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C_4AF ettringite and calorific synergic effect contribution

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Abstract The need for cements or other cementitious materials that afford high early age mechanical strength has led to the use of extremely reactive pozzolanic additions such as silica fume, nanosilica, metakaolin and similar. The inclusion of the right proportion of such pozzolanic additions stimulates portland cement hydration, i.e., *directly*, as they are initially moistened by the mixing water, *non-directly* when they act as "seed crystals", and *indirectly*, because of the pozzolanic reaction between the addition particles and the portlandite forming from the portland cement components hydration; since this reaction is characterized by its intensity and speed, when its occurs it prevails over the other two. *Indirect* stimulation also causes the fraction of portland cement in the blend to release more heat of hydration than pure portland cement, and its does so on a scale consistent with the existence of a *calorific synergic effect*. Such greater heat is released in the early stages of hydration primarily by C_3A and C_3S that react with the mixing water to respectively generate ettringite and hydrated calcium silicates. When portland cements have a low to nil C_3A content, less heat of hydration is released due to the absence of an *AFt* phase that could be transformed into *AFm*. However, when extremely active pozzolanic additions, such as silica fume, are used, ettringite forms from C_4AF, further contributing to origin amounts of hydration heat released comparable to the above *calorific synergic effect*.

Keywords Portland cements · Silica fume · C_4AF ettringite · Calorific synergic effect

Introduction

The use of active mineral additions in cement manufacture or for inclusion in concrete is beneficial:

- economically, for less portland clinker is needed, with the concomitant energy savings,
- ecologically, because for the same reason as above, less CO_2 is emitted, and
- technologically, in connection with certain questions related [1–4] or otherwise [4] to high initial mechanical strength values and/or the chemical durability [2] of reinforced concrete structures.

By interacting with portland cement (PC), certain pozzolans, silica fume (SF) among them, contribute either to the physical–chemical [5–8] or, in the case of metakaolin (MK) [9–11], the chemical–physical densification of the paste. Others may section the capillary pores [5, 11], but this does not prevent the decline in portlandite crystal size [12], all else being equal, from favouring the subsequent carbonation-mediated decay of the mineral at an earlier age than when the crystals are formed from pure portland cement. This finding must be taken very seriously into account in cement design to ensure a suitable service life.

The rate of this interaction depends on the chemical composition, physical–chemical state, morphology and particle size of the active mineral additions. Other factors

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to be considered include the type of portland cement [9, 10, 13, 14] and the replacement ratio used [9, 10, 13, 14]. In most cases, the reaction rate has been found to be slow [4, 13], while in others, more specifically silica fume [14] or metakaolin [14], it has been observed to take place very quickly. Such pozzolanic additions are required where high mechanical strength [1–4] (because both, SF and MK, stimulate the portland cement fraction hydration with which they are blended [14]) or greater resistance is needed to aggressive media (sulphates [15, 16], chlorides [5, 17], seawater [18], carbonation [19] and alkali aggregate reaction [20, 21]), in the case of silica fume, and chlorides [11] and alkali aggregate reaction [22–24], in the case of metakaolín. In contrast and generally speaking, metakaolin decreases the resistance in front of sulfates [25–29] (this detrimental effect derived from gypsum attack is such an extent that it could be described as "rapid gypsum attack" [26]), marine environment [18] and carbonation [30].

Further consequences of the *direct* [13, 14, 31], *non-direct* [31], but most notably the *indirect* [14] stimulation of Portland cement hydration by these two specific pozzolanic additions, silica fume and metakaolin, were high mechanical strength [1–4] and the rise in the amount of heat of hydration released per gram of portland cement [14], especially when the cement had a high C_3A content [13, 14, 31]. Hence, the hydration stimulated

- *directly*, is due to the mixing water that initially moistened the outer and inner surface of more or less spherical particles,
- *non-directly*, is due in the very early stages, to the positive and negative electrostatic charges on these particles, which would respectively attract the OH^- and Ca^{2+} ions from the portlandite, and subsequently to the Z potential; as a result, the mineral addition (SF in this case) particles would ultimately behave like "seed crystals", facilitating the initial precipitation of portlandite as hexagonal plates prior to the pozzolanic reaction with the SF (although when mineral additions are not pozzolanic but crystalline, the pozzolanic reaction does not take place [31], as logical), and
- *indirectly*, is due to the substantial, speedy and early (after only 2 days) pozzolanic activity exhibited by such active pozzolanic additions [14] (SF, nano-silica, MK and so on).

While all the mineralogical components of portland cement are known to release a certain amount of heat during hydration, the amount released at such early ages depends primarily on C_3A hydration, given the intensity and speed of this reaction, and C_3S hydration, in light of the amount and reactivity of this component, although its reaction rate is slower [14, 32]. The initial formation of *ettringite, phase AFt* (tri-substituted aluminium–ferrite phase), from C_3A and its subsequent transformation into *phase AFm* (mono-substituted aluminium–ferrite phase) together with the formation of C–S–H gels from C_3S and the concomitant generation of portlandite, also contribute to heat of hydration.

Silica fume, in turn, reacts with portlandite to form C–S–H gel, which in this case is pozzolanic in origin, thereby stimulating C_3S hydration to generate more portlandite as the system responds to the shortage of this mineral in the liquid phase [14]. In addition to the foregoing, the initial formation of *ettringite* from C_3A and its subsequent transformation into *AFm* after reacting with the remaining anhydrous C_3A would prompt the release of even more heat of hydration on a scale that may on occasion be comparable to a *calorific synergic effect, CSE* [14].

The other majority components of portland cement are C_2S and C_4AF. The former, as the least reactive of all the hydraulic components of portland cement, releases the lowest amount of heat of hydration, whereas C_4AF has a higher hydration rate than C_2S and lower than C_3A [33]. Nonetheless, under certain circumstances, C_4AF may also drive the formation and serve as the source of *ettringite* and its transformation into *AFm*, further contributing to the aforementioned *calorific synergic effect*.

Purpose

The present study aims to prove that the formation of ettringite, *phase AFt*, from C_4AF origin and its transformation into *phase AFm* also contributes to promoting the above-mentioned *calorific synergic effect*, CSE.

Materials and methodology

The materials selected were:

- two portland cements (PC) of industrial origin and very different mineralogical composition (Bogue): one with a high C_3A content (PC1), 51% C_3S, 16.5% C_2S, 14% C_3A and 5.5% C_4AF ($Na_2O = 0.90\%$, $K_2O = 0.52\%$, $SO_3 = 3.50\%$ and LOI = 1.60%), a density of 3.08 and a Blaine fineness of 319 m^2/kg; and the other (PC2), with a low (almost nil) C_3A and a high C_3S content, 79.5% C_3S, 2.5% C_2S, ≈0% C_3A and 10% C_4AF ($Na_2O = 0.43\%$, $K_2O = 0.20\%$, $SO_3 = 2.34\%$ and LOI = 1.11%), a density of 3.21 and a Blaine fineness of 329 m^2/kg.
- silica fume (SF) with a SiO_2 content of over 90%, a reactive silica content, SiO_2^{r-}, of 88.46% [34], a density of 2.10 and a specific surface area of 22,100 m^2/kg.

- very pure ($CaSO_4 \cdot 2H_2O > 95\%$; $Na_2O = 0.02\%$ and $K_2O = 0.01\%$) natural gypsum, ground to the particle size distribution stipulated in standard ASTM C 452-68 [35].

The two PC were blended (in dry) with SF at replacement ratios of 5% and 15%. Two series of pastes were then made: one with sufficient gypsum for SO_3 to account for 7.0% of the total cementitious material in each sample, with a view to enhancing system kinetics, and the other gypsum-free.

The analyses conducted included: the pozzolanicity test or Frattini test [36], conduction calorimetry and X-ray diffraction. The pozzoalanicity test [36] was performed at the age of 2 days. Conduction calorimetry was determined on pastes with a water/solid ratio (by mass) of 0.5 for pure PC, and, to obtain pastes with the same workability, of 0.5625 and 0.6875 for cements with 5% and 15% replacement ratios, respectively. Heat release rates were measured using an isothermal conduction calorimeter operating at 25 °C. Data were determined up to 2 days of hydration and the total heat produced was calculated as the integral below the heat dissipation rate curve versus time. X-ray diffraction tests were conducted on 2 days pastes prepared with the same water/solid ratios as used for the calorimetry samples. The measurements were performed on a diffractometer (Philips X'Pert) equipped with a graphite monochromator using CuKα radiation and operating at 40 kV and 20 mA. Step scanning was made from 5 to 60° 2θ using scan speed of 2°/min and sampling interval of 0.02° 2θ. The XRD patterns are illustrated from 5 to 25° 2θ because the more significant peaks of early compounds formed during cement hydration, such as *AFm*, *AFt* and CH, are detected in this range.

Results and discussion

Figure 1a and b show the results of the pozzolanicity test. This test implies the determination of the amount of calcium cation (Ca^{++}) and hydroxyl anion (OH^-) containing in the water in contact with the tested samples at 40°C. In this case the test was made at 2 days. Then, comparing the amount of CH in the contact water with the solubility isotherm of CH in an alkaline solution at the same temperature, the addition is considered hydraulically active when the concentration of CH in the sample solution is below the solubility isotherm.

According to these results, SF stimulated the hydration reactions, as the points representing these concentrations in the 5% blended cements were positioned above the solubility isotherm. At the same time, the positions below the solubility isotherm observed for the 15% blended cements were an indication of high, early and fast pozzolanic activity in SF; this pattern was found in both PC. The foregoing re-confirmed that SF is not only a pozzolanic, but over all a highly reactive addition. Moreover, Fig. 1a and b show that when excess of gypsum was added (7.0% SO_3), the concentration values were also positioned above the solubility isotherm. This, in conjunction with the observation that the [OH^-] values declined in the PC1 and PC2 blends, due to the physical *dilution* effect of the Na_2O and K_2O contents existing in PC1 ($Na_2O_{eq} = 1.24\%$) and in PC2 ($Na_2O_{eq} = 0.56\%$), with the addition of the gysum excess; indicated that part of the excess of gypsum was soluble in the liquid phase, justifying of this way, the increases in [CaO] originated in comparison with their respective blended cements without excess of gypsum.

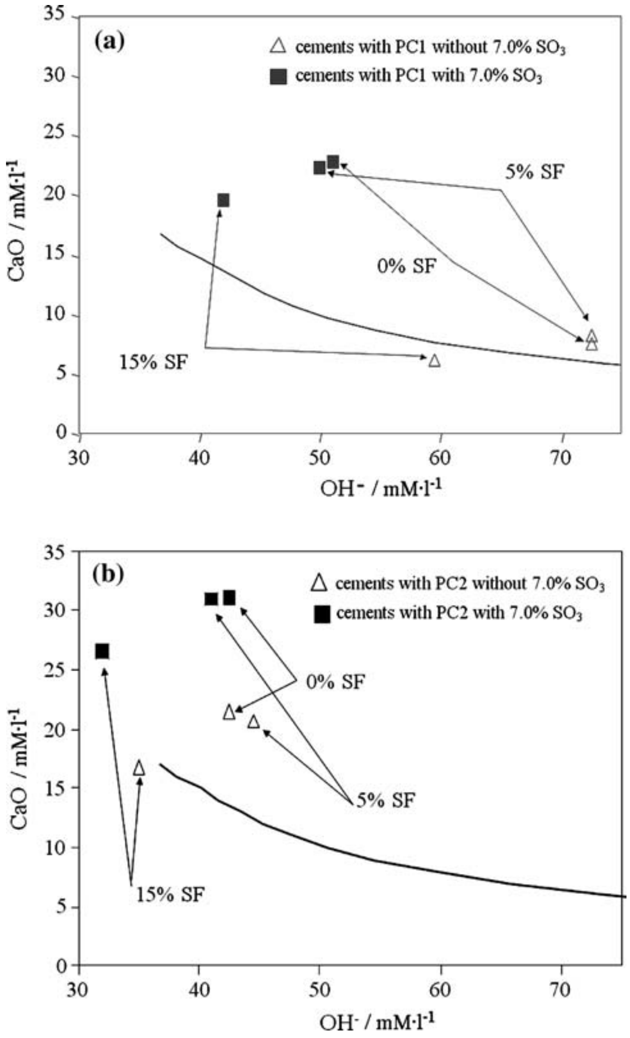

Fig. 1 Pozolanicity test (Frattini test). Results at 2 days. **a** For PC1 and its blended cements. **b** For PC2 and its blended cements

Moreover, SF cannot be regarded to have behaved inertly but if SF were assumed to have behaved inertly, in the 95/05 blends with and without 7.0% SO_3, SF would

Table 1 Pozzolanicity test (Frattini test). Results. Age: 2 days

Cements	-7.0% SO_3				$+7.0\%$ SO_3			
	$[OH^-]$ (mM L^{-1})		[CaO] (mM L^{-1})		$[OH^-]$ (mM L^{-1})		[CaO] (mM L^{-1})	
	Real value	*	Real value	*	Real value	*	Real value	*
P1 100/00	72.50	–	7.60	–	51.00	–	22.75	–
P1/SF 95/05	72.50 >	68.88	8.25 >	7.22	50.00 >	48.45	22.25 >	21.61
P1/SF 85/15	**59.50** <	61.63	**6.25 <**	6.46	42.00 <	43.35	19.50 >	19.34
P2 100/00	42.50	0.00	21.50	0.00	42.50	0.00	31.10	0.00
P2/SF 95/05	44.50 >	40.38	20.65 >	20.43	41.00 >	40.38	30.95 >	29.55
P2/SF 85/15	**36.00** <	36.13	**16.80 <**	18.28	32.00 <	36.13	26.50 >	26.44

The paired values in *bold* mean that the point is in the subsaturation region (= +result)

* Values assuming inertness of SF

< pozzolanic activity ⇒ *indirect* stimulation

> non pozzolanic activity ⇒ *direct* and *no-direct* stimulation

have stimulated the PC fraction hydration with which it was blended more *directly* and *non-directly* [31] than *indirectly* [14]: for not only did the respective specimen fail to pass the 2-day Frattini test, but also the real [CaO] in its liquid phases was always higher than the "theoretical" concentration (Table 1), i.e., the concentration expected from inert behaviour (Table 1). By contrast, in the 85/15 blends with no 7.0% SO_3, the contrary was observed: *indirect* stimulation prevailed over *direct* and *non-direct* stimulation, for not only did the specimen pass the two-day Frattini test (confirming once more that SF is a rapid-acting pozzolanic addition), but also the real [CaO] in its liquid phases was always lower than the concentration expected from inert behaviour (Table 1). In the same blends with 7.0% SO_3 (Table 1), however, *direct* and *non-direct* stimulation predominated.

Proof of the veracity of all the foregoing reasoning and/or justification in general, and of this last premise in particular, lies in the fact that the chemical parameter $[OH^-]$ (involved also like [CaO] in the pozzolanic reaction) behaved in each blend of "real" and "inert" SF (Table 1), in the same way as [CaO], except precisely with respect to the solubilization of the excess of gypsum (=7.0% SO_3) in the liquid phase of the 85/15 blends, where *indirect* stimulation prevailed (Table 1), as expected, over *direct* and *non-direct* stimulation. This would be the result of the own specific pozzolanic activity of OH^-, especially with the reactive silica, SiO_2^{r-}, in the SF, giving rise initially to silanol groups Si–OH and subsequently to silicic acid later on. The above would occur despite the presence of such excess gypsum, which in any event would affect [CaO] very directly via its solubilization, and $[OH^-]$ indirectly, with the latter declining would in any event due to the physical dilution of the alkaline ions Na^+ and K^+ released by the PC with which the SF was blended (the $Na_2O_{eq.}$ content (%) in PC1 was 1.24% and in PC2 less than half that amount, a very small 0.56%, making it possible so that the $[OH^-]$ content in the liquid phase of the 95/05 PC2/SF without 7,0% SO_3 to be nonetheless higher than for its plain PC2. This would be an indication that at such early test ages—only 2 days—seemingly, the OH^- and Ca^{2+} ions were not equally involved in the considerable pozzolanic activity exhibited by the SF, as a result of other physical and/or chemical agents by which their respective [CaO] and $[OH^-]$, specially in small very small amount, may have been affected, such as the mixing water initially moistening the particles of pozzolan and/or other anions and/or chemical elements unrelated to the water, its possible chemical inter-action among them, and other possible causes [7] insignificant for the main objective of this study).

The graphs in Fig. 2 show the heat of hydration curves; each peak and valley represents a significant event in the reaction. The first peak, for instance, indicates the release of dissolution heat with the attendant formation of *AFt*, after which hydration gradually slows until it hits a nadir, whose duration depends on the pH required for the following reactions to take place. Similarly, the second peak, associated with the formation of hydrated calcium silicates, precedes the next trough. Lastly, where *AFt* is formed previously and anhydrous C_3A is still present, a third peak appears that denotes the conversion of *AFt* into *AFm*. This peak, in turn, is followed by the third valley.

A closer look at Fig. 2a reveals that the second and third peaks shifted to earlier ages in PC1 and the heat release rates rose; both these effects were more accentuated in the blends with the higher replacement ratio, an indication that SF stimulated the hydration of the mineralogical components in PC1. The heat of hydration released in the first 2 days, calculated as the integral of these curves, came to

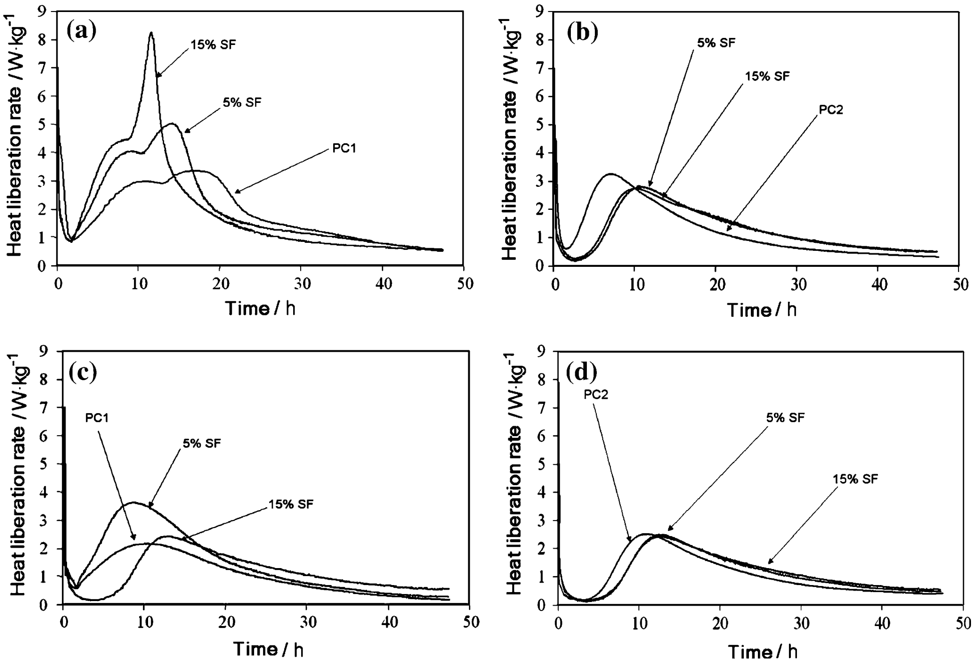

Fig. 2 Calorimetry test for (**a**) PC1 and its blended cements without 7.0% SO_3, (**b**) PC2 and its blended cements without 7.0% SO_3, (**c**) PC1 and its blended cements with 7.0% SO_3, and (**d**) PC2 and its blended cements with 7.0% SO_3

298, 337 and 335 kJ/kg of cementitious material for replacement ratios of 0, 5 and 15%, respectively. Such results require no further analysis to support the hypothesis that the interaction generated leads to values comparable to *CSE* figures.

By contrast, in the samples prepared with PC2 (Fig. 2b), the ages at the first valley and second peak were lowered and the respective intensity did not rise. Nonetheless, the values of the total heat of hydration released in the first 2 days were very similar for the three cements (212, 210 and 215 kJ/kg of cementitious material for 0%, 5% and 15% replacement, respectively). If SF had behaved inertly, the total heat released by the blends should have been 5% and 15% lower than the figure for pure portland cement, PC2 in this case. This pattern was not observed, however, for the values mentioned above were much higher than the theoretical values obtained assuming SF to be an inert material. This proved that during the early hours of hydration, the interaction between SF and PC2 (with a significantly different mineralogical composition than PC1) also stimulated hydration, although substantially less than in PC1, as discussed below.

Foremost among the mineralogical components of portland cements that traditionally release early age heat of hydration are C_3A, characterized by intense, rapid reactions, and C_3S, whose contribution is due to its volume and reactivity. The findings of this study, as in prior research [14], showed that C_3A-mediated stimulation prevailed over the action of C_3S, inasmuch as PC1 (with 14% C_3A and 51% C_3S) was stimulated by 18% and 27.5% by 5% and 15% SF, while the same replacement ratios stimulated hydration in PC2 (with $\approx$0% C_3A and 79% C_2S) by only 4% and 16%.

In the series containing 7.0% SO_3 (Fig. 2c, d), the total heat released declined with respect to the respective gypsum-free blended cements (180, 245 and 205 kJ/kg of cementitious material for PC1 and its 5% and 15% blends, respectively, and 177, 185 and 203 kJ/kg of cementitious material, for PC2 and its blends, also respectively). In the blended cements with 7.0% SO_3, however, hydration was stimulated by 41% and 20% in the case of PC1, but only by 9.5% and 31% in PC2, in pastes with 5% and 15% replacements, respectively. The deduction is that the presence of gypsum also stimulated the hydration reactions.

This may not be attributed entirely to the pozzolanic reaction initiated by the SF, since the pozzolanicity test points for the series with 7.0% SO_3 were positioned above the solubility isotherm (see Fig. 1a, b). Consequently, the components involved in the interaction in this case would be the gypsum and the aluminous fraction only of portland cements (since silica fume contains no reactive alumina, $Al_2O_3^{r-}$ [37]). In PC1, C_3A (14%) would have obviously taken part in the above reaction; in the case of PC2, however, with a very low to nil ($\approx$0%) C_3A content, the reagents must have been gypsum and C_4AF. The detection of *AFt* and *AFm* phases on the diffractograms of the respective samples verified this hypothesis.

The compounds identified by X-ray diffraction are shown in Fig. 3. In the series without 7.0% SO_3 (Fig. 3a, b), portlandite, appeared in both PC1 and PC2, but not in the blends containing 15% SF, showing that it was depleted during the pozzolanic reaction. The *AF* phase in PC1—consisting in

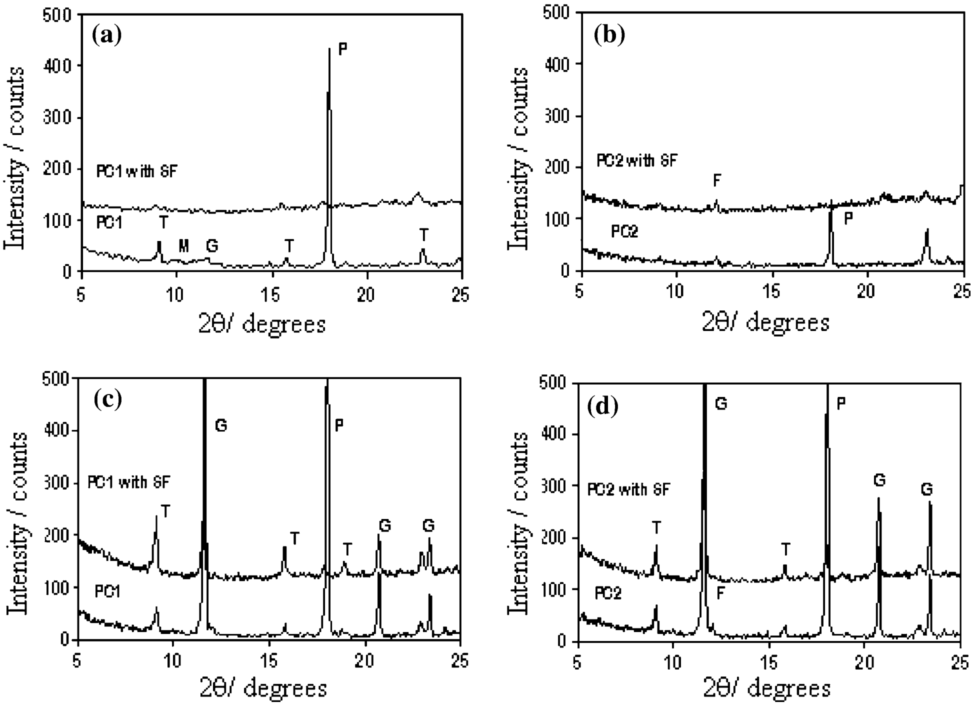

Fig. 3 XRD analyses. Results at 2 days: **a** PC1 and its blended cements without 7.0% SO_3, **b** PC2 and its blended cements without 7.0% SO_3, **c** PC1 and its blended cements with 7.0% SO_3, and **d** PC2 and its blended cements with 7.0% SO_3. Key: *P* $Ca(OH)_2$, *T* AFt, *M* AFm, *G* gypsum ($CaSO_2 \cdot H_2O$), *F* C_4AF

14% C_3A + 5.5% C_4AF, in turn, clearly declined as phases *AFt* and *AFm* rose; the *AF* phase in PC2— ≈0% C_3A + 10% C_4AF, i.e., consisting nearly entirely in C_4AF which reacts more slowly with water, showed no perceptible change in intensity at the age of 2 days, however.

As noted above, hydration was stimulated in the series containing 7.0% SO_3 (Fig. 3c, d) on a scale comparable to the *CSE*, as observed in the total amount of heat of hydration released in 2 days. In PC1 and its blends, this effect could be largely attributed to ettringite formation from C_3A (Fig. 3c); for PC2 and its blends, however (since $C_3A \approx 0\%$ and SF contains no $Al_2O_3^{r-}$), the sole possible origin of ettringite was C_4AF.

The preceding analysis therefore shows that at least in these circumstances, ettringite may form from C_4AF at early ages, 2 days or sooner, releasing heat of hydration that would contribute to the aforementioned *CSE*.

Conclusions and recommendations

Pursuant to the experimental results obtained in this study, the following conclusions and recommendations can be drawn:

- Ettringite forming from C_4AF may appear at an early age (less than 2 days) in these circumstances (with SF, PC with ≈0% C_3A, gypsum and water), and therefore, contributes to the *CSE*.
- The inclusion of silica fume in portland cements stimulates hydration reactions *directly*, *non-directly* and *indirectly* on a scale that may even lead to a *Calorific Synergic Effect, CSE*, which is more pronounced in portland cements with a higher C_3A content.
- The differences in the amount of heat produced per gram of Portland cement were more significant in Portland cement blends with a high C_3A and low C_3S content than in PC blends with a very small or nil low C_3A and high C_3S content.
- Whilst the addition of gypsum retarded and attenuated the hydration reactions in all cases, leading to a decline in the amount of total heat released, it nonetheless, also stimulated the hydration reactions because it generated greater heat of hydration per gram of Portland cement than observed in the blends with no excess gypsum.
- In works calling for a considerable volume of in situ concrete with highly reactive pozzolanic additions such as silica fume, attention should be paid, not only to the weather conditions, but also to any measures required to lower the risks of (thermal and hydraulic) cracking due to concrete overheating (because of the heat of hydration released). Such precautions involve the informed choice of both the type of Portland cement and the type and quantity of pozzolanic addition used.

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