformation mode H-O-H (ν_2) of the molecular water absorbed.

The bands of 1480, 872 and 712 cm^{-1} (the latter not well defined in this case) are attributed to ν_3 , ν_2 and ν_4 CO_3^{2-} , respectively. The presence of CaCO_3 is attributed to the atmospheric CO_2 absorbed during the air hydration sample.

The main characteristic of the hydrated samples is the displacement of stretching mode Si-O (ν_3) from 925 cm^{-1} in the non-hydrated cement to 970 cm^{-1} in the hydrated one. This accounts for the polymerization of the units SiO_4^{4-} present in C_3S and C_2S . The intensity decrease of ν_4 in 522 cm^{-1} and the increase of ν_2 in 452 cm^{-1} also reflect a decrease in the freedom of movement caused by the polymerization of the ortosilicate⁷. The present SO_4^{2-} ions account for the acute peak in 1115 cm^{-1} .

Figure 2b shows the IR spectrum of C3 hydrated to 28 days.

Comparing the bands of silicate in the zone 930-995 cm^{-1} with the ones corresponding to C0, it is observed that zinc incorporation retards the formation of C-H-S because this band is not so reinforced by the polymerization as the reference is. On the other hand, a change of the relative intensities of ν_4 and ν_2 SiO_4 in C3 is not shown; thus indicating the advance of the hydration process.

It has been reported⁵ that the simultaneous presence of calcium and zinc carbonate determines the split of ν_3 carbonate from 1421 and 1352 cm^{-1} and a slight displacement of ν_2 and ν_4 in 876 and 714 cm^{-1} , respectively. These differences cannot be clearly seen due to the acute peak in 1384 cm^{-1} corresponding to the nitrate anion, which deforms the band.

Finally, the acute peak in 3645 cm^{-1} , which increases with the advance of hydration, is less intense in C3 than in C0, thus showing the retardation of cement hydration in the presence of zinc ions. Also in C3 the peak in 3645 cm^{-1} shows a split in 3645 and 3616 cm^{-1} due to presence of Ca and Zn hydroxide, respectively⁵.

The split previously mentioned is not observed in C1 and appears weakly in C3 to 7 and 28 hydration days. However, as it is observed in Figure 3, in C5 to 7 hydration days the new peak has the same intensity as the corresponding to the stretching O-H of $\text{Ca}(\text{OH})_2$. This difference in intensity indicates that this peak depends exclusively on the amount of Zn^{2+} ions present and, due to its placement in the zone of stretching OH, they must correspond to groups of this kind joined to Zn ions.

The IR technique allows the corroboration of the existence of species like $\text{Zn}(\text{OH})_3^-$, $\text{Zn}(\text{OH})_4^{2-}$ and/or $\text{Ca}(\text{Zn}(\text{OH})_2)_2 \cdot 2\text{H}_2\text{O}$ as reported.

3.3. Differential calorimetry

In Figure 4 the calorimetric curves corresponding to the studied samples are presented. Here the differences between C02 and C05 with the reference (C0) can be comparatively observed. In C0, the first peak is generated as soon as water is put in contact with the cement. The heat developed corresponds to the wetting and surface solubilization of the particles. Water is saturated with calcium hydroxide produced by the C_3S hydrolysis and calcium aluminate. Together with the dissolution of these ions, the alkaline hydroxides of the clinker are quickly dissolved. Kinetics of this process is fast and the control is chemical.

Then a period of apparent inactivity, known as dormant period can be observed. This stage determines that the cement remains in plastic state for some hours. From a chemical point of view, it is caused by the need to have a determined concentration of ions in solution before starting the precipitation of the hydration products. The end of the dormant period indicates the beginning of the setting of portland cement as it is defined by test methods in which the time at which the pure cement paste shows a resistance to particular deformation is arbitrarily defined¹⁷.

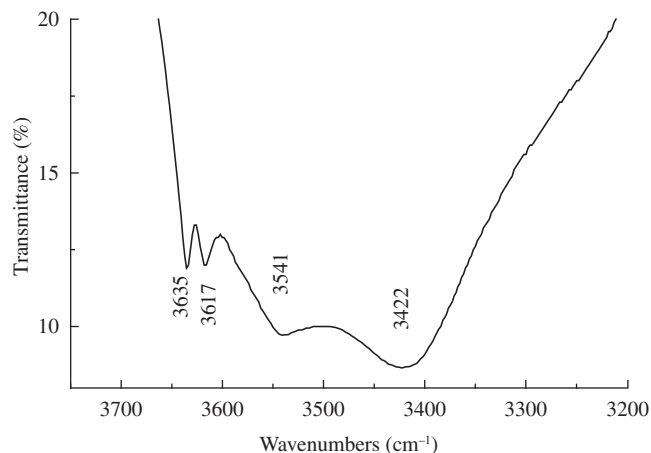
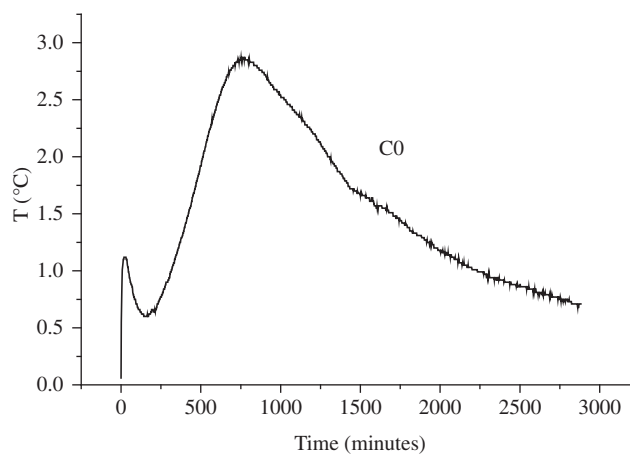
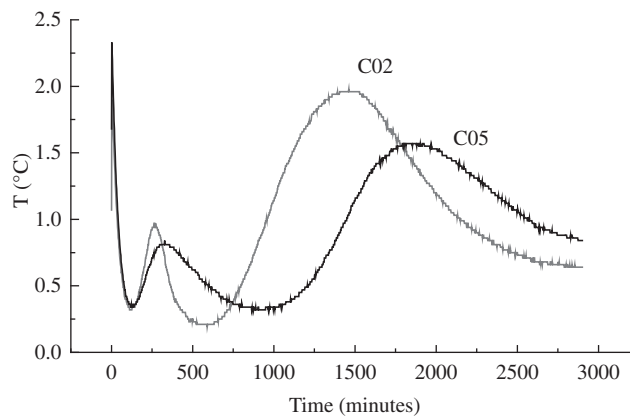


Figure 3. IR – spectra of C5 at 7 hydration days, high zone.



(a)



(b)

Figure 4. Calorimetric curves of C0 and C02 – C05.

In the calorimetric curve, the start of setting determines an acceleration period that culminates in a second maximum. The second maximum of the hydration curves determines the end of the formation processes of hydrate nuclei and the beginning of the gain of paste resistance due to the growing and crossing of the hydrates formed. For this reason, this maximum is frequently correlated with the final set¹². This process, chemically controlled, is caused by the formation of hydration products from silicates.

Apparently¹⁸, the CH crystallizes from the solution, while the C-S-H is developed on the surface of the C₃S grain and forms a coating covering the grains not hydrated yet. Thus, when the hydration goes on, the thickness of the hydrated layer increases and forms a barrier between the non-hydrated material and the water. For this reason, the water must diffuse to reach the anhydrous material and the ions diffuse in the opposite direction to reach the growing zones; thus a deceleration period chemically and diffusionally controlled occurs. The movement of ions through the C-S-H layers determines the reaction rate of this stage, which is controlled by diffusion. These processes are lower as the layer thickness increases; consequently the second maximum is completed at a very long delay. This stage determines the resistance gain rate.

When analyzing the curves corresponding to the study samples C02 and C05, Figure 4, both the appearance of a new peak and the significant retardation of setting time are observed.

It was reported that Zn is rapidly hydrolyzed and adsorbed into solid surfaces, and due to the high pH of porous water, the dominant species are Zn(OH)₃⁻^{5,6}.

The retardation may be caused by a reaction similar to one suggested by Jawed and colleagues and cited by Stephan⁴ for the retardation of C₃S by ZnCl₂. The Zn in the cement can react to form Zn(OH)₂; this Zn(OH)₂, which has additional hydroxyl ions, can produce a complex oxyanion which may precipitate as an insoluble calcium salt: Ca(Zn(OH)₃)₂·2H₂O. The hydration will be retarded until these reactions are completed because both OH⁻ and Ca²⁺ concentrations are kept low.

In the same way, Asavapit¹¹ reported that the severe retardation caused by the Zn waste indicates the formation of a very low permeability membrane which coats cement particles formed by the Ca(Zn(OH)₃)₂·2H₂O previously mentioned.

This compound would precipitate during the induction period and consequently the hydration would not continue because the required concentrations in solution are not enough for the formation of the hydration products until the formation of Ca(Zn(OH)₃)₂·2H₂O is not completed. Consequently, the higher the concentration of zinc ions in the porous solution is, the higher the hydration retardation is. This would be the specie that originates the second peak in the samples hydrated in the presence of zinc ions.

Once this stage is overcome, the hydration process of silicate continues the formation of C-S-H, but very retarded in time.

4. Conclusions

The combined use of the XRD, IR and differential calorimetry techniques permits to study the hydration of portland cement in the presence of zinc ions; thus evaluating the hydration retardation and the formation of phases incorporated to zinc.

The XRD technique permits to identify the main crystalline hydration phases and to evaluate the PC hydration velocity in the presence of Zn²⁺ ions. No new hydration phases that involve Zn were identified by this technique.

The IR technique permits to identify the existence of species like Zn(OH)₃⁻, Zn(OH)₄²⁻ and/or Ca(Zn(OH)₃)₂·2H₂O reported for PC hydration in the presence of Zn²⁺ ions. The identification is carried out from the split of the peaks (3645 – 3616 cm⁻¹) attributed to O-H stretching, in Ca-OH and Zn-OH respectively.

The differential calorimetry makes it possible to quantify both, the PC hydration retardation and the formation age of the phase Ca(Zn(OH)₃)₂·2H₂O generated by the incorporation of Zn²⁺ ions into the hydration water.

In all the cases, the effect depends on the percentage of zinc incorporated.

References

- Deja J. Immobilization of Cr⁶⁺, Cd²⁺, Zn²⁺ and Pb²⁺ in alkali-activated slag binders. *Cement and Concrete Research*. 2000; 32(12):1971-1979.
- Ziegler F, Johnson C. The solubility of calcium zincate (CaZn₂(OH)₆·2H₂O). *Cement and Concrete Research*. 2001; 31(9):1327-1332.
- Stephan D, Maleki H, Knöfel D, Eber B, Härdtl R. Influence of Cr, Ni and Zn on the properties of pure clinker phases Part II. C₃A and C₄AF. *Cement and Concrete Research*. 1999; 29(5):651-657.
- Stephan D, Maleki H, Knöfel D, Eber B, Härdtl R. Influence of Cr, Ni and Zn on the properties of pure clinker phases Part I. C₃S. *Cement and Concrete Research*. 1999; 29(4):545-552.
- Mollah MYA, Parga JP, Cocke DL. An infrared Spectroscopic examination of Cement-Based Solidification/Stabilization Systems-Portland Types V and IP with Zinc. *Journal Environment Science Health*. 1992; A27(6):1503-1519.
- Mollah MYA, Vempati RK, Lin L-C, Cocke DL. The interfacial chemistry of solidification/stabilization of metals in cement and pozzolanic material systems. *Waste Management*. 1995; 5(2):137-148.
- Mollah MYA, Hess TR, Tsai YN, Cocke DL. An FTIR and XPS investigations of the effects of carbonation on the solidification/stabilization of cement based systems-portland type V with Zinc. *Cement and Concrete Research*. 1993; 23(4):773-784.
- Hill J, Sharp JH. The hydration products of Portland cement in presence of tin(II) chloride. *Cement and Concrete Research*. 2003; 33(1):121-124.
- Stumm A, Garbev K et al. Incorporation of zinc into calcium silicate hydrates, Part I. *Cement and Concrete Research*. 2005; 35(9):1665-1675.
- Ouki SK, Hills CD. Microstructure of Portland cement pastes containing metal nitrate salts. *Waste Management*. 2002; 22(2):147-151.
- Asavapit S, Fowler G, Cheeseman CR. Solution chemistry during cement hydration in the presence of metal hydroxide wastes. *Cement and Concrete Research*. 1997; 27(8):1249-1260.
- Alunno Rossetti V, Medici F. Inertization of toxic metals in cement matrices: effects on hydration, setting and hardening. *Cement and Concrete Research*. 1995; 25(6):1147-1152.
- Oriol M, Pera J. Pozzolanic activity of metakaolin under microwave treatment. *Cement and Concrete Research*. 1995; 25(2):265-270.
- Dutta D, Bordoloi D, Bothakur P. Hydration of Portland cement clinker in the presence of carbonaceous materials. *Cement and Concrete Research*. 1995; 25(5):1095-1102.
- Mollah MYA, Palta P, Hess H. Chemical and physical effects of sodium lignosulfonate superplasticizer on the hydration of Portland cement and solidification/stabilization consequences. *Cement and Concrete Research*. 1995; 25(3):377-385.
- Bensted J, Varma SP. Some applications of IR and Raman. Spectroscopy in cement chemistry, Part III: Hydration of Portland cement and its constituents. *Cement Technology*. 1974; 5(5):440-450.
- Taylor HFW. *La química de los cementos* (in spanish). Urmo ed. Bilbao, España; 1967.
- Mindess S, Joung JF. *Concrete*. Prentice Hall ed. New York, USA; 1981.