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Fast physics-chemical and calorimetric characterization of natural pozzolans and other aspects

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Abstract This research reports on the effects of including natural pozzolans in two Portland cements with different mineralogical compositions, with and without excess gypsum at amounts equivalent to 7.0% SO_3. The main analytical techniques used to study these effects were: the amount of water needed to make a paste of normal consistency, the 2-day Frattini pozzolanicity test and conduction calorimetry. The results obtained showed that these natural pozzolans caused contradictory (accelerating and retarding) effects on the rheology of the resulting cements, depending on the mineralogical composition of the respective Portland clinkers as well as the reactive chemical composition of the pozzolans, in particular their reactive alumina content ($Al_2O_3^{r-}$). The addition of gypsum also caused acceleration and delays in the calorimetric evolution of the resulting pastes, which proved to be heavily dependent upon the more or less *aluminic* chemical *character* of the natural pozzolans studied. This, in turn, was conditioned by the higher or lower $Al_2O_3^{r-}$ content (for the SiO_2^{r-} content was of a very similar order of magnitude in all three pozzolans analyzed). The $Al_2O_3^{r-}$ content was likewise responsible for paste behaviour in the afore-mentioned trials and analyses, and the pozzolanic activity exhibited by the compound was found to be more *specific* than *generic*, *indirectly* stimulating C_3A hydration more intensely and rapidly than C_3S hydration in PC1, one of the two Portland cements used. Indeed, when these natural pozzolans exhibited such prior pozzolanic activity in the second cement studied, PC2, the hydration of its 79.5% of C_3S was not *indirectly* stimulated to the same degree; rather, the contrary effect was observed, i.e., this cement was physically *diluted* by the three pozzolans. Pozzolan **O** stimulated hydration *directly* and *non-directly* more than *indirectly*, while pozzolan **C** acted conversely, and **A** exhibited varying combinations of the two patterns. The physical state of the reactive alumina, $Al_2O_3^{r-}$, in these three natural pozzolans, must be more amorphous than vitreous, i.e., resembling metakaolin more than fly ash in this regard. That notwithstanding, the reactive alumina content in each pozzolan must have conditioned the water/cementitious material ratio obtained for the respective blends with both types of Portland cement (a finding that could be used in future for speedy, simple, reliable and economical *characterization*), as well as their *specific* pozzolanicity developed and the rate and total heat of hydration generated by such blended cements.

Keywords Conduction calorimetry · Natural pozzolans · Portland cements · Pozzolanicity · Setting times

Introduction

The use of natural pozzolans dates back to antiquity. Lime and pozzolan mortars were used by the Romans in many types of works, including maritime structures. The fact that many of these structures are still standing today and in good condition is proof of the durability of the binder used [1]. Pozzolans are used in mortars today and as mineral

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admixtures in concrete and as very ground components in pozzolan cements or in Portland cement-pozzolan blends.

The reactivity of pozzolanic additions with portlandite defines their greater or lesser pozzolanicity and hydraulicity, which is essentially associated with the vitreous and/or amorphous nature of their structure [2], i.e., with the amount of reactive silica (SiO_2^{r-}) [3–5] and reactive alumina ($Al_2O_3^{r-}$) they contain [1–3]. Irrespective of whether natural or artificial pozzolanic additions are *siliceous* or *siliceous-aluminous* in nature [6], the determination of their chemical *character* has been based on their behaviour when exposed to sulphates [7–12], on the one hand, and chlorides [13, 14], on the other. As a result, regardless of their natural or artificial origin and nature [6], they have been classified by Talero [7] as *silicic, aluminic* or a mixture of these two extreme chemical characters, i.e., *silicic-aluminic* or *aluminic-silicic*, depending, respectively, on whether the *silicic* or *aluminic* chemical *character* prevail. In addition, when pozzolans on occasion also exhibit certain *ferric* characteristics, they are said to have a *silicic-ferric-aluminic* chemical *character* or any other combination of those three characters [7].

Be it said in this regard that *aluminic* pozzolanic additions reduce (sometimes very rapidly) the sulphate resistance of the Portland cement with which they are blended, even when the initial PC is highly sulphate resistant [7–11]. In the absence of sulphate, however, they raise cement mechanical strength, particularly at early ages [7, 10, 11, 13]. By contrast, they prevent or at least hinder chlorides from attacking reinforcing steel: first chemically and then physically [13, 14].

Conversely, *silicic* pozzolanic additions enhance ordinary Portland cement sulphate resistance [7, 12], reduce its mechanical strength [7] and increase reinforcement exposure to chloride attack [13, 14]. One exception to this rule is found in silica fume, which not only raises sulphate resistance and mechanical strength [12], but also prevents or at least hinders the effects of chloride ions on reinforcement [13, 14], albeit only physically, for its predominantly vitreous condition and small particle size provide for substantial, speedy and early age pozzolanic activity [15].

Most natural and artificial pozzolanic additions constitute a random mixture of these two *behaviours*; in these cases, naturally, one or the other condition or chemical *character*, *aluminic* or *silicic*, should predominate, depending on whether the effects deriving from their $Al_2O_3^{r-}$ content prevail or otherwise over the effects of their SiO_2^{r-} content. Nonetheless, in the best of cases, such *characterizations* take at least 28 days [7, 10–12], while the same results can be obtained with conduction calorimetry in only 48 h [15].

Moreover, in both pozzolan <> tricalcium silicate (C_3S) and pozzolan <> tricalcium aluminate (C_3A) systems, pozzolans accelerate hydration of the mineralogical components of Portland clinker and its setting regulator [16]. Such stimulation is the result of the rise in temperature and the lime/pozzolan ratio [1, 16]. In calorimetric studies of cement/pozzolan pastes (60/40, by weight), both the second peak, representing the mass hydration of tricalcium silicate, and the third peak, representing the transformation of ettringite into hydrated calcium monosulphoaluminate, have been observed to appear earlier than in the pure PC. When the percentage of the pozzolanic addition was varied from 0 to 90, however, the effect observed in blends with lower percentages was the stimulation of hydration reactions, while in those with higher percentages, heat dissipation centres were generated [17]. At the same time, as the heat of hydration declined with the rise in the replacement ratio, setting times were also found to rise with a decline in early age workability and mechanical strength, although the latter effect tended to disappear with age [18].

The pozzolanic activity of this type of mineral additions has been evaluated in terms of the uptake or fixation of calcium hydroxide and/or portlandite, CH, as revealed by X-ray diffraction [19, 20] and electrical resistance [20]. Infrared spectroscopy is another technique used to assess addition pozzolanicity, in which spectra are analyzed before and after treatments such as: acid–base attack and subsequent calcination at 1000 °C, calcination at 1000 °C and treatment with salicylic acid in a methanol medium [21]. Nonetheless, the results of these analytical methods do not always concur, for in some cases mineral additions that exhibit pozzolanic activity with lime [22–24] fail to do so with cement and vice versa [25].

The inclusion of gypsum, in turn, stimulates constituent hydration in Portland cement, although it affects the aluminate more intensely than the silicate phase [26, 27].

Objective

The studies cited above did not address variations in behaviour in terms of differences of the mineralogical composition of the Portland cements containing pozzolanic additions with different chemical *character*, or the possible effect of including gypsum in the blend. With a view to contributing to the understanding of such questions, the present paper describes a study on the effect of natural pozzolans and gypsum on the hydration of two Portland cements with widely varying mineralogical compositions.

Materials and methodology

The materials selected for the study were as follows: two Portland cements: one, with a high C_3A content, denominated PC1, and the other, with a minimum C_3A content, denominated PC2; three natural pozzolans, with very similar Blaine specific surface, BSS, values, "**O**" from Olot, Gerona: *silicic-ferric-alumic* [7]; "**A**" from Almagro, Ciudad Real: *silicic-aluminic* [7]; and "**C**" from the Canary Islands: *aluminic-silicic* [7]; natural, 98% pure ground gypsum ($CaSO_4 \cdot 2H_2O$); and distilled water for mixing.

The chemical composition, density and BSS for the Portland cements and pozzolanic additions are given in Table 1. The Bogue calculations performed on the grounds of the chemical composition yielded the following potential composition for the Portland cements: for PC1, 51% C_3S, 16% C_2S, 14% C_3A and 5% C_4AF; and for PC2, 79.5% C_3S, 2% C_2S, 0% C_3A and 10% C_4AF. The samples analyzed and studied were: two pure Portland cements (PC) and the respective blended cements prepared by mixing each with each natural pozzolan (NP). The proportion, by weight, was PC/NP 60%/40% (=60/40), with and without additional gypsum in proportions of up to 7.0% SO_3. The 100/00 ratio denotes a pure Portland cement. The setting times [28] and respective water/cementitious material ratios (w/cm) by weight used are given in Table 2.

Pozzolanic activity was evaluated with the Frattini test [29] by storing the hydrated sample in an aqueous solution at 40 °C for a given period of time (in this case, 2 days) and comparing the amount of calcium hydroxide in the solution with the solubility isotherm for calcium hydroxide stored in an alkaline solution at the same temperature. Samples are regarded to test positive when the calcium hydroxide concentration in the solution is lower than on the solubility isotherm (Table 3).

Lastly, the heat release pattern was ascertained by heat conduction calorimetry for pastes. Measurements were taken at a temperature of 25 °C throughout the 48-h trial period (Fig. 1a–d).

Table 1 Chemical-physic determinations of cementing materials

Materials	Portland cements		Natural pozzolans		
Parameters	PC1	PC2	**O**	**A**	**C**
L.O·I (%)	1.60	1.11	0.40	3.92	6.92
IR (%)	0.70	0.15	1.10	–	0.43
SiO_2 (%)	19.18	21.70	45.12	41.38	54.18
Al_2O_3 (%)	6.44	1.52	13.84	19.36	20.10
Fe_2O_3 (%)	1.75	4.11	13.82	12.05	3.12
CaO (%)	63.94	67.97	10.48	11.11	2.38
MgO (%)	1.48	0.42	9.54	10.58	2.04
Na_2O (%)	0.90	0.43	3.18	1.24	5.64
K_2O (%)	0.52	0.20	2.40	0.44	5.17
SO_3 (%)	3.50	2.34	0.46	0.00	0.00
Total (%)	100.01	99.95	100.94	100.08	99.98
Density	3.08	3.21	3.08	2.41	2.68
BSS (m^2/kg)	319	301	404	403	402

Results and discussion

Table 2 gives the results for setting times and the *w/cm* (water/cementitious materials) ratio. The deduction drawn from these data is that in both PC1 and PC2, with and

Table 3 Pozzolanicity test (Frattini test). Results at 2 days

Cements	-7.0% SO_3 (mM/l)		$+7.0\%$ SO_3 (mM/l)	
	$[OH^-]$	[CaO]	$[OH^-]$	[CaO]
PC1 100/00	72.50	7.60	51.00	22.75
PC1/O 60/40	61.00	11.30	47.50	26.00
PC1/A 60/40	59.50	10.35	45.50	15.55
PC1/C 60/40	**83.50**	**2.30**	**81.00**	**1.80**
PC2 100/00	42.50	21.50	42.50	31.10
PC2/O 60/40	47.00	21.60	42.50	31.80
PC2/A 60/40	46.00	19.90	35.00	27.75
PC2/C 60/40	**61.50**	**5.00**	**39.00**	**15.10**

Table 2 Times of setting and water/binder ratios (w/mc)

Cements -7.0% SO_3	Setting times (h:min)		w/mc (in weight)	Cements $+7.0\%$ SO_3	Setting Times (h:min)		w/mc (in weight)
	Initial	Final			Initial	Final	
PC1 100/00	3:20	5:10	0.31	PC1 100/00	3:55	6:15	0.34
PC1/O 60/40	2:50	4:45	0.32	PC1/O 60/40	2:45	4:50	0.32
PC1/A 60/40	2:40	5:15	0.35	PC1/A 60/40	2:40	5:10	0.32
PC1/C 60/40	2:45	3:50	0.37	PC1/C 60/40	2:15	4:20	0.37
PC2 100/00	4:30	6:15	0.28	PC2 100/00	4:15	6:10	0.28
PC2/O 60/40	3:45	6:25	0.27	PC2/O 60/40	4:55	7:40	0.28
PC2/A 60/40	1:25	4:45	0.30	PC2/A 60/40	1:20	4:40	0.30
PC2/C 60/40	4:35	6:35	0.36	PC2/C 60/40	4:40	6:25	0.36

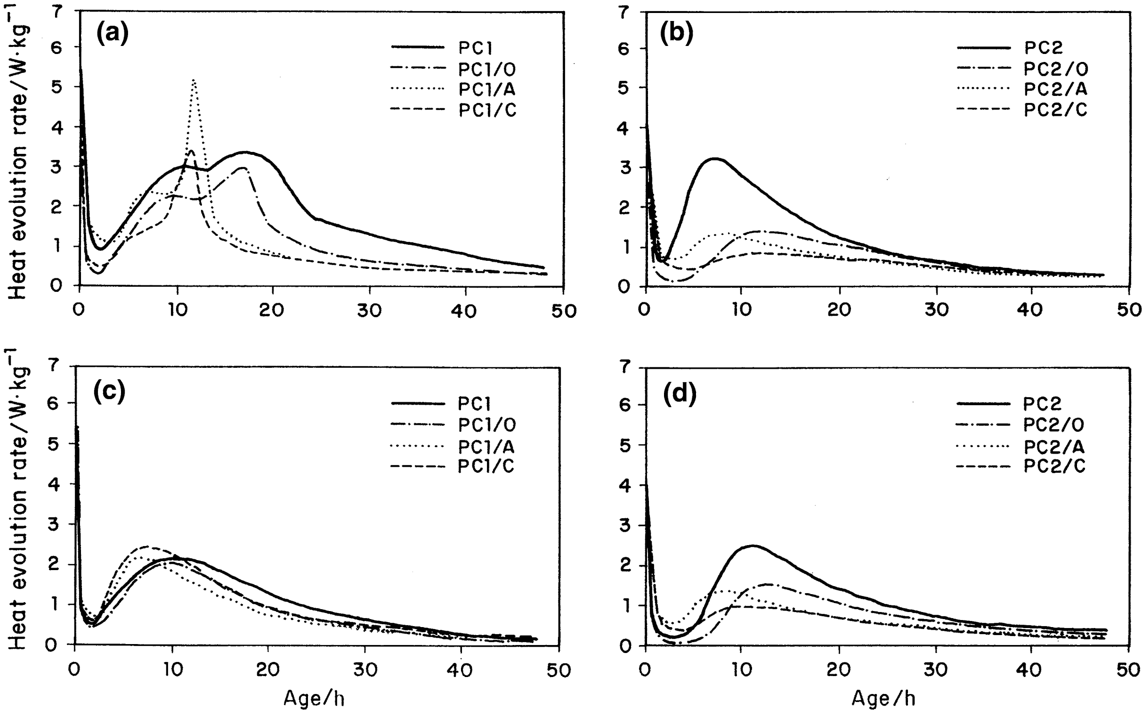

Fig. 1 Calorimetric curves of PC1 and PC2 and their blends with the three natural pozzolans: **a, b** without 7.0% SO_3; **c, d** with 7.0% SO_3

without excess gypsum (=7.0% SO_3), the ratio rose in direct proportion to the reactive alumina ($Al_2O_3^{r-}$) content [1] in the pozzolan, which was: 5.5% in **O**; 8.0% in **A**; and 11.5% in **C**. That finding signifies that:

- the reactive alumina ($Al_2O_3^{r-}$) in the three natural pozzolans must have been closer to the amorphous state characteristic of metakaolin than the vitreous state characteristic of fly ash;
- when they reacted with the portlandite released during the initial hydration of the two PC, the pozzolans must have generated proportional amounts of hydrated calcium aluminates and sulphoaluminates [8, 9, 11], which require water of crystallization to form; and finally
- this simple, reliable, reproducible and economical method [28] could well be used to rapidly determine the chemical *character* of a given natural and/or artificial pozzolan, and as a consequence, its certain chemical *character* can then be used to deduce its likely behaviour in an aggressive medium (sulfates, chlorides, sea water, carbonation, ASR, etc.).

Table 3 gives the 2-day [OH$^-$] and [CaO] found with the Frattini test. The points positioned below the solubility isotherm are shown in **boldface** type. According to the Table 3, in both PC1 and PC2, pozzolan **C** exhibited pozzolanicity at that early age, i.e., 6 days prior to the 8 [4] stipulated for the first test [29] (and 13 days before to the 15 [4] stipulated for the second and final test [29], for cases where the first 8-day trial is negative) for classifying a Portland cement-pozzolan blend as a type IV pozzolanic cement [4]: that is to say, to accept or reject the mineral admixture as a pozzolan, on the basis of chemical testing. In this case, then, **C** can be regarded to be a genuine pozzolan from the age of only 2 days, for it exhibited pozzolanic activity within that time frame, both with and without excess gypsum (=7.0% SO_3). This is a fairly significant finding, for as Talero [7, 10, 11], Mejía et al. [13, 14] and Talero and Rahhal [30–32] have amply proven [8–16], more or less intensely *aluminic* pozzolans are the only ones that, mixed in appropriate proportion with calcium hydroxide and/or portlandite and excess gypsum, yield materials with hydraulic properties. This, among others, may be the underlying basis for cement types CEM II/A-V [4] and II/B–V, II/A-P and II/B–P [4], II/A-T and II/B-T [4], II/A-M and II/B-M [4], type IV/A and IV/B [4] and type V/A and V/B [4], as well as so-called "expansive hydraulic cements" [33].

Table 3 also shows that the OH$^-$ concentrations in the PC1 blends containing **O** and **A** were lower than in pure PC1 (reflecting the *dilution* effect [31]). Even so, they were higher than the values that would have been obtained if the pozzolans had behaved inertly, which stands as partial proof of the fact that they stimulated the hydration reactions, in addition to supplying more alkaline cations (**O**: 4.76% $Na_2O_{eq.}$ and **A**: 1.53% $Na_2O_{eq.}$) than PC1 (1.24%). This latter effect was consistently greater in pozzolan **C**, which contained 9.04% Na_2O_{eq}, which would explain why the liquid phase of its paste had a higher [OH$^-$] than pure PC1. The same trend was observed in the PC2 samples, although in this case the supply of alkaline cations from pozzolan **C** was much more significant, for the alkaline content in PC2 itself was considerably lower (=0.56% of Na_2O_{eq}).

The [CaO] in the pozzolan **O** and **A** blends, in turn, was higher than in PC1 as a result, again, of the *direct* and *non-direct* stimulation of the hydration reactions by the pozzolans because of to the amount of mixing water that moistened each one of their particles when the trial began and to their behaviour like "*seed crystals*" [34, 35] (due, very in the beginning, to the positive and negative electrostatic charge acquired by the particles of pozzolan during grinding and/or mixing, and subsequently, to the zeta potential specially originated as PC hydration progresses), respectively; in pozzolan **C**, by contrast, the value was not only lower than in PC1, but also lower than would be expected if the 40% pozzolan in the blend had been inert. Such behaviour evinced the high pozzolanicity exhibited by **C** at the early age of 2 days.

The CaO concentration in the PC2 blends containing additions **O** and **A** was comparable to the concentration in PC2, likewise confirming once again the *direct* and *non-direct* stimulation referred to above, for the 60/40 blends obviously contained less Portland cement PC2 from which to release portlandite. By contrast, pozzolan **C**'s considerable early age pozzolanicity was again confirmed by the low [CaO] found in its liquid phase [29]. When these samples contained excess gypsum (=7.0% SO_3), the [CaO] rose in general due to the dissolution of this salt in the water, whereas the [OH^-] declined due to the physic *dilution* of PC2, despite which they passed the Frattini [29] test at the early age of 2 days. This decline in [OH^-] would logically be greater for PC1 than PC2, for the N_2O_{eq} and K_2O_{eq} content were higher in the former than in the latter. Such behaviour may have been due to the lower calcium silicate content in PC1 able to react and, consequently, to release OH^- (in the form of portlandite)

Briefly, then, natural pozzolans **O** (which is *silicic-ferric-aluminic* in chemical *character*) and **A** (*silicic-aluminic* in chemical *character*) exhibited different Frattini [29] test results depending on the type of Portland cement with which they were blended; while the behaviour pattern observed for natural pozzolan **C** (*aluminic-silicic* in chemical *character*) was the same in the two Portland cements, regardless of the differences in their mineralogical compositions. Moreover, by including gypsum in the blend a distinction could be drawn between the *silicic-ferric-aluminic* (**O**) and the *silicic-aluminic* (**A**) pozzolans; perhaps because the *aluminic* fraction of **A** was more reactive than the *ferric* component of **O**, [CaO] (despite the dissolution of the gypsum) was consistently lower in pozzolan **A** than in **O** (particularly, in the PC1 blend, which had a high C_3A content: 14%).

Figure 1a, b, c, and d, respectively, show the first 48-h calorimetric curves for the PC1 blended cements containing **O**, **A** and **C**, with and without excess gypsum (=7.0% SO_3). The PC1 calorimetric curve shows a first stage with a high rate of heat (of hydration) release, as a result of the initial hydrolysis and reaction of its calcium aluminate phases, primarily C_3A, with water (forming the *AFt* phase [30–32]). After 2 h, the value declined to 0.91 W/kg, when the first nadir on the curve was recorded. This was followed by the formation of CSH gels that accelerated the hydration reactions; during this interval (2:00–11:12 h:min) the heat release rate peaked for a second time, concurring with PC1 setting (Table 2). Thereafter the rate of the hydration reactions declined to a second nadir (at 13:00 h), to subsequently rise again to a third peak (at 3.3 W/kg) on the calorimetric curve, at 17:24. During this time CSH gel formation overlapped with the transformation of *AFt* into *AFm* (which takes place when the SO_3/Al_2O_3 molar ratio is less than 3, in this case, 0.69). Finally, the hydration reactions as reflected by the rate of heat release slowed and remained low through the end of the 48-h trial.

The first nadir and second and third peaks appeared earlier on the heat release curves for the PC1 blends with and without excess gypsum (=7.0% SO_3) than on the curve for pure PC1. This finding provided further proof of the stimulation of the hydration reactions. But since the heat release rates recorded for each of the pozzolan-containing blended cements at the first nadir and second peak were consistently lower than the rate found for the Portland cement control, PC1, while the third peak rates for the pozzolan **A** and **C** blends were higher than the PC1 rate, the hydration reactions must clearly have also been subject to *indirect* stimulation [30–32]. This would have been due primarily to the prior pozzolanic activity mediated by the 8.0% and 11.50% $Al_2O_3{}^{r-}$ content, respectively, in these blends. Indeed, the activity attributed to the respective proportions of $SiO_2{}^{r-}$(%) [5] in the three pozzolans, i.e., **O**, 40.7%; **A**, 37.7%; and **C**, 38.8%, must have been of a very similar order of magnitude. For this reason, while in pozzolan **O** *direct* and *non-direct* stimulation [34, 35] must have prevailed over the *indirect* model [30–32] (hence its short duration, for only the first nadir appeared earlier than in PC1, while all the other peaks appeared later and were less intense), in pozzolans **A** and **C**, on the contrary, *indirect* stimulation must have predominated. Pozzolan **C** in particular, with the highest $Al_2O_3{}^{r-}$ content of the three, when blended with PC2 generated three attenuated peaks (Fig. 1b), while the pozzolan **A** blend peaks were even less intense (Fig. 1b). Consequently, the predominance of *indirect* over *direct* and *non-direct* stimulation was not as clear in **A** as in **C**; and neither, if predominance was the contrary as in **O**.

At the same time, the prior pozzolanic activity observed in pozzolans **A** and particularly **C** was also more *specific* than *generic*, stimulating C_3A hydration more rapidly and intensely than C_3S hydration in pure PC1 [30–32]. As discussed below, for this very reason, when these natural pozzolans exhibited such prior pozzolanic activity in PC2, its 79.5% C_3S was not stimulated to the same degree, but rather, the contrary effect was observed, i.e., the PC2 was physically *diluted* by the three pozzolans.

When excess gypsum (=7.0% SO_3) was added to PC1, the calorimetric curve was substantially attenuated and the third peak, attributed to the transformation of phase *AFt* into *AFm*, disappeared, perhaps due to the increase in the SO_3/Al_2O_3 ratio (1.50). In the pastes made with the pozzolanic blends, by contrast, when gypsum was added the first nadir appeared later and the second peak earlier than in pure PC1, likewise denoting the stimulation of the hydration reactions. In addition, the interaction of the *aluminic* fraction of the pozzolans was again reflected in the rate attained at the second peak, which, as noted above, climbed to higher values with the increasing reactive alumina ($Al_2O_3^{r-}$) content in such pozzolans.

Moreover, the PC2 calorimetric curve (Fig. 1b) initially showed a high rate of heat release in the induction period, which was followed by the drop to the first nadir at 0.64 W/kg, after 1:37 h:min. The second peak was recorded at 7:39, during the mass generation of CSH gels, when the hydration reaction rate rose to 3.25 W/kg and then declined. The third peak, attributed to the transformation of phase *AFt* into *AFm*, failed to appear on the pure PC2 cement curves due to the 0% C_3A content in this cement. The first nadir and second peak on the PC2-pozzolan blend curves appeared later than on the curve for pure PC2, while the rate of heat release was also lower in the blends than in the pure PC2. In this case also, the higher $Al_2O_3^{r-}$ content in pozzolan **C** led to the appearance of a second attenuated nadir after the second peak, followed by an even less intense third peak, which in turn preceded the final sustained decline through the end of the trial. Lastly, adding excess gypsum (=7.0% SO_3) to Portland cement PC2 (Fig. 1d) significantly attenuated and retarded the first nadir and second peak with respect to the pure Portland cement control. The patterns for the respective pozzolan blend pastes initially exhibited similar behaviour, for they were all retarded and attenuated, although as a rule the second peak appeared earlier and exhibited a higher rate of heat release than the control. Such behaviour may have been due to the chemical interaction between the gypsum and the above-mentioned $Al_2O_3^{r-}$ fraction in the pozzolans.

In short, the rate of heat release patterns found for the pozzolan blend cements showed that their behaviour differed depending on the Portland cement with which they were blended. The significant points on the PC1 blend calorimetric curves appeared earlier than on the pure PC1 curve, due perhaps to the simulation of the hydration reactions reported by some authors [16] and classified by others [30–32, 34, 35] by the *indirect* and/or *direct* and *non-direct* way of such stimulation; in the PC2 blends, by contrast, the appearance of such points was delayed.

Table 4 Total heat released at 48 h

Cements	Total heat (kJ/kg)
PC1 100/00 −7.0% SO_3	298
PC1 100/00 +7.0% SO_3	180
PC1/O 60/40 −7.0% SO_3	196
PC1/O 60/40 +7.0% SO_3	144
PC1/A 60/40 −7.0% SO_3	231
PC1/A 60/40 +7.0% SO_3	138
PC1/C 60/40 −7.0% SO_3	149
PC1/C 60/40 +7.0% SO_3	171
PC2 100/00 −7.0% SO_3	212
PC2 100/00 +7.0% SO_3	177
PC2/O 60/40 −7.0% SO_3	117
PC2/O 60/40 +7.0% SO_3	110
PC2/A 60/40 −7.0% SO_3	113
PC2/A 60/40 +7.0% SO_3	111
PC2/C 60/40 −7.0% SO_3	105
PC2/C 60/40 +7.0% SO_3	88

Finally, the total heat released in the first 48 hours of sample hydration is given in Table 4. The values obtained showed, here also, that the pozzolans *diluted* physically the PC, for the values of the 60/40 blends were consistently lower than the values for the respective controls or standards [16]. But at the same time, further proof was gathered of the pozzolan particle-mediated stimulation of the hydration reactions, clearly concurring with the results of prior research [15–17, 34, 35], as well as of heat *dissipation* [17, 36]; these latter values are shown because they proved to be the total heat values, respectively higher and lower than the proportional values for the respective standards or controls (179 and 108 kJ/kg for a 40% replacement ratio in PC1, with and without excess gypsum; and 127 and 106 kJ/kg for a 40% replacement ratio in PC2, with and without excess gypsum).

Conclusions

The conclusions that may be drawn from the experiments conducted with two types of Portland cement with very different mineralogical compositions, mixed with the natural Spanish pozzolans used, with and without excess gypsum (=7.0% SO_3) are as follows:

- The three natural pozzolans exhibited different pozzolanicity depending on the mineralogical composition of the Portland cement with which they were tested, although such differences were attributable more to their $Al_2O_3^{r-}$ than to their SiO_2^{r-} content. For further details, see the final two conclusions.

- As a rule, the earlier or later appearance of the significant points on the calorimetric curves depended more on the type of Portland cement than on the chemical *character* of the pozzolans. Hence, they appeared earlier in blends with C_3A-rich Portland cements, and later in the cements with a low C_3A content.
- The total heat of hydration values obtained after 48 h revealed the various effects of the pozzolanic additions: PC *dilution,* the *indirect* and/or *direct* and *non-direct* stimulation of hydration reactions and behaviour as heat *dissipation* centres, particularly as regards pozzolan **O**.
- The combined addition of pozzolans and gypsum stimulated hydration even more intensely in all the Portland cements with which they were blended.
- The physical state of the reactive alumina, $Al_2O_3^{r-}$, in these three natural pozzolans must be more amorphous than vitreous, resembling metakaolin more than fly ash. That notwithstanding, pozzolan composition must have conditioned the water/cementitious material ratios obtained for their respective PC1 and PC2 blended cements (a finding that could be used in the future for speedy, simple, reliable and economical *characterization*), as well as the *specific* pozzolanic activity and rate and total amount of heat of hydration generated by such cements.
- The substantial, speedy and early age prior pozzolanicity exhibited by the $Al_2O_3^{r-}$ in natural pozzolan **C**, in particular, but also in **A**, was also more *specific* than *generic*, *indirectly* stimulating C_3A hydration more rapidly and intensely than C_3S hydration [30–32] in PC1. Indeed, when these substances exhibited such prior pozzolanic activity in PC2, the hydration of its 79.5% of C_3S was not *indirectly* stimulated to the same degree; rather, the contrary occurred, i.e., the PC2 was physically *diluted* by the three pozzolans. Consequently, pozzolan **O** stimulated hydration *directly* and *non-directly* more than *indirectly*, while pozzolan **C** acted conversely and **A** exhibited varying combinations of the two patterns.

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References

1. Taylor HFW. La química de los cementos, vol. II, cap. 14—Ediciones Urmo, C/Espartero, 10, Bilbao, España, 1971 (in Spanish).
2. Mehta PK. Pozzolanic and cementitious byproducts as mineral admixtures dor concrete—a critical review. Fly ash, silica fume slag & other mineral by products in concrete. ACI SP 79-1. 1993. pp. 1–46.
3. Moya JS, Aza S, Sanz J, Madani A, Serratosa JM. Aluminum-27 and silicon-29 magic-angle spinning magnetic resonance study of the kaolinite-mullite transformation. J Am Ceram Soc. 1988; 71(10):C-418.
4. Instrucción para la Recepción de Cementos RC-03 (R.D. 1797/2003, de 26 de diciembre; B.O.E. núm. 14 de 16 de enero 2004).
5. EN 197-1 Standard = UNE 80-225-93 Standard. Test methods for cements: chemical analysis. Determination of the reactive silica (SiO_2) content in cements, pozzolans and fly ashes. AENOR, Calle Génova no 6, 28004, Madrid, Spain.
6. ASTM C 618-94a Standard. Standard specification for coal fly ash and raw or calcined natural pozzolan for use as a mineral admixture in Portland cement concrete. Annual Book of ASTM Standards, Section 04, Vol. 04.02 Concrete and aggregates. 1995. p. 304–6.
7. Talero R. Contribution to the analytical and physical-chemistry study of the system: pozzolanic cements–gypsum–water (at 20 ± 2 °C). Ph.D. Thesis, Complutense University of Madrid, Ftad. CC. Químicas, 20 November 1986.
8. Mehta PK. Effect of the fly ash composition on sulfate resistance of cement. ACI J Mater. 1986;83(6):994–1000.
9. Tikalsky PJ, Carrasquillo RL. Influence of fly ash on the sulfate resistance of concrete. ACI J Mater. 1992;89(1):69–75.
10. Talero R, Bollati M-R, Hernández-O F. Manufacturing non-traditional mortars and concretes by OPC, metakaolin and gypsum (15.05%). Mater Constr. 1999;49(256):29–41.
11. Talero R. Kinetochemical and morphological differentiation of ettringites by the *Le Chatelier-Ansttet* test. Cem Concr Res. 2002; 32:707–17.
12. Martín-L MP. Sulfate resistance and mechanical strengths behaviour of some crystalline and amorphous components in fly ashes. PhD Thesis, Autónoma University of Madrid, Spain, 29 May 1997.
13. Mejía R. Contribution to the analytical and physical-chemistry study of the system: Portland cements–Pozzolans–GGBS–Water (at 20 ± 2 °C). Ph.D. Thesis, Complutense University of Madrid, Ftad. CC. Químicas, 29 November 1997.
14. Mejía R, Delvasto S, Talero R. Chloride diffusion measured by a modified permeabilty test in normal and blended cements. Adv Cem Res 2003;15(3):113–8.
15. Rahhal V. Characterization of pozzolanic additions by conduction calorimetry. Ph.D. Thesis, Politechnic University of Madrid, E.T.S. Ings. Caminos, Canales y Puertos, 12 December 2002.
16. Takemoto K, Uchikawa H. Hydratation des ciments pouzzolaniques. In: Proceedings of 7th International congress on the chemistry of cement. 1980. Vol. I, Theme IV, p. 2/1–2/29.
17. Rahhal V, Batic O. Mineral admixtures contribution to heat of hydration development. Cem Concr Aggreg. 1994;19:150–8.
18. Shannag MJ, Yeginobali A. Properties of pastes, mortars and concretes containing natural pozzolan. Cem Concr Res. 1995;25: 647–57.
19. Rahhal V, Batic O. Seguimiento de la reacción puzolánica de cementos compuestos por DRX. Anales de la Asociación Química Argentina, 1995;83(1–2):35–47.
20. Tashiro Ch, Ikeda K, Inoue Y. Evaluation of pozzolanic activity by the electric resistance measurement method. Cem Concr Res. 1994;24:1133–9.
21. de Luxán MP. Estudio de las puzolanas de origen volcánico mediante espectroscopia de absorción infrarroja. Cuadernos de Investigación, Instituto Eduardo Torroja. 1976;32:5–21.
22. Amer AA. Thermal analysis of hydrated fly ash-lime pastes. J Therm Anal Calorim. 1998;54:837–43.

23. Giergiczny Z. Effect of some additives on the reactions in fly ash-$Ca(OH)_2$ system. J Therm Anal Calorim. 2004;76:747–54.
24. El-Shimy E, Abo-El-Enein SA, El-Didamony H, Osman TA. Physico-chemical and thermal characteristics of lime-silica fume pastes. J Therm Anal Calorim. 2000;60:549–56.
25. Mullick AK, Babu KH, Bhaskara Rao P. Evaluation of pozzolanic activity and its impact on specification of blended cements. In: 8th international congress on the chemistry of cement. 1986. Vol. VI, p. 308–11.
26. Mindess S. Young J. Concrete. Englewood Cliffs, NJ: Prentice-Hall, Inc. 1981.
27. Ushiyama H, Shigetomi Y, Inoue Y. Effect of gypsum on the hydration of alite and belite. In: 10th international congress on the chemistry of cement, Gothenburg, Sweden. 1997. Vol. II, 4 p., June 2–6.
28. Norma UNE-EN 196-3:2005. Método de ensayo de cementos. Parte 3: determinación del tiempo de fraguado y de la estabilidad de volumen. AENOR, Calle Génova, 6, 28004, Madrid.
29. Pliego de Prescripciones Técnicas Generales para la Recepción de los Conglomerantes Hidráulicos RC-75 (BOE no 206 de 28 de agosto de 1975) $\approx$ EN 196-5 Standard (Pozzolanicity test for POZCs). AENOR (= Frattini, N. Ann .Chim. Applicata, 1949;39: 616–20).
30. Talero R, Rahhal V. Influence of *aluminic* pozzolans, quartz and gypsum additions on portland cement hydration. In: Proceedings of 12th international congress on the chemistry of cement, W2-05.2, Montreal, Canada. 8–13 July 2007.
31. Rahhal V, Talero R. Calorimetry of portland cements with metakaolíns, quartz and gypsum additions. J Therm Anal Calorim. 2008;91:825–34.
32. Talero R, Rahhal V. Calorimetric comparison of portland cement containing silica fume and metakaolin: is silica fume, like metakaolin, characterized by pozzolanic activity that is more specific than generic?. J Therm Anal Calorim. 2009;96(2):383–93.
33. ASTM C 845-90 Standard. Specification for expansive hydraulic cement. Annual Book of ASTM Standards, Section 4 Construction, Vol. 04.01 Cement; Lime; Gypsum. 1995. p. 390–3.
34. Rahhal V, Talero R. Early hydration of portland cement with crystalline mineral additions. Cem Concr Res. 2005;35:1285–91.
35. Rahhal V, Bonavetti V, Delgado A, Pedrajas C, Talero R. Scheme of the portland cement hydration with crystalline mineral admixtures and other aspects. Silicates Industriels, Ref. No.: C-188. 19 January 2009 (accepted for publication; in press).
36. Rahhal V, Talero R. Influence of two different fly ashes on the hydration of portland cements. J Therm Anal Calorim. 2004;78: 191–205.