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INFLUENCE OF TWO DIFFERENT FLY ASHES ON THE HYDRATION OF PORTLAND CEMENTS

V. Rahhal[1*] *and R. Talero*[2**]

[1]Departamento de Ingeniería Civil, Facultad de Ingeniería, U.N.C.P.B.A. Avda. del Valle 5737, (B7400JWI) Olavarría, Argentina
[2]Instituto de Ciencias de la Construcción 'Eduardo Torroja', C.S.I.C. Serrano Galvache, 4, 28033 Madrid, Spain

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Abstract

Fly ashes from the combustion of coal thermal power stations are commonly incorporated into portland cements and/or concretes and mortars. The chemical and morphological composition of fly ashes, together with their particle size, make them suitable as pozzolanic(non-calcic) or pozzolanic/hydraulic(highly calcic) additions to manufacture such building materials. This work focuses on the incorporation of two different fly ashes (non-calcic but of very different Fe_2O_3(%) contents, fineness and morphology) to two ordinary portland cements (of very different mineralogical composition as well), to determine the effects those have and the interactions they produce in the hydration reactions of portland cement. The main techniques employed for this study have been: conduction calorimetry and Frattini test; secondary techniques applied have also been: determination of setting times and analysis by X-ray diffraction and SEM. Analysis of the results obtained permitted to find different effects of fly ash addition on the hydration reactions of portland cements. Thus, dilution and stimulation effects augment with the increased fly ash percentage. Delay and acceleration of the reactions depend mainly on the type of portland cement and are accentuated with increased fly ash contents. Their behaviour as concerns heat dissipation mainly, depends on the type of fly ash used and is more pronounced with increased cement replacement. On the other hand, the pozzolanic activity of these fly ashes has been revealed at 7 and 28 days, but not at 2 days. Finally, pozzolanic cements can be manufactured using different portland cements and/or types of fly ashes, in the appropriate proportions and compatible qualities, depending on the effect(s) one wish to enhance at a specific age, which is according to previous general conclusions drew out of sulphate attack and chloride attack researches.

Keywords: conduction calorimetry, fly ashes, portland cements, pozzolanic cements, pozzolanicity, setting times, XRD

Introduction

Fly ashes are added to portland cement or directly to mortars or concretes. Therefore the need of numerous studies on the mechanical and durability properties of the re-

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[*] Author for correspondence: E-mail: vrahhal@fio.unicen.edu.er
[**] Author for correspondence: E-mail: rtalero@ietcc.csic.es

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sulting final products appeared. Similarly, legislation has been developed to classify the ashes, and to lay down the specifications for fly ash cements. On one hand, ASTM C 618 Standard [1], stipulates the differences between Class C and Class F fly ashes (calcic and non-calcic ones). EN 197 Standard [2] classifies fly ash cements into CEM II A or CEM II B, according to whether the fly ash content incorporated is between 6 and 20% or between 21 and 35%, respectively. In Argentina, although fly ash cements are not regulated by the Iram, the Cirsoc 201 Standard contemplates their implementation after testing if they have no harmful effects on the properties of cements or not.

Their pozzolanic properties and hydraulicity are most closely associated with the amorphous and/or vitreous status of their structure [3–8]. Distinction between the properties of the admixtures used is based on general behaviour in response to attack by sulphates, on the one hand [4, 5], and chlorides, on the other [6]; classifying these into silicic, aluminous-ferric, silicic, silicic-aluminous and aluminous [4–8].

The effects of fly ash (FA) incorporation to portland cements (PC) on hydration reactions, corresponded to a delayed appearance of the second peak on calorimetric curves and reduced intensity of the heat dissipation rate as compared to the plain PC [9–12]. This resulted in an overall reduction of total heat evolved at the start of the hydration reactions (12, 24, 48, 72, 120 h) [13, 14]. However, in the first few hours (before 12 h), the total amount of heat evolved was greater than for the plain PC [10]. Similarly, fly ash incorporation accelerated alite hydration, and this visible as the water-cement ratio increased [15]. Nevertheless, elevated percentages of ash incorporated and the water-cement ratio increased resulted in increasing setting times of the mixtures [11].

When studying lime consumption by the fly ashes in the pozzolanic reaction, the cement–ash mixtures or blended cements or pozzolanic cements (POZC), were observed to initially release calcium hydroxide, just like a plain PC (up to 7, 28 and 90 days, depending on the case), which was later consumed in the pozzolanic reaction [9, 12, 14–19]. However from 1 day of age and by DTA method, calcium hydroxide consumptions also were observed in PC pastes with fly ashes [20].

Strong correlations were also found between the amount of lime fixed and the hydration heat for the same age [21], and between the reactivity degree of a fly ash with its soluble silica content and its fineness [22]. There was also a strong tendency for reactivity to increase with the ground fineness of the fly ashes [16].

Numerous studies have been carried out on cements with variable contents of different types of fly ash, mainly concerned with such properties as mechanical strengths and durability in different aggressive media.

In the experiments thus reported, the behavioural variability of the fly ash portland cements supplemented with fly ashes of different chemical compositions are not comparable.

Objectives

In an attempt to put some new light on these aspects, this work proposes to study the influence of different percentages of fly ashes, with different chemical composition, on the hydration of portland cements with extreme mineralogical compositions (approximately 50 and 80% of C_3S, and 14 and 0% of C_3A, respectively).

Material and methods

The materials selected for the experiment were:

- Two portland cements, one with a high C_3A content, PC1, and another with a minimum C_3A content, called PC2.
- Two industrial fly ashes – fly ash CV 19: aluminous-ferric-silicic [4–8], and fly ash CV10: silicic-aluminous [4–8] – with very similar fineness which moreover satisfied the specification of the ASTM C 618-95 Standard for fly ashes – amount retained when wet-sieved on 45 μm (No. 325) sieve <34%.
- Distilled water as mixing water in all cases.

The chemical composition, density and Blaine's fineness of the ordinary portland cements and the fly ashes are presented in Tables 1 and 2.

From the Table 1, it results that although the fly ashes appear to be chemically similar, in fact they are not because their Fe_2O_3(%) contents are very different (Table 1) and their mineralogical differences as well (Figs 1 and 2). Thus, their XRD pat-

Table 1 Chemical composition of cementing materials

Components/%	Portland cements		Fly ashes	
	PC1	PC2	CV19	CV10
LOI	1.60	1.11	0.83	6.92
IR*	0.70	0.15	0.12	0.18
SiO_2	19.18	21.70	45.47	49.29
Al_2O_3	6.44	1.52	30.09	29.63
Fe_2O_3	1.75	4.11	16.12	4.22
CaO	63.94	67.97	4.03	2.86
MgO	1.48	0.42	1.12	1.81
Na_2O	0.90	0.43	0.20	0.50
K_2O	0.52	0.20	2.80	3.60
SO_3	3.50	2.34	1.92	0.94
Total	100.01	99.95	102.70	99.95
Density	3.08	3.21	2.43	2.09
BSS, $m^2\ kg^{-1}$	319	301	399	401

*Insoluble residue

Table 2 Potential phase composition (Bogue) of PC

Components/%	PC1	PC2
C_3S	51.05	79.43
C_2S	16.48	2.29
C_3A	14.11	0.00
C_4AF	5.33	10.19

terns reveal the presence of quartz (Q), hematite (He), maghemite (Ma) and mullite (Mu), and mainly, a diffuse band which is generally assigned to fly ash glassy component [7], and it is different too. This diffuse band can be observed as belonging to the vitreous fraction in each of these fly ashes, being most significant in CV10. On the other hand, their respective SEM analysis show them to have also very different shapes, sizes, diameters and quantities (Figs 3a and b and 4a and b).

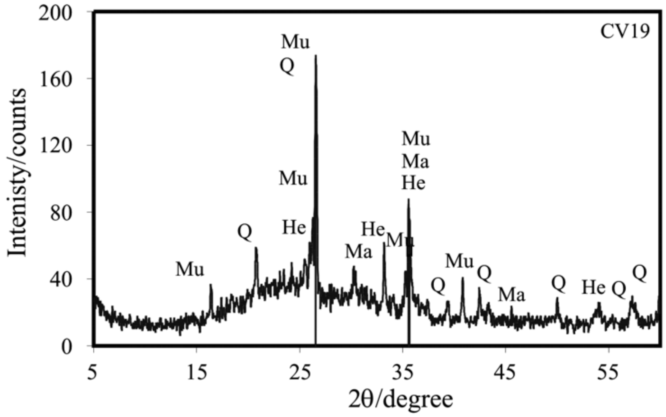

Fig. 1 XRD pattern of fly ash CV19

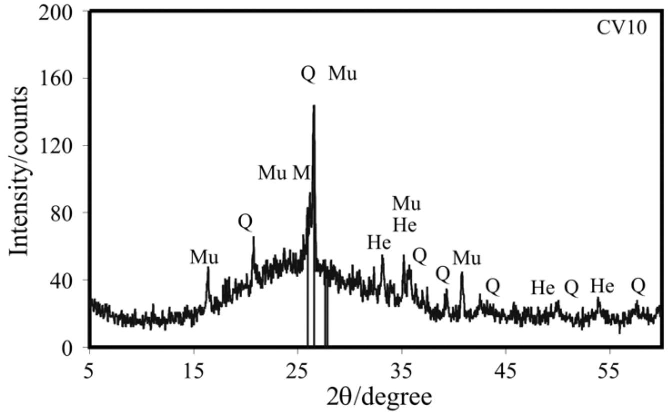

Fig. 2 XRD pattern of the fly ash CV10

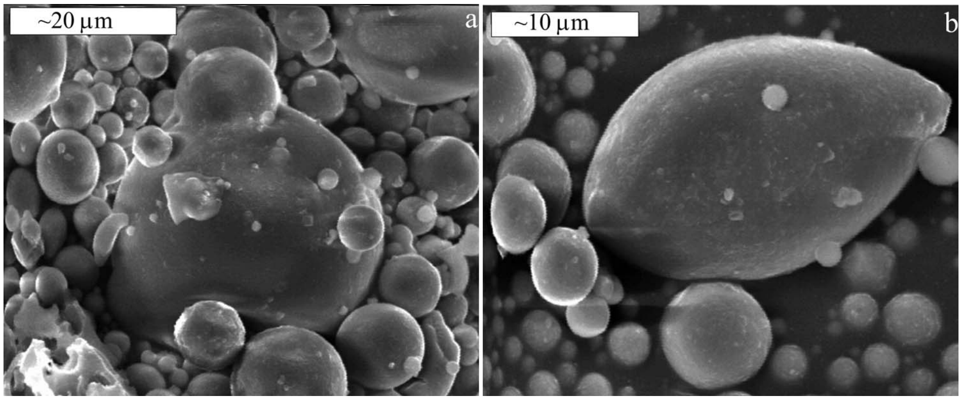

Fig. 3 SEM of fly ash CV19

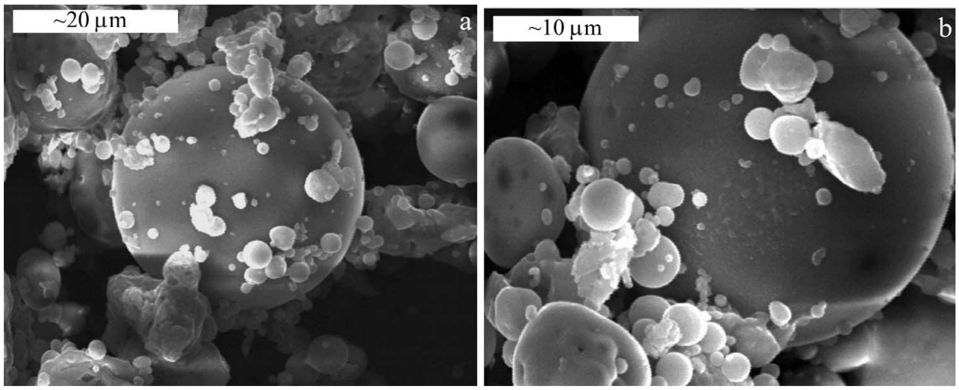

Fig. 4 SEM of fly ash CV10

First of all, 8 POZC with 80%/20% and 60%/40% (%PC–*n*/%FA – *n*º ratios) were prepared with 2 portland cements (PC) – PC1 and PC2 – and 2 fly ashes (FA) – CV19 and CV10 –. Secondly, all these POZC were analysed by the Frattini test [2, 23–25] in order to confirm their pozzolanic characteristics at 2, 7 and 28 days (Table 3). Thirdly, times of setting and water/binder-ratio (*w/b*, in mass) were also determined (Table 4). Fourthly, each POZC and each PC, were submitted to the conduction calorimeter test (for this test, the water/binder-ratio – *w/b* – used was always 0.5) (Tables 5 and 6 and Figs 5 and 6). Lastly, each PC and POZC paste was analysed by XRD for the most significant minimum points or troughs, of its calorimetric curve (Figs 7–10).

Pozzolanicity was assessed by the Frattini test [2, 23–25] which consists in comparing the amount of calcium hydroxide in the aqueous solution in contact with the sample (pozzolanic cement, POZC, with %PC–*n*°/%FA – *n*° ratio) hydrated at 40°C at 2, 7 and 28 days with the isotherm of calcium hydroxide solubility in an alkaline solution also at 40°C. This test is considered positive for a pozzolanic addition, when at 7 or 28 days, before [23], and at 8 or 15 days, now [24], the calcium hydroxide con-

Table 3 Pozzolanicity (Frattini test): results at 2, 7 and 28 days

Cements	2 days/mM L^{-1}				7 days/mM L^{-1}				28 days/mM L^{-1}			
	*	[OH]	*	[CaO]	*	[OH]	*	[CaO]	*	[OH]	*	[CaO]
PC1 100		72.50		7.60		71.25		6.80		78.00		6.45
PC1/CV19 80/20	58.0	68.00	6.08	9.55	57.0	**63.50**	5.44	**6.50**	62.4	**71.50**	5.16	**4.30**
PC1/CV19 60/40	43.5	61.00	4.56	11.55	42.75	**54.50**	4.08	**5.60**	46.8	**61.50**	3.87	**1.50**
PC1/CV10 80/20	58.0	67.50	6.08	11.20	57.0	69.75	5.44	6.55	62.4	**77.50**	5.16	**4.25**
PC1/CV10 60/40	43.5	60.50	4.56	9.50	42.75	**60.00**	4.08	**3.80**	46.8	**71.00**	3.87	**2.10**
PC2 100		42.50		21.50		39.45		16.55		42.00		16.10
PC2/CV19 80/20	34.0	44.00	17.2	20.65	31.56	**41.50**	13.24	**13.95**	33.6	**40.50**	12.88	**10.00**
PC2/CV19 60/40	25.5	45.00	12.9	21.05	23.67	**35.50**	9.93	**11.20**	25.2	**35.50**	9.66	**4.25**
PC2/CV10 80/20	34.0	45.50	17.2	21.75	31.56	**40.50**	13.24	**10.25**	33.6	**47.50**	12.88	**8.75**
PC2/CV10 60/40	25.5	45.50	12.9	21.35	23.67	**35.00**	9.93	**8.45**	25.2	**43.50**	9.66	**5.50**

The paired values in **bold** mean that the point is in the subsaturation region (=+result) *Values assuming inertness of fly ash

Table 4 Setting times and *w/b* ratios

Cements	Setting times (h:m)			*w/b* ratio (in mass)
	initial	final	total	
PC1 100	3:20	5:10	1:50	0.310
PC1/CV19 80/20	2:45	4:45	2:00	0.300
PC1/CV19 60/40	3:10	5:10	2:00	0.275
PC1/CV10 80/20	2:55	4:40	1:45	0.330
PC1/CV10 60/40	3:05	4:55	1:50	0.345
PC2 100	4:30	6:15	1:45	0.280
PC2/CV19 80/20	3:10	7:30	4:20	0.285
PC2/CV19 60/40	3:40	7:50	4:10	0.275
PC2/CV10 80/20	3:35	8:00	4:25	0.320
PC2/CV10 60/40	6:05	8:20	2:15	0.340

Table 5 Ages of the most significant points of each calorimetric curve

Cements	Induction period/h:m	2nd peak/h:m	3rd peak/h:m
PC1 100	2.00	11.20	17.40
PC1/CV19 80/20	1.75	9.71	15.05
PC1/CV19 60/40	2.30	11.26	20.30
PC1/CV10 80/20	1.75	9.68	15.11
PC1/CV10 60/40	2.18	11.08	17.98
PC2 100	1.62	7.35	–
PC2/CV19 80/20	2.23	9.43	–
PC2/CV19 60/40	2.34	13.96	–
PC2/CV10 80/20	2.56	10.63	–
PC2/CV10 60/40	3.43	17.16	–

Table 6 Total heat at 48 h

Cements	Total heat/kJ kg^{-1}		Cements	Total heat/kJ kg^{-1}	
	*	measured		*	measured
PC1 100		298	PC2 100		212
PC1/CV19 80/20	238.4	264	PC2/CV19 80/20	169.6	175
PC1CV19 60/40	178.8	173	PC2/CV19 60/40	127.2	108
PC1/CV10 80/20	238.4	260	PC2/CV10 80/20	169.6	171
PC1/CV10 60/40	178.8	74	PC2/CV10 60/40	127.2	67

*Values assuming inertness of fly ash

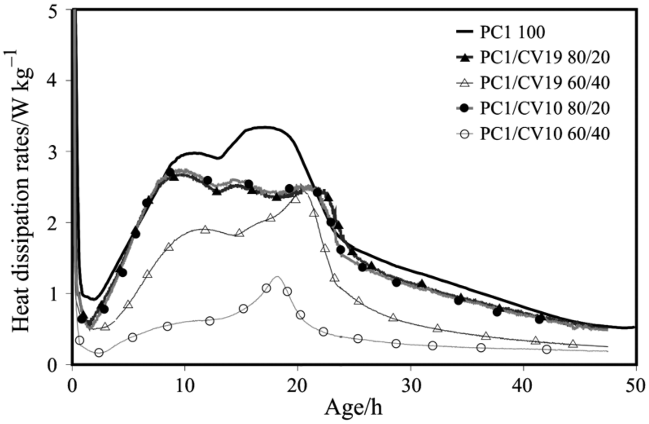

Fig. 5 Calorimetric curves with PC1

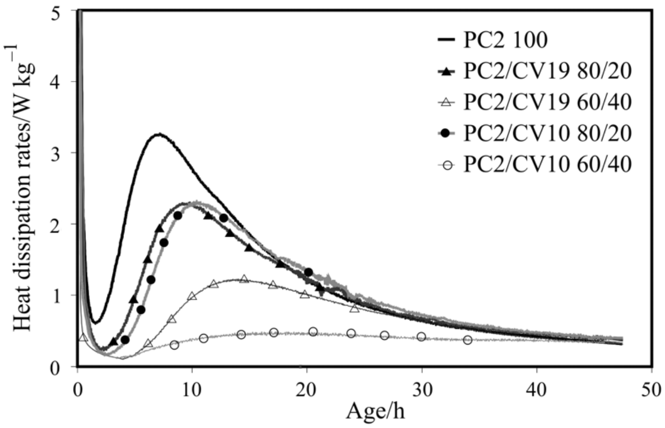

Fig. 6 Calorimetric curves with PC2

centration (which must be reported as [CaO]) in the sample solution, is below the solubility isotherm (positive pozzolanicity result, or simply, + result).

The mechanism of the initial hydration in cementitious systems with different mineral admixtures can be investigated by use of calorimetry [26]. In this work, the evolution of the heat generation rate was determined by conduction calorimetry for cement pastes. The baseline temperature for measurements was 25°C. Registers were completed for the first 48 h of hydration. The total heat was obtained from the integral under the heat generation curve *vs*. time.

X-ray diffraction of the cement pastes was conducted to measure the change in the production and/or consumption of calcium hydroxide (semiquantitative or comparative analysis only) at the ages of the different troughs (Table 5) obtained from the calorimetric curves:

- In the case of POZC 60/40 with PC1 (Figs 7 and 8): first depression or the so-called induction period or lowest point, second depression (between the second and third maximum or highest point or peak) and third depression (at the end of the calorimetric test).

- In the case of POZC 60/40 with PC2 (Figs 9 and 10): first depression and second depression (at the end of the calorimetric test).

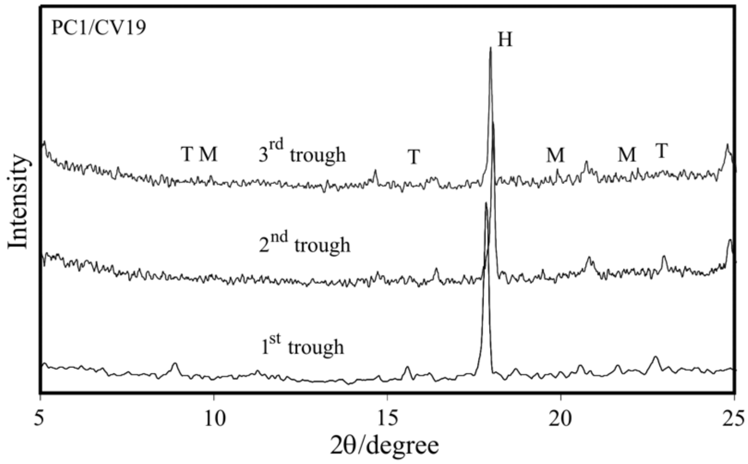

Fig. 7 XRD patterns of the POZC PC1/CV19 60/40

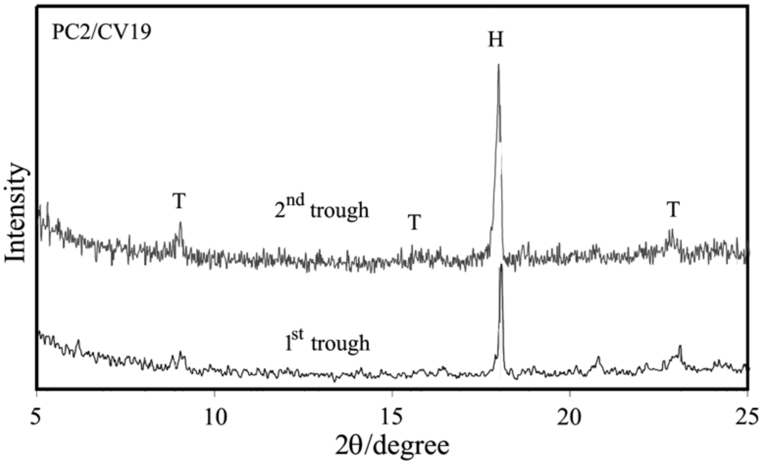

Fig. 8 XRD patterns of the POZC PC2/CV19 60/40

Results and discussion

Table 3 shows the specified concentrations determined for [OH^-] and [CaO] in the sample solution (or liquid phase of its Frattini test), at 2, 7 and 28 days. Points which intersect below the solubility isotherm are marked in bold (=positive pozzolanicity

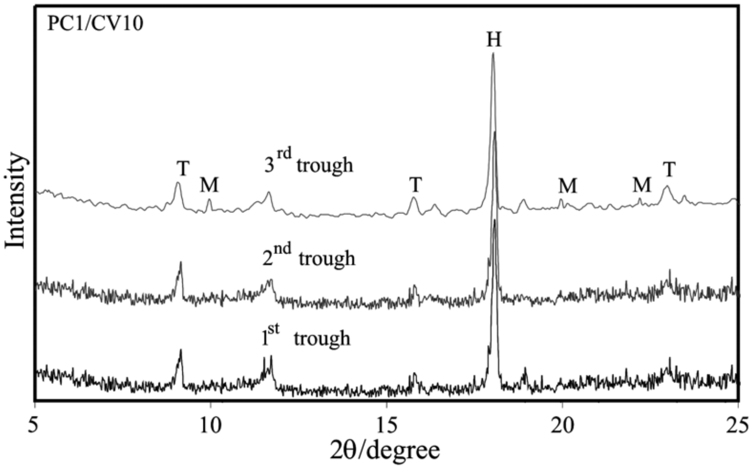

Fig. 9 XRD patterns of the POZC PC1/CV10 60/40

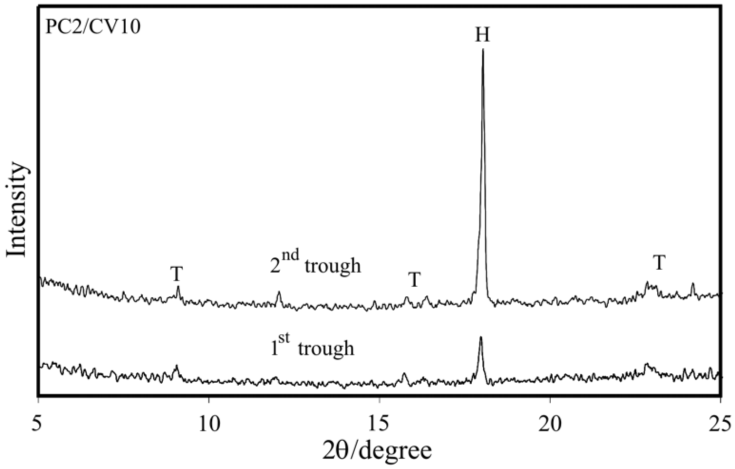

Fig. 10 XRD patterns of the POZC PC2/CV10 60/40

results or simply + results). It can be observed in this Table 3, that no POZC showed pozzolanic activity at 2 days old; at 7 days all the POZC, except for PC1/CV10 80/20, presented pozzolanic activity, and finally at 28 days, all the POZC presented positive pozzolanicity (naturally, both plain PC showed no pozzolanic activity). The reason of that consisted in lower C_3S content in PC1 than in PC2, and as a consequence, in its liquid phases (plain and of its POZC) composition with always reduced [CaO] contents, as it occurred in this research (Table 3).

On the other hand, the decrease of $[OH^-]$ and [CaO] from 2 until 28 days due to both fly ashes presence in the mixture, could also be observed. In parallel with the decline in [CaO] and $[OH^-]$ until 28 days, these reductions also increased with percentage replacement. This shows the progress of the pozzolanic reaction as demonstrated in other studies [9, 12, 15–19].

Also, stimulation of the hydration by its PC fraction, by means of ‘through way’ or ’direct way’, or simply ‘direct stimulation’ – promoted by the initial adsorbed water of the fly ashes (from the mixing water) –, was verified for all the samples since the [OH^-] and [CaO] values were higher than those estimated mathematically assuming inertness of the fly ashes, but particularly for the CV19 fly ash. Furthermore and in relation to the augmented percentage of PC replacement by fly ashes, the tendency to achieve a positive pozzolanic behaviour after 7 days increases, but this trend is not observed for CV19 POZC at 2 days of age, but direct stimulation effect only, which would also be reported by other authors [6, 9, 11, 16]. In contrast, a quite different behaviour is observed for CV10 POZC at 2 days, although logically to the detriment of its direct stimulation behaviour for the hydration reactions. These different qualitative and quantitative behaviours point out that the chemical composition of both fly as concerns mainly the vitreous fraction, must be logically different. It has been verified by XRD – their diffuse bands [7] are also different (Figs 1 and 2) – and further on by SEM analysis – their shapes, sizes, diameters and quantities are different as well (Figs 3a and b and 4a and b).

When the behaviours of every fly ash with two PC of different mineralogical composition, were compared, in both cases the similar tendencies were found, except of the relative positions of the dots (respective points which intersect below or over the referred solubility isotherm). Generally, the higher [OH^-] presented by the CV10 POZC at 7 and/or 28 days, compared to the CV19, could be perhaps due to the greater proportion of Na_2O and K_2O of the CV10. This accounted for the two POCZ families, 80/20 to themselves and 60/40 to themselves.

Figures 5 and 6, show the calorimetric curves drawn up during the first 48 h. for PC1 and PC2, respectively. The heat dissipation curves for the POZC with CP1 (Fig. 5 and Table 5), presented in the first depression and in the second and third peaks, an advance for the 80/20 POZC and a delay for the 60/40 POZC, except the 2nd peak of POZC PC1/CV10 60/40. For POZC with CP2 (Fig. 6 and Table 5), the first depression and the second peak were delayed. But in relation to the heat dissipation rate, there was an attenuation compared to its respective plain PC2, which augmented with increasing percentage of fly ash in both cases. Once again, different behaviours of these two fly ashes CV19 and CV10 with both PC resulted in higher hydration rate of the C_3A than that of the C_3S, and as a consequence, the C_3A would have been more susceptible for hydration (wetting) by initial absorbed water of the fly ash, than C_3S. The earlier was the age of test thus considered, the more susceptible for hydration was C_3A than C_3S. And another consequence, all the setting times of the POZC with PC1 should have been always shorter than those of its plain PC1, and in contrast, some POZC with PC2 should have not been, as it occurred in this research (Table 4). However, the greater density of CV19 than CV10, because of its greater Fe_2O_3(%) content, should have,

- lower *w/b* ratios than CV10,

- shortened initial setting times of their plain PC as compared to CV10, but in addition, initial and final setting times lower than with CV10, and as a final consequence,
- decreased total heat of its plain PC, but being always greater than with CV10,

as it occurred in this research as well (Tables 4 and 6). By the way, it can not be forgotten that density, setting times and total heat are physical parameters.

As it results from analysis of the calorimetric curves, the effect of fly ashes is different depending on to the portland cement used and the percentage of fly ash incorporated. Thus, in the case of POZC with PC1, for a 20% replacement, the advanced appearance of individual dots could be due to the stimulation of the hydration reactions as cited previously [10, 15, 22]. However, a delay was recorded with increased percentage addition like that described by other authors [9–12, 14], due to the dilution effect probably (but between two solid materials: PC-n^o and FA-n^o, in this case). This was also corroborated for the POZC with CP2.

Table 6 shows the total heat delivered during the first 48 h of POZC and PC hydration. The values thus obtained reveal a stimulating effect of the fly ash particles on hydration reactions for POZC with 20% replacement since the total heat values were higher than those estimated mathematically assuming inertness of the fly ashes. However for POZC with 40% replacement, it was not observed. Probably, it was caused by their common 'hollowed' sphericity, which would have made fly ash particles show their best and most intense behaviour as sources ('nuclei') of indirect heat emission – that is, being equivalent to heat 'dissipation' or 'evacuation', really –, when 40% replacement.

Finally, a step-by-step measurements were carried out by calorimetric conduction, starting at the moment when the water firstly came into contact with the POZC or the PC, up to the first 48 h, and then from 2 to 28 days, followed by a pozzolanicity test. Thus, with the purpose of corroborating the course of the reactions during the first 48 h, the compounds thus formed were identified by XDA and the progress of hydration at every age (see the age of every peak in Table 5) was followed. Figures 7 and 8 show XRD patterns of the CV19 POZC with CP1 and CP2, respectively; and in Figs 9 and 10, those of the CV10 POZC.

The increase in the amount of calcium hydroxide (H) (in the solid phase or cement paste) in the advancement of the troughs, has demonstrated a stimulatory effect on hydration reactions that was also shown in the pozzolanicity test, in the total amount of heat originated at 48 h and in the final and/or initial setting times. On the other hand, the formation of the AFt phase (T) and its transformation into the AFm phase (M) in the case of POZC with CP1, was verified (Figs 7 and 9), corresponding with the third maximum or third peak, of the calorimetric curve. In the case of POZC with CP2, Figs 8 and 10, the absence of the AFm phase was also verified corresponding with the absence of the third peak of the calorimetric curve, after all, C_3A content present in PC2 was practically 0.00%.

Generalising the behaviour observed according to the experimental results obtained, the incorporation of fly ashes, regardless of the mineralogical composition of the portland cements with which they are blended, can be considered to stimulate the hydration reactions within the time shorter than 2 days. This is due to the fly ash particles acting first of all, as points adsorbing water initially, and secondly, as centres for calcium hydroxide nucleation (Figs 7, 8, 9 and 10). For this reason, its representative dots in the pozzolanicity test or Frattini test, were in the supersaturated region, that is to say, all were negative at 2 days old samples (Table 3). Nevertheless, after the first few hours, this effect diminishes and the dilution effect caused by the percentage replacement, demonstrated by a significant reduction in the heat evolution rates, becomes more evident (Figs 3 and 4 and Table 6). For cements with high C_3A contents, the incorporation of these fly ashes stimulates the hydration reactions to a specific percentage between 20 and 40% replacement; and after this, the process slows down. However, for cements with low C_3A contents, the hydration reactions slow down as the percentage of these fly ash increases. All this, coincides with the start and finish of the setting process and the appearance of individual dots on the calorimetric curves. Hence after first 48 h, these fly ash particles act as nuclei which evacuate or dissipate heat previously evolved by PC1 or PC2 particles (when PC particles are hydrated with water) attached to those fly ash particles, or perhaps also sources of heat evolved indirectly and not directly like PC particles evolve it, since the total heat of the 60/40 mixtures was less than 60% of the total heat released by plain PC (Table 6). The type of fly ash affects this mode of 'calorific' behaviour, and fly ash CV10 has been more effective to reduce hydration heat due to its greater size and particle diameter, precisely because of its 'silicic-aluminous' character [4, 7, 8]. Furthermore, the pozzolanic activity is improved with increased replacement and with time (that is, at the final of the test the result is better than at the beginning), since the relative decrease in [CaO] increases with both parameters (Table 3).

Conclusions

By means of conduction calorimetry, pozzolanicity (Frattini) test, setting time determination and analysis by XRD and SEM, the following conclusions were obtained:

The incorporation of fly ashes, CV19 and CV10, to portland cements of different mineralogical composition stimulated the hydration reactions of portland cements components. Thus, for portland cements with high C_3A contents, the incorporation of these fly ashes stimulated the hydration reactions up to a specific cement replacement (between 20 and 40). However, for portland cements with low C_3A contents, the reactions slowed down with the rise of fly ash percentage.

As the fly ash content in blended cement rises, the stimulatory effect begins to be less evident, masked by the obvious dilution effect; this is observed within the first few hours.

Behaviour of fly ash particles as sources ('nuclei') of heat indirect emission depends mainly on the type of fly ash, and consequently of its morphology, and is enhanced with increased percentage. Subsequently, the pozzolanic activity is manifested; it is stimulated with increased fly ash percentage, with C_3S content and with time. Logically, at the end the pozzolanicity test results are better than at the beginning.

According to all the experimental results thus obtained, the chemical composition of the vitreous fraction of these fly ashes must be different, and as a consequence in relation to the evolution of the heat and the total heat values, POZC can be manufactured using different PC and/or types of fly ashes, mixed in the appropriate proportions and compatible qualities. It should depend on the effect(s) one wish to enhance at any age; here one can take into account the general conclusions from references [4, 7, 8].

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