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

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HIGHLIGHTS

- 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.

ABSTRACT

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.

Keywords:

Rheology
Portland cement
Fresh pastes
Fillers
Hydration stimulus

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 -SiO₂), 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 C₃A(%) content, whose mineralogical composition was found to be followed: 51.0% C₃S, 16.5% C₂S, 14.0% C₃A and 5.5% C₄AF, a density of 3.08, a Blaine specific surface, BSS, of 319 m²/kg and a loss on ignition of 1.6% and Na₂Oeq. of 1.24% (>0.6%). On the other hand, the second Portland cement, PC2, was selected due to its low C₃A(%) and high C₃S(%) contents; its detail mineralogical composition was: 79.5% C₃S, 2.5% C₂S, ≈0.0% C₃A (<1.0%) and 10.0% C₄AF, a density of 3.21, a BSS of 329 m²/kg and a loss on ignition of 1.1% and Na₂Oeq. 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 SiO₂ content of over 99%, a density of 2.70, a BSS of 395 m²/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 CaCO₃ content of over 95%, a density of 2.71, a BSS of 362 m²/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].

Fig. 1. Particle size distribution for fillers Q and C (laser granulometry findings).

Fig. 2. XRD pattern for filler Q.

Fig. 3. XRD pattern for filler C.

2.2. Rheological tests

The rheological trials were conducted on a rotational rheometer fitted with a profiled rotor blade with serrated surface (internal diameter (R_i) = 19.010 mm; height (h) = 55 mm), a profiled cylinder, a temperature control unit for coaxial cylinders and a circulation thermostat. After analysing the effect of varying the aforementioned parameters, a scheme was designed with 10-s intervals, three velocities and down ramping preceding up ramping which made the evolution of cement pastes become the biggest hysteresis loop (thixotropic behaviour). The Doherty-Hurd method was proposed which is based in a reconstruction-destruction of the structure. A continuous variation of shear rate between a maximum and minimum value was applied, assuming at the maximum, the structure is close to destroyed and at the minimum is not rebuilt [18]. So, this control shear rate test (CR) proposed gave an extra information about the specific behaviour of each fresh cement paste as a result of the mineralogical composition of Portland cement and the physical state and chemical composition of the additions used.

A control shear rate test (or CR test) was chosen for every case. The scheme designed (Fig. 4) was as follows: 10" from 0 to 45 rad/s [A_1 point]; 30" at 45 rad/s [A_2 point]; 10" from 45 to 27 rad/s; 10" at 9 rad/s; 10" from 9 to 0 rad/s [C_1 point]; 10" rest [C_2 point]; 10" from 0 to 9 rad/s; 10" from 9 to 27 rad/s; 10" at 27 rad/s; 10" from 27 to 45 rad/s [A_2 point]; 30" at 45 rad/s [B_2 point] and 10" from 45 to 0 rad/s [C_3 point]. Trials were conducted during latent hydration at 25 °C because the viscosity of these materials is strongly dependent on the shear rate applied and on the degree of hydration of the cement paste, so this experimental scheme minimizes the different cement hydration rate influence [7–11,19].

Fig. 4 shows the cycle applied to each fresh paste. Points A_1 , B_1 , C_1 , C_2 , A_2 , B_2 and C_3 obtained from each curve are labelled on the graph. Yield stress (σ_0) parameter values were determined too, but these shear stress points were chosen to try to find the best way to explain the dynamic behaviour of cement pastes and predict the mixing and application processes. In fact, the yield stress values were also adjusted with the model that provides a better regression, in this case was Casson equation (Eq. (1)) [8,18,19].

$$\tau = \left[\tau_0 + \left(\eta_p \cdot \dot{\gamma} \right)^{1/2} \right]^2 \quad (1)$$

For the rheometric trials, the samples were hydrated at a water:binder (cement + filler) ratio (w/b) of 0.5 in every case. The fresh pastes were mixed manually for 2 min in a porcelain capsule, were stored in water bath at 25 °C until they were tested and poured into the viscometer annulus. Test times were made to concur with the hydration latency period. The latency period was determined with prior calorimetric trials [1–5]. X-ray dif fraction was applied to identify the hydrated and unhydrated compounds present in the resulting pastes, likewise during hydration latency.

The effect of the two fillers, Q and C, on the two Portland cements, PC1 and PC2, was also analysed by determining the zeta potential of each fresh paste from initial hydration through setting on a Malvern Instruments ZETASIZER 2000, in light of the direct relationship between that parameter and fresh cement paste viscosity [20]. Fresh paste rheological behaviour clearly depends upon the colloidal stability of the system. In this test, when the scatter from a laser beam focused on a sample is recorded, the data are used to calculate the zeta potential of the double-layered particles. In this study the sample was an aqueous solution in contact with the fresh paste during hydration at 25 °C. The zeta potential was determined for the pastes at a total of seven ages: at 20 min, 60 min and 120 min, at the outset and end of setting and at the first nadir and second peak on their calorimetric curve [1–5].

3. Results and discussion

3.1. Preliminary tests

Table 1 gives the key physical characteristics of the two Portland cements studied, with and without each of the two fillers, Q and C, namely water demand for a normal consistency and initial and end setting times.

First of all, the presence of both fillers have produced an accelerating effect on the setting times of both PC1 and PC2, (except PC2/Q samples, (Table 1)). This phenomenon was favoured with the presence of filler C and Portland cement PC1. Such observed influences are related to the different inner texture of these materials (the C filler texture is very granulated and with very sub-microscopic and microscopic particles as a result of its geochemical

Table 1
Physical characteristics of PC1 and PC2 with and without filler Q or C.

Physical parameter	Cement				
	PC1 100/00	PC1/Q 80/20	PC1/Q 60/40	PC1/C 80/20	PC1/C 60/40
Water demand ¹ (w/c ²)	0.31	0.32	0.32	0.33	0.33
Initial setting (h:min)	3:20	2:45	3:15	1:00	0:50
Final setting (h:min)	5:10	4:30	4:45	2:15	2:10
Physical parameter	Cement				
	PC2 100/00	PC2/Q 80/20	PC2/Q 60/40	PC2/C 80/20	PC2/C 60/40
Water demand ¹ (w/c ²)	0.28	0.29	0.30	0.30	0.29
Initial setting (h:min)	4:30	5:05	5:00	2:55	2:40
Final setting (h:min)	6:15	7:00	8:00	4:35	4:40

¹Water needed for normal consistency; ²w/c = water cement ratio.

Fig. 4. Proposed scheme for CR test.

origin [21,22] and it is not totally compact like for Q filler and, therefore, improves the moisture absorption capacity of C filler which is higher than it occurs for Q filler). This phenomenon was confirmed by lab tests (Table 2). In addition, it justifies the better behaviour as an inner moist closed, which finds reflection in its water for normal consistency (Table 1) and the water needed for its storage values. Hence, the set of its PC is as easier as faster, where its C₃A(%) is always more receptive than its corresponding C₃S(%) content.

The higher shortening of the setting times has once again been provoked by the stimulation effect of the corresponding PC fraction hydration by both, fillers Q and C, by *direct* [1,23] and *non-direct* [3] stimulation. These stimulation hydration phenomenon's are more intense in C₃A phase than C₃S phase and, as a consequence, greater reduction of the PC setting times. Further proof lies in the observation that the BSS (362 m²/kg) of C filler is nonetheless lower than the BSS (395 m²/kg) of Q filler.

As expected, PC1 had a higher water demand than PC2, given its greater capacity to form sulfoaluminates and calcium aluminate hydrates, which have substantial amounts of chemically combined water. On the other hand, the setting times for PC1 were also shorter than for PC2, in keeping with its high C₃A content (14%), which should exhibit greater fresh paste shear stress at the later

stages of the rheological trial, although not in the earliest ages because of its higher Na₂Oeq.: 1.24 and 0.56%, respectively [11].

In the same way, the water demand for normal consistency remained practically unaltered in both cements after Q filler was added. That may be due, in part, to the low moisture in quartz (Table 2) as well as to its lack of pozzolanic or hydraulic activity. Even though for PC1/Q 60/40 blended cement, the first point of Frattini test at the age of 20 min, strangely developed a positive result in its pozzolanic activity. Therefore, the following questions arise: What is the reason that the Q filler has shown pozzolanic characteristics at the age of 20 minutes, because it isn't a pozzolan?. According to the previous question, the pozzolanic activity shown by the filler Q at the age of 20 minutes is it real or fictitious?. In this case and according to the chemical-physical characteristics of the filler Q whose nature is siliceous, acid in chemical character and with compact intimate texture, it behaves like an inhibitor of PC1 hydration at that early age by provoking a phenomenon of electrostatic repulsion between filler particles and the dipolar ones of mixing water. Therefore, it had to prevent that the particles of PC1 began to hydrate from the first moment. To this phenomenon would have to add the effect of physical dilution that its replacement by PC1 causes. Therefore, blended cement P1/Q 60/40 has given a "false positive" result at the age of 20 minutes, whereas filler C hasn't given it, because it is calcareous in nature, basic in chemical character and it has a granular texture. This is one of the causes but there may be more that are being investigated at this time that complete the knowledge of this phenomenon. However, the setting times changed depending on the percentage of Portland cement replaced. In PC1 both the initial and final times were shortened, while both were lengthened in PC2. The former was indisputably due to *direct* [1,23] and *non-direct* [3] hydration stimulation by Q filler and the considerable C₃A content in the PC1 fraction in the blend, as well as to the respective C₃S content, although to a much lesser extent. That setting times in PC2 (with a high C₃S content –79%– and nil C₃A content) were retarded more with rising replacement ratios (see Table 1) was proof of the physical *dilution* effect induced.

As shown in earlier studies, in the cement pastes containing C filler, *direct* stimulation induced greater and faster hydration in C₃A than in the majority clinker phase C₃S. Unsurprisingly, then, the blended cements prepared with PC1 (with 14% C₃A) exhibited

Table 2
Humidity absorption for fillers Q and C.

Crystalline Mineral Additions (fillers)	Humidity Absorption (%)					
	Age (days)					
	1	3	7	14	21	28
Q	0.41	0.49	1.38	1.76	2.75	2.75
C	2.07	2.53	3.35	3.90	6.67	6.67

earlier initial and end setting times, given the stimulation of hydration in its C_3A fraction. Such stimulation would be:

- *direct* [1,23], prompted by the mixing water that differentially moistened the particles of the fillers Q and C;
- and *non-direct* [3], prompted by the zeta potential generated as hydration progressed.

Hence, the particles of the two fillers ultimately behaved like nucleation or precipitation sites, respectively, for the calcium hydroxide with which their respective liquid phases were supersaturated.

At the same time, stimulation would also be *indirect* in filler C [24], albeit with no pozzolanic activity, for its $CaCO_3$ was wholly crystalline and *basic* in chemical character [3]. Under those circumstances, the calcium carbonate would be able to react with the C_3A to form calcium tri- and mono-carboaluminate hydrate and especially calcium hemi-carboaluminate hydrate. Nonetheless, calcium mono-carboaluminate would be favoured to the detriment of the AFm forming at the outset of the hydration of the cement in the blend, in turn converted into slow-forming ettringite or *ett-lf* [25].

When fillers Q and C partially replaced PC1 in the respective blends, the pH of the liquid phase of the resulting pastes (tested with the Frattini test at 25 °C [17]) declined as the replacement ratio rose. That finding attested to the physical *dilution* effect and hence of the Na_2O_{eq} content in PC1 and the portlandite generated after initial hydration. As a result, the $[OH^-]$ decreased in its liquid phase at all the Frattini test ages in all but blended cement PC1/C 80/20. In that cement, *direct* [1,23], *non-direct* [3] and *indirect* stimulation of hydration (albeit in the absence of pozzolanic activity [24]) induced by the C calcareous filler fraction prevailed in the clinker over the *dilution* effect observed for all the other blends. The same pattern was observed and for the same reasons in the fluctuations in $[CaO]$, which declined at 120 min and the second peak on its calorimetric curve [1] in all cases with the exception once again of blended cement PC1/C 80/20 (see Fig. 5).

In contrast, when PC2 was partially replaced by the fillers (Fig. 5), medium basicity rose in the early hydration reactions, a development that was intensified with rising replacement ratios. At longer test ages, however, the liquid phase in all the blended

cements was less alkaline than the respective pure Portland cement. That finding inferred that both fillers stimulated Portland cement hydration more effectively when the C_3A content was high than when C_3S was high. Therefore, of the two PC phases, C_3A was more logically prone to greater and faster hydration stimulation.

3.2. Rheological tests

Figs. 6 and 8 plot the yield stress against the shear applied (CR test) to the fresh pastes made with pure Portland PC1 and its blends with fillers Q and C, whereas Figs. 7 and 9 graph the same parameters for the fresh pastes made with pure PC2 and its blends with the two fillers.

The singular points shown in Fig. 4 were identified for all the rheological tests. The fresh paste values for the PC1 and its family of blended cements are given in Table 3 and for PC2 and its family in Table 4. These Tables also include a column showing the age (or latent period) of each paste when tested, along with a column with the pH of the liquid phase found with the Frattini test [17], conducted at 25 °C. The Casson [8,18,19] rheological model was used to determine the yield stress for each fresh cement paste.

3.2.1. Comparative study of PC1 and PC2

After 120 min of hydration, fresh paste PC1 reached a shear stress at point A₁, i.e., after the first 10 s of rotation at 45 rad/s, of 91.91 Pa. At point B₁, after 30" of constant rotation, stress decreased sharply, to nearly 38 Pa [(91.91–54.07) Pa] (thixotropic behaviour). When the rotor blade was stopped (point C₁), the shear stress remaining in the paste was 11.48 Pa. After a 10-second pause, the paste recovered part of its shear stress (point C₂), which rose to 12.30 Pa. Nonetheless, the particles in the fresh paste and its liquid phase must not have been the same at point C₂ as when the fresh paste was placed in the rheometer. Rather, new hydration products must have formed, particularly from C_4AF and C_3A origin specially (calcium aluminate hydrates) and from C_2S and C_3S origin (calcium silicate hydrate (CSH) gels, in addition to the portlandite in the liquid phase up to the supersaturation level, see Fig. 5).

The resulting viscosity sufficed to lower shear stress by approximately 50% when the fresh paste was subjected to the same

Fig. 5. Frattini test results for PC1 and PC2 with and without filler Q or C.

Fig. 6. Rheological behaviour of fresh PC1 paste with and without filler Q.

Fig. 7. Rheological behaviour of fresh PC2 paste with and without filler Q.

Fig. 8. Rheological behaviour of fresh PC1 paste with and without filler C.

Fig. 9. Rheological behaviour of fresh PC2 paste with and without filler C.

Table 3

CR test results for fresh PC1 pastes with and without filler Q or C.

Cement	pH [*]	w/c ratio ^{2*}	Age ^{3*} (min)	τ_0 (Pa)	Shear stress values for PC1 with and without filler Q or C (Pa)						
					A ₁	B ₁	C ₁	C ₂	A ₂	B ₂	C ₃
PC1 100/00	12.38	0.50	120	71.98	91.91	54.07	11.48	12.30	47.20	46.15	11.35
PC1/Q 80/20	12.18	0.50	100	34.34	78.50	55.34	12.81	13.90	36.97	34.77	12.76
PC1/Q 60/40	11.98	0.50	125	41.42	122.70	74.48	15.09	13.60	48.06	44.98	13.75
PC1/C 80/20	12.28	0.50	50	74.54	86.21	46.01	9.102	9.526	36.34	34.21	8.682
PC1/C 60/40	12.29	0.50	80	69.54	95.47	53.50	11.79	13.52	42.68	39.23	10.19

^{*}Liquid phase during latent period as per the Frattini test [15] at 25 °C; ^{2*}water:cement ratio; ^{3*}duration of latent period as per conduction calorimetry [1].

Table 4

CR test results for fresh PC2 pastes with and without filler Q or C.

Cement	pH [*]	w/c ratio ^{2*}	Age ^{3*} (min)	τ_0 (Pa)	Shear stress values for PC2 with and without filler Q or C (Pa)						
					A ₁	B ₁	C ₁	C ₂	A ₂	B ₂	C ₃
PC2 100/00	12.35	0.50	100	40.32	162.50	75.78	13.44	12.04	46.15	42.87	12.83
PC2/Q 80/20	12.37	0.50	180	38.93	138.70	77.92	12.99	12.77	48.77	45.19	10.58
PC2/Q 60/40	12.24	0.50	95	26.10	119.40	74.46	11.19	11.30	47.37	44.77	11.36
PC2/C 80/20	12.31	0.50	80	33.20	154.60	83.73	16.23	16.14	54.14	50.48	15.90
PC2/C 60/40	12.31	0.50	95	31.33	146.10	77.95	17.27	17.10	55.30	51.83	14.69

^{*}Liquid phase during latent period as per the Frattini test [15] at 25 °C; ^{2*}water:cement ratio; ^{3*}duration of latent period as per conduction calorimetry [1].

controlled rate of 45 rad/s at point A₂, while subsequently, at point B₂ where the stimulus was the same as at B₁, stress dipped by a mere 15%. Lastly, at the end of the test, i.e., at point C₃, the remaining shear was similar to the value recorded at point C₁. The foregoing showed, in short, the high degree of thixotropic recovery in fresh paste PC1.

In fresh PC2 paste, after 100 min of hydration, the shear stress at point A₁ (after the first 10 s of the rheological trial, when the rotational speed was 45 rad/s) came to 162.5 Pa. In this case, the shear stress was much higher than in PC1, due firstly to the lower Na₂Oeq. content (0.56 compared to 1.24%) [7,11] and hence lower liquid phase pH: 12.35 compared to 12.38, as shown in Tables 3 and 4, respectively.

And this in spite of that the proportions of usual and less usual hydration products (especially slow-forming ettringite, *ett-lf*, with its hexagonal prismatic needles and rosettes [25,26,27] and alumina, ferric oxide, mono-sulfate, *Afm* with its hexagonal plates) generated must have varied widely between the two Portland

cements because their potential mineral composition likewise differed (see diffractograms in Figs. 10 and 11). Similarly, after fresh PC2 paste was rotated at a constant rate up to point B₁, its shear stress decreased by nearly 87 Pa (thixotropic behaviour).

In both PC1 and PC2, shear stress decreased by around one half of the value reached at points A₁. But the rest of findings for the two fresh pastes can be summarised as follows. Firstly, at point C₁, the shear stress remaining in fresh PC2 paste was 13.44 Pa, although with a clear tendency to decrease over time, slipping to 12.04 Pa at point C₂. Under the same circumstances, the shear stress in fresh PC1 paste rose from 11.48 Pa at point C₁ to 12.30 Pa at point C₂. Secondly, at point A₂ the shear stress of the fresh paste PC2 was approximately only one quarter lower than at point A₁, while in fresh PC1 paste the shear stress at A₂ was around half of the A₁ value. Thirdly, at point B₂, where the stimulus was the same as at point B₁, the shear stress in fresh PC2 paste dropped by 45%, whereas in fresh PC1 paste stress decreased by a mere 15%.

Fig. 10. XRD patterns for fresh PC1 pastes with and without filler Q or C (60/40), during the latent period of hydration.

Fig. 11. XRD patterns for fresh PC2 pastes with and without filler Q or C (60/40), during the latent period of hydration.

This very different behaviour of the two Portland cements in rheology test is due to:

- Their different mineralogical compositions and $\text{Na}_2\text{O}_{\text{eq}}$ (%) contents very specially.
- Their different Frattini test results at all ages (Fig. 5).
- Their different water demand for normal consistency and setting times (Table 1).
- The different amount and type of hydration products generated when controlled rate rheological tests were conducted (Figs. 10 and 11).
- The different higher yield stress of PC1 than PC2 calculated by Casson model (Tables 3 and 4).

All these differences explain their different behaviours in rheology test. The explanation must lie either in the higher C_3A and $\text{Na}_2\text{O}_{\text{eq}}$ contents (%) in PC1, the higher C_3S content (%) in PC2 or any combination of the three. Nonetheless, the higher hydration rate of C_3A in PC1 must have played a lead role, but its greater $\text{Na}_2\text{O}_{\text{eq}}$ content (%) holding priority always. Hence that fresh paste's "settability", with the resulting rotational consequences observed.

The zeta potential value for fresh cement paste was higher for PC1 than PC2 (Fig. 12). Those findings were closely related to the pH values obtained for the liquid phase of the respective pastes.

At all ages, fresh paste PC1 generated a more basic medium than fresh paste PC2, which led to higher absolute zeta potential values, more negative in this case, due to the higher Na^+ and K^+ concentration in the liquid phase, in turn attributable once again to the higher $\text{Na}_2\text{O}_{\text{eq}}$ (%) content.

For that reason, the fresh PC1 pastes exhibited higher absolute zeta potential values. As a result, the individual particles were dispersed more widely due to the greater width of the double layer induced by the greater strength of the repulsion forces. In other words, the PC1 fresh paste system was moving into a more stable region, rendering its viscosity lower than in cement PC2, yet another consequence of the major differences in the mineralogical and chemical composition of the Portland cements studied, but above all, of its higher $\text{Na}_2\text{O}_{\text{eq}}$ (%) content: 1.24% and 0.56, respectively.

3.2.2. Comparative study of PC1 and PC2 with Q and C fillers

3.2.2.1. With Q filler. When Q filler was added to PC1, shear strength rose at most of the singular points and where that was the case, the effect intensified when the replacement ratio was raised to 40%. That increase in the apparent viscosity of the fresh paste induced by the inclusion of Q filler was due to the larger number of Q particles present in the paste (which, as wholly crystalline, were neither pozzolanic nor hydraulic). Their presence stimulated hydration of the fraction of PC1 directly [1,23] and

Fig. 12. Zeta potential of fresh PC1 and PC2 pastes with and without filler Q or C, during the latent period of hydration.

non-directly [3] and with it the formation of the respective hydration products sourced primarily from C_3A , namely *slow-forming* ettringite, *ett-lf* [25–28] and AFm (Fig. 10). These latter prompted a decline in fresh paste fluidity. The greater amount of the hydration products that could form, which would be proportional to the amount of hydration water available to the PC1 in the blend with Q filler (in this case, PC1/Q 60/40), the steeper would be the decline.

Furthermore, in fresh paste, these stimulating effects were curbed at some ages as a result of the physical *dilution* of PC1 by Q filler. That would be supplemented by chemical *dilution* because what was in fact *diluted* was the liquid phase of the paste, and therefore its major constituents, portlandite and especially Na_2O_{eq} . These phases were generated during initial PC1 hydration (for in such circumstances, paradoxically, the amounts of *ett-rf* and AFm formed by the 60% PC1 in the blend should potentially be greater than the amounts of pure PC1: see Fig. 10). The inescapable result would be greater fresh paste viscosity. The foregoing is reinforced by the opposite rheological behaviour observed in families PC1/Q and PC2/Q at the same singular points.

- Viscosity was higher in the PC1/Q family fresh paste when the blend contained 40% filler (see Table 3). Conversely, in PC2/Q, viscosity was observed to be higher with a 20% replacement ratio.
- After the 10 s pause in each PC1/Q fresh paste, point C2 shear strength was greater in the two blends, 80/20 and 60/40, than in pure PC1 (Table 3), whereas in PC2, shear strength should have been and was greater in the 80/20 blend only.
- Fresh paste shear strength at point C₁ was greater than at point C₂ in the PC1 family, and vice versa in the PC2 family.
- Fresh paste shear strength at point C₃ was greater in PC1/Q than in pure PC1 and rose with the replacement ratio. In contrast, PC2/Q strength at that point was lower than pure PC2 strength.

3.2.2.2. *With C filler.* Lastly, all the Portland cements were blended with C filler. An analysis of the respective yield stress values (σ_0 , Tables 3 and 4) showed, firstly, that the addition of C filler induced greater hydration stimulation *directly* [1,23], *non-directly* [3] and *indirectly* [24] (in the absence of pozzolanicity) in the PC1 with which it was blended, and in particular in its C_3A fraction. The effect was such that in PC1/C 80/20, yield stress was reached at a higher shear strength value. This pattern was not observed in

PC2 due to the total absence of C_3A in this cement, with a substantial weakening of the stimulus attributable to fraction C filler. Under these circumstances, physical *dilution* prevailed over all other developments.

Moreover, when C filler was added to PC1, shear strength rose at most of the singular points in the first CR cycle and where that was the case, the effect intensified when the replacement ratio was raised to 40%. That increase in the apparent viscosity of the fresh paste induced by the inclusion of C filler was due once again to the larger number of C particles present in the paste. Their presence stimulated hydration of the fraction of PC1 *directly* [1,23] and *non-directly* [3] as well as *indirectly* in the absence of pre-existing pozzolanicity [24], with the concomitant formation of the respective hydration products characteristic of PC1, namely *slow-forming* ettringite, *ett-lf* [25–28], AFm and calcium tricarboaluminate hydrate (Figs. 10 and 11). These latter prompted a decline in fresh paste fluidity to the point of decomposition due to shear stress. The greater the amount of the hydration products that could form, which would be proportional to the amount of hydration water available to the PC1 in the blend with C filler (in this case, PC1/C 60/40), the steeper would be the decline.

In all the fresh pastes containing C filler, this stimulating effect prevailed over the physical *dilution* of the PC by the C filler and over the associated effect of the chemical *dilution* of the liquid phase of the paste and its main constituents, portlandite and Na_2O_{eq} . More specifically, the *non-direct* stimulation of hydration [3] prompted by C filler was favoured in PC2. That finding is closely related to the zeta potential findings for the fresh pastes from the onset of hydration through the end setting time (Fig. 12). In contrast, *direct* and *indirect* stimulation of hydration was favoured in PC1. More precisely, it cannot be contended that *non-direct* stimulation is not favoured by C filler in PC1, inasmuch as such stimulation was in fact present, given that the zeta potential rose as hydration progressed. Rather, the explanation may lie in that the C_3A content in the blend may have been depleted because its hydration was stimulated much earlier via the *direct* and *indirect* routes.

3.3. X-ray diffraction and Z potential analysis

The hydration compounds during the latent period of hydration are identified in the XRD patterns illustrated in Figs. 10 and 11 for PC1 and PC2 cements, respectively, and for 60/40 blended cements containing Q and C crystalline mineral additions filler type.

For PC1 and PC2 pastes with Q and C crystalline mineral additions filler type, the intensity of CH peak was stronger than the corresponding to PC1 and PC2 pastes. XRD results confirm the stimulation effect on the hydration reactions that has also been shown in the physical and rheological tests. On the other hand, the formation of the tri-substituted aluminum ferrite compounds was demonstrated (AFt: Ts or Tc), and its very early transformation to the mono-substituted aluminum ferrite compound phase (AFm: Ms) for cement based made on PC1. In the case of PC2 and PC2 blends, the practical absence of the mono- and tri-substituted particularly aluminum ferrite phases (AFt and AFm) was verified in correspondence with the absence of C₃A in the PC2.

At very early ages, Tc formation is especially interesting in blends with the filler C having been formed from the C₃A derived from the PC1. These compounds have been found previously in other experiments [1–4]. Similarly, the formation of carbonate hydrated calcium silicate (CS) has also been detected previously [1–3].

In both cases, irrespective of the filler used (Q or C), the deflocculating conditions in the PC1 cementitious system were more intense [20], since its zeta potential values exhibited higher absolute values throughout the hydration latency period (Fig. 12). For that reason, the fresh PC2 cements blended with either filler generated a more electrostatically stable and more viscous medium. That finding was clearly impacted by the alkalinity of the liquid phase of the paste and therefore by the amount of soluble Na₂O and K₂O present and of portlandite forming from its clinker.

An explanation can also be given for the higher apparent viscosity in general in the blends of both PCs with both percentages of both fillers (Tables 3 and 4) than in the pure PCs. These blends were closer to the isoelectric point at which the charge distribution of any solution is nil [7] and tends toward electrostatic equilibrium. That favours a higher fresh paste viscosity.

In addition, both fillers acted as nucleation-precipitation sites [3], respectively, for portlandite crystals, stimulating hydration *non-directly* [2,3]. C filler exhibited higher performance in this respect, adopting the role of “seed crystal” in portlandite crystal precipitation, although the epitaxial phenomenon is absent [29,30].

4. Conclusions

1. Very early-age hydration in both Portland cements studied was stimulated *directly*, *non-directly* and *indirectly* by the presence of mineral fillers, although only C filler prompted *indirect* stimulation (see conclusion 4 for a fuller discussion). Stimulation intensified with the percentage of Portland cement replaced by filler, without prejudice to the effect associated with the physical *dilution* of the cement and the liquid phase in its fresh paste, which prevails when stimulation weakens.
2. Q filler has strangely fulfilled the Frattini test at the age of 20 minutes when it was mixed with PC1 in the 60/40 blend ratio. This result is not real, it was fictitious and it is a “false positive” result, which has been duly justified, because the Q filler does not have any pozzolanic characteristic because it is a totally crystalline α-quartz.
3. The viscosity of any Portland cement fresh paste and their yield stress depends on:
 - on the qualitative and quantitative mineralogical and chemical composition, Na₂O_{eq}(%) content especially of the cement, i.e., the alkaline element content in the liquid phase of their fresh paste, and
 - on the amount and types of hydrated compounds generated during the hydration latency period, when the fresh paste is fluid.

4. Further to conclusion 3, the inclusion of crystalline fillers in Portland cement induces greater viscosity in its fresh paste due to the quicker formation of more hydration products (such as ettringite, AFm and C-S-H gels) due to the stimulation referred to in conclusion 1. In some cases, that increase in product formation is further favoured by the chemical *dilution* affecting the liquid phase of the blend, but not by the effect of the physical *dilution* of the Portland cement present in the fresh paste, for in that case stimulation would be attenuated. Nonetheless, the equilibrium between those effects is reached when the ‘boundary’ replacement ratio is used.
5. The three routes for hydration stimulation induced by Q and C fillers in Portland cement have a greater or lesser impact depending on the composition of the cement itself, as well as on the siliceous or calcareous nature of the filler. *Direct* hydration stimulation prevails when the Portland cement at issue has a high aluminate phase, such as C₃A (%). The *non-direct* route predominates when the aluminate phase content in the Portland cement is low, i.e., when its silicate phase content is high, C₃S especially. Lastly, *indirect* stimulation in the absence of pozzolanicity is present only where the C₃A content is high and only when calcareous filler is used.

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