Role of the filler on Portland cement hydration at very early ages: Rheological behaviour of their fresh cement pastes

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H I G H L I G H T S

- The effects of *Q* and *C fillers*, on rheological behaviour of PC at very early ages.
- *Direct* and *non-direct* stimulations of the PC hydration, consequence about plastic viscosity.
- Chemical interaction: *Specific* of Q and C fillers with portlandite and C_3A, respectively.
- Technical consequences in PC-*Q* or *C* pastes: yield stress, shear stress and plastic viscosity.

A B S T R A C T

The rheological behaviour of fresh Portland cement (PC) pastes with different chemical and potential mineralogical compositions was analysed when were blended with crystalline mineral additions (fillers). These two fillers were very different: a siliceous, Q, α-quartz type, and another limestone, C. Trials were conducted during latent hydration at 25 °C. The findings showed that apparent viscosity was higher in the PC with low C_3A and high C_3S content, consequently, the $Na_2O_{eq.}$(%) content of everyone also contributed very significantly. Moreover, it was also observed that the incorporation of each filler affects differently the rheological behaviour of fresh cement pastes. The different influence is due to the different physical and chemical properties of each filler (nature, chemical composition and character and texture intimate of the particles), and also of the type of PC to interact. Finally and at these very early ages, both fillers stimulated the hydration of the PC which they were mixed by *direct* and *non-direct* way, and in the case of C filler by *indirect* way as well, but without any pozzolanic activity. Despite the fact that blended cement P1/Q 60/40 has proved to be a "false positive" in Frattini test.

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1. Introduction

Global warming, one of the symptoms of climate change, is regarded as a serious threat to the environment. Many scientific studies associate climate change with greenhouse gas emissions, of which CO_2 is the primary component. In response to those concerns, the inclusion of crystalline mineral fillers as additions is standard practice in cement manufacture. In this vein:

– in 2005 the authors published an article entitled 'Early hydration of Portland cement with crystalline mineral additions' [1] and

– in 2012 as second entitled 'Role of the filler on Portland cement hydration at early ages' [3].

In retrospect, some of the authors of those papers believe that, inasmuch as both focused on the early-age heat of hydration generated by Portland cement (PC) in the presence of absence of finely ground crystalline mineral additions such as α-quartz (α-SiO_2) or calcite [1] and on the type of physical and chemical interactions between the PC and each type of filler [3], their titles were overly ambitious. Neither actually encompassed all the actually takes place in PC early-age hydration, from the very instant when its particles and the filler particles come into contact with the mixing water.

Conduction calorimetry tests were run on the same two PCs chosen for this study, with or without the two mineral additions mentioned at the replacement ratios specified. The trials were

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begun on fresh paste and terminated after 48 h [1]. The parameters monitored during the tests were absolute and relative total heat released and heat released at significant ages, such as hydration latency [1–5] and a number of other ages. In calorimetric studies of cement pastes, the heat release rate is high during the solution period primarily as a result of initial hydrolysis. Thereafter the rate drops to a minimum constituting the first nadir on the calorimetric curve. This is followed by acceleration of the hydration reactions and mass precipitation of reaction products, primarily CSH gel. The heat release rate at the second peak representing the mass hydration of tricalcium silicate and the third peak, representing the transformation of ettringite into hydrated calcium mono-sulphoaluminate. These parameters were monitored irrespective of the fact that:

- some of the heat of hydration values were released by the fresh paste, i.e., while still in a fluid state;
- other amounts were released in a pseudo-fluid state (after setting had commenced), and
- the rest of the heat, through the end of the 48 h test, was released after the specimens hardened (long after setting had come to an end).

Consequently, further to the titles of the two articles [1,3], one at least should have included information on the fresh paste rheology. Including such findings would have rendered the paper unfit for publication, however, for it would have been too lengthy. That is why the authors wish to publish those findings hereunder.

As shown in the aforementioned studies and other calorimetric research conducted [1–6], the effect of mineral additions the length of the latency period and on the properties of the paste up to that age depends on whether the filler is crystalline [1–4] or otherwise [5], the type of Portland cement and the replacement ratio. Moreover, despite their crystallinity, these mineral additions interact physically and may interact chemically with Portland cement [3]. For those reasons, both prior studies [1,3] determined the type of physical and chemical interaction that took place between the Portland cement and the siliceous and the limestone filler. Whilst an early-age hydration mechanism was also described, the ages addressed were not as early as in this new endeavour: prior to fresh paste setting.

The filler<>Portland cement paste interaction has a heavy impact not only on the heat released in early-age cement [1–6], but also on the rheological behaviour of the resulting fresh paste. One of the major rheological properties is viscosity, of considerable significance for concrete or mortar mixing, shipping, pouring and on-site casting, as well as their workability and consolidation. This parameter is particularly important in self-consolidating or mechanically pumped concrete and mortar.

Viscosity may be assessed with rheometric trials to determine, for instance, shear stress or stress (σ) by varying the rotational speed. Stress also depends on the type of PC, type of mineral addition and replacement ratio, as well as on the temperature, water: cement ratio and the acceleration/deceleration cycles applied. The resulting flow curves provide a measure of fluidity.

In light of those considerations, a number of tests were conducted to analyse the effect of fillers and the type of variables that impact fresh paste viscosity during the latency period, in particular with respect to the timing of rheological behaviour. The findings were also applied to determine the most appropriate type of cycle to be used for each fresh paste. Suitability was defined in terms of the area of the hysteresis loop characteristic of the thixotropic behaviour of fresh pastes [7–10] (the larger the better) and the response observed in the Portland cements with different potential mineralogical compositions [11]. The best results were analysed and the rheological behaviour of the fresh Portland cement pastes

studied after the inclusion of apparently inert (i.e., non-pozzolanic) fillers with variable origin, chemical composition, mineralogy, geology and particle size, shape and intimate texture.

The two types of mineral additions filler type consisted in the excess generated during crushed aggregate grinding. The effect of these fillers on fresh Portland cement paste rheology was ascertained by using two very different mineral additions: one siliceous in nature and *acid* in chemical character, (α-SiO$_2$), Q, and the other calcareous in nature and *basic* in chemical character, C, i.e., with different chemical compositions, types of crystallinity, geochemical origin, nature, chemical character, particle size, shape and intimate texture. Both were ground to approximately cement fineness.

2. Materials and methodology

2.1. Selection of materials and preliminary tests

Two Portland cements (PC) with widely different potential mineralogical compositions were chosen to ensure that the results would be extensive to any type of PC. The first one, denominated PC1 and characterized by its high C$_3$A content, whose mineralogical composition was found to be followed: 51.0% C$_3$S, 16.5% C$_2$S, 14.0% C$_3$A and 5.5% C$_4$AF, a density of 3.08, a Blaine specific surface, BSS, of 319 m^2/kg and a loss on ignition of 1.6% and Na$_2$Oeq. of 1.24% (>0,6%). On the other hand, the second Portland cement, PC2, was selected due to its low C$_3$A(%) and high C$_3$S(%) contents; its detail mineralogical composition was: 79.5% C$_3$S, 2.5% C$_2$S, $\approx$0.0% C$_3$A (<1.0%) and 10.0% C$_4$AF, a density of 3.21, a BSS of 329 m^2/kg and a loss on ignition of 1.1% and Na$_2$Oeq. of 0.56% (<0,6%). Finally, the crystalline mineral additions (i.e. non-pozzolanic) chosen as fillers [12,13] were as follows:

- a quartz one, Q (ground ASTM C 778-92a sand [14]), with a SiO$_2$ content of over 99%, a density of 2.70, a BSS of 395 m^2/kg and a loss on ignition of 0%, being therefore additionally, *siliceous* in nature and *acid* in chemical character; and the other,
- a limestone one, C (ground Spanish limestone routinely used to manufacture cement concretes, and mortars) with a CaCO$_3$ content of over 95%, a density of 2.71, a BSS of 362 m^2/kg and a loss on ignition of 42.5%, being therefore additionally, *calcareous* in nature and *basic* in chemical character.

Both fillers were ground to a size which ≤20% of the material passed through a No. 325 sieve in a wet sieving process (mesh size 45 μm) [15]. Further to laser diffraction test findings (Fig. 1), after grinding, the two fillers exhibited similar fineness. They were also analysed with XRD to verify their crystallinity (Figs. 2 and 3).

Finally and in order to examine the moisture absorption or adsorptivity of both fillers, the equal amounts of ≈1.0 g of the each (C and Q) was separately placed in porcelain vials and then stored in a desiccator (with water distilled at bottom –instead of silica gel– to guarantee the RH ≥ 95% conditions). The experiment was carried out at 23 ± 1.7 °C and the findings are present in Table 2. Thus, their adsorptivity values were also determined and found to be approximately 65% lower in Q than in C. The explanation for that difference is discussed in reference [1].

The replacement ratios used were 20 and 40% for both fillers Q and C, all by Portland cement mass. So, blended cements used in the survey were batched in a proportion of 80/20 and 60/40, Portland cement (%)/filler (%). The 100/00 ratio denotes a pure Portland cement. The water demand for normal consistency and initial and final setting times determined in accordance with EN 196-3 standard [16] for the cements studied are given in Table 1.

Also on the other hand, all pure and blended cements mentioned were analysed by testing Frattini [17], although it wasn't applicable for any of them. According to Spanish cement code RC-16 [12] and European standard EN 197-1 [13], the Frattini test is required of pozzolanic cements only. Although none of the pure or blended cements used in this study was pozzolanic, all were tested with this procedure in the understanding that the respective findings would help explain their rheological behaviour.

In the Frattini test for every blended cements, the calcium hydroxide content in the aqueous solution in contact with the hydrated sample kept at 40 °C for first hydration hours (20 and 60 min, first nadir and second peak of conduction calorimetric findings, one and two days) was compared to the solubility isotherm for calcium hydroxide in an alkaline solution kept at the same temperature. The mineral addition is regarded to produce pozzolanic activity (=positive result) when the calcium hydroxide concentration in the sample solution was below the solubility isotherm curve, but as both PC are plain, i.e., both of them had not any pozzolan amount, the [CaO] and [OH$^-$] contents of their respective liquid phase have to be, in contrast, necessarily over the solubility isotherm curve for calcium hydroxide in alkali solution (=negative result).

It is necessary to say that initial and final setting times were determined according to EN 196-3 [16] standard and first nadir and second peak of conduction calorimetric findings times were determined in a previous research [23].