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Cement and Concrete Research 35 (2005) 1285–1291

Cement and Concrete Research

# Early hydration of portland cement with crystalline mineral additions

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Received 16 July 2003; accepted 8 December 2004

## Abstract

This research presents the effects of finely divided crystalline mineral additions (quartz and limestone), commonly known as filler, on the early hydration of portland cements with very different mineralogical composition. The used techniques to study the early hydration of blended cements were conduction calorimeter, hydraulicity (Fratini's test), non-evaporable water and X-ray diffraction. Results showed that the stimulation and the dilution effects increase when the percentage of crystalline mineral additions used is increased. Depending on the replacement proportion, the mineralogical cement composition and the type of crystalline addition, at 2 days, the prevalence of the dilution effect or the stimulation effect shows that crystalline mineral additions could act as sites of heat dissipation or heat stimulation, respectively.

*Keywords:* Calorimetry; Hydration; Kinectics; Filler; X-ray diffraction

## 1. Introduction

Nowadays, different types of mineral additions are added to portland clinker during the milling process or directly to the cement. Current European cement standard [1] authorizes the use of different types of additions including pozzolanic (natural pozzolans, low calcium fly ash, silica fume), autopozzolanic (high calcium fly ash and blast furnace slag) and crystalline (generally knows as filler). For these additions, their pozzolanic activity or their greater or lesser hydraulicity is mainly associated with their vitreous and/or amorphous structure [2]. However, the crystalline compounds of addition introduce to its mineralogical classification and it exerts least influence on their hydraulic property [3]. Therefore, completely crystalline additions only act as fillers "to dilute" the portland cement. Even so, a study incorporating non-hydraulic filler (rutile powder) to the main components of cement has showed that fillers increase the hydration degree of each of this [4]. Similar tendency has been reported on the mechanical strength of mortars when non-hydraulic fillers of different origins (calcareous, granitic and siliceous) were incorporated, and this increase of mechanical strength was attributed to the particles of filler acting as nucleation sites of the CH crystals [5].

It has been reported that the incorporation of calcareous filler (finely divided limestone or calcium carbonate) accelerates the hydration reactions of portland cements. This was proved by behavioral analysis of the mechanical strengths, the hydration degree, the amount of CH released, the time of appearance of characteristics points on the calorimetric curves, the total dissipated heat at determinate age and the setting time [6–10]. Moreover, calcareous filler also reacts with the aluminate phase of cement producing calcium hemicarboaluminate, calcium monocarboaluminate and calcium tricarboaluminate [6,9–14]. During the hydration of silicate phases small amounts of filler are incorporated to the C–S–H [6] and the formation of carbonated hydrated calcium silicate compound has been reported [9].

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doi:10.1016/j.cemconres.2004.12.001

Several comparative studies have been done about the influence of calcareous and siliceous fillers on pastes and mortars, and on the influence of calcareous and siliceous coarse aggregates on concretes. In cement pastes, the incorporation of both fillers increases the hydration degree of portland cement at the early ages. However, the mechanical strength increase was greater for pastes containing siliceous filler at later ages [15] and the amount of CH in the samples containing siliceous fillers was lower than that in the calcareous samples under the same curing conditions at 28 days [16]. Also, the increase of mechanical strength (from 1 to 56 days) was greater for the mortars containing siliceous filler [17]. For concretes made with calcareous or siliceous coarse aggregate, both the increases of mechanical strength and the hydration degree of portland cement, between 3 and 60 days, were greater for concretes containing siliceous aggregates [18]. It was also found that the mortar–siliceous aggregate interface is less permeable than the mortar–calcareous aggregate interface [19] and it could be assigned to the interface improvement due to the reactions generated on the surface of the aggregate [20].

The aims of this work are to contribute in the identification of the benefits and limitations of different fillers and to explain the similarities and differences between their behavior as crystalline mineral additions to the portland cement. This work studies the effects that produce the incorporation of different percentages of crystalline mineral additions (finely divided quartz and limestone) on the hydration of portland cements with extreme mineralogical compositions (approximately 50 and 80% $C_3S$, and 14 and 0% $C_3A$, respectively).

## 2. Materials and methods

The materials selected for this experimental plan were two portland cements, one with high $C_3A$ contents (CP1) and another with zero $C_3A$ content (CP2); two finely divided crystalline mineral additions with similar Blaine fineness – quartz (Q) ($SiO_2$=99%) and limestone (C) ($CaCO_3$=96%) –, and distilled water as mixing water.

The chemical composition, density and specific surface of portland cements and crystalline mineral additions used are shown in Table 1. The mineralogical composition (Bogue) of the portland cements was $C_3S$=51%, $C_2S$=16%, $C_3A$=14% and $C_4AF$=5% for CP1; and $C_3S$=79%, $C_2S$=2%, $C_3A$=0% and $C_4AF$=10% for CP2.

In this study, two plain portland cements (CP1 and CP2) and twelve blended cements composed with cement replacement of 20, 30 and 40% in mass by crystalline mineral addition (Q or C) were analyzed.

The hydraulic activity of the additions was determined using the Fratini's test standardized by EN 196:5 [21]. This test implies the determination of the amount of calcium cation ($Ca^{2+}$) and hydroxyl anion ($OH^-$) containing in the water in contact with the tested samples at 40 °C. In this case the test was made at 2, 7 and 28 days. Then, comparing the amount of CH in the contact water with the solubility isotherm of CH in an alkaline solution at the same temperature, the addition is considered hydraulically active when the concentration of CH in the sample solution is below the solubility isotherm.

Table 1
Characteristics of the materials

| Materials | Cements | | Additions | |
|---|---|---|---|---|
| Parameters | PC1 | PC2 | Q | C |
| LOI (%) | 1.6 | 1.1 | – | 42.5 |
| IR (%) | 0.7 | 0.1 | – | 0.5 |
| $SiO_2$ (%) | 19.2 | 21.7 | 99.9 | 1.6 |
| $Al_2O_3$ (%) | 6.4 | 1.5 | – | 0.1 |
| $Fe_2O_3$ (%) | 1.7 | 4.1 | – | 0.5 |
| CaO (%) | 63.9 | 68.0 | – | 53.5 |
| MgO (%) | 1.5 | 0.4 | – | 0.1 |
| $Na_2O$ (%) | 0.9 | 0.4 | – | – |
| $K_2O$ (%) | 0.5 | 0.2 | – | – |
| $SO_3$ (%) | 3.5 | 2.3 | – | 0.0 |
| Density | 3.08 | 3.21 | 2.70 | 2.71 |
| Blaine ($m^2$/kg) | 319 | 301 | 395 | 362 |

The heat dissipation rate of blended cements was measured on paste ($w/b$=0.5) using an isothermal conduction calorimeter operating at 25 °C. Data were determined up to 2 days of hydration and the total heat produced was calculated as the integral below the heat dissipation rate curve versus time. Around the world, this methodology has been accepted to study the hydration process of plain and blended portland cement [22,23].

To determine the amount of hydrated cement in the samples at the end of the calorimetric test, the non-evaporable water was estimated using the procedure proposed by Power [24]. For calculations, it is assumed that both additions behave as hydraulically inactive.

The evolution of the hydration compounds in cement paste was evaluated by X-ray diffraction at the time derived from the characteristic points in the calorimetric curves. For this purpose, a new set of pastes containing 40% of addition ($w/b$=0.5) was made at 25 °C and, at the time previously determined by calorimetric test, they were removed and the hydration stopped by immersion in acetone. Then the paste was dried at 40 °C during a week and was ground to a particle size minor than 45 μm for XRD analysis. XRD measurements were performed on a diffractometer (Philips X'Pert) equipped with a graphite monochromator using CuKα radiation and operating at 40 kV and 20 mA. Step scanning was made from 5 to 60° $2\theta$ using scan speed of 2°/min and sampling interval of 0.02° $2\theta$. The XRD patterns are illustrated from 5 to 25° $2\theta$ because the more significant peaks of early compounds formed during cement hydration, such as AFm (tri-substituted aluminum ferrite phase), AFt (mono-substituted aluminum ferrite phase) and CH, are detected in this range [25]. Three and two XRD analyzes were made for each CP1 and CP2 blended cement, respectively.

## 3. Results and discussion

### 3.1. Fratini's test

Table 2 reports the concentration of calcium cation, expressed in oxide [CaO], and hydroxyl anion, [OH$^-$], for water in contact with the studied cements after 2, 7 and 28 days. Fig. 1 shows these values plotted on the [OH$^-$] versus [CaO] diagram, all points are located above the solubility isotherm of CH indicating that a large proportion of CH released from blended cement producing contact solutions saturated in CH. These results confirm that both crystalline mineral additions have no hydraulicity or pozzolanic activity (negative hydraulicity result).

For PC1 blends with both additions, an increase of [OH$^-$] was found from 2 to 7 days, and no significant change was measured from 7 to 28 days. For each age, the hydroxyl concentration decreases when the percentage of addition in cement is increased, suggesting the dilution effect. However, all experimental values obtained for these blends were higher than theoretical calculations in which the addition was assumed to be hydraulically inactive. This reveals a stimulation of the reactions that release CH during the early hydration stage. It can be attributable to the fact that the presence of addition particles acts as nucleation sites for compound precipitation. From 7 to 28 days, in spite of a rise in the [OH$^-$] for PC1, the concentrations of the blends remained almost constant showing that the nucleation effect was the most important in the early ages. On the other hand, the [CaO] declines with the age for PC1 blends containing both used additions, as occurred for PC1. However, their values were higher than those of the PC1, and they increase when increase the replacement percentage, confirming the high hydration degree produced by stimulation owing to the presence of particles of the crystalline mineral additions.

For PC2 blends, the [OH$^-$] decreased with the age, although at 2 and 7 days, the values were always higher than the [OH$^-$] corresponding to the PC2, demonstrating the stimulation of the hydration reactions. At 28 days, the [OH$^-$] for PC2 blends were lower than those of PC2, revealing that the stimulation effect was tailing off. In the same way of PC1 blends, the [CaO] for PC2 blends decreases with the age and these values were higher than those theoretical values. At 2 and 28 days, the [CaO] of PC2 blends with both additions Q and C were similar to those of PC2, revealing, once again, the stimulation effect produced by the crystalline mineral additions.

Table 2
Results of Fratini's test at 2, 7 and 28 days

| Sample | 2 Days (mM/l) | | 7 Days (mM/l) | | 28 Days(mM/l) | |
|---|---|---|---|---|---|---|
| | [OH$^-$] | [CaO] | [OH$^-$] | [CaO] | [OH$^-$] | [CaO] |
| PC1 100 | 72.5 | 7.6 | 71.2 | 6.8 | 78.0 | 6.5 |
| PC1/Q 80/20 | 65.0 | 9.5 | 67.0 | 8.9 | 68.0 | 8.3 |
| PC1/Q 70/30 | 60.0 | 10.3 | 63.5 | 9.5 | 63.0 | 9.5 |
| PC1/Q 60/40 | 57.0 | 11.6 | 59.5 | 10.5 | 59.0 | 10.1 |
| PC1/C 80/20 | 65.0 | 9.0 | 68.0 | 8.0 | 68.5 | 7.6 |
| PC1/C 70/30 | 61.0 | 9.8 | 64.5 | 8.6 | 64.5 | 8.3 |
| PC1/C 60/40 | 55.0 | 10.5 | 58.0 | 9.8 | 59.0 | 9.1 |
| PC2 100 | 42.5 | 21.5 | 39.5 | 16.5 | 42.0 | 16.1 |
| PC2/Q 80/20 | 44.5 | 21.9 | 41.5 | 16.8 | 40.5 | 16.3 |
| PC2/Q 70/30 | 44.0 | 22.2 | 41.0 | 15.5 | 40.0 | 16.4 |
| PC2/Q 60/40 | 43.5 | 22.3 | 40.0 | 14.4 | 39.5 | 16.7 |
| PC2/C 80/20 | 42.5 | 20.1 | 42.0 | 17.9 | 40.0 | 16.0 |
| PC2/C 70/30 | 43.5 | 20.3 | 41.0 | 18.1 | 40.0 | 16.4 |
| PC2/C 60/40 | 44.0 | 20.6 | 40.0 | 18.2 | 40.0 | 16.5 |

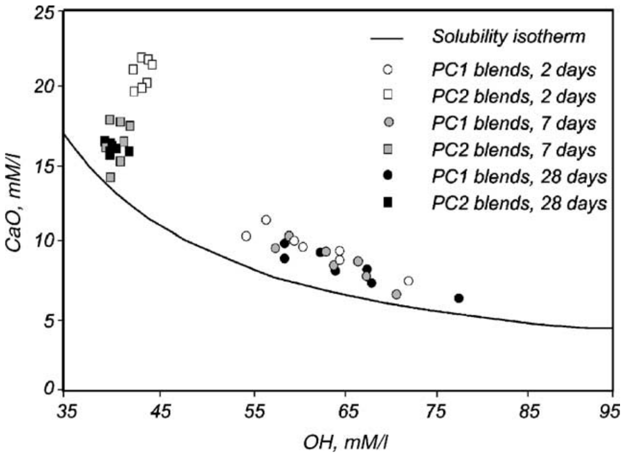

Fig. 1. Results of Fratini's test at 2, 7 and 28 days.

When the same crystalline mineral addition was incorporated to two cements of different mineralogical composition, the effects were the same in both cases except that between 2 and 7 days, the [OH$^-$] of the PC1 blends increased while those of PC2 blends decreased. Regarding the [CaO], for PC1 blends, it increases when the percentage of replacement by both additions is increased at all ages. Results presented here prove that Fratini's test is an appropriate and sensitive test in order to determine the stimulation effects produced by crystalline additions during the early hydration of cement. These results present a similar tendency that previously investigations carried out using other techniques [7–11].

### 3.2. Calorimetric test

Figs. 2 and 3 show the calorimetric curves up to 2 days for blends containing PC1 and PC2, respectively. Fig. 2 presents a typical calorimetric curve for an ordinary portland cement with several characteristic points (three peaks and three valleys). The first peak corresponds to dissolution process during the initial hydration and the first valley is the dormant period. The second peak is the acceleration due to the silicate hydration and third peak appears due to the transformation of ettringite (AFt) to monosulfoaluminate (AFm). For high $C_3A$ cement with medium fineness, the second valley appears between the second and the third peak in the calorimetric curve. After this stage, the desacceleration of cement hydration occurs and the paste reaches to the steady period determining the third valley. For PC2 cement

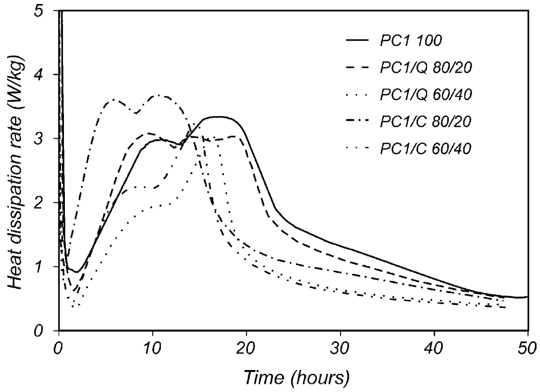

Fig. 2. Influence of Q and C on heat dissipation rate of PC1.

Table3
Total heat and non-evaporable water at 2 days

| Sample | Total heat dissipated (kJ/kg) | Total heat dissipated (kJ/kg$_{cement}$) | Non-evaporable water (g$_{water}$/g$_{cement}$) |
|---|---|---|---|
| PC1 100 | 298 | 298 | 0.139 |
| PC1/Q 80/20 | 283 | 354 | 0.152 |
| PC1/Q 70/30 | 256 | 366 | 0.164 |
| PC1/Q 60/40 | 180 | 300 | 0.180 |
| PC1/C 80/20 | 276 | 345 | 0.144 |
| PC1/C 70/30 | 262 | 374 | 0.151 |
| PC1/C 60/40 | 192 | 320 | 0.158 |
| PC2 100 | 204 | 204 | 0.093 |
| PC2/Q 80/20 | 189 | 236 | 0.110 |
| PC2/Q 70/30 | 148 | 211 | 0.128 |
| PC2/Q 60/40 | 132 | 220 | 0.145 |
| PC2/C 80/20 | 187 | 234 | 0.101 |
| PC2/C 70/30 | 185 | 264 | 0.106 |
| PC2/C 60/40 | 117 | 195 | 0.113 |

(Fig. 3), the absence of $C_3A$ in its composition determines that the third peak and the second valley are absent in the calorimetric curve.

The calorimetric curves for PC1 blends (Fig. 2) presented the first valley and the second and third peaks in advance for the 80/20 blends compared to PC1 and a delay in the 60/40 blends compared to the 80/20 blends. For the PC2 blends (Fig. 3) containing Q addition, the first valley and the second peak were delayed for the 80/20 blend and advanced for the 60/40 blend. In the blends containing C addition, the first valley and the second peak were advance with the 80/20 blend and delayed for the 60/40 blend. Nevertheless, the PC1 blends in the second and third peaks of the 80/20 blends had similar or even higher values than those of PC1 alone. There was a reduction in the heat dissipation rate when increases the percentage replacement in all characteristics points for the other blends.

From the analysis of the calorimetric curves, it can be observed that the behavior of crystalline mineral additions differs according to the portland cement used and with the percentage of addition incorporated. On the one hand, for PC1 blends with 20% replacement advances in characteristic points could be due to an acceleration of the hydration reactions, as mentioned previously [6–10]. However, when the percentage of addition increases, it produces a delay. On the other hand, for PC2 blends, the behavior according to the percentage of addition was reversed: it advances when increases percentage of addition Q and it delays when increases percentage of addition C.

### 3.3. Behavior at 2 days

For all studied cements, Table 3 summarizes the cumulative hydration heat and the non-evaporable water at 2 days of hydration. The obtained values of cumulative heat reflect the stimulation effect on the hydration reactions of portland cement by the particles of each addition. It can be observed that all blends (except PC2/C 60/40) have a cumulative heat per gram of cement higher than those recorded for plain portland cements. The dilution effect at early ages is also demonstrated by the decrease of cumulative heat value that register all blends when increasing the percentage of addition from 20 to 40% in the cement.

Fig. 4 shows the relationship between the relative cumulative heat of hydration and the relative amount of non-evaporable water at 2 days for the samples containing

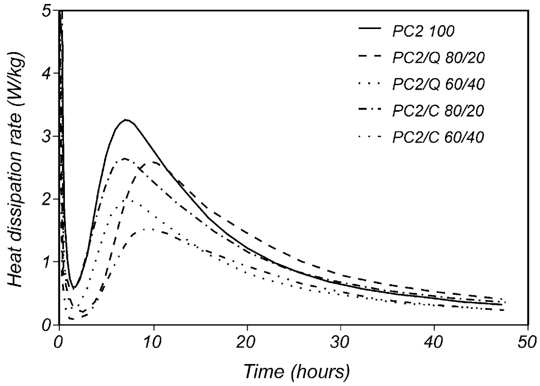

Fig. 3. Influence of Q and C on heat dissipation rate of PC2.

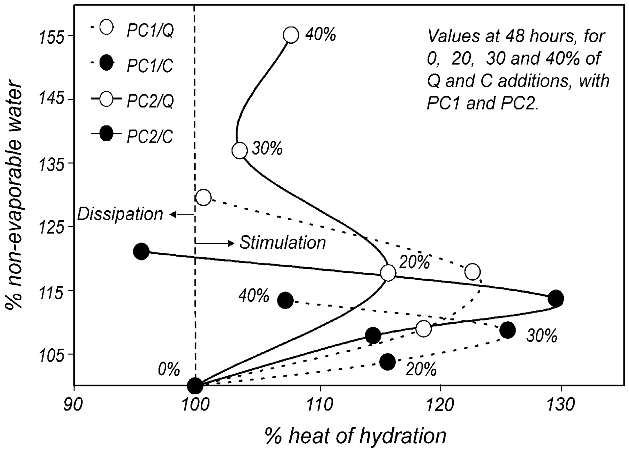

Fig. 4. Effects of dissipation and stimulation on heat of hydration.

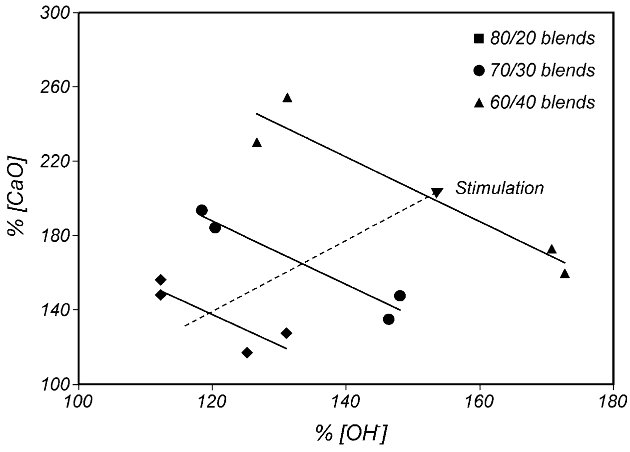

Fig. 5. Effect of stimulation on [CaO] and $[OH^-]$.

20, 30 and 40% replacement of both additions with each portland cement. The vertical line corresponding to 100% heat of hydration separates the region in which the stimulation effect predominates (>100% heat of hydration) from the region in which the addition acts as sites of heat dissipation (<100% heat of hydration).

$[OH^-]$ and [CaO] per gram of cement at 2 days obtained in the Fratini's test (2 days) also shown a relative incremental tendency for the 80/20, 70/30 and 60/40 blends for both portland cements used (see Fig. 5). This observation confirms that the stimulation effect on the early hydration reactions is directly proportional to the percentage of crystalline mineral addition incorporated.

### 3.4. X-ray diffraction analysis

The hydration compounds during 2 days are identified in the XRD patterns illustrated in Figs. 6 and 7 for CP1 and CP2 cements, respectively, Figs. 8 and 9 for blend cements containing Q addition; and in Figs. 10 and 11 for blended cements made with C addition.

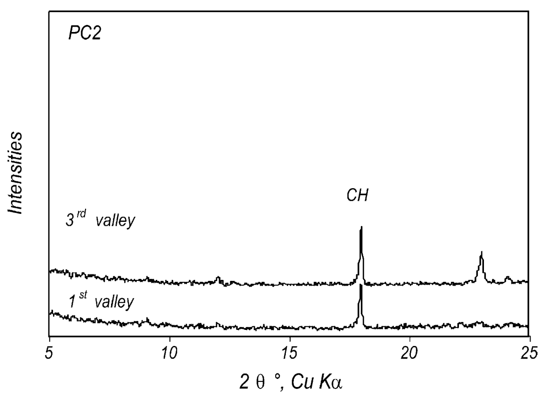

Fig. 7. X-ray diffraction of PC2. Q—quartz, C—calcite, CH—calcium hydroxide, Ts—tri-sulphate aluminum ferrite hydrate, Tc—tri-carbonate aluminum ferrite hydrate, Ms—mono-sulphate aluminum ferrite hydrate, Mc—mono-carbonate aluminum ferrite hydrate, CS—carbonated hydrated calcium silicate.

For PC1 pastes with additions, the intensity of CH peak was similar to intensity of CH peak on PC1 paste, instead of the content of calcium silicate was reduced 40% by mass. On the other hand, the intensity of CH peak for PC2 pastes with additions was stronger than the corresponding to PC2 paste. XRD results confirm the stimulation effect on the hydration reactions that has also been shown in the hydraulicity test, calorimetric curves, the total amount of heat dissipated at 2 days and in the non-evaporable water. On the other hand, the formation of the tri-substituted aluminum ferrite compounds was demonstrated (AFt: Ts or Tc), and its transformation to the mono-substituted aluminum ferrite compound phase (AFm: Ms or Mc) for cement based made on PC1 (Figs. 6, 8 and 10)). In the case of PC2 and PC2 blends (Figs. 7, 9 and 11)), the absence of the tri- and mono-substituted aluminum ferrite phases (AFt and AFm) was verified in correspondence with the absence of $C_3A$ in the PC2.

The formation of Tc and Mc is especially interesting in blends with the C addition formed from the $C_3A$ derived

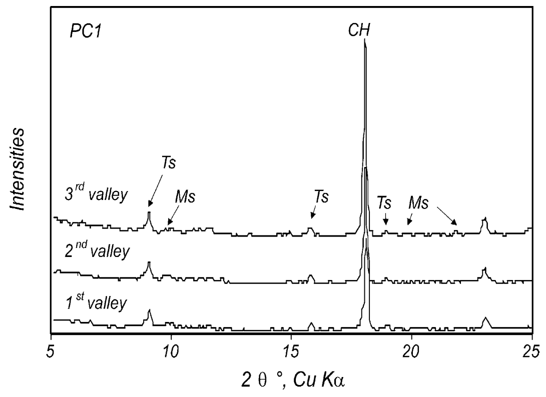

Fig. 6. X-ray diffraction of PC1. Q—quartz, C—calcite, CH—calcium hydroxide, Ts—tri-sulphate aluminum ferrite hydrate, Tc—tri-carbonate aluminum ferrite hydrate, Ms—mono-sulphate aluminum ferrite hydrate, Mc—mono-carbonate aluminum ferrite hydrate, CS—carbonated hydrated calcium silicate.

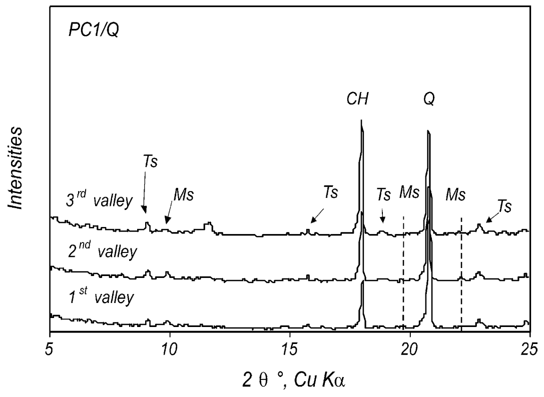

Fig. 8. X-ray diffraction of PC1/Q 60/40. Q—quartz, C—calcite, CH—calcium hydroxide, Ts—tri-sulphate aluminum ferrite hydrate, Tc—tri-carbonate aluminum ferrite hydrate, Ms—mono-sulphate aluminum ferrite hydrate, Mc—mono-carbonate aluminum ferrite hydrate, CS—carbonated hydrated calcium silicate.

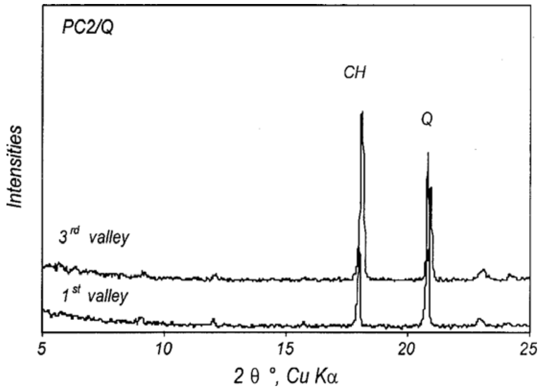

Fig. 9. X-ray diffraction of PC2/Q 60/40. Q—quartz, C—calcite, CH—calcium hydroxide, Ts—tri-sulphate aluminum ferrite hydrate, Tc—tri-carbonate aluminum ferrite hydrate, Ms—mono-sulphate aluminum ferrite hydrate, Mc—mono-carbonate aluminum ferrite hydrate, CS—carbonated hydrated calcium silicate.

from the PC1. These compounds have been found previously in other experiments [6,9–14]. Similarly, the formation of carbonate hydrated calcium silicate (CS) has also been detected previously [9].

### 3.5. Summary

According to the behavior observed, the incorporation of crystalline mineral additions, regardless of their mineralogical composition of the portland cements to which they are added, stimulates the hydration reactions of the portland cement components (see non-evaporable water in Table 3 and the results of Fratini's test in Fig. 5). After the first few hours, this effect begins to diminish and the dilution effect caused by the percentage replacement becomes more evident, revealed by the important reduction in heat dissipation rate when the addition contents increases (Figs. 2 and 3).

For cement with high $C_3A$ content (PC1), the incorporation of both crystalline mineral additions accelerates the hydration reactions. However, its heat dissipation rate increases when the replacement was up to 30%; while for high replacement percentages (40%), it decreases due to dilution effect. In contrast, for cement with low $C_3A$ content (PC2), the behavior of blended cements depends more closely on the nature of the addition: when increases Q content in the blend, the reactions accelerate and when increases C content they are slowed down. Therefore, at 2 days the particles of C addition appears to act as sites of heat dissipation since the heat of hydration of the 60/40 blend was less than 100% (Fig. 4).

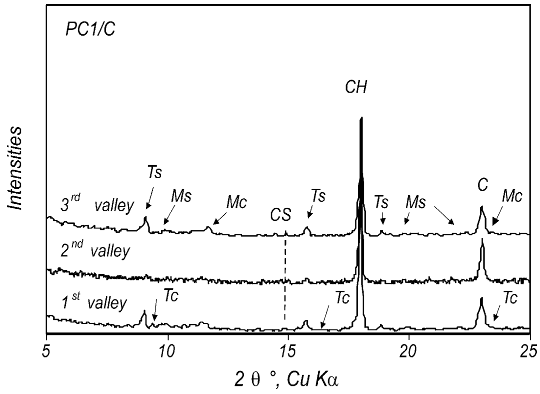

Fig. 10. X-ray diffraction of PC1/C 60/40. Q—quartz, C—calcite, CH—calcium hydroxide, Ts—tri-sulphate aluminum ferrite hydrate, Tc—tri-carbonate aluminum ferrite hydrate, Ms—mono-sulphate aluminum ferrite hydrate, Mc—mono-carbonate aluminum ferrite hydrate, CS—carbonated hydrated calcium silicate.

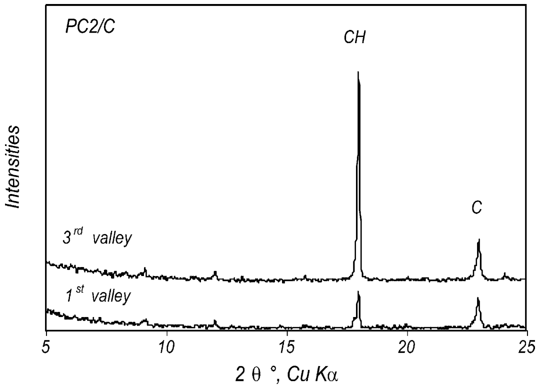

Fig. 11. X-ray diffraction of PC2/C 60/40. Q—quartz, C—calcite, CH—calcium hydroxide, Ts—tri-sulphate aluminum ferrite hydrate, Tc—tri-carbonate aluminum ferrite hydrate, Ms—mono-sulphate aluminum ferrite hydrate, Mc—mono-carbonate aluminum ferrite hydrate, CS—carbonated hydrated calcium silicate.

## 4. Conclusions

From the experiments conducted with the materials studied here, it can be concluded that:

- The incorporation of crystalline mineral additions to portland cements of different mineralogical compositions stimulates the hydration reactions of the portland cement components.
- The effect of stimulation increases with the percentage incorporation. However, when this is superposed by the dilution effect, which is also increasing, from a calorimetric viewpoint the crystalline mineral addition particles can begin to behave as sites of heat dissipation.
- For the portland cements with high $C_3A$ content, the incorporation of crystalline mineral additions accelerates the reactions up to a specific percentage, whereas for portland cements with low $C_3A$ contents, the reactions slow down with the increased percentage of crystalline mineral addition.
- Depending on the prevalence of these effects at a given age, blended cement can be formulated considering the proportion, the mineralogical composition of portland cement and the mineralogical composition of crystalline mineral addition.

## Acknowledgments

We would like to thank, the Fundación Rotaria and the Universidad Nacional del Centro de la Provincia de Buenos Aires for financing the research on which this work is based, and also, the Instituto de C.C. "Eduardo Torroja"–CSIC for having allowed to use its equipments.

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