CALORIMETRIC INFLUENCE OF TWO CRYSTALLINE ADDITIONS ON HYDRATION OF PORTLAND CEMENTS

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Abstract

This research presents the effects of finely divided crystalline mineral additions - filler - (quartz and limestone) on the hydration of portland cements with very different mineralogical composition. the techniques used were conduction calorimeter, hydraulicity (fratini test), chemically combined water and x-ray diffraction. results showed that the stimulation and the dilution effects depend on the percentage of crystalline mineral additions used. depending on the mineralogical cement composition and the type of crystalline admixture, at 48 hours, the dilution effect is higher or lower than the stimulation effect, showing the behavior of such crystalline mineral additions like sites of heat dissipation or heat stimulation, respectively.

Resumen

El presente trabajo analiza la influencia las adiciones cristalinas molidas (cuarzo y caliza) sobre la hidratación de cementos portland con diferente composición mineralógica. Las técnicas usadas fueron calorimetría de conducción, ensayo de hidraulicidad (ensayo de fratini), agua químicamente combinada y difracción de rayos x. los resultados mostraron que la estimulación de las reacciones, aumenta con el porcentaje de reemplazo y también la dilución del cemento. Dependiendo del tipo de adición y de cemento, el efecto de dilución resulta mayor o menor que el de estimulación, comportándose las adiciones a las 48 horas, como de focos de disipación o de generación de calor, respectivamente.

Introduction

Nowadays, different kinds of crystalline mineral additions are being added to Portland clinker during the milling process or directly to the cement. Current Argentinean cement legislation [1, 2], provides for the use of different types of additions including pozzolanic, autopozzolanic or hydraulically active (pozzolanic or slags) ones, and crystalline or hydraulically inactive (filler) another ones. Their reactivity conditions points out their greater or lesser hydraulicity; which is mainly associated with their vitreous and/or amorphous structure [3]. However, their crystallinity is the property that has the least influence and which least classifies them although it is the property that best distinguishes them [4]. Hence, completely crystalline additions only act as fillers "to dilute" the ordinary Portland cement. However, in a study which incorporated non-hydraulic filler (rutile) individually to the main components of a cement, this was shown to increase the degree of hydration of each of these [5]. this same tendency was observed in the mechanical resistance of mortars to which non-hydraulic fillers of different origins

were incorporated (calcareous, granitic and siliceous), and the increased mechanical strengths was attributed to the particles of each filler acting as nucleation sites of the calcium hydroxide crystals [6].

It has been observed that the incorporation of calcareous filler (finely divided limestone or calcium carbonate), accelerates the hydration reactions of ordinary Portland cements. this was demonstrated by behavioral analysis of the mechanical strengths, the hydration degree, the amount of calcium hydroxide generated, the age of appearance of isolated points on the calorimetric curves, the total heat dissipated at different ages and the setting times [7 - 11]. moreover, it has been found to react with the aluminate phase to produce hydrated calcium hemicarboaluminate, hydrated calcium monocarboaluminate and hydrated calcium tricarboaluminate [7, 10 - 15]; and with the silicate phases, given that small amounts of filler are incorporated to the hydrated calcium silicate [7] and that carbosilicate is produced [10].

Table 1: *Characteristics of the materials*

Materials	Cements		Additions	
Parameters	PC1	PC2	Q	C
PF (%)	1.6	1.1	-	42.5
IF (%)	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
Total (%)	100.0	99.9	99.9	98.8
Density	3.08	3.21	2.70	2.71
BSS, m^2/kg	319	301	395	362

A comparative study has been done on the influence of calcareous and siliceous fillers on pastes and mortars, and the influence of coarse calcareous and siliceous aggregates on concretes. In pastes, the incorporation of both fillers has been found to increase the hydration degree in Portland cement in the first ages. However, the increase in resistance over this period was greater for pastes with finely divided quartz additions [16] and the amount of calcium hydroxide for the quartz samples at 28 days was less than for the calcareous samples under the same curing conditions [17]. In the case of mortars, the increase in mechanical strengths between 1 and 56 days was greater for the mortars which used siliceous filler [18]. For concretes with coarse calcareous or siliceous aggregates, both the increased mechanical strengths and the hydration degree, between 3 and 60 days, were greater for concretes with siliceous aggregates [19]. It was also found that the mortar-siliceous aggregate interface is less permeable than the mortar-calcareous aggregate interface [20]. The improvement in the interface brought about by the use of

siliceous aggregate was studied by other authors [21], who assigned this improvement to a reaction induced on the surface of the aggregates.

Initially, this work aims to identify the benefits and limitations of each of the fillers and to explain the similarities and differences between their behaviors as crystalline mineral additions to the Portland cement. This is done by studying the effects of incorporating different percentages of crystalline mineral additions (finely divided quartz and limestone) on the hydration of Portland cement with extreme mineralogical compositions (approximately 50 and 80% C3S, and 14 and 0% C3A, respectively).

Materials and methods

The materials selected for the experiment were: two Portland cements, one with a high C3A contents, called CP1, and another with a minimum C3A content, called CP2; two crystalline mineral additions with a similar fineness - finely divided quartz, Q and finely divided limestone, C -, and distilled water as mixing water in all cases.

The chemical composition, density, specific surface Blaine of the Portland cements, and the crystalline mineral additions are shown in Table 1. The potential composition (Bogue) of the Portland cements was CP1: 51 % C3S, 16 % C2S, 14 % C3A, 5 % C4AF and CP2: 79% C3S, 2 % C2S, 0 % C3A, 10 % C4AF.

The cements used for the study were two plain Portland cements and blended cements in mass proportions of 80/20 and 60/40 ratio. The hydraulic activity of the additions was determined by comparing the amount of calcium hydroxide in the aqueous solution in contact with the hydrated sample at 40 °C at 2, 7 and 28 days; with the solubility isotherm of calcium hydroxide in an alkaline solution at the same temperature (Fratini test). The result is considered to be positive when the concentration of calcium hydroxide in the sample solution is below the solubility isotherm. This test has applicability to cementitious materials. The European Standard EN 197 indicates its methodology [22].

Table 2, shows the [OH-] and [CaO] at 2, 7 and 28 days, for the samples studied. All the points are logically located above the solubility isotherm because generally crystalline mineral additions have no hydraulicity or pozzolanic activity (negative hydraulicity result).

The evolution of the heat dissipation curve was studied using a conduction calorimeter for pastes. The baseline temperature for the measurements was 25°C. Data were determined for the first 48 hours of hydration and the total heat produced corresponded to the integral below the heat dissipation rate curve versus age. In pure Portland cement this methodology is used in order to observe its process of hydration [23], in cement with mineral additions is used too [24]. In order to establish the amount of hydrated cement in the samples the chemically combined water was estimated at the end of the calorimetric test using the model proposed by Power [25], making the assumption that the additions behave as inert compounds.

The evolution of the generation and/or consumption of calcium hydroxide were evaluated by X-ray diffraction of the samples at the ages derived from the calorimetric curves. In the case of the CP1 blends: first trough, second trough (between the second peak and the third) and the third trough (at the end of the calorimetric test). And in the case of CP2 blends: first trough and second trough (at the end of the calorimetric test). In

$2\theta = 25°$ the more significant AFm (tri-substituted aluminum ferrite phase), AFt (mono-substituted aluminum ferrite phase) and some calcium hydroxide peaks are present. For this reason, the X-Ray is diffracted until this angle [26]. On the other hand, quartz and calcite peaks are excluded in this analysis because its intensity minimizes the AFm and AFt peaks and their identification is not important for this research.

Table 2: *Hydraulicity results at 2, 7 and 28 days*

Sample	2 days (mm/l)		7 days (mm/l)		28 days(mm/l)	
	[HO-]	[CaO]	[HO-]	[CaO]	[HO-]	[CaO]
PC1 100	72.5	7.6	71.2	6.8	78.0	6.4
PC1/Q 80/20	65.0	9.5	67.0	8.8	68.0	8.3
PC1/Q 60/40	57.0	11.6	59.5	10.5	59.0	10.0
PC1/C 80/20	65.0	8.9	68.0	8.0	68.5	7.5
PC1/C 60/40	55.0	9.7	58.0	9.8	59.0	9.0
PC2 100	42.5	21.5	39.4	16.5	42.0	16.1
PC2/Q 80/20	44.5	21.9	41.5	16.8	40.5	16.2
PC2/Q 60/40	43.5	22.2	40.0	14.3	39.5	16.6
PC2/C 80/20	42.5	20.1	42.0	17.9	40.0	16.0
PC2/C 60/40	44.0	20.2	40.0	18.1	40.0	16.5

Results and discussion

Hydraulicity (Fratini test):

In the blends of PC1 with both additions Q and C, the [OH-] were found to increase from 2 to 7 days, and changed very little between 7 and 28 days. Also, for each age the concentrations dropped with increasing percentage replacement, reflecting a dilution effect. However, all the values of the blends were higher than theoretical calculations in which the additions were assumed to be inert. This revealed a stimulation of the calcium hydroxide generating reactions owing to the additions particles acting as nucleation sites for these reactions. Nevertheless, between 7 and 28 days, in spite of a rise in the [OH-] of the PC1, the concentrations of the blends remained almost constant showing that the nucleation effect was the most important in the younger ages.

On the other hand, the [CaO] of the blends with PC1 continued to drop with aging, both with the addition of Q and of C, as occurred with the [CaO] for PC1. However, its values were higher than those of the PC1, and furthermore, grew with increased percentage replacement, confirming the high degree of hydration stimulation by the particles of the crystalline mineral additions.

In the PC2 blends with both additions Q and C, the [OH-] decreased with age, although at 2 and 7 days, the values were always higher than the [OH-] of CP2, demonstrating stimulation of the hydration reactions. At 28 days, the [OH-] of the blends, were lower than those of CP2, revealing that the stimulation effect was tailing off.

On the other hand, the [CaO] of the blends with PC2, in general, decreased with age as also occurred with the PC1 blends. All these values were higher than those calculated theoretically assuming the additions to be inert. Both at 2 and at 28 days the

[CaO] of the blends with both additions Q and C, were similar to those of PC2, revealing, once again, a stimulatory effect of the crystalline mineral additions.

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 PC1 blends increased while those with PC2 decreased. The greatest different in [CaO] lay in the increase in PC1 blends with increased percentage replacement at all ages. When this technique was applied to assess hydration stimulation it was found to be adequate and sensitive since this was detected at early ages as has also been demonstrated for other techniques [7 - 11].
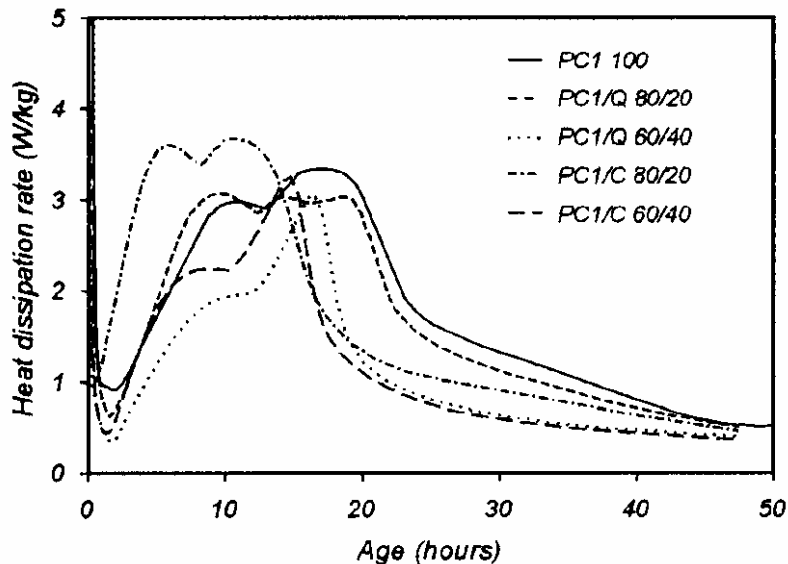
Figure 1: Influence of Q and C on heat dissipation rate of PC1

Calorimetric test

Figures 1 and 2, show the calorimetric curves for the first 48 hours for samples with PC1 and PC2, respectively. The heat dissipation curves for the samples with PC1 (Figure 1), presented in the first trough and the second and third peaks an advance in the 80/20 blends compared to PC1 and a delay in the 60/40 blends compared to the 80/20 blends. For the PC2 samples (Figure 2), in the blends with addition Q the first trough and the second peak were delayed for the 80/20 blend and advanced for the 60/40 blend; and in the blends with addition C the first trough and the second peak were advanced with the 80/20 blend and delayed for the 60/40 blend.

There was a reduction in the heat dissipation rate with increased percentage replacement in all isolated points in both cases. Nevertheless, the PC1 blends in the second and third trough of the 80/20 blends had similar or even higher values than those of PC1 alone. In this case, from the analysis of the calorimetric curves, the behavior of crystalline mineral additions differs according to the Portland cement used and also with the percentage of admixture incorporated. On the one hand, for PC1 blends with 20%

replacement advances in isolated points could be due to an acceleration of the hydration reactions, as mentioned previously [7 - 11]. However, as the percentage addition increases this produces a delay. On the other hand, for PC2 blends, the behaviors in percentage replacement with the additions were reversed: advances with increased percentage replacement of addition Q and delays with increases of addition C.
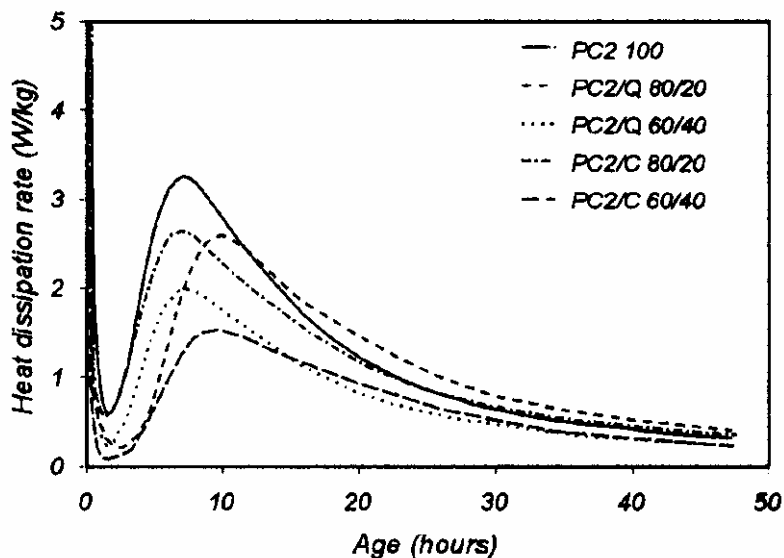

Figure 2: Influence of Q and C on heat dissipation rate of PC2

Behavior at 48 hours

Table 3 shows the total heat dissipated during the first 48 hours of sample hydration and the chemically combined water. The total heat values obtained reflect a stimulatory effect on the hydration reactions by the particles of each addition admixture and the dilution effect. This was deduced from both of these having values higher than those recorded for the pure Portland cements and for presenting lower total heat values with increasing percentage addition, respectively.

Figure 3 shows the variation between the heat of hydration and amount of chemically combined water, for each Portland cement, at 48 hours. The same sample shows the variation obtained for a 40% replacement of either of the two additions with either of the two Portland cements. The vertical line corresponding to 100% heat of hydration separates the region in which the stimulatory effect predominates (>100% heat of hydration) from the region in which the admixtures act as sites of heat dissipation (< 100 % heat of hydration).

Figure 4 also shows at 48 hours the trends obtained for the [OH⁻] and [CaO] per gram of cement in the 80/20, 70/30 and 60/40 blends, relative to each Portland cement. This also shows that the degree of stimulation of the reactions is directly proportional to the percentage of crystalline mineral addition incorporated.
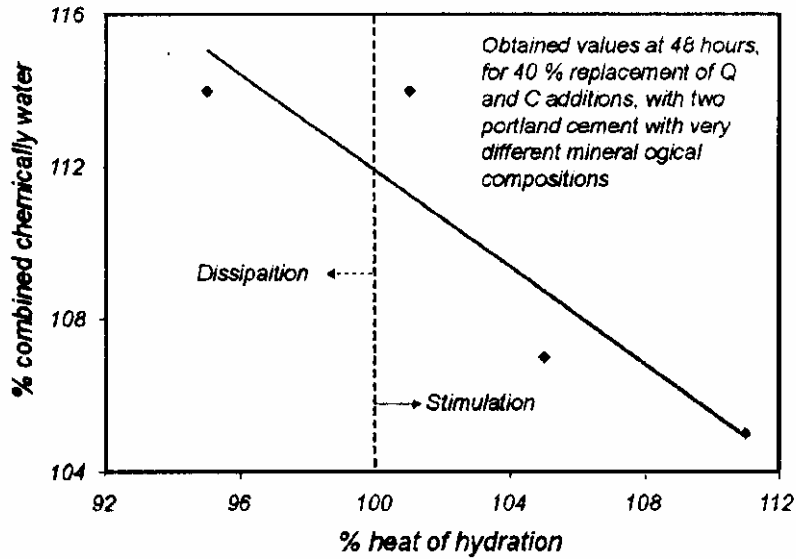
Figure 3: Effects of dissipation and stimulation on heat of hydration

Table 3: Total heat and chemically combined water at 48 hours

Sample	Total heat (kJ/kg cement)	CCW (g water/g cement)
PC1 100	298	0.138
PC1/Q 80/20	353	---
PC1/Q 60/40	301	0.157
PC1/C 80/20	348	---
PC1/C 60/40	330	0.145
PC2 100	212	0.122
PC2/Q 80/20	236	---
PC2/Q 60/40	223	0.130
PC2/C 80/20	235	---
PC2/C 60/40	201	0.139

X-ray diffraction analysis

In an attempt to determine the reaction course over the first 48 hours, the compounds present were identified and the evolution of each of these with age was established. Figures 5 and 6 show the XRD patterns of the blends of addition Q with CP1 and CP2, respectively and Figures 7 and 8, blends of addition C.

The increase in the amount of calcium hydroxide (H), in the advanced troughs, reflects a stimulatory effect on the hydration reactions that has also been shown in the hydraulicity test, calorimetric curves, the total amount of heat dissipated at 48 hours and in the chemically combined water. On the other hand, formation of the tri-substituted

aluminum ferrite was demonstrated (AFt: Ts or Tc), and its transformation to the mono-substituted aluminum ferrite phase (AFm: Ms or Mc) in the case of the PC1 blends (Figures 5 and 7). In the case of PC2 blends, Figures 6 and 8, the absence of the tri- and mono-substituted aluminum ferrite phases (T and M) was verified in correspondence with the absence of C3A in the PC2.
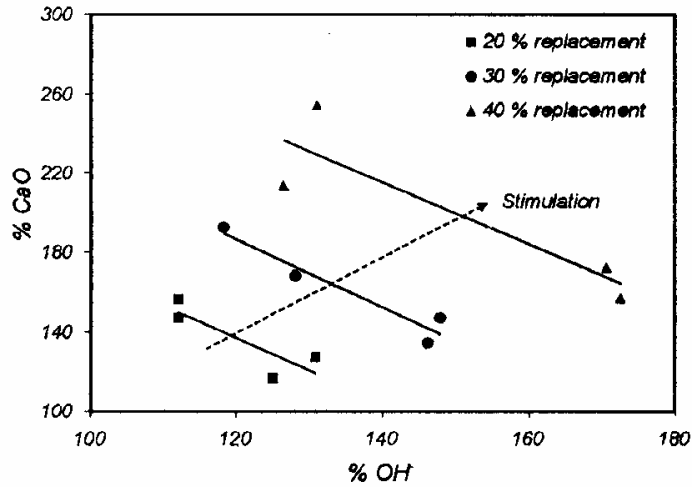

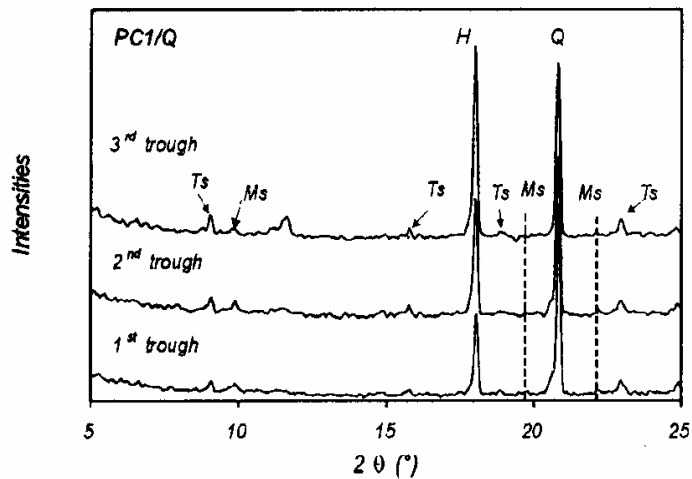**Figure 4:** *Effect of stimulation on [CaO] and [OH-]*

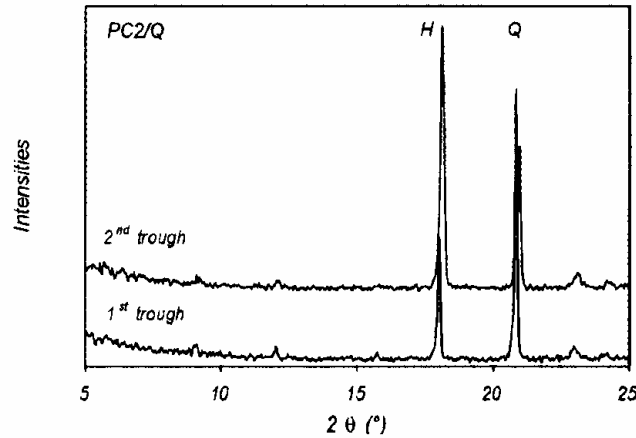**Figure 5:** *x-ray diffraction of PC1/Q 60/40*

Figure 6: *X-ray diffraction of PC2/Q 60/40*

The formation of Tc and Mc is especially interesting in blends with the C addition formed from the C3A derived from the PC1. These compounds have been found previously in other experiments [7, 10 - 15]. Similarly, the formation of carbosilicate (CS) has also been detected previously [10].
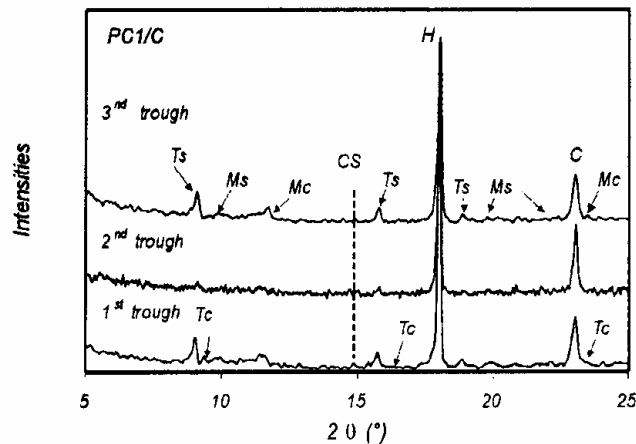

Figure 7: *X-ray diffraction of PC1/C 60/40*

Behaviors

Generalizing the behaviors observed, the incorporation of crystalline mineral additions, regardless of the mineralogical composition of the Portland cements to which they are added, stimulates the hydration reactions of the Portland cement components (Figures 5 - 8). Hence, its representative points in the hydraulicity test are above 100% (Figure 4). 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 rates as the addition contents increases (Figures 1 and 2).

For cements with a high C3A contents, the incorporation of crystalline mineral additions accelerates the reactions until certain percentage of incorporation, and later slows them down. In contrast, for cements with a low C3A contents the behavior depends more closely on the nature of the addition. With increased Q contents the reactions accelerate and with increased C addition they are slowed down. Therefore, after 48 hours the particles of C addition act as sites of heat dissipation since the heat of hydration of the 60/40 blend was less than 100% (Figure 3).

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 stimulation effect 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 a high C3A contents, the incorporation of crystalline mineral additions accelerates the reactions up to a specific percentage, whereas for Portland cements with a low C3A contents, the reactions slow down with the increased percentage of crystalline mineral addition. Depending on the effect or effects one wants to encourage at a specific age, cement blends can be obtained with appropriate proportions of appropriated Portland cements and/or crystalline mineral additions.
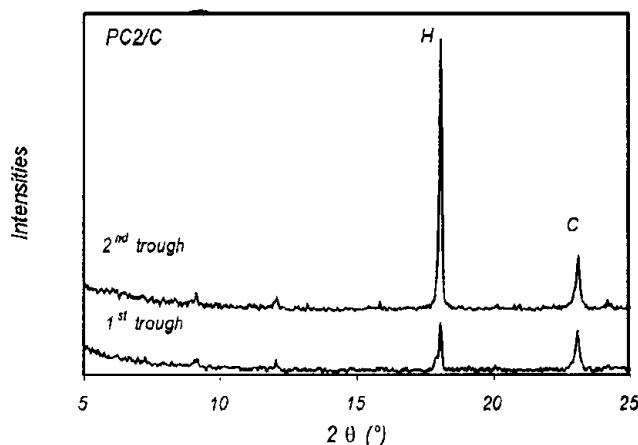

Figure 8: *X-ray diffraction of PC2/C 60/40. Q: quartz, C: calcite, H: calcium hydroxide, TS: tri-sulphate aluminum ferrite hydrate, TC: tri-carbonate aluminum ferrite hydrate, MS: mono-sulphate aluminum ferrite hydrate, MC: mono-carbonate aluminum ferrite hydrate, CS: carbosilicate*

Acknowledgments

based, and also, the Instituto de C.C. "Eduardo Torroja"-CSIC for having allowed the use of equipment and Library.

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