



Very early age detection of ettringite from pozzolan origin



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HIGHLIGHTS

- Q filler and M pozzolan effect on Portland cement (PC) hydration at very early ages.
- Direct, non-direct and indirect stimulations of the PC hydration by Q and M.
- Chemical interactions: Generic of Q with any PC and specific of M with C₃A of PC.
- Expansive Synergic Effect of ettringite from MC waste and from OPC has been originated.

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ABSTRACT

The mineralogical composition of special purpose Portland cements must conform to certain requirements. Sulphate-resistant Portland cements, for instance, the tricalcium aluminate (C₃A) and tetracalcium aluminoferrite (C₄AF) phase's contents must be very low to minimize the consequences of the hydration of large amounts of sulphates and the wide fluctuations in volume that would entail. At the same time, for economic, technical and environmental reasons, primarily pozzolanic additions, some of which are *aluminic* in chemical character, are included in Portland cements. When thermally activated clays such as metakaolin (*aluminic* pozzolan) are added to Portland cements with low (to nil) C₃A content, an *Aft* phase of pozzolan origin may also form. The present study corroborated previous reports of the formation, but at very early ages (48 h), of such an *Aft* phase of pozzolan origin, mainly, in a Portland cement blend containing minimal C₃A content, an *aluminic* pozzolan in chemical character (*metakaolin*, M pozzolan) and excess gypsum, 15.05% (=7.0% SO₃); and if C₃A content in OPC is high, the *Aft* phase originated is of pozzolan origin as well, and in addition, of such C₃A content, generating so greater or lesser *Expansive Synergic Effect*, ESE, according to the greater or lesser pozzolanic activity amount originated previously by M pozzolan in this case, and for this reason, being the ettringite from M pozzolan its chief *direct* and *indirect* cause. On the other hand, it also proved that such excess gypsum acted as a *setting regulator* in blended cements with metakaolin and a *retarder* in all the other cements tested, whether they were pure Portland cements or blends containing a crystalline mineral addition, Q, and also some blended cements with metakaolin can be regarded as being "*hydraulic expansive cements*" according to ASTM C 845-90 Standard.

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1. Introduction

A series of studies on the interaction between pozzolanic additions and Portland cement in sulphate media have shown that different origins determine different behaviour, with some additions protecting the cement against aggressive sulphate attack [1–3] and others heightening the effects of such attack [4–9]. In the latter case, the origin of the decay lay in the large volume of tricalcium aluminate phase (C₃A) and tetracalcium aluminoferrite phase (C₄AF) hydration products generated when Portland cement

reacts with gypsum. These may include ettringite or *Aft* and/or *AFm* (hydrated calcium monosulphoaluminate) deriving from C₃A [10], C₄AF [10], or from the reactive alumina, Al₂O₃⁻, whose physical state may be vitreous and/or amorphous, or more exactly, tetra- or penta-coordinated aluminium, recently confirmed to be a meta-stable near χ -alumina [11]) present in pozzolans with *aluminic* chemical character [4–9].

In pozzolanic additions, this variable response to sulphates attack is largely due to the chemical character of the addition. Distinctly pozzolanic additions *silicic* in character chemical, for instance, mitigate the effects of sulphates attack [1–3], due to their high reactive silica, SiO₂⁻, content (diatomites, silica fume, nanosilica, opaline stones, etc.); while pozzolanic additions with *aluminic* chemical character intensify their effects due to the presence of its

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Al_2O_3^- [4–9] because their contents are significant (metakaolins, activated clays, burnt shale, calcined paper sludge, etc.). The formation of ettringite in a Portland cement with pozzolanic additions depends not only on the characteristics of the Portland cement, but on the chemical character of the pozzolanic addition [1–9]. Ettringite formation from C_3A present in PC was verified by previous papers [4–9]; likewise, it was also shown by XRD analysis at 7 days [4–9], that pozzolanic additions form ettringite with exposure to the same sulphate bearing solutions [4–9]. These minerals were termed “**rapid forming**” (“**ett-rf**”) (formed from the Al_2O_3^- present in pozzolans) and “**slow forming**” (“**ett-lf**”) (formed from the C_3A present in OPC) –ettringite, respectively. Moreover, around 10-fold less **ett-rf** than **ett-lf** was observed to form [4–9]. Quantitatively speaking, their co-precipitation in a common plaster-bearing solution is always more *synergic* than *additive* [8,9]. That can be attributed to the fact that in the presence of *aluminic* pozzolans such as metakaolin, more of the anhydrous C_3A in the OPC is hydrated quicker and earlier than in its absence because the activity induced by their Al_2O_3^- phase is more *specific* than *generic* [9]. Finally, the **ett-rf** induced by the Al_2O_3^- present in *aluminic* pozzolans is the *chief direct and indirect* cause of the more or less intense **Expansive Synergic Effect, ESE**, jointly generated with the ettringite formed from the C_3A in OPC [9], due to its very *specific* pozzolanic activity in such gypsum media.

No consensus has been reached among researchers about the effect of *aluminic* pozzolans on the chemical kinetics, morphology and particle size of ettringite, its co-precipitation with ettringite forming from the C_3A in PC or the respective technical consequences. Nonetheless, as the present findings show, a Portland cement with low or nil C_3A (%) content blended with an *aluminic* pozzolan (metakaolin), gypsum and water, can form pozzolan-induced ettringite or *ett-rf* at very early ages (at 48 h: 5 days earlier than in prior studies [4–8]), irrespective of its high or low C_3A content.

2. Objective

The present study aimed to corroborate previous findings [8,9] on the presence and effect of ettringite from pozzolan origin at very early ages (48 h).

3. Materials and methodology

Two mineral additions were selected for this study. One, metakaolin (pozzolan *M*), is a pozzolan with a 29% Al_2O_3^- content [12] a 48% SiO_2^- content [13], a density of 2.52 and a Blaine specific surface, BSS, of 333 m^2/kg . Previous studies [4–9,14–16] showed pozzolan *M* to be an *aluminic* phase, exhibiting very high pozzolanic and hydraulic activity when mixed with portlandite either in the presence or absence of excess gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (=7.0% SO_3) (the results of such substantial and early pozzolanic and hydraulic activities can be found in references [4–9,11,14–16]). The second, completely crystalline non-pozzolanic [14,15,17] mineral addition, quartz (*Q*), used as a control, had an SiO_2 content of over 99%, 0% Al_2O_3 , a density of 2.80 and a BSS of 395 m^2/kg .

The Portland cements blended with the above mineral additions were: *PC1*, a cement with a high (14%) C_3A content, as well as, 51% C_3S , 16.5% C_2S and 5.5% C_4AF ; a density of 3.08 and a BSS of 319 m^2/kg ; and a low \approx 0% C_3A content cement, *PC2*, with 79.5% C_3S , 2.5% C_2S and 10% C_4AF , a density of 3.21 and a BSS of 329 m^2/kg .

The 20% and 40% replacement ratios used are shown here as 80/20 and 60/40, respectively, while the two pure Portland cements used as a control, are represented as 100/00. The behaviour of all the resulting cements was analysed with and without excess gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, up to an SO_3 content of 7.0%.

The 48h materials were analysed and tested for pozzolanicity (Frattini test) [18], mechanical strength [19] (for pozzolan *M* only), setting times [20] and heat of hydration (measured on a conduction calorimeter for pastes with a water/binder ratio of 0.5 at a temperature of 25 °C). The new mineralogical compounds generated in *PC1* and *PC2* and their 60/40 blends with *M* and *Q* were identified on a Philips X'pert diffractometer fitted with a $\text{Cu K}\alpha$ 40-kV, 20-mA graphite monochromator.

The Frattini test [18] was also conducted on the 2-, 7- and 28-day plain and blended cements with the pozzolan (*M*) and crystalline (*Q*) additions to determine the existence or otherwise of pozzolanic properties, with and without excess

gypsum (7.0% SO_3) (Tables 1(a) and 1(b)). This test compares the calcium hydroxide concentration in an aqueous solution containing the hydrated sample after a given time (2, 7 and 28 days in this study) to the solubility isotherm of calcium hydroxide in an alkaline solution at 40 °C. Calcium hydroxide concentrations lower than the solubility isotherm are indicative of pozzolanic activity in the sample (=+result).

4. Results and discussion

Tables 1(a) and 1(b) give the 2-day $[\text{OH}^-]$, $[\text{CaO}]$ and pozzolanicity findings for the four pozzolan-PC blends. Quartz, naturally, exhibited no pozzolanic activity with either portland cement, although with its inclusion the hydration rate was observed to rise. Initially, this higher reaction rate in the PC fraction would be due, among others, to:

- mixing water adsorption on the surface of the mineral addition particles, in what may be termed “*direct*” stimulation [17], and
- the electrical charge resulting from mixing itself, but especially from the zeta potential generated as hydration progresses in what may be termed “*non direct*” stimulation [17],

(which not the same as “*indirect*” stimulation [14–16]).

Such *direct* and *non-direct* stimulation was once again observed in the PC/Q blended cements, in which $[\text{OH}^-]$ and $[\text{CaO}]$ were higher than mathematically predicted when *Q* was assumed to be physically and chemically inert in 2-day materials, an assumption that recent research has called into question [17].

Table 2 shows $[\text{CaO}]$ and the $[\text{OH}^-]$ per gram of Portland cement for each plain PC, in per cent. The cements blended with metakaolin only clustered, respectively, below of 100% $[\text{CaO}]$ and $[\text{OH}^-]$, as logical. The PC/Q blended cements, however, located above 100% $[\text{CaO}]$ and $[\text{OH}^-]$, as logical too. The proportion of dissolved calcium hydroxide tended to grow with rising quartz content in the cement blends containing this crystalline mineral addition

These results may be interpreted to mean that more calcium hydroxide is released in the presence of mineral additions and would remain in solution when the addition is crystalline or non-pozzolanic but combine with pozzolanic substances where present.

The very low rate of calcium hydroxide generation in *M*-containing cement pastes during the first 48 h was consistent with the high 2-day pozzolanic activity exhibited by this pozzolan (Tables 1(a) and 1(b)). The amount of CH generated was observed to increase in both portland cements when blended with *Q*, providing further evidence that this mineral *stimulates* hydration reactions *directly*.

Mechanical strength: the pozzolanic activity index for *M* pozzolan, found as described in ASTM standard C 311 [19], was 77.2%, and the water demand was 110.0%. For *Q* mineral addition was not needed, as logical.

Setting times are given in Table 3. As the values listed show, in the *PC1* group of blended cements with and without 7.0% SO_3 , the initial and final setting times were shorter than in the control portland cement, while the contrary was observed for the *PC2* group of blended cements.

The cements blended with crystalline addition *Q*, in turn, behaved uniformly, for while all the setting times lengthened with increasing replacement ratios. Such delays may have been the outcome of the rise in the effective water: cement ratio, which would have made the pastes less resistant to Vicat needle penetration.

The behaviour of the cements blended with *M* pozzolan, differed depending on the type of Portland cement used. With *PC1*, generally speaking, setting time declined, but the *PC2/M* blends containing 7.0% SO_3 , took longer to set. This behaviour can be attributed to the formation of a new chemical compound which, in addition to resisting Vicat needle penetration, may also call for

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