

CALORIMETRIC COMPARISON OF PORTLAND CEMENTS CONTAINING SILICA FUME AND METAKAOLIN

Is silica fume, like metakaolin, characterized by pozzolanic activity that is more specific than generic?

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This new study must be regarded to be a direct outcome of two previous studies published by these same authors, which were conducted to respond to interesting questions brought out about the effect of silica fume, SF and metakaolins, M and MQ, on the heat of hydration of portland cements, PC, with very different C₃A and C₃S contents. The answer to these so interesting questions has been the primary objective of the present research. For this purpose, the same PC, PC1 (14% C₃A) and PC2 (≈0% C₃A), metakaolins, silica fume and blended cements were once again used more 60/40 for sulphate attack, and the same analytical techniques (CC, pozzolanicity and XRD analysis) and parameters determined as well. In this new research, the sulphate attack was determined by two accelerated methods: Le Chatelier-Ansttstet and ASTM C 452-68.

The experimental results of sulphate attack mainly, have demonstrated definitively that the high, rapid and early pozzolanic activity exhibited by SF also is, as in the case of the two metakaolins, more specific than generic, for it indirectly stimulated greater C₃A than C₃S hydration, but only in the first 16 h monitored in this study. Thereafter it is the contrary, i.e., anti- or contra-specific for the same purpose. And the longer the hydration time, the more anti- or contra-specific it became, since, when exposed to sulphate attack, SF blended cements resisted or even prevented the aggressive attack against PC1 which, with a higher C₃A content than PC2, was the more vulnerable of the two. By contrast, metakaolin MQ not only failed to hinder or prevent the attack, but heightened its effects, rendering it more intense, aggressive and rapid, leading to what could be called a rapid gypsum attack.

Keywords: heat of hydration, metakaolins, portland cements, silica fume, sulphate attack

Introduction

The use of pozzolanic additions in portland cements is a long-standing practice [1–6]. The pozzolanic reactivity of such materials is closely associated with the amorphous and/or vitreous nature of their structure [7, 8]. Pozzolanic additions can also be differentiated in terms of their 'silicic' [9–14] or 'aluminic' [15–18] character, irrespective of whether they are 'siliceous' or 'siliceous and aluminous' pozzolans [19].

According to the findings of previous research conducted by Talero, Mejía, Martín-L. and Rahhal [10–18], 'aluminic' pozzolans have high reactive alumina, Al₂O₃^{r-}, content. Reactive alumina is tetra- or penta-coordinated alumina [20]. Commonly, the Al₂O₃^{r-} content of metakaolin is high and for this reason precisely, metakaolin develops very high, fast and significant pozzolanic activity at early ages, and as a result, metakaolin reduce (sometimes very rapidly) the sulphate resistance of the portland cement with which they are blended, even when the PC used is sulphate-resistant portland cement, SRPC [9, 10], due to the ett-rf [10, 16–18] which origin. Nonetheless, in

the absence of sulphates they raise mechanical strength, particularly at earlier ages [10, 15]. By contrast, they prevent or at least hinder chloride attack on steel reinforcements, first chemically, and then, physically [12, 14].

In contrast, 'silicic' pozzolans have high reactive silica, SiO₂^{r-}, content [20, 21], and for this other opposite chemical reason precisely, they increase the sulphate resistance of the portland cement with which they are blended [10, 11] and decrease its mechanical strengths [10] and also its resistance to the chloride attack to the reinforcements of steel [12], except silica fume, SF, [12, 14] and nanosilica which increase them as well, due to its vitreous and/or amorphous state and to the very small size of their particles, and as a consequence, to their very high, fast and significant pozzolanic activity at early ages as well.

In connection with these two very different families of pozzolanic additions, SF and metakaolins, the authors of the present paper recently published two articles in this journal [22–24] proving the effect of each on the heat of hydration of PC with very differ-

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ent percentages of C_3A and C_3S . The same portland cements have naturally been used in this follow-up study. Thus, while the first study [22] dealt with the effect of SF, the second [23, 24] analyzed the effect of two metakaolins, M and MQ (the metakaolin content was nearly twice as high in M, practically pure metakaolin, as in MQ, whose composition included around 50% quartz), whose respective $Al_2O_3^{r-}$ con-

tents, mainly, show pozzolanic activity at 48 h, which induce, in turn, stimulation of the hydration reactions by 'indirect way', mainly, but SF as well, even though due to its reactive silica, SiO_2^{r-} , content. But in addition, such prior and very significant pozzolanic activity of both M and MQ pozzolans, due to their respective $Al_2O_3^{r-}$, contents, mainly, is, at least at very early ages, more specific than generic, prompting more in-

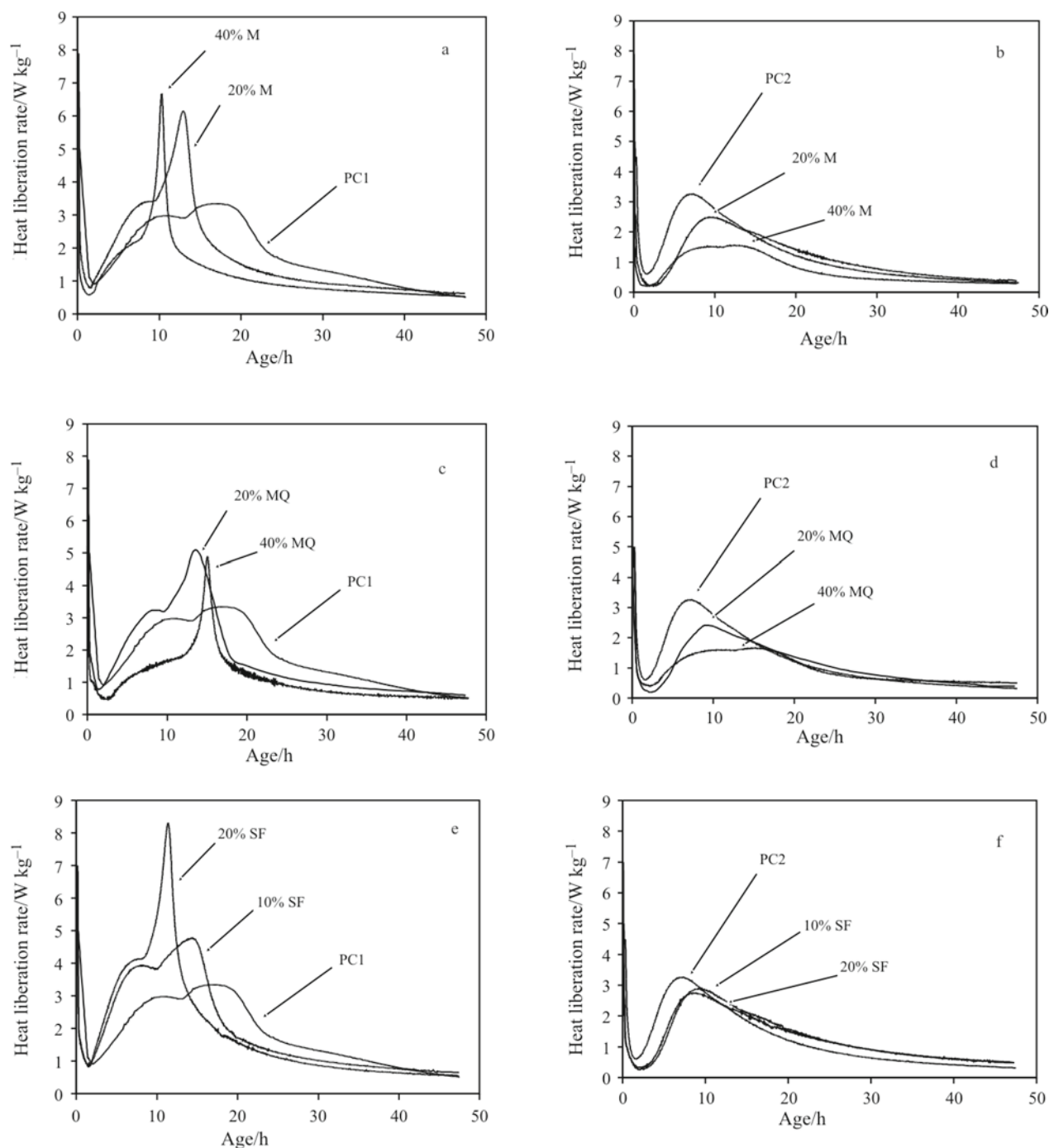


Fig. 1 Calorimetric curves for both plain PC and for their mixes: a – PC1, PC1/M 80/20 and 60/40, b – PC2, PC2/M 80/20 and 60/40, c – PC1, PC1/MQ 80/20 and 60/40, d – PC2, PC2/MQ 80/20 and 60/40, e – PC1, PC1/SF 90/10 and 80/20 and f – PC2, PC2/SF 90/10 and 80/20 [22–24]

tense C_3A than C_3S hydration. Is also such high, early and rapid pozzolanic activity of SF more specific than generic for the same result? And there being high sulphate contents present, as well? Or perhaps for SF is not... due to its reactive silica, SiO_2^r , content?

The following three conclusions, among others, were drawn from the results of the second of these latter studies with metakaolins [23, 24]: See conclusions 3 and 4 in [24] and in [23] if necessary; finally the latest conclusion (7th) is as follows, '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? (1st question) (the same result is stimulation by *indirect way* prompting more intense C_3A than C_3S hydration as well, i.e., the amount of heat of hydration released per gram of PC is greater than when this PC is plain; 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?' (2nd question).

Initially, in light of the values obtained for the rate of heat release through the age of 48 h in both prior studies [22, 24] (Figs 1a–d), conclusions 3 and 4, and in particular 4, are perfectly applicable to the first, that is, to the SF (Figs 1e and f) [22].

This similar behaviour in two such very different pozzolanic additions, one, the metakaolins, with aluminic character, and the other, SF, with silicic character, might appear to infer that when all these hydration reactions take place in a medium with a higher sulphate content, both the metakaolins and the silica fume favour an aggressive attack on the C_3A existing in the fraction of the PC1 with which they are blended, and even render that attack more rapid and intense and harmful...or perhaps they do not...? (3rd question).

Consequently, this new paper should be regarded to be a direct outcome of the previous studies [22–24] which contains a new study conducted to respond to these so interesting questions, which are, then, the primary objective of the present research.

Experimental

Objective

The present study aims, therefore, to determine whether the high, rapid and at early age pozzolanic activity observed for SF [22] is, like in metakaolin [23, 24], also more specific than generic, indirectly

stimulating greater hydration of the C_3A (with and without excess of gypsum) than of the C_3S , both existing in the ordinary portland cement, OPC, or otherwise and in any event, to identify the cause, and finally, to answer the rest of questions.

Materials and methods

The following cementitious materials were selected for finding the answer to so interesting questions made:

- two portland cements, one –PC1–, with high C_3A content, 14% C_3S , 51% C_2S , 16.5% and C_4AF , 5%, being its density, 3.08, its Blaine specific surface, BSS, 319, and its N_2O and K_2O contents, 0.90 and 0.52%, respectively, and the other –PC2–, with minimum C_3A content ($\approx 0\%$) and very high C_3S content, 79.5%, C_2S , 2% and C_4AF , 10%, being its density, 3.21, its BSS, 329 $m^2 kg^{-1}$, and its Na_2O and K_2O contents, 0.43 and 0.20%, respectively,
- three very active pozzolanic additions:
 - a nearly pure metakaolin M ($\geq 95.0\%$), with a 48% reactive silica content [21] and a 29% reactive alumina content [9], being its density 2.52 and its BSS, 333 $m^2 kg^{-1}$, and BET SS, 9000 $m^2 kg^{-1}$,
 - a metakaolin blended with quartz, MQ, (≈ 50 mass%) having a 38% reactive silica content [21] and a 15% reactive alumina content [9], being its density 2.55, and its BSS, 398 $m^2 kg^{-1}$, and BET SS 7260 $m^2 kg^{-1}$ (the metakaolins were prepared by calcining kaolin, with and without $\approx 50\%$ quartz, at 750°C), and
 - a silica fume, SF, which contains over 90% SiO_2 and 88.5% SiO_2^r contents [20, 21] being its density 2.70 and its BET SS very high, 22100 $m^2 kg^{-1}$.
- The particle size composition of the three pozzolanic additions conformed to standard ASTM C 595M-95 [25] (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 [26] was used throughout.

Finally, all pastes were made with distilled water [22–24]. Thus and with all these cementing materials, firstly, a total of six blended cements with PC/pozzolanic addition 'Z' ratios of 60/40 by mass for both metakaolins (and 80/20 for sulphate attack tests, only), and 90/10 and 80/20 for SF (60/40, for sulphate attack tests, only), were prepared with the two portland cements –PC1 and PC2– and the three pozzolanic additions –M, MQ and SF–, separately.

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 at 2, 7 and 28 days (Table 1) [22–24].

Thirdly, a series of paste parameters were determined, namely the water/binder ratio (w/b, by mass) for normal consistency cement paste, setting times [28] (results in Table 2 of [22] for SF, and in Table 4 of [24] for M and MQ), volume stability [28] (results in [24]) and mechanical strengths [29] (Table 2).

The heat release pattern was ascertained by heat conduction calorimetry for pastes. Measurements were taken at a temperature of 25°C. Data were recorded during the first 48 h of hydration and the total heat released was computed by integrating the area under the rate of release-age curve. This methodology is widely used to monitor hydration in pure portland cement [30] as well as for cements containing mineral additions [31]. To obtain equally workable pastes, the

water:cementitious material ratios used were 0.5 for plain portland cements and for their mixes with 40% M and 40% MQ, and 0.625 and 0.75 for their mixes with 10 and 20% SF, respectively. The mixes with 20 and 40% SF were not needed for this test but for sulphate attack only.

Lastly, each POZC and each PC, were subjected to the Le Chatelier-Ansttet (L-A) [32] and ASTM C 452-68 [26] tests.

Table 2 Pozzolanic activity index, PI (ASTM C 311) [29]

Pozzolans	PI/%	Water/%
M	77.2	110.0
MQ	75.1	106.0
SF	90.6	108.0

Table 1 Pozzolanicity (Frattini test) of the PC, PC1 and PC2, and of their POZC with M, MQ and SF pozzolan [22–24]

Cements		Age/day					
		2		7		28	
		CaO/OH ⁻ / mM L ⁻¹	CaO/OH ⁻ / mM L ⁻¹	CaO/OH ⁻ / mM L ⁻¹	CaO/OH ⁻ / mM L ⁻¹	CaO/OH ⁻ / mM L ⁻¹	CaO/OH ⁻ / mM L ⁻¹
PC1	100/00	7.60	72.50	6.80	71.25	6.45	78.00
	90/10	6.95	65.00	6.00	55.00	5.05	66.00
PC1/SF	80/20*	5.50	55.50	4.90	40.00	2.35	45.00
	70/30*	2*		2.75	15.11	2*	
	60/40*	2*		1.95	4.95	2*	
PC1/M	80/20	4.15	51.50	4.25	58.00	1.75	58.00
	70/30	1.55	41.00	1.50	45.75	0.75	46.00
	60/40	1.00	31.00	1.35	33.60	0.75	33.50
PC1/MQ	80/20	6.35	55.00	6.25	63.00	8.15	71.50
	70/30	5.50	48.50	2.20	48.50	5.00	58.00
	60/40	2.15	35.00	1.65	44.50	1.45	43.00
PC2	100/00	21.50	42.50	16.55	39.45	16.10	42.00
	90/10	19.50	42.00	14.90	33.50	14.10	39.00
	80/20*	15.25	32.00	11.75	27.00	7.50	21.50
PC2/SF	70/30*	2*		6.20	12.20	2*	
	60/40*	2*		4.35	7.22	2*	
	80/20	13.25	32.00	8.90	32.00	8.00	29.50
PC2/M	70/30	10.50	26.50	4.60	22.00	2.95	17.50
	60/40	9.25	25.00	2.55	15.00	2.35	15.00
	80/20	16.60	41.00	12.30	36.00	15.00	44.50
PC2/MQ	70/30	13.50	34.50	9.00	27.90	5.80	24.50
	60/40	11.15	28.00	5.30	19.80	5.05	21.50

The paired values in bold mean that the point is in sub-saturation region (= + result).

* The specified SF amounts to design high performance concrete are commonly between 5 and 10%, although sometimes 15 and 20% at the most, also are used, but 30 and 40% are never used. Nevertheless, both have been used here for the sulphate resistance tests only (Tables 4 and 5).

2* These values were not needed.

Results and discussion

Pozzolanicity test or Frattini test (Table 1)

Table 1 show [CaO] and [OH⁻] determined at 2, 7 and 28 days old. Note that all the pastes with SF, M and MQ showed pozzolanic activity at 48 h (i.e., 6 and 13 days before its first and second respective specified ages, 8 and 15 days [34]), in the case of PC1, but in the case of PC2, some paste SF and MQ did not, at (addition-PC2) replacement rates of 10 and of 20%, respectively. These mixes failed to show pozzolanicity at that age because the rate of the hydration reaction was so high that it could not be countered or compensated for by the fixation of the calcium hydroxide resulting from the pozzolanic reaction.

On the other hand, Table 1 gives 2-day [OH⁻] and [CaO] as well as the two-day results of the pozzolanicity or Frattini test for the three pozzolan-cement blends with SF, M and MQ, respectively ($\approx 50\%$ quartz in MQ, naturally, exhibited no pozzolanic activity with either of the two portland cements [23, 24]). 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 pozzolanic additions, a process that may be termed 'direct' induction or stimulation [22–24, 35], which differs from 'indirect' stimulation [22–24], a mechanism discussed below.

Furthermore, the rate of calcium hydroxide, CH, 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 pozzolans (Table 1). Nonetheless, the amount of CH generated was observed to increase more in both PC when blended with MQ. It was due more to the direct stimulation of its $\approx 50\%$ Q (providing further evidence that this crystalline mineral stimulates hydration reactions directly [23, 24]) than to the lesser Al₂O₃^{r-} content of MQ (≈ 0.5 Al₂O₃^{r-} content of M). This direct stimulation of its $\approx 50\%$ Q will also be discussed below with other different parameter.

Calorimetric curves for the plain PC and for their mixes with M, MQ and SF and %total heat released per gram of PC (Figs 1a–f, 2a and b)

The discussion and interpretation from results shown in Figs 1a–f can be found in references [22–24], and for this reason, its repetition is not considered necessary. Nonetheless, it is strongly recommended to read them previous to the next additional discussion. Despite this fact, the main conclusion of these results [22–24] has to be quoted here, it said: The high, fast and early pozzolanic activity of the Al₂O₃^{r-} present in M and MQ is more specific than generic, prompting more intense C₃A than C₃S hydration; that is, C₃A hydration was more *stimulated* than C₃S hydration. This type of stimulation of hydration reactions was termed 'indirect' [22–24] to differentiate it from the 'direct' one, as explained above. But on the other hand, the pozzolanic activity of the SiO₂^{r-} present in SF is high, fast and early as well, but is it also more specific than generic prompting more intense C₃A than C₃S hydration?; i.e. was C₃A hydration also more stimulated than C₃S hydration? Or, was it not? And finally if it was, was it produced by indirect way and/or by direct way?

In the present new and comparative discussion and interpretation, that behaviour also was in fact verified in M, MQ and SF pozzolans, whose randomly granulated and nothing or very spherical texture, SF mainly, as a result of its artificial origin, enabled it to absorb more moisture at laboratory temperature than M and MQ, (whose texture is not spherical but compact), when ≈ 1.0 g of each was separately stored in porcelain vials and placed in a desiccator (with water distilled at bottom instead of silica gel) at $23 \pm 1.7^\circ\text{C}$ and $\text{rh} \geq 95\%$ (Table 3). This would mean that from the outset, when it was mixed with the portland cement to form a 80/20 blend, the SF pozzolan comprising the 20% fraction must have adsorbed more of the initial mixing water ($w/c=0.75$) (and $w/c=0.625$ for the 90/10 POZC) than M and MQ pozzolans. Hence as noted earlier, when these three pozzolanic admixtures were mixed separately with each portland cement, account must likewise be taken of the fact that more water amount was needed to mix the POZC containing 10 and 20% SF, i.e., the water/cementitious material

Table 3 Humidity absorption for M, MQ and SF pozzolan

Pozzolans	Humidity absorption/%					
	Age/day					
	1	3	7	14	21	28
M	2.48	4.04	5.75	7.44	8.78	9.62
MQ	2.24	3.59	5.39	6.83	8.44	8.76
SF	5.59	9.26	12.20	16.67	18.88	21.50

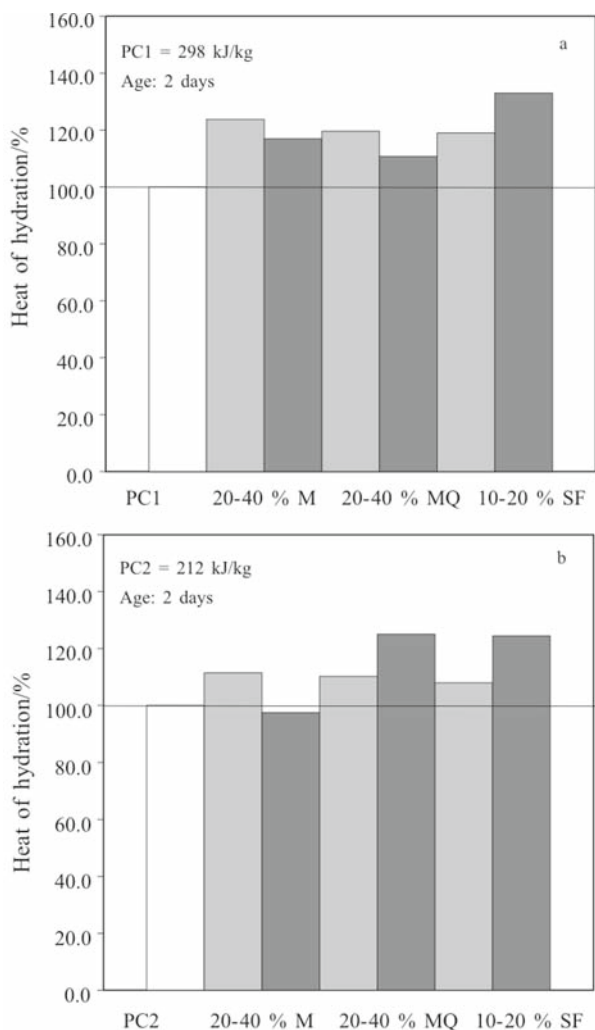


Fig. 2 % total heat released per gram of PC: a – PC1, PC1/M 80/20 and 60/40, PC1/MQ 80/20 and 60/40, and PC1/HS 90/10 and 80/20; b – PC2, PC2/M 80/20 and 60/40, PC2/MQ 80/20 and 60/40 y PC2/HS 90/10 y 80/20

ratio was higher (0.625 and 0.75, respectively), than to mix the respective POZC containing M and MQ (0.5 in all cases).

All this, in turn, must have facilitated greater direct than indirect stimulation of SF hydration in the early and very early ages. Proof of this hypothesis lies in the fact that the greater pozzolanic activity consistently exhibited by the two metakaolins up to the age of two days (Table 1) (and at 7 days, but at 28 days, nearly always) was reflected in a higher rate of heat release in the third peak of both 80/20 POZC PC1/M and PC1/MQ in comparison with the third peak of 90/10 POZC PC1/SF only, i.e., the peak denoting the greater transformation of Phase AFt into Phase AFm [24]. Nonetheless, it was not reflected in either of the two second peaks nor their respective previous valleys or in the third peak for any of the 60/40 POZC, because the greatest values were always for blended cements with SF. This was the case

despite the fact that hydration was always faster for the M blends. The foregoing constitutes further evidence that the pozzolanic activity of the Al_2O_3^r in the two metakaolins is more specific than generic, in order for the C_3A in the PC fraction with which they are blended to hydrate more and more quickly than C_3S . By contrast, SiO_2^r activity must be considerably less specific than generic in this same respect as hydration progresses. For this reason, the only PC1/SF cement that exhibited a higher rate of heat release than any of the blends containing metakaolin was the 80/20 blend, which was mixed with the highest water/cementitious material ratio used, namely 0.75.

Hence, the higher rate of heat release both in the third peak and the rest of the peaks prior thereto considered must be attributable more to the mixing water used than to the high, rapid and early pozzolanic activity exhibited by the blended cements as a result of their very high SiO_2^r content. In other words, it must be due more to direct than indirect stimulation of hydration. While the latter may also be present to some extent, this would be limited to the initial stages of hydration and taper as the reaction progresses and the amount of CSH gel (subsequently transformed into tobermorite) and silanol groups, Si–OH (later converted into hydrated silicic acid) newly formed from the SiO_2^r in the SF, hinders and ultimately obstructs the process altogether.

In short, at the most significant ages of the conduction calorimetry test, the PC1 blended cements with 10 and 20% of SF almost always exhibited higher values of rate of heat release than the 80/20 and 60/40 metakaolin blended cements. This behaviour is more consistent with

- the larger amounts of mixing water or higher water:cementitious material ratios that had to be used to be able to mix the pastes, 0.625 and 0.75, respectively (compared to the 0.5 needed to mix the cements with the two metakaolins), than with
- high pozzolanic activity in SF through the age of 2 days, for in fact it was consistently lower and even considerably lower than exhibited by the two metakaolins

This would constitute a further indication that the SF particles must have stimulated early age hydration more directly than indirectly. The metakaolins, in turn, must have acted conversely, i.e., more indirectly than directly, for the w/c ratio used to mix their respective cements was smaller than in the case of SF (0.625 and 0.75 compared to 0.5), while the pozzolanic activity exhibited up to the age of 2 days was consistently greater than recorded for SF. In other words, the pozzolanic activity of the Al_2O_3^r in the two metakaolins is more specific than generic, prompting greater and quicker hydration of the C_3A than of the C_3S present in the OPC with

which the two metakaolins were mixed. The SiO_2^- pozzolanic activity, by contrast, appears to be less specific than generic at nearly all the early hydration ages, even though the exception being the most initial stages.

But at the same time, given the greater amount of mixing water used and the greater pozzolanic activity exhibited in PC1 cement blended with SF, the increase in the rate of heat release with the SF replacement ratio might be interpreted to mean the contrary, i.e., that SiO_2^- pozzolanic activity is likewise more specific than generic, stimulating greater C_3A than C_3S hydration. But if this were the case, it would hold for only a short time, 16 h at most according to the present findings.

In order to clearly and indisputably determine whether the pozzolanic activity generated by SiO_2^- is or is not (or ceases to be and when) more specific than generic, stimulating greater and faster C_3A than C_3S hydration, further sulphate attack tests were found to be needed with SF 80/20 and 60/40 blended cements, i.e., cements with the same ratios as the two metakaolin blends (these quantities, 20 and 40%, are never used, however, to make high mechanical strength or high performance concrete in light of the possible setting and hardening anomalies they generate, not to mention the risk of premature carbonation decay involved; the proportions in fact used do not as

a rule exceed 10% of the total amount of portland cement by mass). For the foregoing reason, the 5 blended cements plus the two pure PC, PC1 and PC2, were tested to the Le Chatelier–Ansttet (L–A) (gypsum cement paste) (Table 4) and ASTM C 452-68 (gypsum cement mortar) accelerated methods (Table 5).

The experimental results obtained when such blended cements were subjected to sulphate attack do not support such hypothesis, but rather indicate that the behaviour of these two very different pozzolanic additions (with aluminic character, metakaolins, and with silicic character, SF) is diametrically opposed. While MQ (with around 50% of Q) intensified the aggressive sulphate attack in both OPC and SRPC, rendering it very fast [15, 16, 18] (an effect that would have been even more visible if M pozzolan have been used), silica fume hindered and even obstructed the attack altogether, depending on the test method used and/or blended cement tested (Tables 4 and 5).

Pursuant to the experimental findings on pozzolanicity (Table 1), heat of hydration, Fig. 1 (and [22, 24]) and sulphate attack (Tables 4 and 5), then, it may be validly sustained that in this study, the pozzolanic activity of the SiO_2^- in the SF is also more specific than generic, much the same as Al_2O_3^- , but at most only during the first 16 h of hydration; be-

Table 4 Le Chatelier-Ansttet test. Results of some cement

Age/day	$\Delta\varnothing_{x \text{ days}}/\%$ for two PC and of their POZC with MQ or SF pozzolan						
	OPC		SRPC	POZC with MQ or SF pozzolan			
	PC1	PC2	PC1/MQ 80/20	PC1/MQ 60/40	PC2/MQ 80/20	PC1/SF* 80/20*	PC1/SF* 60/40*
1	1.62	0.00	0.50	14.46	0.25	0.25	0.37
7	4.74	0.25	5.30	26.50	1.75	1.81	1.12
14	6.92	0.40				2.49	1.25
21	7.42	0.60				2.87	1.00
28	8.23	0.75	19.95	27.43	10.24	2.99	1.00
60	12.28	1.00				3.24	1.00
90	14.71	1.20	23.22	27.51	23.94	3.24	1.00
120	15.60	1.58				3.24	1.00
150	16.25	2.02				3.24	1.00
180	16.58	2.24	28.94	27.12	43.21	3.49	1.25
275	24.15	2.79				3.49	1.56
365	25.94	3.49	40.96	26.68	48.25	3.49	1.75
545	42.14	6.23	44.14	27.06	59.73	3.49	1.81
730	49.37	9.42	45.14	26.31	56.36	2.56	0.94

*Specifications of sulphate resistance:

For PC and for POZC as well, but at the proposal of Talero [10, 15]:

HSR $\Rightarrow \Delta\varnothing_{28 \text{ d}} \leq 1.25\%$; MSR $\Rightarrow 4.0\% \leq \Delta L_{28 \text{ d}} < 1.25\%$; LSR $\Rightarrow \Delta L_{28 \text{ d}} \geq 4.0\%$, HSR, MSR and LSR = High, Moderate and Low sulphate resistance.

*The specified SF amounts to design high performance concrete are commonly between 5 and 10%, although sometimes 15 and 20% at the most, also are used, but 30 and 40% are never used.

Table 5 ASTM C 452-68. Results of some cement

Age/day	$\Delta L_{x \text{ days}}/\%$ for two PC and of their POZC with MQ or SF pozzolans						
	OPC		SRPC	POZC with MQ or SF pozzolan			
	PC1	PC2	PC1/MQ 80/20	PC1/MQ 60/40	PC2/MQ 80/20	PC1/SF* 80/20*	PC1/SF* 60/40*
7	0.094	0.004	0.099	0.148	0.025	0.045	0.033
14	0.176	0.008	0.101	0.150	0.044	0.055	0.044
21	0.277	0.009	0.101	0.153	0.069	0.064	0.046
28	0.474	0.009	0.101	0.156	0.067	0.070	0.046
60	1.954	0.010	0.101	0.157	0.081	0.080	0.046
90	0.959	0.010	0.104	0.159	0.083	0.085	0.052
120	0.961	0.011	0.102	0.160	0.081	0.085	0.051
150	0.962	0.012	0.101	0.160	0.083	0.087	0.053
180	0.962	0.014	0.107	0.166	0.085	0.091	0.057
275	0.963	0.016	0.109	0.169	0.089	0.091	0.057
365	0.965	0.023	0.108	0.168	0.094	0.095	0.060
545	0.966	0.027	0.109	0.169	0.094	0.106	0.067
730	0.974	0.040	0.108	0.168	0.093	0.126	0.073

Specifications of sulphate resistance: (a) For PC, from ASTM C 150-95 Standard (23): HSR $\Rightarrow\Delta L_{14 \text{ d}}\leq 0.040\%$ and (b) For PC and for POZC as well, but at the proposal of Talero [10, 15]: HSR $\Rightarrow\Delta L_{28 \text{ d}}\leq 0.054\%$; MSR $\Rightarrow 0.073\%\leq\Delta L_{28 \text{ d}}<0.054\%$; LSR $\Rightarrow\Delta L_{28 \text{ d}}\geq 0.073\%$, HSR, MSR and LSR = high, moderate and low sulphate resistance

*The specified SF amounts to design high performance concrete are commonly between 5 and 10%, although sometimes 15 and 20% at the most, also are used, but 30 and 40% are never used.

cause after those first 16 h, specifically wanes more and more rapidly as hydration progresses, due to that the new CSH gels and silanol groups, Si–OH, formed when the compound reacts with the portlandite hinder and even completely obstruct, depending on the amount present, such indirect stimulation of C₃A hydration with gypsum, so that the higher the SF replacement ratio the less intense is the sulphate attack on the rest of the anhydrous C₃A as well, it would seem, as on the C₃A initially stimulated after the first 16 h. This, then, is the reason that the presence of a sufficient amount of SiO₂^{r-} in SF can hinder or even prevent aggressive sulphate attack on the C₃A and/or the C₄AF in PC (Tables 4 and 5), and chloride attack to the reinforcements as well [12, 14]. By contrast, Al₂O₃^{r-} is unable to prevent or even hinder the sulphate attack: rather it favours these reactions with gypsum and water to such an extent that they can be classified as fast gypsum attack [15, 16, 18].

Therefore and according to this very different behaviour of these three pozzolanic additions, M and MQ and SF, in front of gypsum attack (Tables 4 and 5), it can finally be reasserted that the prior and very rapid and significant pozzolanic activity of both M and MQ pozzolans (due primarily, to their respective Al₂O₃^{r-} (%) content) is at all ages, more specific than generic, prompting more intense C₃A than C₃S hydration, and conversely, this prior pozzolanic activity must be seen as unspecific, or perhaps more pre-

cisely, insufficiently specific in the stimulation of C₃S hydration, inasmuch as the specific indirect stimulation of its hydration declines. In contrast, the prior and also very rapid and significant pozzolanic activity of silica fume (due to its SiO₂^{r-} (%) content) is not also finally more specific than generic at all ages for the same purpose, but only up to the first 16 h, in this work; but after the first 16 h, it is unspecific. And the more reaction time goes on, the more unspecific is because in the case of sulphate attack, silica fume can specifically hinder C₃A hydration, but M and MQ cannot, since M and MQ can not only promote it but also accelerate it [15, 16, 18]. It is due to that SiO₂^{r-} reacts more and more with portlandite giving rise to more and more CSH gel and silanol groups, Si–OH, which can specifically hinder C₃A hydration. In contrast, Al₂O₃^{r-} gives rise to calcium aluminate hydrates and sulphate–aluminate hydrates (AFt and AFm phases, [24]) which can not specifically hinder C₃A hydration but accelerate it.

Conclusions

The conclusions that may be drawn from the comparative experiments conducted with two types of portland cement, with very different mineralogical compositions, mixed separately, with metakaolins and silica fume, both with different character as well, are as follows:

1 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. In contrast, for sulphate attack is not, because the final behavior is more or less fine, with SF, and not fine always, with M and/or MQ, even though at different speed depending on whether the C_3A content of PC is high or not.

2 Irrespective if M, MQ or SF is used, the differences in the amount of heat produced per gram of PC were more significant in mixes with PC1, with a high C_3A and low C_3S content, than in mixes with PC2, with low C_3A and high C_3S content.

3 The pozzolanic and hydraulic activities of both aluminic pozzolans, M and MQ, depend extensively on the non-crystallinity of their structure (amorphous structure), and more specifically, on their $Al_2O_3^{r-}$ contents, mainly. Indeed, at 48 h-ages, 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 its $Al_2O_3^{r-}$ content. It goes hand-in-hand with a decrease in CH and an increase in heat of hydration originated per gram of PC.

This conclusion can also be regarded to be wholly applicable to the silicic pozzolan SF, even though in contrast, its pozzolanic and hydraulic activities depend extensively on its vitreous structure, and more specifically, on its high SiO_2^{r-} content, whose also highly significant pozzolanic activity at very early ages (2nd paragraph in Conclusion 6) stimulates hydration, primarily indirectly as well. But also this effect can be regarded to be direct in light of the high mixing water amounts used for blended cements with SF (Conclusion 4).

4 SF, which exhibited also pozzolanic activity at 48 h-age, must have stimulated the hydration reactions in the PC fractions with which it was mixed, both:

- Directly, in the first place, because of its size and shape (very small spheres, high specific surface), it demands greater amounts of mixing water, which would ultimately be the actual cause of this direct stimulation, and then overlapping.
- Indirectly, because of its very small size, vitreous state and chemical properties favour its very significant pozzolanic activity at very early stages as well (2nd paragraph in Conclusion 6), due to its high SiO_2^{r-} content.

Nonetheless, both metakaolins, M and MQ, also behaved in the same way but with lesser mixing water amount than SF and greater pozzolanic activity at 2 days old than SF. Therefore, their direct

stimulation must have been lesser than for SF and their indirect stimulation, even though in any case, the overlapping between indirect and direct stimulation must have been higher.

Finally, this consequential effect of both pozzolan families, M and MQ and SF, is so intense that in some cases the amount of heat of hydration released may be assimilated to a Synergistic Calorific Effect (SCE).

5 When metakaolin and/or SF are 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 due to the possible SCE referred.

6 Such high and fast pozzolanic activity is observed in both M and MQ pozzolans, due primarily to their respective $Al_2O_3^{r-}$ contents, mainly, is more specific than generic, prompting more intense C_3A than C_3S hydration (i.e., giving rise to a decrease in CH and an increase in heat of hydration released per gram of PC). Not only at early ages of hydration (up to 48 h) but also from beginning to the end of the sulphate attack test. Conversely, this prior pozzolanic activity must be seen as unspecific, or perhaps more precisely, insufficiently specific in the stimulation of C_3S hydration for the same purpose, inasmuch as the specific indirect stimulation of its hydration declines, even though the sulphate attack is neither hindered nor stopped, but made easier and faster.

In contrast, such high, fast and early pozzolanic activity also observed in the SF (even though due primarily to its high SiO_2^{r-} content), must be more specific than generic as well, prompting more intense C_3A than C_3S hydration, but only at very early ages of hydration (up to the first 16 h in this work), because after 16 h, it is unspecific for the same purpose; and the more unspecific is, the more the hydration moves forward. But from point of view of sulphate attack only, SF is unspecific from beginning of the sulphate attack for prompting more intense C_3A than C_3S hydration with (and without) excess of sulphate, and for this reason precisely, SF is protective of sulphate attack in adequate amount for PC1 and for any OPC. Conversely, this prior pozzolanic activity of SF must also 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 also declines, even though the sulphate attack is hindered.

7 Irrespective of the previous conclusions, and according to,

- L-A test [32] and the following specifications, HSR ($=\Delta\varnothing_{28 \text{ days}} \leq 1.25\%$ [33]), MSR ($=\Delta\varnothing_{28 \text{ days}} \leq 4.00\%$ [33]) and LSR= $\Delta\varnothing_{28 \text{ days}} > 4.00\%$ [33]), both PC could be

qualified as follows: PC1 with LSR, and PC2 with HSR or SRPC, while 80/20 and 60/40 POZC PC1/SF with MSR and HSR, respectively, and 80/20 and 60/40 POZC PC1/MQ and 80/20 PC2/MQ with LSR (H – high, M – moderate and L – low sulphate resistance).

- ASTM C 452-68 [26] and the following specifications, (a) for PC, from ASTM C 150-95 Standard [36]: $HSR \Rightarrow \Delta L_{14d} \leq 0.040\%$, and (b) for PC and for POZC as well, but at the proposal of Talero [10, 15, 33]: $HSR \Rightarrow \Delta L_{28d} \leq 0.054\%$; $MSR \Rightarrow 0.073\% \leq \Delta L_{28d} > 0.054\%$; $LSR \Rightarrow \Delta L_{28d} \geq 0.073\%$, both PC could be qualified as follows: PC1 with LSR and PC2 with HSR or SRPC, while 80/20 and 60/40 POZC PC1/SF with HSR and 80/20 and 60/40 POZC PC1/MQ and 80/20 PC2/MQ with LSR.

In short, irrespective of the accelerated test used, all cements were characterized with the same or very similar qualification, but there being always a notable difference: SF blended cements did not fail to hinder or prevent the sulphate attack against PC1 (due to the high, fast and early pozzolanic activity from the SiO_2^{r-} content present in SF), which with a higher C_3A content than PC2, was the more vulnerable of the two PC to the sulphate attack; by contrast, metakaolín MQ not only failed to hinder or prevent the sulphate attack to its MQ blended cements (due to the also high, fast and early pozzolanic activity from its $Al_2O_3^{r-}$ content, mainly), but heightened its negative effects, rendering it more intense, aggressive and rapid, leading to what could be called rapid gypsum attack [15–18].

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