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CALORIMETRY OF PORTLAND CEMENT WITH SILICA FUME AND GYPSUM ADDITIONS

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The use of active mineral additions is an important alternative in concrete design. Such use is not always appropriate, however, because the heat released during hydration reactions may on occasion affect the quality of the resulting concrete and, ultimately, structural durability. The effect of adding up to 20% silica fume on two ordinary Portland cements with very different mineralogical compositions is analyzed in the present paper. Excess gypsum was added in amounts such that its percentage by mass of SO_3 came to 7.0%.

The chief techniques used in this study were heat conduction calorimetry and the Frattini test, supplemented with the determination of setting times and X-ray diffraction. The results obtained showed that replacing up to 20% of Portland cement with silica fume affected the rheology of the cement paste, measured in terms of water demand for normal consistency and setting times; the magnitude and direction of these effects depended on the mineralogical composition of the clinker. Hydration reactions were also observed be stimulated by silica fume, both directly and indirectly – the latter as a result of the early and very substantial pozzolanic activity of the addition and the former because of its morphology (tiny spheres) and large BET specific surface. This translated into such a significant rise in the amounts of total heat of hydration released per gram of Portland cement at early ages, that silica fume may be regarded in some cases to cause a synergistic calorific effect with the concomitant risk of hairline cracking. The addition of excess gypsum, in turn, while prompting and attenuation of the calorimetric pattern of the resulting pastes in all cases, caused the Portland cement to generate greater heat of hydration per gram, particularly in the case of Portland cement with a high C_3A content.

Keywords: *gypsum, heat of hydration, Portland cements, pozzolanicity, silica fume*

Introduction

Cement studies range from the individual analysis of each of the component phases, to research into highly complex systems with all their variables. Joint studies of Portland clinker components and their interaction with the gypsum ($CaSO_4{\cdot}2H_2O$) added to regulate setting time, for instance, have found that:

- The C_3A and C_4AF in ordinary Portland cement compete for gypsum, but as it is more reactive, C_3A consumes higher quantities of the addition more rapidly. This, in conjunction with constraints on the amount of gypsum used to ensure that only the setting time is regulated, leads to the formation of less ettringite than might otherwise be expected [1].
- Gypsum also accelerates the hydration rate of calcium silicates, which likewise compete for sulphate ions during hydration, given the significant amount of sulphates included in the CSH gel. The inclusion of 2 to 6% of gypsum has been found to accelerate alite hydration, and from 2 to 4%, belite hydration [2].

A high gypsum content contributes to the formation of large amounts of ettringite, however, which 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 monosulphoaluminate solid solutions before the end of the latent period of C_3S hydration, thereby retarding the acceleration period of this compound [1].

The study of mineral pozzolanic additions has also developed from the analysis of discrete systems [3–5]. In the case of silica fume, which is a highly pozzolanic addition, it has been found that:

- After three days, at addition rates of 5 and 10%, C_3A hydration is retarded [6].
- Additions of 5–10% accelerate alite hydration up to the age of 28 days [6, 7].
- Lastly, including the addition also heightens the hydration rate of βC_2S during the first 28 days [8].

The outcome of all the foregoing is to produce greater heat of hydration at early ages [9], an effect that grows more intense as the percentage of the addition is raised from 5 to 10% [10]. The high BET specific surface of silica fume has been identified as the cause of its over-stimulation of Portland cement hydration reactions [11]. In addition, however, an indirect stimulatory effect on such reactions has been attributed to the substance, due to the fixation of cal-

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cium hydroxide in the pozzolanic reaction from the earliest ages [12]. On the one hand, the pozzolanic reaction has been confirmed to take place even in the first few days, chiefly on the grounds of the consumption of Ca^{2+} ions in the liquid phase, but also of the uptake – in descending order – of OH^- and K^+ ions [13–17]. And on the other, the amount of heat released per gram of Portland cement in pastes with silica fume has been found to amply exceed the amount of heat released by the respective plain pastes [18].

Experimental

Objective

In light of these considerations on substances such as gypsum and silica fume; the objective or purpose of the present study is, to analyze their overall effect on the hydration of two Portland cements with widely varying compositions, with a view to limiting their use in high performance concrete.

Materials and methods

Two Portland cements with widely differing mineralogical compositions were chosen for this study. One, with a very high C_3A content, called PC1, and the other, with a minimum C_3A content (<1%) and a maximum C_3S content, called PC2; the other constituents were a very active pozzolanic mineral addition (silica fume, SF) and rich ground natural gypsum. Distilled water was used in the mortar in all cases.

The chemical composition, density and BET specific surface of the Portland cements and the addition are given in Table 1. The potential composition of the Portland cements found from their chemical composition and the Bogue equations was as follows: 51% C_3S, 16% C_2S, 14% C_3A and 5% C_4AF for PC1 and 79% C_3S, 2% C_2S, 0% C_3A and 10% C_4AF for PC2.

Table 1 Chemical composition of cementing materials

Parameters	Materials		
	Portland cements		Silica fume
	PC1	PC2	SF
SiO_2/%	19.2	21.7	92.0
Al_2O_3/%	6.4	1.5	0.7
Fe_2O_3/%	1.7	4.1	0.4
CaO/%	63.9	68.0	0.0
MgO/%	1.5	0.4	0.0
Na_2O/%	0.9	0.4	0.0
K_2O/%	0.5	0.2	0.0
SO_3/%	3.5	2.3	0.1
L.O.I./%	1.6	1.1	6.3
I.R./%	0.7	0.2	–
Density	3.08	3.21	2.10
BSS/m^2 kg^{-1}	319	301	–
BET/m^2 kg^{-1}	–	–	22100

The different chemical and mineralogical compositions of the two cements Portland are partly reflected in the difference in their densities; their fineness, on the contrary, is comparable. SF contains: over 90% SiO_2, 88.46% SiO_2^{r-} (reactive silica) [19, 20] and yet has a much lower density than quartz (2.70) and a very high specific surface. Its diffractogram, shown in Fig. 1, reveals the presence of cristobalite (C); the diffuse pattern is indicative of the substance's primarily vitreous nature [21].

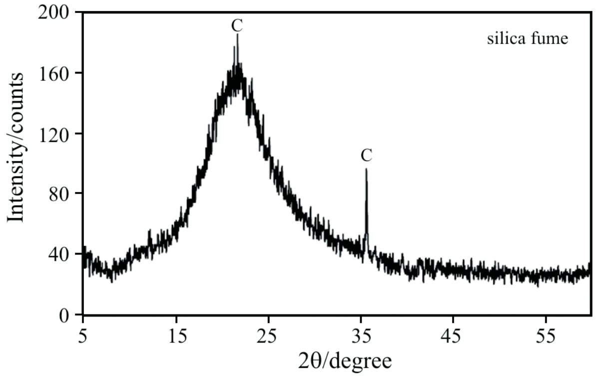

Fig. 1 XRD pattern of the SF

The pastes for the study were made by mixing each Portland cement separately with SF, in percentages by mass of 90/10 and 80/20, in the absence of gypsum or with sufficient amounts to bring the total SO_3 content to 7.0%. Table 2 gives the setting times and water demand for 500-g samples. These two physical parameters were determined as laid down in European standard EN 196, part 3 [22].

It may be deduced from Table 2 that particle size and morphology had a significant effect on water demand. The SF spheres separated the Portland cement particles, making a greater surface area available for hydration. Moreover, given its density and specific surface, the silica fume comprised a larger number of particles than the Portland cement replaced, significantly increasing the water demand.

Pozzolanic activity was evaluated chemically by Frattini's test [23], by comparing the amount of calcium hydroxide in an aqueous solution covering the hydrated sample at 40ºC for a given period of time (in this case, 48 h), with the solubility isotherm for calcium hydroxide in an alkaline solution at the same temperature. The indication of pozzolanic activity was defined to a lower calcium hydroxide concentration in the sample solution than on the solubility isotherm, due to its uptake in the pozzolanic reaction (=+result) (Fig. 2).

The heat release pattern was ascertained by heat conduction calorimetry for pastes. Measurements were taken at a temperature of 25ºC. 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 [1] as well as for cements containing mineral additions [24]. To obtain equally workable pastes, the water:cementitious material ratios used were 0.5 for pure Portland cements, 0.625 for mixes with 10% SF and 0.75 for mixes with 20% silica fume.

Results and discussion

Figure 2 shows [OH^-] and [CaO] determined at 48 h. Note that the pastes with SF showed pozzolanic activity at 48 h (i.e., 6 days before its first specified age, 8 days [25]), in the case of PC1 at (addition-cement) replacement rates of 10%, and in PC2 at rates of 15% or higher. Some of 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.

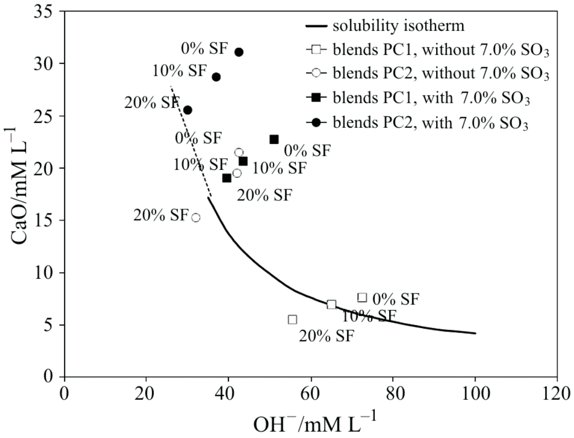

Fig. 2 Pozzolanicity (Frattini test) at 48 h: results

When gypsum was added to the samples, the [CaO] increased due to its partial dissolution in water, whereas [OH^-] declined, partially because of the effect dilution of the Portland cement, although no pozzolanic activity was detected in any of the samples within the first 48 h.

Figures 3 and 4 show the first 48-h calorimetric curves for the samples containing PC1 and PC2, respectively. The first stage or induction period for plain PC1, visible in Fig. 3, shows a high rate of heat release due to initial hydrolysis and the hydration of the aluminous phase (primarily C_3A); the rate dropped to 0.91 W kg^{-1} after 2 h, accounting for the first trough on the calorimetric curve. This was followed by the acceleration of hydration reactions – with the initial precipitation of the CSH gel, primarily from C_3S –, until the rate of heat release peaked for a second time at 2.97 W kg^{-1} at reaction time 11:12. During acceleration, PC1 began to set (Table 2). Thereafter the rate of the hydration reactions declined through the 13th hour, overlapping in this stage with the aluminous phase transformation reactions, which take place when the SO_3/Al_2O_3 molar ratio falls to under 3 (in this case, 0.69). But the most prominent effect of the reaction was the enormous amount of heat released, which rose to 3.33 W kg^{-1}, forming the third peak on the calorimetric curve, 17 h and 24 min into the reaction. Finally, the hydration reactions slowed to and remained at a low rate.

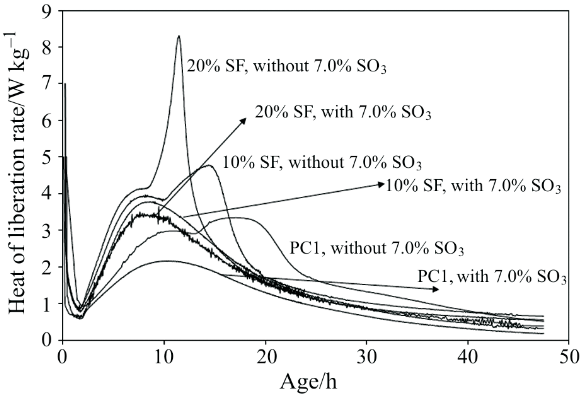

Fig. 3 Calorimetric curves for mixes with PC1

The test was considered completed after 48 h, taking the reading at that time as the third trough on the calorimetric curve.

Although when 10 and 20% SF was added to the PC1 the calorimetric phases or stages observed were essentially the same as for the plain PC1, certain differences were noted. During the first stage, for instance (from t=0 to the first trough), the effect of the SF particles was to dilute the Portland cement, with rates of 0.83 and 0.88 W kg^{-1}, respectively. At the same time, however, the hydration reactions were enhanced in the fraction of the PC1 with which they were mixed, given that the first trough appeared earlier than in plain PC1 (1:36 and 1:42 h, respectively). This was followed by the acceleration of the hydration reactions – with the initial formation, in this case, of gels of chiefly C_3S and SF origin and silanol groups of SF origin – with the second trough recorded at reaction times of 10:12 and 7:54, respectively. That is to say, both minima appeared earlier than in plain PC1, and the interval between the first and second troughs was narrower with both 10 and 20% replacement rates. This confirmed that the hydration reaction was stimulated by the SF, an effect that was further corroborated by the higher rate of heat release values

Table 2 Times of setting and normal consistency

Cements	Setting times (h:m)		Normal consistency/%
	initial	final	
PC1, without 7.0% SO_3	3:20	5:10	31
PC1, with 7.0% SO_3	3:35	6:15	32
PC1/SF 90/10, without 7.0% SO_3	1:40	4:10	36
PC1/SF 90/10, with 7.0% SO_3	2:20	4:45	35.7
PC1/SF 80/20, without 7.0% SO_3	0:35	3:55	45
PC1/SF 80/20, with 7.0% SO_3	0:50	4:35	43.5
PC2, without 7.0% SO_3	4:30	6:15	28
PC2, with 7.0% SO_3	4:15	6:10	28
PC2/SF 90/10, without 7.0% SO_3	4:45	8:55	36
PC2/SF 90/10, with 7.0% SO_3	5:00	8:55	35.4
PC2/SF 80/20, without 7.0% SO_3	3:30	9:20	44
PC2/SF 80/20, with 7.0% SO_3	3:40	9:45	46.2

(3.92 and 4.11 W kg^{-1}) found for the mixes than for plain PC1. Subsequently, the low SO_3/Al_2O_3 molar ratios in the two cement mixes (0.68 and 0.67, respectively) prompted aluminous phase transformation. The outcome was third peak reaction times of 14:24 and 11:34, respectively, for 10 and 20% replacement, both higher than for plain PC1. Moreover, the rate values at these third peaks were 4.77 and 8.20 W kg^{-1} – higher than for plain PC1 –, again providing dual confirmation (troughs appearing in shorter times and higher heat of hydration release values) of hydration stimulation as a result of replacing PC1 with SF.

In short, the first troughs on the heat release curves for the samples containing PC1 appeared earlier and were attenuated for all mixes, and the second and third peaks appeared earlier for all mixes and their intensities were higher than in plain PC1.

When gypsum was added to the PC1, the calorimetric curve was substantially attenuated and the third peak disappeared; when gypsum was included in the SF – PC1/SF mixes –, in turn, all the curves were slightly retarded and the first trough and second peak were slightly attenuated. As in the case of plain PC1, the third peak disappeared altogether.

The first stage or induction period for plain PC2, visible in Fig. 4, is also characterized by a high rate of heat release due to initial hydrolysis; after 1:37 h, the rate dropped to 0.64 W kg^{-1}, accounting for the first trough on the calorimetric curve. This was followed by the acceleration of hydration reactions – with initial precipitation, this time at a higher rate, of the CSH gel, primarily from the C_3S –, up to a second heat release rate peak of 3.25 W kg^{-1}, reached at 7:39 h (the fact that this value was higher than for PC1 confirmed that PC2 had a higher C_3S content). PC2 also began to set during acceleration (Table 2). The reactions slowed thereafter and although hydration continued, the rate remained low. The test was considered completed after 48 h, taking the reading at that time as the second trough on the calorimetric curve. In this case, there was no transformation of the aluminous phase, since the C_3A content in PC2 was nil, virtually.

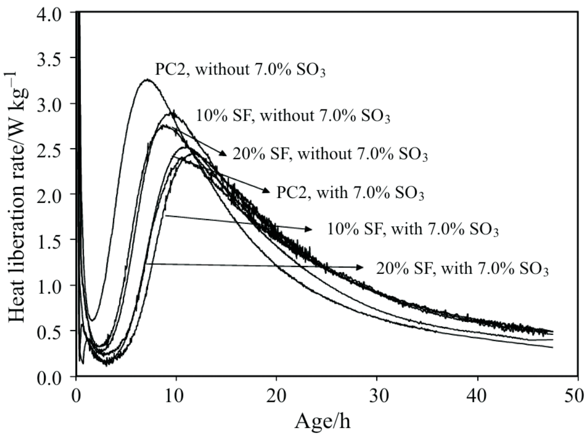

Fig. 4 Calorimetric curves for mixes with PC2

Although when 10 and 20% SF was added to the PC2 the calorimetric phases or stages observed were essentially the same as for the plain PC2, certain differences were noted. During the first stage, for instance (from time=0 to the first trough), the effect of the SF particles was to dilute the PC2, with rates of 0.27 and 0.26 W kg^{-1}, respectively. Moreover, the hydration reactions were observed retarded, with the troughs appearing at reaction times of 2:27 and 1:51, respectively. The hydration taking place between the first trough and the second peak lasted longer, with the second peak appearing at 9:24 and 8:55, respectively, for 10 and 20% replacement: i.e., not only later than in the case of PC2, but with a longer interval between the first trough and the second peak. The time lapsing between initial and end setting times was also longer and final setting was retarded in all these pastes. And yet, in this stage also, SF was observed to stimulate the hydration reactions in the fraction of the Portland cement with which it was mixed, with rates of release at the second peak equal to and greater than (2.92 and 2.84 W kg^{-1}), respectively, the proportional rate for PC2 (2.92 and 2.60 W kg^{-1}). For the same reason as in the case of plain PC2, the third stage (transformation of the aluminous phase) was absent.

In short, both the first trough and the second peak were retarded and attenuated in all the mixes, and although stimulation was observed, it was much less pronounced than for mixed cements containing PC1. This is an unequivocal sign that the higher C_3A content in the latter is a determining factor in the enhanced stimulation of the hydration reaction.

Adding gypsum to PC2 significantly attenuated and retarded the first trough and second peak with respect to plain Portland cement. Similarly, adding gypsum to the mixes retarded the first trough and the second peak and widened the interval between the two.

The percentage of total heat of hydration released per gram of Portland cement after 48 h is shown in Fig. 5. It will be noted that both the nature of the additions and the composition of the cements affected mix behaviour, as did the presence or absence of gypsum up to an SO_3 content of 7.0%.

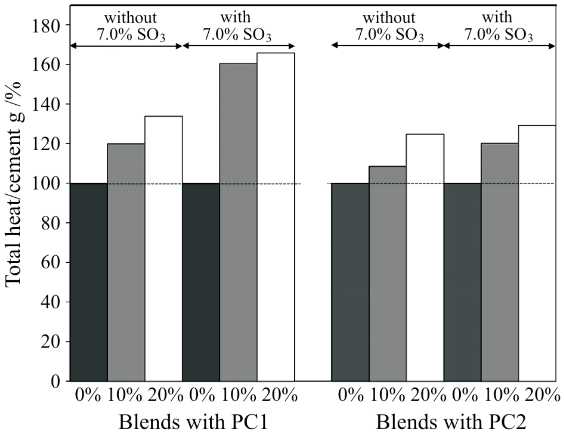

Fig. 5 Changes of hydration heat per gram of Portland cement for PC/SF mixes

Silica fume, at percentages of both 10 and 20%, produced mixes that generated greater heat of hydration with PC1 than with PC2. This behaviour can be explained by the composition of the Portland cements used. The high C_3A content in PC1 naturally produced more heat of hydration at the early ages. After 48 h of hydration, SF indirectly prompted the respective fraction of the PC with which it was mixed to generate a larger amount of heat of hydration than the plain PC. (This involved direct stimulation of hydration via the internal and external humidification of each particle from the time the mixing water was initially added and/or indirect stimulation, due to the substantial pozzolanic activity of the silica fume in the early ages.)

When gypsum was added to the mix, the total heat after 48 h declined in all cases (calorimetric curves in Figs 3 and 4). Nonetheless, more heat per gram of Portland cement was released by the samples with gypsum.

Conclusions

The conclusions that may be drawn from the experiments conducted with two types of Portland cement with very different mineralogical compositions, mixed with silica fume and gypsum, are as follows:

- Silica fume, which exhibited pozzolanic activity at 48 h, stimulated the hydration reactions in the PC fractions with which it was mixed, both:
  - directly: 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
  - indirectly: its chemical properties favour very significant pozzolanic activity at early stages.

This effect was so intense that in some cases it could be compared to a synergistic calorific effect. For this reason, when SF is added to cement to be used 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, the risk of cracking, among others.

- Whilst the addition of gypsum retarded and attenuated the hydration reactions in all cases (with a smaller amount of total heat after 48 h), it also generated greater heat of hydration per gram of Portland cement than when no gypsum was added.
- The differences in the amount of heat produced per gram of Portland cement were more significant in mixes with Portland cement with a high C_3A and low C_3S content than in Portland cement with a low C_3A and high C_3S content.

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