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CALORIMETRY OF PORTLAND CEMENT WITH METAKAOLINS, QUARTZ AND GYPSUM ADDITIONS

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In this work two aluminic pozzolans (metakaolins) and a non-pozzolan were added to two Portland cements with very different mineral composition, to determine the effect on the rate of heat release and the mechanisms involved. The main analytical techniques deployed were: conduction calorimetry, pozzolanicity and XRD.

The results showed that the two metakaolins induced stimulation of the hydration reactions due to the generation of pozzolanic activity at very early stage, because of their reactive alumina, $Al_2O_3^{r-}$ contents, mainly. Such stimulation was found to be more specific than generic for more intense C_3A hydration than C_3S, at least at very early on into the reaction, and more so when 7.0% SO_3 was added, and for this reason, such stimulation is described as 'indirect' to differentiate it from the 'direct' variety. As a result of both stimulations, the heat of hydration released is easy to assimilate to a Synergistic Calorific Effect.

Keywords: *calorimetry, gypsum, metakaolin, Portland cement, pozzolanicity, quartz, reactive alumina, setting control, synergy, XRD*

Introduction

Cement studies range from the individual analysis of each of the component phases to research into highly complex systems in which all the variables are addressed. Studies of Portland clinker components and their interaction with gypsum ($CaSO_4\cdot 2H_2O$) have shown that:

- The C_3A and C_4AF in ordinary Portland cement compete for gypsum, but as C_3A is more reactive, it takes up greater quantities more rapidly. This, in conjunction with content constraints to ensure that no more gypsum is added than required to control setting, leads to the formation of less ettringite than might otherwise be expected [1].
- Gypsum also accelerates calcium silicate hydration; these compounds also compete for sulphate ions during hydration, for the CSH gel contains significant amounts of sulphates. The inclusion of 2 to 6% of gypsum has been found to hasten alite hydration, and from 2 to 4%, belite hydration [2].
- A high gypsum content contributes to the formation of large amounts of ettringite, whose presence retards paste setting and hardening and prompts substantial changes in volume as a result of microstructural expansion and cracking. A low gypsum content, in turn, favours the formation of solid monosulphoaluminate solutions before the end of the latent period of C_3S hydration, thereby retarding the onset of accelerated reactions in this compound [1].

The use of mineral additions in Portland cements is a long-standing practice. Today different types of mineral compounds are added to Portland clinker during grinding or directly to the cement itself. Consequently, the analysis of discrete systems such as hydraulically active (pozzolanic and self-pozzolanic) and inactive (lacking in pozzolanic activity) minerals has given rise to the study of pozzolanic additions [3–8]. The pozzolanic reactivity of such materials is closely associated with the amorphous and/or vitreous nature of their structure [9, 10]. Additions can also be differentiated in terms of their 'silicic' [11–16] or 'aluminic' [17–20] character, irrespective of whether they are 'siliceous' or 'siliceous and aluminous' pozzolans [21].

According to the findings of previous research conducted by Talero, Mejía, Martín-L. and Rahhal [12–20], 'aluminic' pozzolans reduce (sometimes very rapidly) the sulphate resistance of the Portland cement with which they are blended, even when the PC used is SRPC [11, 12]. Nonetheless, in the absence of sulphates they raise mechanical strength, particularly at earlier ages [12, 17]. By contrast, they prevent or at least hinder chloride attack on steel reinforcements, first chemically and then physically [14, 16]. They are able to afford physical protection because the volume of the Friedel's salt generated is similar to the molecular volume of the calcium aluminate hydrates in the OPC. In other words, since the salt is not expansive it fills in the pores and micropores in the concrete or mortar. While characterization by conventional methods takes

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at least 28 days [12, 14, 17–19], the same results can be obtained in 48 h with conduction calorimetry [15].

Totally crystalline (hydraulically inactive) mineral additions are used as fillers solely to contribute to PC dilution. A non-hydraulic filler (rutile, TiO_2) added to each of the main components of cement separately was found to increase the hydration rate in all cases [22]. Similarly, the increase in mortar mechanical strength observed with the inclusion of non-hydraulic limestone, granite and siliceous fillers was attributed to their ability to form filler particles that acted as nucleation sites for calcium hydroxide crystals [23].

To date, however, experimental research has not determined how Portland cements differing in their mineral composition behave when blended with mineral additions containing varying proportions of reactive alumina, $Al_2O_3^{r-}$ (tetra- or penta-coordinated alumina [24]). The aim of the present study was to obtain such data by exploring the effect of the $Al_2O_3^{r-}$ content of pozzolanic mineral additions on the hydration of Portland cements with widely varying mineralogical compositions.

Experimental

Objectives

The present paper addresses the effect of adding aluminic pozzolans, with and without excess gypsum (≈7.0%), on the rate of hydration of Portland cements varying widely in mineralogical composition.

Materials and methods

The following cementitious materials were selected for the experiment: two Portland cements, one –PC1– with a high C_3A (14%) content and the other –PC2– with a minimum C_3A content (≈0%). Of the three mineral additions, two were pozzolanic: a nearly pure metakaolin M (≥95.0%), with a 48% reactive silica content [25] and a 29% reactive alumina content [11], and a metakaolin blended with quartz, MQ, (≈50% by mass) having a 38% reactive silica content [25] and a 15% reactive alumina content [11]. The third, non-pozzolanic or crystalline addition consisted in ground crystalline quartz, Q, with very high α-SiO_2 content (ground siliceous sand from Ottawa, Illinois, USA). The metakaolins were prepared by calcining kaolin (with and without ≈50% quartz) at 750°C. The particle size composition of the three mineral additions conformed to standard ASTM C 595M-95 [26] (maximum retained when wet-sieved on No. 325 (45–(m)sieve=20%). Natural stone gypsum (with a high $CaSO_4 \cdot 2H_2O$ content) whose particle size composition conformed to standard ASTM C 452-68 [19] was used throughout. All pastes were made with distilled water.

The chemical composition, density and Blaine specific surface of the Portland cements and mineral additions are given in Table 1. The potential composition of the Portland cements studied, found by substituting the chemical composition in the Bogue formulae, was as follows: 51% C_3S, 16% C_2S, 14% C_3A, 5% C_4AF, 0.90% N_2O and 0.52% K_2O for PC1, and 79% C_3S, 2% C_2S, 0% C_3A, 10% C_4AF, 0.43% Na_2O and 0.20% K_2O for PC2.

The differences in the chemical and mineralogical compositions of the two Portland cements were also partially reflected in their varying density, while their fineness (Blaine specific surface, BSS) was comparable.

The XRD patterns of the mineral additions are reproduced in Figs 1a and b; the more or less diffuse band observed [10] is indicative of the primarily amorphous

Table 1 Characteristics of cementing materials

Chemical composition/%	Portland Cements		Mineral Additions		
	PC1	PC2	M	MQ	Q
L.O.I.	1.6	1.1	0.4	0.6	–
I.R.	0.7	0.2	–	0.2	–
SiO_2	19.2	21.7	57.5	73.6	99.9
Al_2O_3	6.4	1.5	41.6	23.1	–
Fe_2O_3	1.7	4.1	0.5	1.2	–
CaO	63.9	68.0	0.0	0.6	–
MgO	1.5	0.4	0.0	0.0	–
Na_2O	0.9	0.4	–	0.1	–
K_2O	0.5	0.2	–	0.7	–
SO_3	3.5	2.3	0.0	0.0	–
Density/g cm^{-3}	3.08	3.21	2.52	2.55	2.70
Blaine specif. surf./m^2 kg^{-1}	319	301	333	398	395

Table 2 Pozzolanicity (Frattini test) at 48 h.

Cements without 7.0% SO_3	48 h/mM L^{-1}		Cements with 7.0% SO_3	48 h/mM L^{-1}	
	$[OH^-]$	[CaO]		$[OH^-]$	[CaO]
PC1	72.5	7.6	PC1	51.0	22.8
PC1 M 60/40	31.0	1.0	PC1M 60/40	39.5	3.0
PC1 MQ 60/40	35.0	2.2	PC1MQ 60/40	44.5	5.5
PC1 Q 60/40	57.0	11.6	PC1Q 60/40	46.0	25.7
PC2	42.5	21.5	PC2	42.5	31.1
PC2 M 60/40	25.0	9.3	PC2M 60/40	11.0	3.9
PC2 MQ 60/40	28.0	11.2	PC2MQ 60/40	25.5	18.5
PC2 Q 60/40	43.5	22.3	PC2Q 60/40	41.5	32.2

Note: Points of intersection below the solubility isotherm appear in bold

nature of M (density, 2.52) and MQ (density, 2.55). No such diffuse band appears on the diffractogram in Fig. 1c, whose well-defined peaks reflect the highly crystalline natures of Q. Moreover, these additions have much lower densities than either of the PCs.

Firstly, a total of six blended cements with PC/mineral addition ratios of 60%/40% (=60/640) (by mass) were prepared with the two Portland cements –PC1 and PC2– and the three mineral additions –M, MQ and Q– in the absence of excess gypsum or with sufficient amounts of gypsum to bring the total SO_3 content to 7.0%.

Secondly, the Frattini test [27] was conducted on all these blended cements at the age of two days to confirm whether or not they exhibited pozzolanic properties (Table 2 and Fig. 2). This test compares the calcium hydroxide concentration in an aqueous solution containing the hydrated sample after a given time, two days in this study, to the solubility isotherm of calcium hydroxide in an alkaline solution, in both cases at 40°C. A lower calcium hydroxide concentration than the solubility isotherm is indicative of pozzolanic activity in the sample.

Thirdly, the variation in the heat released by the cement pastes was then measured with conduction calorimetry technique (AJFK calorimeter at 25°C registering a data value every 2 min) (Figs 3a–d). The baseline temperature for the measurements was 25°C and the water/binder (*w*/*b*) ratio for all the cement pastes was 0.5 by mass. Data were recorded for the first 48 h of hydration. The total heat generated at this age was found by integrating the area under the heat of hydration curve (Figs 4, 5), a universally accepted method for studying plain and blended Portland cement hydration [1, 28].

Afterwards, XRD analyses were also conducted on the pastes to confirm the evolution of the hydration reactions over the first 48 h (semi-quantitative or comparative analysis only) at sample ages defined by the valleys on the calorimetric curves. For this purpose, a new set of pastes containing 40% of

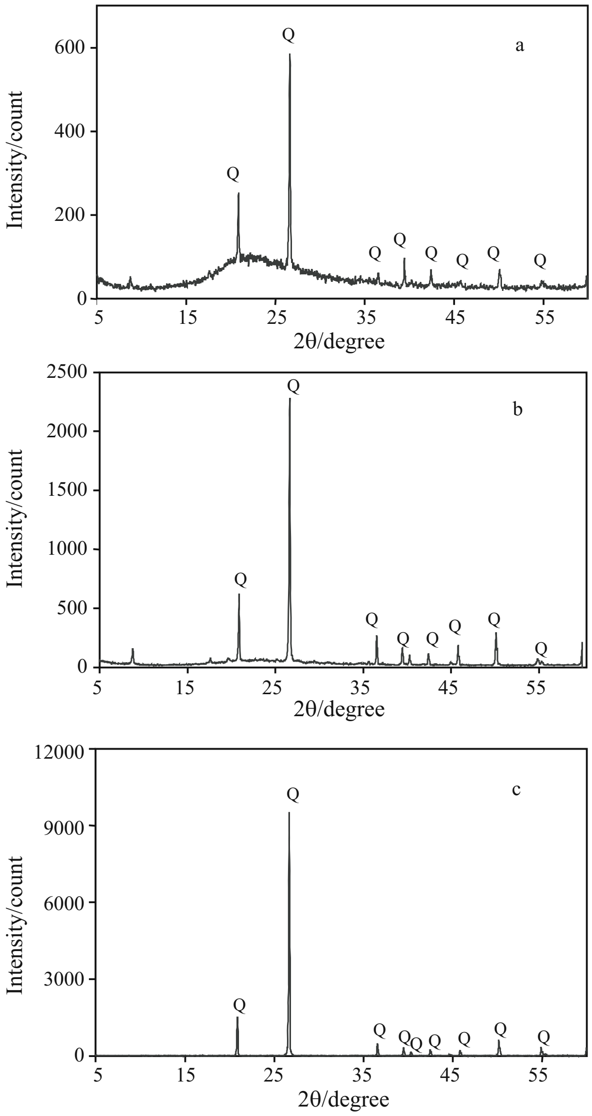

Fig. 1 XRD patterns. a – M pozzolan, b – MQ pozzolan, c – Q mineral addition

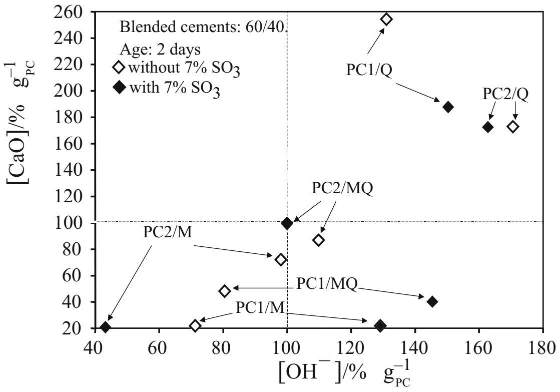

Fig. 2 Blended cements. % [OH$^-$] % [CaO] per gram of PC

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 (Phillips X´Pert) equipped with a graphite monochromator using CuK$_\alpha$ radiation and operating at 40 kV and 20 mA. Step scanning was made from 5 to 60° 2θ. For blended cements containing PC1, the points were the first, second (between the second and third peaks) and third (final point on the curve) valleys. For blended cements containing PC2, the points were first and second (final point on the curve) valleys (Table 3).

Lastly, a series of paste parameters were determined, namely the water/binder ratio (*w*/*b*, by mass) for normal consistency and setting times (Table 4), volume stability (Table 5) and mechanical strengths (Table 6, for plain and PC/M and PC/MQ blended cements, but not, naturally, PC/Q blends). Blends with other ratios, specifically 80/20 and 70/30, were also prepared for the sole purpose of determining volume stability, to acquire a fuller understanding of expansion processes taking place in the presence of the two metakaolins.

Results and discussion

Table 2 gives two-day [OH$^-$] and [CaO] as well as the two-day results of the pozzolanicity or Frattini test for the four pozzolan-cement blends. Quartz, naturally, exhibited no pozzolanic activity with either of the two portland cements, although the rate of hydration was observed to rise. Initially, this higher rate of reaction in the PC fraction is due, among other possible reasons, to water (from the mixing water) adsorption on the surface of the particles of the mineral additions, a process that may be termed 'direct' induction or

Table 3 DRX analysis: Results (relative intensity)

Cements without 7.0% SO$_3$	CH			AFt Phase			AFm Phase		
	1st m	2nd m	3rd m	1st m	2nd m	3rd m	1st m	2nd m	3rd m
PC1	P	↑	↑↑	P	=	=	P	↑	↑↑
PC1/M 60/40	P	↑	↑↑	P	↑	↑↑	P	↑	↑↑
PC1/MQ 60/40	P	↑	↑↑	P	↑	↑↑	P	↑	↑↑
PC1/Q 60/40	P	↑	↑↑	P	=	=	P	↑	↑↑
PC2	P	↑	–	A	A	–	A	A	–
PC2/M 60/40	P	↑	↑↑	P	↑	↑↑	P	↑	↑↑
PC2/MQ 60/40	P	↑	↑↑	P	↑	↑↑	A	A	A
PC2/Q 60/40	P	↑	–	A	A	–	A	A	–
Cements with 7.0% SO$_3$									
PC1	P	↑	–	P	↓	–	A	P	–
PC1/M 60/40	P	↑	–	P	↑	–	P	↑	–
PC1/MQ 60/40	P	↑	–	P	↑	–	P	↑	–
PC1/Q 60/40	P	↑	–	A	A	–	A	A	–
PC2	P	↑	–	P	↑	–	A	A	–
PC2/M 60/40	P	↑	–	P	↑	–	P	↑	–
PC2/MQ 60/40	P	↑	–	P	↑	–	P	=	–
PC2/Q 60/40	P	↑	–	P	↑	–	A	A	–

CH: Calcium hydroxide; 1st m: first minimum; 2nd m: second minimum; 3rd m: third minimum;
A: Absence; P: Presence; ↑: increase; ↓: decrease; =: unchanging

Table 4 Times of setting and water/binder ratios

Cements without 7.0% SO_3	Setting times (h:m)			w/b/by mass
	Initial	Final	Time	
PC1	3:20	5:10	1:50	0.31
PC1/M 60/40	2:40	5:05	2:25	0.43
PC1/MQ 60/40	3:10	5:10	2:00	0.43
PC1/Q 60/40	3:15	4:45	1:30	0.32
PC2	4:30	6:15	1:45	0.28
PC2/M 60/40	5:10	6:20	1:10	0.45
PC2/MQ 60/40	6:20	8:20	2:00	0.42
PC2/Q 60/40	5:00	8:00	3:00	0.30
Cements with 7.0% SO_3				
PC1	3:55	6:15	2:20	0.32
PC1/M 60/40	3:25	5:15	1:15	0.43
PC1/MQ 60/40	3:30	5:30	2:00	0.42
PC1/Q 60/40	3:35	5:45	2:10	0.32
PC2	4:15	6:10	1:55	0.28
PC2/M 60/40	5:15	7:05	1:50	0.45
PC2/MQ 60/40	5:50	7:50	2:00	0.39
PC2/Q 60/40	5:40	8:25	2:45	0.30

stimulation [29–31], which differs from ‘indirect’ stimulation [31], a mechanism discussed below. Such ‘direct’ stimulation was verified in the PC/Q blended cements, in which [OH^-] and [CaO] were higher than mathematically predicted when Q was assumed to be inert (physically and chemically) at these early ages (up to 2 days age).

Figure 2 shows [CaO] and the [OH^-] per gram of Portland cement for each plain PC, in per cent. The cements blended with metakaolin only clustered below and to the left, respectively, of 100% [CaO] and [OH^-]. The cements containing metakaolin and 50% quartz were either below 100% [CaO] or to the left of 100% [OH^-]. The PC/Q blended cements located above 100% [CaO] and [OH^-]. Greater proportions of calcium hydroxide tended to remain in solution with rising quartz content in the blended cements.

These results may be interpreted to mean that the rate of release of calcium hydroxide grows in the presence of mineral additions, with the compound remaining in solution when the addition is crystalline or non-pozzolanic and combining when it is pozzolanic, as logical.

The rate of calcium hydroxide generation and evolution was very low in M- and MQ-containing cement pastes during the first 48 h, which is consistent with the high two-day pozzolanic activity exhibited by these two additions (Table 2). The amount of CH generated was observed to increase in both Portland cements when blended with Q, providing further evidence that this mineral stimulates hydration reactions directly.

Figures 3a–d shows the calorimetric curves plotted during the first 48 h for PC1 and PC2 alone and with M, MQ and Q.

The three peaks on the PC1 curve (Fig. 3a) correspond to initial hydrolysis, C_3S hydration and transformation of the AFt to the AFm phase, respectively. The PC1 blended cements also exhibit three peaks on their respective calorimetric curves. The first valley is shifted to the left and attenuated, while the second and third peaks are likewise shifted to the left and larger for all the blended cements containing metakaolins M and MQ. These findings denote dilution of the silicate phase due to replacement of the PC1 by the respective metakaolin, and simultaneously, the Synergistic Calorific Effect, SCE, produced between the C_3A from the PC1 and the $Al_2O_3^{r-}$ from the metakaolin. SCE, was verified by XRD monitoring of *AFm* phase evolution (Table 3).

Table 5 Volume stabilities

Cements			Le Chatelier needles/mm							
			In water/days							
			Hot 100°C	Cold (21±2°C)						
			7	7	14	21	28	60	90	120
PC1	3.50% SO_3	100/00	0.7	1.70	1.70	1.70	1.70	1.70	1.70	1.70
PC1/MQ	7.00% SO_3	80/20	0.5	3.33	5.65	7.20	9.35	12.00	12.15	12.15
PC1/MQ	7.00% SO_3	70/30	0.5	5.15	6.00	6.33	6.65	6.71	6.75	7.75
PC1/MQ	7.00% SO_3	60/40	0.5	5.75	5.75	5.75	5.75	5.75	5.75	5.75
PC2	2.34% SO_3	100/00	1.0	0.30	0.30	0.30	0.30	0.30	0.30	0.30
PC2/MQ	7.00% SO_3	80/20	0.5	2.00	3.50	3.55	3.60	3.90	4.00	4.50
PC2/MQ	7.00% SO_3	70/30	0.0	3.20	3.70	3.80	4.00	4.60	4.60	4.70
PC2/MQ	7.00% SO_3	60/40	0.5	5.00	5.00	5.00	5.00	5.00	5.00	5.00

Blended cements with M pozzolan and 7.0% SO_3 reached slightly greater values

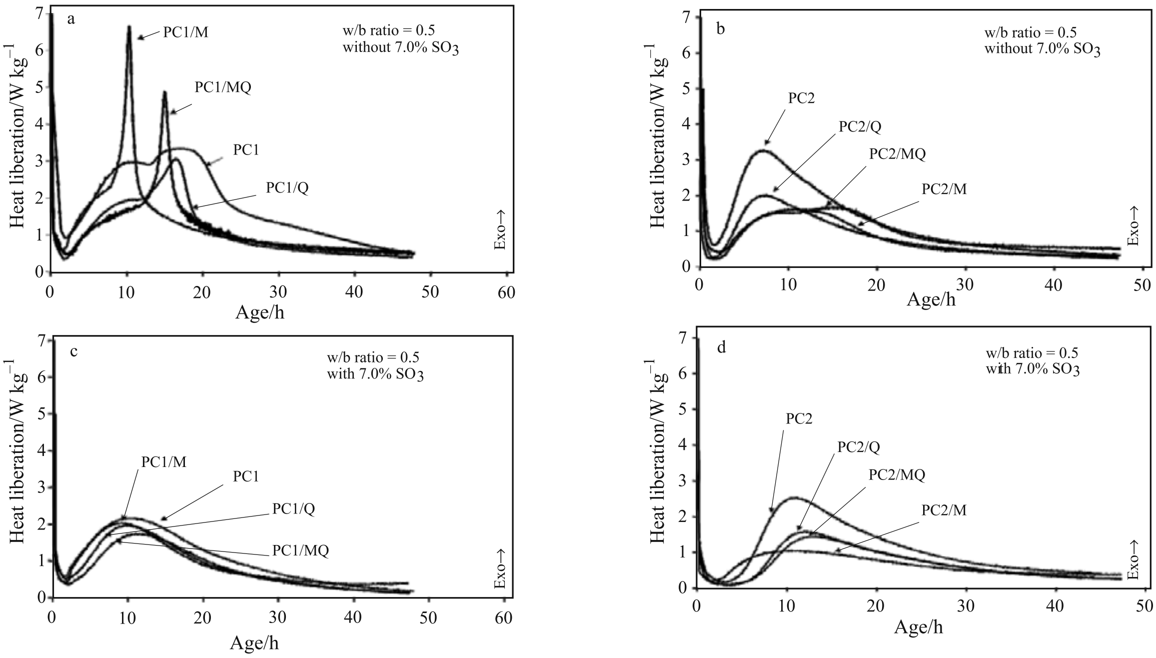

Fig. 3 Calorimetric curves. a – PC1 without 7.0% SO_3, b – PC2 without 7.0% SO_3, c – PC1 with 7.0% SO_3, d – PC2 with 7.0% SO_3

In the presence of excess gypsum (=7.0% SO_3) (Fig. 3c), however, the PC1 blended cements all had two peaks. The third failed to appear because with the rise in the SO_3/Al_2O_3 molar ratio occasioned by the excess gypsum, the *AFt* either did not convert into *AFm* or did so too slightly to generate detectable heat. Both phases were detected by XRD, however, except in the blended cements containing Q as the addition, in which only *AFt* was observed.

The calorimetric curve for PC2 (Fig. 3b) shows only two peaks, corresponding to initial hydrolysis and C_3S hydration. There is no third peak due to the absence of C_3A in this PC2, which also logically precludes the existence of *AFt* and *AFm*. The PC2 blended cements also had two peaks on their calorimetric curves, on which both the first valley and second peak were found to be retarded and attenuated. Here also, the intensity of the first peak and second valley declined with higher replacement percentages, reflecting the dilution of the silicate phase due to the replacement of PC2 by metakaolin. Nonetheless, even though the C_3A content was practically nil in PC2, the third peak was clearly insinuated in the PC2/M and especially PC2/MQ pastes between the tenth and the twentieth hours of hydration. This behaviour was indicative of the transformation of the own aluminic phase in the two metakaolins, a development that could be corroborated by XRD analysis (Table 3). In addition, this behaviour also was indicative of that when the transformation *AFt* in *AFm* of the own aluminic phase in the two metakaolins was carried out in presence of C_3A of PC1, the third peak was very much greater, which in turn also proves that at least at very early ages, the pozzolanic activity of $Al_2O_3^{r-}$ is more specific than generic, prompting more intense C_3A than C_3S hydration. See more details later on.

Table 6 Mechanical strengths at 28 days

Cements	Mechanical strengths/MPa	
	Flexural	Compressive
PC1	7	47.7
PC1/M 60/40	7.7	44.7
PC1/MQ 60/40	8.6	48.3
PC2	7.8	54.3
PC2/M 60/40	5.9	35.3
PC2/MQ 60/40	7.3	54.3

In the presence of excess gypsum (=7.0% SO_3), these PC2 blended cements also showed two calorimetric peaks (Fig. 3d). *AFt* was detected in the cement containing Q as the mineral addition, perhaps because of gypsum stimulation of the C_4AF phase. Both *AFt* and *AFm* were identified when the pozzolan added was M or MQ, however, this implies that hydration must have begun, although the amount of heat released was insufficient to generate a third peak on the calorimetric curves.

Figures 4, 5 show the total heat released per gram of Portland cement after 48 h, in per cent. The nature and character of the mineral additions and the mineralogical composition of the Portland cements can be observed to affect the calorimetric behaviour of the respective blends both separately and jointly. Moreover, there is evidence in all cases except

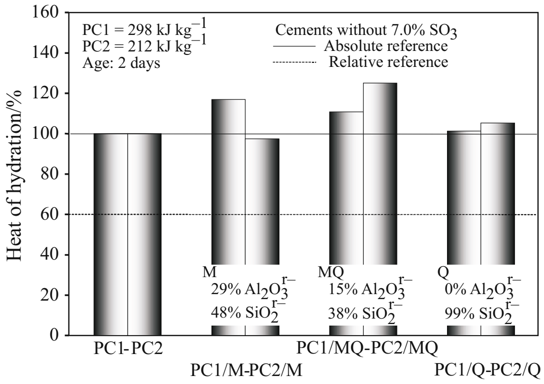

Fig. 4 % total heat released per gram of PC without 7.0% SO_3

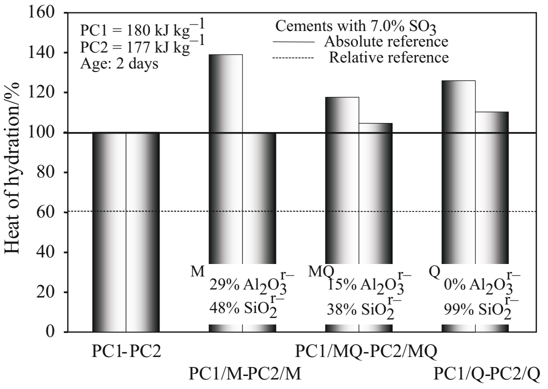

Fig. 5 % total heat released per gram of PC with 7.0% SO_3

7.0%SO_3–free PC2/M, that PC hydration was directly and/or indirectly stimulated, for the total heat values were similar to or greater than the values for the respective plain Portland cement. Logically, they were also greater than the values for the respective blended cements, assuming their mineral addition to be inert. The reason is given in the second part of the following paragraph.

Such stimulation was more intense in the PC1 than the PC2 blends. When the mineral addition contained metakaolin, the effect grew with the reactive alumina, $Al_2O_3^{r-}$, content (the concurrence with the respective total alumina –Al_2O_3%– content, as shown in Table 1, is circumstantial only). Such behaviour is observed for both metakaolins, and proves once again that at least at very early ages, their pozzolanic activity, due primarily to their respective $Al_2O_3^{r-}$ content, is more specific than generic, prompting more intense C_3A than C_3S hydration, particularly with but also without 7.0% SO_3. In the present paper this type of stimulation of hydration reactions has been termed 'indirect' to differentiate it from 'direct' stimulation, as explained above. The effect was less directly proportional (Figs 4, 5) than might have been expected, however, because the *w*/*b* ratio was held constant at 0.5 for all the cements studied. This latter assertion is based on the following logic: in PC2 blended cements, the best results are obtained with MQ, rather than with M. The reason is that at these early ages, the *w*/*b* ratio in both PC2 blended cements (0% C_3A), was 0.5 when the pozzolan added was M. When it was MQ, however, the effective *w*/*b* ratio actually ranged from 0.5 to 0.84 for the pozzolanic activity generated by M (≈50% of the total addition), because the other ≈50% (Q) was non-pozzolanic. Consequently, ≈50% Q can only stimulate hydration 'directly' to the extent that the ≈50% M allows. In addition, the greater BSS of MQ pozzolan and setting times of its blends with PC2 also are in favour of this behavioral hypothesis. This logic is not applicable to PC1 (14% C_3A) blends, however, where account must be taken of the hydration reactions of its high C_3A content (contrasting sharply with the 0% C_3A in PC2), as well as the opposite end result due to the 'indirect' stimulation involved and the SCE generated (Figs 4, 5).

By contrast, 'indirect' stimulation of hydration at very early ages must be seen to be unspecific, or perhaps more precisely, insufficiently specific for C_3S hydration, inasmuch as the specific 'indirect' stimulation of its hydration declines.

In short, while indirect stimulation of hydration in PC1 by the two pozzolanic additions, M and MQ, increases with their respective $Al_2O_3^{r-}$ content, in PC2 it decreases. The same pattern was observed in the presence of excess gypsum (=7.0% SO_3), although indirect stimulation was consistently more intense in PC1. All this can be attributed to the Synergistic Calorific Effect, SCE, between the C_3A in PC1 and the $Al_2O_3^{r-}$ in pozzolans M and MQ. As far as the mineralogical composition of Portland cements is concerned, generally speaking, cements with a high C_3A and low C_3S content exhibited earlier and greater hydration reactions due to direct but particularly to indirect stimulation (Fig. 3a). Cements with a low C_3A and high C_3S content, by contrast, exhibited retarded and attenuated reactions (Fig. 3b). As a result, the differences in the amount of heat of hydration per gram of Portland cement were more significant in PC1 than in PC2 blends.

The differences observed in setting times and *w*/*b* ratios between plain and blended cements (Table 4), in turn, may be explained in terms of the patterns of the calorimetric curves and the other effects discussed above. Moreover, no anomalous setting was found in any of the blended cements, despite the existence of excess gypsum in some of them (=7.0% SO_3).

The 28-day flexural and compressive strength values (Table 6) showed that the stimulation of hydration in both PCs offset the effect of their dilution at later ages. Proof of this was provided by the experimental values, which were higher than mathematically predicted assuming that the mineral additions studied, M and MQ, both with pozzolanic activity, and Q, crystalline quartz, were inert. Account must nonetheless be taken of the fact that mechanical strength values were for 28-day, not 2-day, specimens.

Both metakaolins were found to prompt expansion (Table 5), regardless of the PC/mineral addition ratio. Here also, the difference in the mineralogical composition of the two PCs was clearly visible. More specifically, while expansion increased with the percentage of metakaolin replacing PC2, the opposite trend was observed in PC1 blends from 21 days age but not before. This can be explained by the competition between C_3A and $Al_2O_3^{r-}$ in the formation of different types of ettringite, the explanation for and effect of which have been addressed in a number of papers [17–19]. That notwithstanding, one important consideration should be mentioned here: when metakaolin is added to OPC to make high performance bulk concrete, its direct and indirect effect on the generation of heat of hydration must be borne in mind to minimize undesirable consequences, for the amount of heat of hydration released may be comparable to the amount generated by the Synergistic Calorific Effect, SCE. Even so, expansive hydraulic cements [32] can be manufactured with aluminic pozzolans because they retain important properties such as high early mechanical strengths and significant expansion. The explanation for this benign behaviour lies in the failure of the excess gypsum (=7.0% SO_3) to react aggressively: rather it 'controls setting' in cements blended with pozzolans M or MQ. Indeed, the setting times and mechanical strengths of such blends were of an order of magnitude similar to that observed in any PC (ett-rf and ett-lf [12, 18–20] naturally played a role in these beneficial results). By contrast, the excess gypsum (=7.0% SO_3) behaved aggressively in PC1 and PC2 and their Q-containing blends (more so in the former), which exhibited setting times consistently higher than the respective cements without 7.0% SO_3 (ett-lf only was involved in such adverse results).

Conclusions

The conclusions to be drawn from the above experiments are as follows:

- The initial release and subsequent pattern of heat of hydration as reflected in the hydration curves for the blended cements are substantially affected by the mineralogical characteristics of the respective Portland cements and of their mineral additions as well.
- Adding ground crystalline quartz, Q, a non-pozzolan, stimulates the hydration reactions in the PC fraction of PC/Q blended cements due, among other possible causes, to the adsorption of water on the surface of the quartz particles. This effect, here termed 'direct' stimulation, occurs in conjunction with an increase in CH and higher heat of hydration per gram of PC. As a result, mineral addition Q cannot be regarded to be completely inert, physically speaking, at least up to the age of two days. A fuller discussion and justification of these observations can be found in [15] and [30].
- The pozzolanic and hydraulic activities of both 'aluminic' pozzolans, M and MQ, depend extensively on the non-crystallinity of their structure, and more specifically, on their $Al_2O_3^{r-}$ contents, mainly. Indeed, after 48 h, both M and MQ exhibit pozzolanic activity that stimulates hydration, primarily 'indirectly'. This effect must be regarded to be 'indirect' in light of the highly significant pozzolanic activity in both pozzolans at very early ages, generated primarily by $Al_2O_3^{r-}$. It goes hand-in-hand with a decrease in CH and an increase in heat of hydration per gram of PC.
- Such pozzolanic activity is observed in both M and MQ, due primarily to their respective $Al_2O_3^{r-}$ contents, mainly, and at least at very early ages, is more specific than generic, prompting more intense C_3A than C_3S hydration, especially with but also without 7.0% SO_3. Conversely, this prior pozzolanic activity must be seen as unspecific, or perhaps more precisely, insufficiently specific in the stimulation of C_3S hydration, inasmuch as the specific 'indirect' stimulation of its hydration declines. See conclusion 7.
- When metakaolin is added to OPC to make high performance bulk concrete, account must be taken of its direct and indirect effect on the generation of heat of hydration to minimize undesirable consequences, for the amount of heat of hydration released may be assimilated to the amount generated by the Synergistic Calorific Effect, SCE. Even so, expansive hydraulic cements [32] can be manufactured with aluminic pozzolans for the significant expansion attained when an optimum proportion of excess gypsum is added [33].
- Excess gypsum (=7.0% SO_3) in blended cements retards and attenuates hydration reactions in all cases (with a smaller amount of total heat after 48 h), while also generating more heat of hydration per gram of Portland cement than in the absence of excess of gypsum. Moreover, stimulation of the hydration reactions is much more intense in PC1, with high C_3A and low C_3S contents, than in PC2, with low C_3A and high C_3S. With such significant stimulation and substantial expansion, these M- or MQ-containing blended cements can be classified as expansive hydraulic cements (for specific uses). And for that same reason precisely, they must be

used with caution. In addition, the excess gypsum (=7.0% SO_3) does not behave aggressively, but rather 'controls setting' in cements blended with pozzolans M or MQ. Indeed, the setting times and mechanical strengths of such blends are of an order of magnitude similar to that observed in any PC. Conversely, in all the other cements tested, i.e., PC1 (in particular) and PC2 and their blends with quartz, the excess gypsum did exhibit aggressive behaviour.

- Pursuant to Conclusion 4, the following Final Question can be raised: Why is pozzolanic activity observed to be high two-day cements containing not aluminic but silicic pozzolans, such as silica fume, for instance? Is such pozzolanic activity also more specific than generic for the same result? (the same result is stimulation by indirect way prompting more intense C_3A than C_3S hydration as well; especially with but also without 7.0% SO_3), or perhaps is it more unspecific or insufficiently specific or too low-specific?, or perhaps better yet, is it anti-specific or contra-specific or counter-specific?, or perhaps still more precisely, might it actually specifically hinder C_3A hydration, such as in the case of sulphate attack? The answer is to be found in [12, 13, 31, 34], as well as in subsequent paper on sulphate attack [35], to be released in the very near future.

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