INFLUENCE OF *"ALUMINIC"* POZZOLANS, QUARTZ AND GYPSUM ADDITIONS ON PORTLAND CEMENT HYDRATION

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ABSTRACT

Natural and artificial pozzolanic additions (PA) are added to portland cement (PC) or directly to concretes or mortars. This work focuses on the incorporation of two *aluminic* pozzolanic additions (plain metakaolin, M, and metakaolin doped with quartz, 50% by weight, MQ) to two PCs with very different mineral composition, in order to determine the effects and interactions they produce in the hydration reactions of portland cement. Ground quartz, Q, (non PA), with very high α-SiO_2 content, was a lso needed as standard for both. The main analytical techniques used for this study have been: conduction calorimetry, pozzolanicity (Frattini test) and XRD, while additional determined parameters were: water demand for normal consistency, setting times, volume stabilities and mechanical strengths. The results obtained showed the influence of physical state (more or less c rystalline), chemical comp osition and morphology of these three mineral additions on hydraulicity and interactions they produce on the rate of heat liberation of both portland cements during hydration reactions relative to their respective mineralogy. On the other hand, the resu lts have also shown that both metakaolins induced stim ulation of the hydration reactions due to their very early pozzolanic activities. This induced stimulation of the hydration reactions must be regarded as being by *"indirect way"* for differing it to the induced stimulation by *"direct way"* or *"through way"*, which is mainly due to the initial superficial adsorbed of the quartz particles (without pozzolanic activity, as lo gical) or of the own pozzolan particles. Thus and as a result of the induced stimulation by *"direct"* and/or *"indirect way"* mainly, the releas ed hydration heat amount can be regarded as being comparable to the one of ***Synergistic Calorific Effect , SCE***. Likewise, the results have also s hown that the effects originated by the *aluminic* PA on the calorimetry of PCs are strongly influenced by the mineralogical composition of the PCs and by the greater or lesser *aluminic* character of the PA. Furthermore, it has also been demonstrated that the pozzolanic activity of both metakaolins, due to their respective reactive a lumina, $Al_2O_3^r$, content, is at least at very early ages, more ***specific*** than ***generic*** for a greater hydration reaction of the C_3A of PCs, and more so, when 7.0% SO_3 was added. By contrast, of the C_3S is not, but ***unspecific***, or perhaps more precisely, ***insufficiently specific*** for C_3S hydration . Finally, the excess of gypsum added (= 7.0% SO_3) led to a steady decrease in the hydra tion heat released, despite the simultaneous produced stimulation of the hydration reactions per gram of PC, as well as a steady decrease in the volume stabilities of the blended cements studied; nonetheless this, some would be able to be catalogued as expansive hydraulic cements because this excess of gypsum was not found to behave aggressively but rather as ***"setting regulator"***.

Key words: *Calorimetry, portland cement, m etakaolin, quartz, gypsum, pozzolanicity, reactive alumina, XRD, synergy, setting regulator.*

1. Introduction

Cement studies range from the individual analysis of each of the co mponent phases (Portland clinker [1,2]) to research into highl y complex systems with all variables, including mineral additions. Nowadays, different types of mineral additions are added to portland clinker during the milling process or directly to cement. Thus, the study of mineral pozzolanic additions has also devel oped from the analysis of discrete systems [3 -5]. These include: hydraulically active mineral admixtures (pozzolanic and autopozzolanic), hydraulically inactive ones (lacking in pozzolanic activity). Reactivity of pozzolanic additions is strongly associate d with the vitreous and/or amorphous condition of their structure [6, 7]. These can also be d ifferentiated in relation to their *"silicic"* [8-15] or *"aluminic"* [12-24] character, irrespective of whether they were *"siliceous"* or *"siliceous and aluminous"* poz zolans [25].

According to previous researches of Talero, Mejí a, Ma rtín-L. and Rahhal [9 -24], *"aluminic"* pozzolanic additions decrease (in some cases very quickly) the sulphatic resistance of the portland cement with which they are blended, even when the P C used is an SRPC [8,9] ; nonetheless, in absence of sulphates they raise mechan ical strengths, especially at earlier ages [16]. In contrast, they impede or, a t least, hinder chloride attack to steel reinforcements, first chemically and later physically [10][14,15][17]; it is due to that the molecular volume of Friedel´s salt originate is of similar order of magnitude than the molecular volume of calcium aluminates hydrates of OPC, that is to say, it is not expansive, therefore, it is filling -in porous and m icroporous. In the best case, these characterizations take 28 days [9][15,16][18 -24], whereas the same results can be obtained by conduction calorimetry in 48 hours [12].

Totally crystalline mineral additions only participate as fillers through the physical-dilution of PC. However, in a study in which a non hydraulic filler (ru tile, TiO_2) was incorporated individually to the main cement components this was found to increase the hydration rate of each of them [26]. The same tendency was also observed in mechanical strength of mortars with incorporation of non hydraulic fillers of different origin (limestone, granite and siliceous),where increase in resistance was at tributed to the action of filler particles as nucleation sites for the calcium hydroxide cryst als [27]. Experiments to date have not determined yet the different behaviours resulting from the use of portland cements with different mineralogical compositions, and mineral additions with variable reactive alumina, $Al_2O_3^{r-}$ (tetra- or penta -coordinated alumina [28]), contents. With the aim of acquiring this data, the present work stud ies the influence of the $Al_2O_3^{r-}$ contents of pozzolanic mineral additions on the hydration of portland cements with extreme mineralogical compositions.

2. Objectives

In this work, the effect produced by *aluminic* pozzolanic additions, with and without excess of gypsum (= 7.0%), on the rate of hydration of portland ce ments with very different mineralogical composition is analyzed.

3. Material and methods

The following cementing materials were selec ted for the experiment: two portland cements, one –PC1– with a high C_3A(%) content and the other –PC2– with a minimum C_3A content ($\approx 0\%$); three mineral additions, two pozzolanic, a high purity metakaolin M ($\geq 95.0\%$; total SiO_2 and Al_2O_3 contents, 58% and 42%, respectively), with 48% reactive silica content [29] and 29% reactive alumina content [8] and a metakaolin doped with quartz ($\approx 50\%$ by weight; total SiO_2 and Al_2O_3 contents, 74 % and 23%, respectively), MQ, with 38% reactive sili ca content [29] and 15% reactive alumina content [8], and a non -pozzolanic or crystalline: ground crystalline quartz, Q, with very high $\alpha\text{-}SiO_2$ content (ground siliceous sand from Ottawa -Illinois-USA origin; total SiO_2 content, 99.9%). The m etakaolins (with and without $\approx 50\%$ quartz) were prepared by calcination at 750 °C, being its granular composition in accordance with ASTM C 595M -95 standard [30], amount retained when wet -sieved on No.325 (45 µm) sieve, max.= 20%) ; the granular composition of the ground cry stalline quartz, Q, as well. Natural stone gypsum (with a high $CaSO_{4.2}H_2O$ content) whose particle size composition conformed to standard ASTM C 452 -68 [21] was used throughout. Distilled water was used as mixing water in all cases.

The potential compositi ons of the port land cements according to the Bogue´s formulae, are: 51% C_3S, 16% C_2S, 14% C_3A and 5% C_4AF, for PC1 (its Na_2O(%) and K_2O(%) contents are 0.90% and 0.52%, respectively; BSS, 319 m^2/Kg; density, 3.08), and 79% C_3S, 2% C_2S, 0% C_3A and 10% C_4AF, for PC2 (its Na_2O(%) and K_2O(%) contents are 0.43% and 0.20%, respectively; BSS, 301 m^2/Kg; density, 3.21). The differences in chemical and mineralogical compositions between both por tland cements are also partly reflected in their d ifferent density, whil e their fineness is comparable.

Figures 1a and 1b show DRX patterns of mineral additions, in which a more or less diffuse band [7], reflecting the primarily amorphous nature of the M (density, 2 .52) and MQ (density, 2.55) pozzolanic additions, can be obse rved. Figure 1c shows the absence of a diffuse band and in its place well defined peaks of the high crystalline Q (density, 2.70) . In addition, their densities are much lower than the densities of both PCs.

First of all, a total of six blended cements wit h ratios 60%/40% (= 60/40) (PC - n°/Mineral Addition, by weight) were prepared with both portland cements –PC1 or PC2– and the three mineral additions –M, MQ or Q– in the absence of excess of gypsum or with sufficient amounts to bring the to tal SO_3 co ntent to 7.0%.

Secondly, all these blended cements were analyzed by the Frattini test [31] in order to confirm or not, chemically, their pozzolanic characteristics at 2 days o ld (Table 1 and Fig. 2). There is pozzolanic activity when the calcium hydroxide concen tration in the sample solution studied is below the s olubility isothe rm.

Thirdly, evolution of the rate of heat liberation was measured by conduction calorimetry for cement pastes (Fig. 3 a -d). The base line temperature for the measurements was 25°C and t he water/binder (w/b) ratio to prepare all blended cement pastes was 0.5 by weight. Data records were completed for the first 48 hours of hydration. The total heat produced at this age was obtained from the integral under the heat liberation curve versus t ime (Figs. 4 and 5), it is worthy of notice that this

methodology has been accepted to study the hydration process of p lain and blended portland cements around the world [1][32].

Afterwards, X -ray diffraction of the cement pastes was conducted in order to confirm evolution of the hydration reactions during the first 48 hours (semiquantita tive or comparative analysis only), at specific times derived from the calorimetric curves. For blended cements with PC1: first trough, second trough (between the second a nd the third peak) and the third trough (at the end of the calorimetry test); and f or blended cements with PC2: first trough and second trough (at the end of the calorimetry test) (Table 2; **CH:** Calcium hydroxide; **1st m:** first minimu ; **2nd m:** second minimum; **3rd m:** third minimum; **A:** Absence; **P:** Presence; ↑**:** increase; ↓**:** decrease; **=:** unchanging.).

Lastly, a series of pa ste parameters were determined, namely the water/binder ratio (w/b, by weight) 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 rat ios, specifically 80%/20% (= 80/20) and 70%/30% (= 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.

4. Results and Discussion

Table 1 shows the [OH⁻] and [CaO] at 2 days old and how blended cements with both metakaolin s fulfilled the pozzolanicity test or Frattini test with both portland cements. Quartz does not present pozzolanic activity with either of the t wo portland cements, as logical, even though a stimulation effect on hydration reactions was observed. This stim ulation effect on hydration reactions of the PC fraction is promoted by the initially superficial surrounding adsorbed water of the mineral additions particles (from its mixing water) and it must be regarded as being induced by *"direct way"* or *"through way"* or s imply *"direct stimulation"* [33-35] (which is different in mechanism from the induced stimulation by *"indirect way"* [35] whose justification will be given later on). Finally, this type of stimulation by *"direct way"* was precisely verified for the blended cements with Q mineral addition, since the [OH⁻] and [CaO] values at these early ages were higher than those could be estimated mathe matically assuming inertness of the Q (physic and chemically) .

Figure 2 shows the percentages of [CaO] and the [OH⁻] per gram of portland cement for each plain PC. Pairs of blended cements with plain metakaolin, M, were gathered together below and to the left of 100% [CaO] and [OH⁻], respectively. Blended cements with metakaolin and 50% quartz content, MQ, were either bel ow 100% [CaO] or to the left of 100% [OH⁻]. Blended cements with quartz, Q, are found above 100% [CaO] and [OH⁻]. A tendency to remain in solution for calcium hydroxide can be found with an increase in quartz content in the blended cements.

Interpretation of these results reveals that the presence of the mineral additions increases the rate of calcium hydroxide liberation which remains in solution when the mineral addition is crystalline or non -pozzolanic, and in contrast, it combines when the mineral addi tion is pozzolanic, as logical.

Regarding the generation and evolution of calcium hydroxide, CH, they were very low in the blended cement pastes with M and MQ during the first 48 hours, which is concomitant with the strong pozzolanic activity of both additions at 2 days old (Table 1). 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 *directly*.

Figures 3a-b-c-d show the calorimetric curves drawn up during the first 48 hours for plain PC1 and PC2 and for their blends with M and MQ pozzolans, and Q mineral addition. The calorimetric curve of PC1 (Fig. 3a) presents three peaks corresponding to initial hydrolysis, hydration of C_3S and transformation of the AFt phase to the AFm phase, respectively. Blended cements with PC1 also have three peaks in their respective calorimetric curves. The first trough can be observed to have been advanced and attenuated; an advance and significant augmentation of the second and third peaks are observed for all the blended cements with metakaolins M and MQ. These are the expressions of the physical-dilution effect for the silicate phase due to the replacement of PC1 by each metakaolin, M or MQ, and, simultaneously, the **Synergistic Calorific Effect**, **SCE**, produced between the C_3A from PC1 and the $Al_2O_3^{r-}$ from metakaolin. This **SCE**, was verified by XRD monitoring of AFm phase evolution (Table 2). However, these blended cements with PC1 and excess of gypsum (= 7.0% SO_3) (Fig. 3c) have all shown two peaks, the third one did not appear because the excess of gypsum increased the molar relation SO_3/Al_2O_3, therefore, the transformation of AFt into AFm did not take place or did not attain to be manifest. Nonetheless, both phases could be detected by XRD, except for the blended cement with Q mineral addition where AFt phase could be detected only.

The calorimetric curve of PC2 (Fig. 3b) presents two peaks only, corresponding to initial hydrolysis and to hydration of C_3S, respectively. The third peak does not appear because of the absence of C_3A for this portland cement, which denotes absence of the AFt and AFm phases. Blended cements with PC2 also present two peaks in their respective calorimetric curves, and a delay and also attenuation were observed, both for the first trough and second peak. Once again, the intensities of first peak and second trough both decreased with the increase in percentage of replacement, as above-mentioned; these are the expressions of the physical-dilution effect for the silicate phase due to the replacement of PC2 by metakaolin. Nevertheless, however C_3A content of PC2 was practically zero, third peak was clearly insinuated for its pastes with M pozzolan, and especially with MQ pozzolan, between first 10 and 20 hours of hydration. This behavior has corresponded to the *aluminic* phase transformation of both metakaolins, which could also be corroborated by XRD analysis (Table 2). 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.

These blended cements with PC2 and excess of gypsum (= 7.0% SO_3) (Fig. 3d) have all shown two peaks as well. In the case of blended cement with Q mineral addition, AFt phase could be detected only, perhaps due to the stimulation effect of the gypsum over C_4AF phase, although both AFt and AFm phases were detected when M or MQ pozzolans were present instead of Q mineral addition. This points out that

hydration reacti on must have been originated but its released heat amount could not be showed in their respective calorimetric curves.

Figures 4 and 5 show the percentages of total liberated heat at 48 hours per gram of portland cement. It can be observed that nature and   character of the mineral additions and mineralogical composition of portland cements are involved, separately or jointly, in the calorimetric behaviour of their blends. In all cases, the PC hydration reaction was stimulated *directly* and/or *indirectly* inas much as the total heat values were higher than in the respective blended cement, assuming the mineral addition to be inert.   Compared to the respective PCs, similar or greater total heat values were also generated in all cases except in 7.0% SO_3–free PC2/M, for which the value was slightly lower   than recorded for the control sample. The reason is given in the second part   of the following paragraph.

Thence, generally speaking, Portland cement hydration was stimulated in all the blended cements and this was m ore pronounced in blends with PC1 than in blends with PC2. Also, for metakaolins, this stimulation increases w ith their respective reactive alumina, $A_2O_3^{r-}$, content (its coincidence with their respective total alumina, $Al_2O_3\%$, content is circumstantial onl y). This behaviour of both metakaolins proves once again that their pozzolanic activity due to their respective reactive alumina, $Al_2O_3^{r-}$, content, is at least at very early ages, more *specific* than *generic* for a greater hydration reaction of the C_3A –particularly with and also without 7.0% SO_3–, than of the C_3S. This stimulation type to the hydration reactions has been termed "by *indirect way"* this time, for differing it to the induced stimulation by *"direct way"* which has been justified above, despite the fact that the direct proportionality (Figs. 4 and 5) was lesser than what should have been expected. It was due to that w/b ratio was always co nstant and equal to 0.5 for all the studied cements. In proof whereof, the answer to the very interesting questio n –Why the best results are obtained with MQ pozzolan but not with M pozzolan, when the PC2 is present? – would be the reason and this ans wer is the following: at these very early ages and for both blended cements with PC2 (0% C_3A), w/b ratio is always 0.5 when M pozzolan is present, but when   MQ pozzolan is present, its effective w/b ratio is really greater than 0.5 and lesser than 0.84 for the pozzo lanic activity of its ≈ 50% of M (pozzolan), because its ≈ 50% Q is non -pozzolan, and as a consequence, ≈ 50% Q can stimulate by *"direct way"* only, while its ≈ 50% M allows. However, when PC1 is present (14% C_3A) is not applicable this logical behavioral hypothesis because the hydration reactions of its high $C_3A\%$ content, 14% (which is totally contrary or opposite to the 0% C_3A content of PC2), must also be taken into account but for a contrary or opposite as well, final result, because of its stimulation b y *"indirect way"* and the un derlying **SCE** originated (Figs. 4 and 5).

By contrast, "*indirect*" stimulation of hydration at very early a ges must be seen to be **unspecific**, or perhaps more precisely, **insufficiently specific** for C_3S hy dration, inasmuch as the sp ecific "*indirect*" stimulation of its hydration declines.

In summary, the stimulation by *indirect way* to the PC1, or iginated by both pozzolanic additions, M and MQ, increases with their respective $Al_2O_3^{r-}$ content; but in contrast, to the PC2 decreases. The same tendency is observed when excess of gypsum (= 7.0% SO_3) was present, although still with greater stimulation by *indirect way* to the PC1. All this is due to the **Synergistic Calorific Effect** , **SCE**, between C_3A of PC1 and the $Al_2O_3^{r-}$ of each pozzolan, M and MQ. With respect to the mineralogical composition

of the portland cements, it can be stated that the use of portland cements with high C_3A content and low C_3S content, in general, produced advances and increases in the hydration reactions (Fig. 3a) whi le use of portland cements with low C_3A content a nd high C_3S content caused delays and attenuations (Fig. 3b). Thus, the differences in the amount of hydration heat produced per gram of portland cement were more significant in mixes with PC1 than with PC2.

Regarding technological parameters, differences obtanied between plain PCs and blended cements for their setting times and w/b ratios (Table 3) could be explained with detail as a function of the presented tendencies in the calorimetric curves and all ef fects cited above. On the other hand, it must also be remarked that none very anomalous setting process has been given risen to blended cements, even though some having excess of gypsum (= 7.0% SO_3). Flexural and compressive strength values at 28 days old (Table 5), point out that s timulations of the hydration reactions referred to both PCs maintain balanced the effects of physical -dilution of both PCs to later ages: this behavior has been able to demonstrated because the experimental values have been higher than those estimated mathematically assuming inertness of the mineral add itions studied en this work: M and MQ, both pozzolans, and Q, crystalline quartz. From volume stability results (Table 4), it can be stated that an expansion is produced with MQ, in all ratios PC -nº/Mineral Addition. Here once again, the difference in mineralogical composition of both PCs is clearly manifested. In detail, while MQ produces a steady increase of expansion with the percentage of replacement in PC2, in turn, when they ar e mixed with PC1, the expansion decreases from 21 days age; but before 21 days age, it increases as well. This phenomenon is related with the competitive role of both C_3A and $Al_2O_3^{r-}$ in the formation of different types of e ttringite, whose explanation has been object of several previous works [18 -24]. Despite of that, an important consideration has been found worthy to be stated, th is is 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 hydrat ion heat to minimize undesirable consequences. Because the released hydration heat amount can be comparable to the one of the ***Synergistic Calorific Effect , SCE***. Nevertheless that which, expansive hydraulic cements [36] wit h op timum excess of gypsum [37] can be manufactured with *aluminic* pozzolans due to they keep important properties: high early mechanical strengths and significant expansion, among others. The reason is that the excess of gypsum added (= 7.0% SO_3) has not b een found to behave aggressively but rather as ***"setting regulator"*** for these blended cements with M or MQ pozzolan, only, because their setting times and mechanical strengths were therefore, similar order of magnitude to the pattern observed in any PC (log ically, ett -rf and ett -lf [9][18-24] were involved in this resulting beneficial behavior). In contrast, such excess of gypsum (= 7. 0% SO_3) behaved aggressively towards PC2 but above all towards PC1 and their blended cements with Q addition specially, becau se their respective setting times were always greater than their respective cements without 7.0% SO_3 (logically, ett -lf was only involved in these other resulting adverse behaviors).

5. Conclusions

From the experiments carried out here with two PCs whose m ineralogical compositions have been very different, three mineral additions, M and MQ, both

metakaolins and artificial pozzolans, and Q, crystalline quartz and excess of gypsum (= 7.0% SO_3), it can be concluded that:

1. Initial break through, evolution and development of the heat liberation curves of the blended cements were strongly affected by the mineralogical characteristics of their portland cements.

2. Q mineral addition (ground crystalline quartz or non pozzolanic addition), gives rise to stimulation of the hydration reactions to PC fraction in the ir blended cements. It is promoted by the initially superficial adsorbed water of the Q mineral additions particles. This stimulation effect must be regarded as being induced by *"direct way"* or *"through way"* or simply *"direct stimulation"* and it is accompanied by increase in CH and in grea ter originated hydration heat per gram of PC. As a result, mineral addition Q cannot be regarded to be comple tely inert, physically speaking, at least up to the age of two days . A fuller discussion and justification of these observations can be found in references [12] and [34].

3. The pozzolanic and hydraulic activities of both *"aluminic"* pozzolans, M or MQ, are strongly affected by the amorphous physical state, and more concrete ly, by their respective $Al_2O_3^{r-}$ content. Thus, M and MQ show po zzolanic activity at 48 hours which induce, in turn, stimulation of the hydration reactions by *"indirect way"*, mainly. This stimulation effect must be regarded as being induced by *"indirect way "* due to the prior and very significant poz zolanic activity from $Al_2O_3^{r-}$ origin, mainly, of both pozzolans at very early a ges, and it is accompanied by decrease in CH and increase in hydration heat originated per gram of PC.

4. Such prior po zzolanic activity is observed in bo th M and MQ, due primarily to their respective $Al_2O_3^{r-}$ content, 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. Converse ly, 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 section 7. **Final Question** .

5. When metakao lin is added to OPC to make high performance bulk concrete, account must be taken of its **direct** and **indirect** effect of stimulation on the generation of hydration heat to minimize unde sirable consequences. This released hydration heat amount can be comparab le to the one of **Synergistic Calorific Effect**, **SCE**. Notwithstanding this, expansive hydraulic cements [36] can be manufactured with *aluminic* pozzolans due to their significant expansion with optimum excess of gypsum [37].

6. An excess of gypsum (= 7.0% SO_3) in blended cements retarded and attenuated the hydration reactions in all cases (with a smaller amount of total heat after 48 hours), it also generated greater hydration heat per gram of Port land cement than when no excess of gypsum was added. Moreover, it caused much more significant stimulation of the hydration reactions to the PC1, with high C_3A and low C_3S content, than to the PC2, with low C_3A and high C_3S content. This significant stimulation, but above all, their lower volume stability due to their significant expansions, a llow some of these blended cements with M or MQ pozzolan, met the criteria to be once again catalogued as expansive hydraulic cements (whose use is specific), and for that same reason precisely, caution is also needed when they are used. On the other hand, this excess of gypsum was not found to behave aggressively but rather as *"setting regulator"* for blended

cements with M or MQ pozzolans, because their setting times and mechanical strengths were therefore, of similar order of magni tude to the pattern observed in any PC. In contrast, for the rest of cements tested, PC2 but above all PC1 and their blended cements with Q addition specially, such excess of gypsum behaved aggressively.

6. Final Question

Pursuant to Conclusion 4, the foll owing Final Question can be raised: Why is pozzolanic activity observed to be high two -days 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 y et, is it ***anti-specific*** or ***contra-specific*** or ***counter-specific***, or perhaps still more precisely, might it actually ***spec ifically hinder*** C_3A hydration, such as in the case of sulphate attack? The answer is to be found in references [9][11] and [38] and also in subsequent papers about sulphate attack which will be published in the very near future [39].

7. Acknowledgments

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Table 1: Pozzolanicity (Frattini test) at 48 hours. Results

Cements without 7.0% SO₃	48 hours mM/l [OH⁻]	[CaO]	Cements with 7.0% SO₃	48 hours mM/l [OH⁻]	[CaO]
PC1	72.5	7.6	PC1	51.0	22.8
PC1/M 60/40	**31.0**	**1.0**	**PC1/M 60/40**	**39.5**	**3.0**
PC1/MQ 60/40	**35.0**	**2.2**	**PC1/MQ 60/40**	**44.5**	**5.5**
PC1/Q 60/40	57.0	11.6	PC1/Q 60/40	46.0	25.7
PC2	42.5	21.5	PC2	42.5	31.1
PC2/M 60/40	**25.0**	**9.3**	**PC2/M 60/40**	**11.0**	**3.9**
PC2/MQ 60/40	**28.0**	**11.2**	**PC2/MQ 60/40**	**25.5**	**18.5**
PC2/Q 60/40	43.5	22.3	PC2/Q 60/40	41.5	32.2
NOTE: Points of intersection below the solubility isotherm appear in **bold**					

Table 2: DRX analysis: Results (relative intensity)

Cements without 7.0% SO₃	CH 1ˢᵗ m	2ⁿᵈ m	3ʳᵈ m	AFt Phase 1ˢᵗ m	2ⁿᵈ m	3ʳᵈ m	AFm Phase 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% SO₃	CH 1ˢᵗ m	2ⁿᵈ m	3ʳᵈ m	AFt Phase 1ˢᵗ m	2ⁿᵈ m	3ʳᵈ m	AFm Phase 1ˢᵗ m	2ⁿᵈ m	3ʳᵈ m
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	-

Table 3: Times of setting and water/binde r ratios

Cements without 7.0% SO$_3$	Setting Times (h:m) Initial	Final	Time	w/b (by weight)
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$_3$	Setting Times (h:m) Initial	Final	Time	w/b (by weight)
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 60/4 0	5:50	7:50	2:00	0.39
PC2/Q 60/40	5:40	8:25	2:45	0.30

Table 5: Mechanical Strengths at 28 days

Cements	Mechanical Strengths [MPa] F lexural	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

Table 4: Volume stabilities

CEMENTS			LE CHATELIER NEEDLES (mm)							
				In water (days)						
			Hot 100 ºC	Cold (21 ± 2 ºC)						
			7	7	14	21	28	60	90	120
PC1/MQ	3.50% SO₃	100/00	0.7	1.70	1.70	1.70	1.70	1.70	1.70	1.70
	7.00% SO₃	80/20	0.5	3.33	5.65	7.20	9.35	12.00	12.15	12.15
		70/30	0.5	5.15	6.00	6.33	6.65	6.71	6.75	7.75
		60/40	0.5	5.75	5.75	5.75	5.75	5.75	5.75	5.75
PC2/MQ	2.34% SO₃	100/00	1.0	0.30	0.30	0.30	0.30	0.30	0.30	0.30
	7.00% SO₃	80/20	0.5	2.00	3.50	3.55	3.60	3.90	4.00	4.50
		70/30	0.0	3.20	3.70	3.80	4.00	4.60	4.60	4.70
		60/40	0.5	5.00	5.00	5.00	5.00	5.00	5.00	5.00

NOTE: Blended cements with M pozzolan and 7.0% SO$_3$ reached slightly greater values.
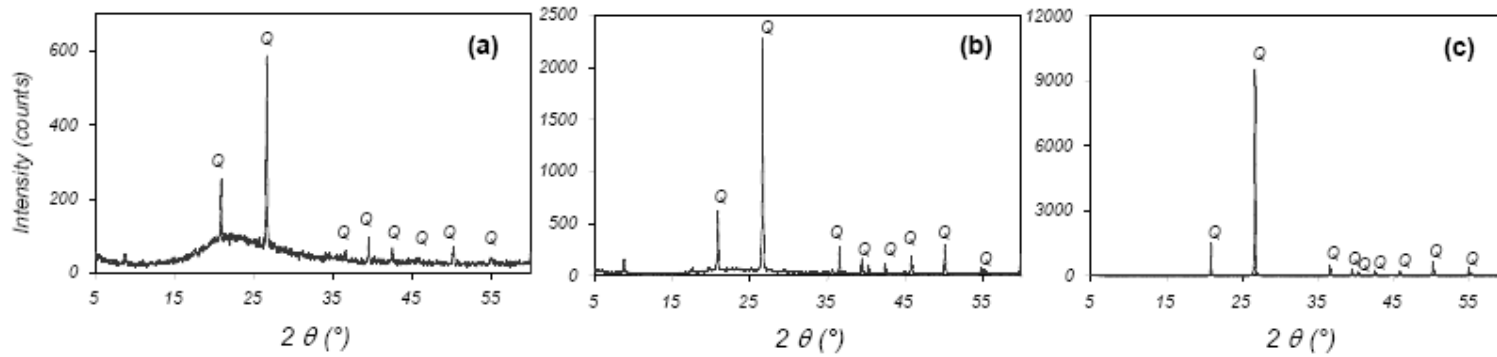
Fig. 1: XRD patterns. (a) M pozzolan, (b) MQ pozzolan, (c) Q mineral addition
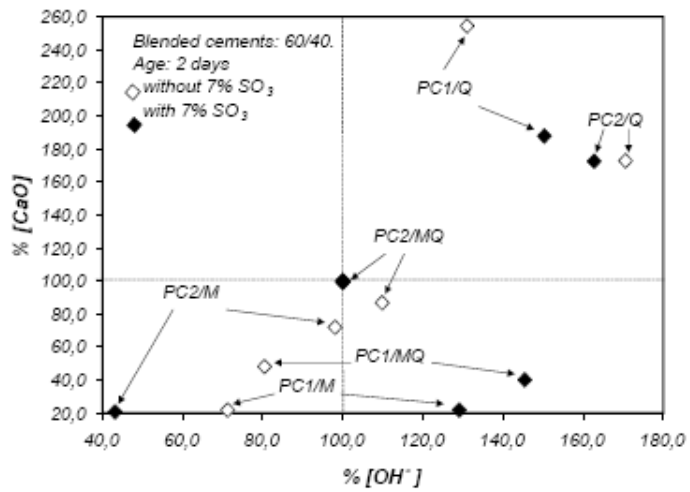

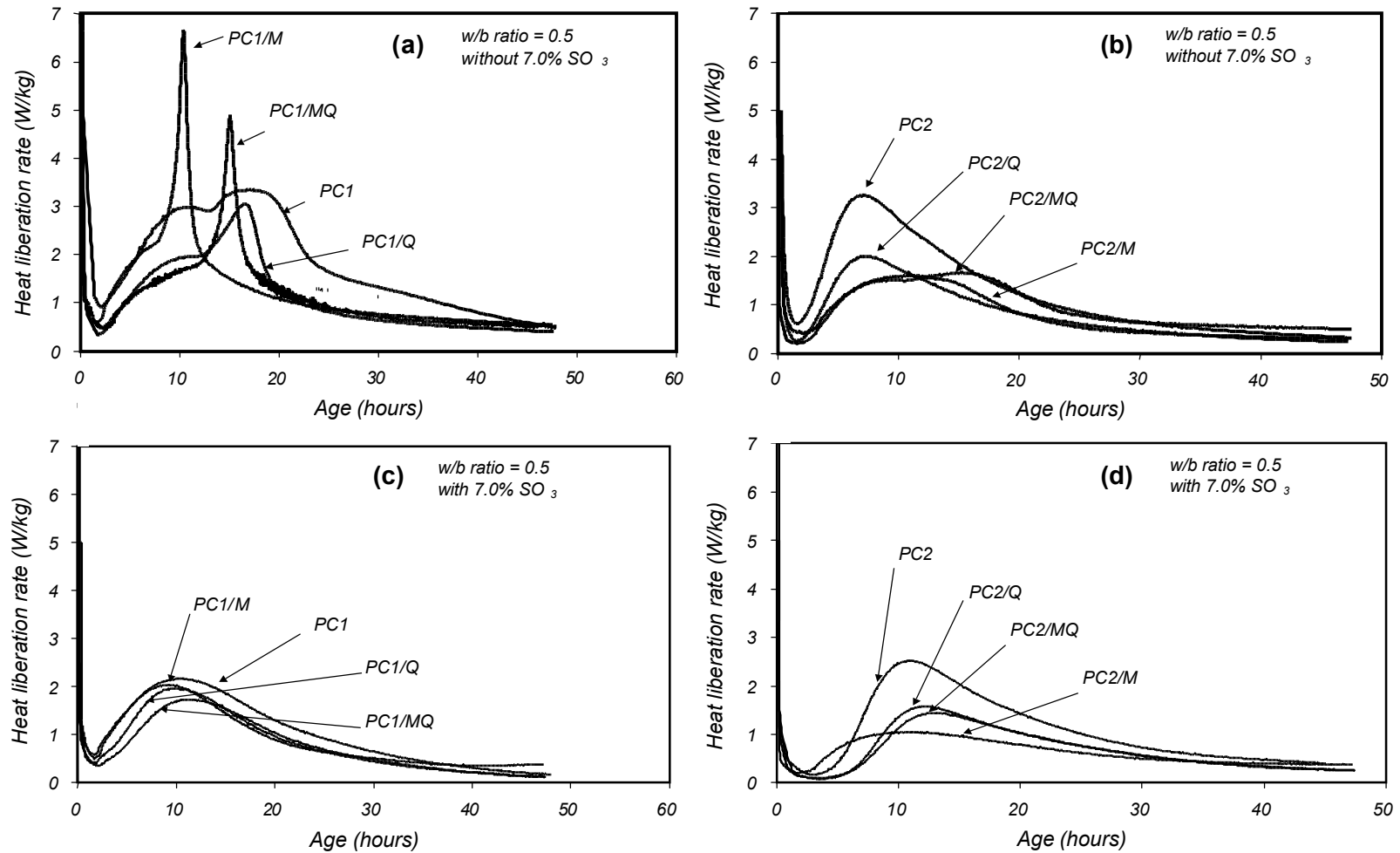**Fig. 2: Blended cements. % [OH⁻] and % [CaO] per gram of PC**

Fig. 3: Calorimetric curves. (a) PC1 without 7.0% SO₃, (b) PC2 without .0% SO₃, (c) PC1 with 7.0% SO₃, (d) PC2 with 7.0% SO₃
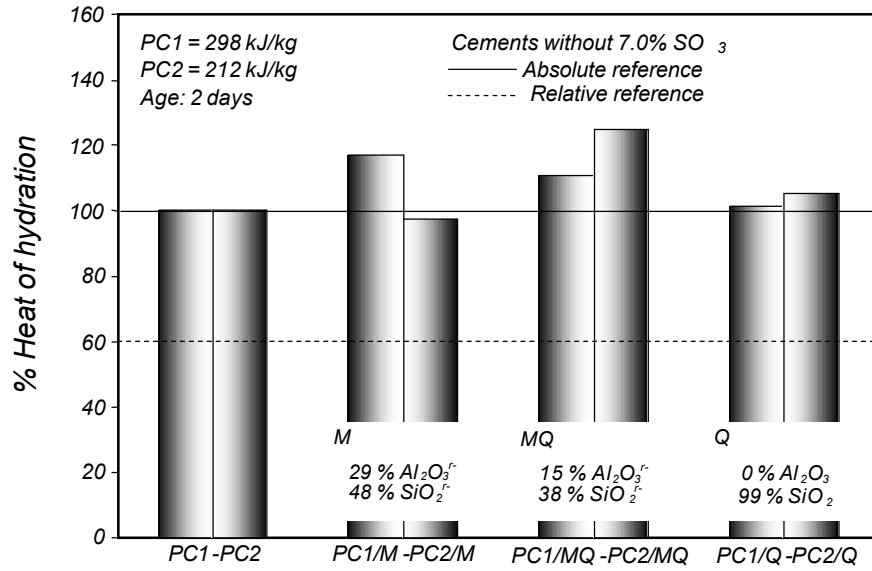
Fig. 4: % total heat released per gram of PC without 7.0% SO₃

Chart 1 annotations:
- PC1 = 298 kJ/kg
- PC2 = 212 kJ/kg
- Age: 2 days
- Cements without 7.0% SO₃
- Absolute reference
- Relative reference
- Y-axis: % Heat of hydration
- M: 29 % Al₂O₃ʳ⁻, 48 % SiO₂ʳ⁻
- MQ: 15 % Al₂O₃ʳ⁻, 38 % SiO₂ʳ⁻
- Q: 0 % Al₂O₃, 99 % SiO₂
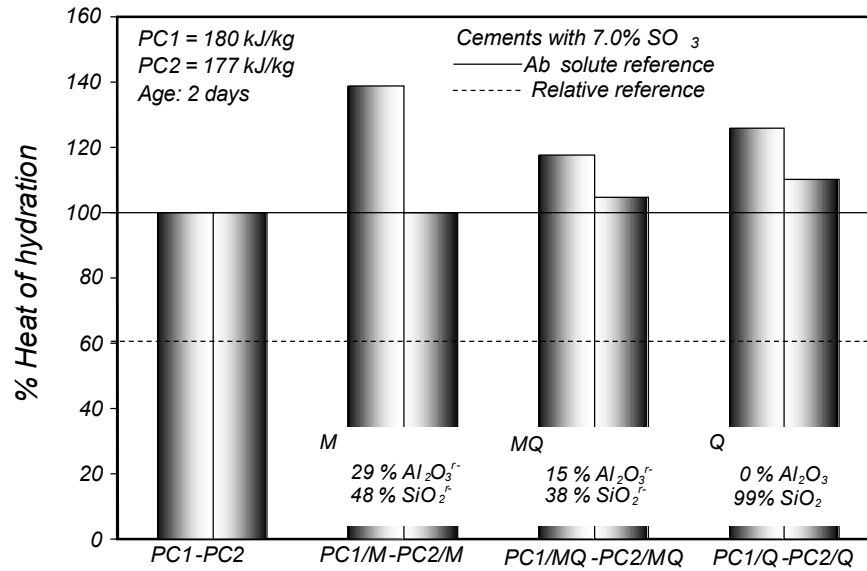- X-axis: PC1 -PC2, PC1/M -PC2/M, PC1/MQ -PC2/MQ, PC1/Q -PC2/Q

Fig. 5: % total heat released per gram of PC with 7.0% SO₃

Chart 2 annotations:
- PC1 = 180 kJ/kg
- PC2 = 177 kJ/kg
- Age: 2 days
- Cements with 7.0% SO₃
- Absolute reference
- Relative reference
- Y-axis: % Heat of hydration
- M: 29 % Al₂O₃ʳ⁻, 48 % SiO₂ʳ⁻
- MQ: 15 % Al₂O₃ʳ⁻, 38 % SiO₂ʳ⁻
- Q: 0 % Al₂O₃, 99% SiO₂
- X-axis: PC1 -PC2, PC1/M -PC2/M, PC1/MQ -PC2/MQ, PC1/Q -PC2/Q