Influence of the synergy between mineral additions and Portland cement in the physical-mechanical properties of ternary binders

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ABSTRACT: The paper deals with the synergistic effect of mineral additions on the physical-mechanical performance of ternary blends prepared with different Portland cements (PC). The effect in setting and heat flow release is also analyzed. The mineral additions used are blast furnace slag (BFS), fly ash (FA) and limestone filler (LF). PCs with different C_3A and alkali content have been tested to study the synergy in ternary blends. Ternary binders with PC low in C_3A and alkali content achieve similar mechanical strength gain as plain PC and refinement of pore size distribution from early hydration ages due to the acceleration of PC hydration induced by the mineral additions. In contrast, ternary binders with PC higher in C_3A and alkali content have a delayed in mechanical strength at early hydration ages, but significantly higher at long hydration times.

KEYWORDS: Blended cement; Hydration; Physical properties; Mechanical properties

RESUMEN: *Prestaciones físico-mecánicas en cementos ternarios dependiendo de la sinergia entre las adiciones minerales y el cemento Portland.* El artículo aborda la interacción sinérgica de las adiciones minerales en el rendimiento físico-mecánico de mezclas ternarias preparadas con dos tipos de cemento Portland (PC). Se analiza desde las edades tempranas la contribución en los tiempos de fraguado y en el flujo de calor liberado. Las adiciones minerales usadas son escoria de alto horno, ceniza volante y filler calizo. Los PC utilizados se han seleccionado en base al contenido en C_3A y álcalis. Mezclas formuladas con PC de bajo contenido en C_3A y álcalis mantienen desde el inicio una ganancia similar en las prestaciones mecánicas y un refinamiento en el tamaño de poro atribuido a la aceleración inducida por las adiciones minerales en la hidratación inicial del PC. En cambio, mezclas ternarias con un PC con mayor contenido en C_3A y álcalis tienen más lenta generación de resistencias mecánicas iniciales, pero mayores a medida que avanza la hidratación.

PALABRAS CLAVE: Cementos con adiciones; Hidratación; Propiedades físicas,; Propiedades mecánicas

1. INTRODUCTION

Cement production in the world is estimated at around 4.3 billion tones in 2014 (1) and it is expected to increase in the future. The manufacture of Portland cement clinker is responsible for about 5–8% of total CO_2 emitted into the atmosphere (2, 3), in fact per ton of PC produced about 1 ton of CO_2 is emitted (3, 4). The high environmental impact of clinker production can be reduced by partial or

total replacement of clinker with mineral additions, by use of alternative fuels or by optimization of the heat transfer in the production of clinker (5).

The replacement of clinker by mineral additions can be total, as in the alkali activated blends (6–8), or partial, as in the blended cements like CEM II type (PC clinker > 65%) plus one mineral addition according to EN 197-1:2011. In fact, in Europe in the last years the CEM II production is twice that CEM I (9) and will increase in next years. The most common mineral additions employed are blast furnace slag (BFS), fly ash (FA), limestone filler (LF) and silica fume (SF). It is well known that the use of these mineral additions in binary mixes have technical, economic and environmental advantages (10–14) but their content is limited since the BFS and especially FA have slower reaction than clinker with the subsequent retardation of developing of technical properties of concrete (13, 15, 16).

Recent studies with ternary blends (PC plus two mineral additions) have demonstrated that they can improve the mechanical performance with respect to binary binders at initial and long-term ages of hydration. This effect is more relevant when additions with different hydration mechanism are combined (11, 15, 17–23). The future of CEN (European Committee for Standardization) is on the way to include the ternary blends in the standards (9).

Results reported in the literature for ternary blends suggest that the effect of the additions depends on the type of PC used (16, 21). Different studies showed that ternary blends using PC with relatively high alkali and C_3A content had lower initial mechanical strength than plain PC (5, 18, 19, 22, 24), while in mixes with PC containing low alkali and/or

C_3A content this effect is less relevant (11, 15, 20, 21, 23, 25). Dehuai and Zhaoyuan (24) found that in ternary blends composed of 50–70% PC with 8% C_3A and 0.9% Na_2O_{eq}. mixed with BFS and FA resulted in 32–59% lower compressive strength than for the plain PC after 7 days of hydration. In contrast, Menéndez et al. (15) saw that ternary blends using PC with 2% C_3A, LF and BFS showed better strength than binary blends and similar than plain PC during hydration from 1 to 90 days, which were attributed to the LF at early ages and to the BFS hydration at long term (11, 15, 21). The good mechanical strength of the ternary blends at long term has been also related to the refinement of the pore structure (21–23) which has a further positive response on durability (26). Besides, present authors in a previous paper (21) found that ternary blends with high blended content formed more C-S-H that contained more Al and less C/S ratio than C-S-H gels formed with plain PC and retained more alkalis in their structure.

The goal of this paper is to analyze the synergistic effect of the combination of two mineral additions (BFS, FA and/or LF) and the type of PC on the early hydration and on the physical-mechanical properties of ternary binders in order to clarify the discrepancies between authors.

2. MATERIALS AND METHODS

Two types of CEM I, that belong to the categories CEM I 42.5 R-SR and CEM I 42.5 R, were used to prepare the blends. The chemical compositions are reported in Table 1. X-ray fluorescence (XRF) was used for element content determination. Both PCs had small $CaCO_3$ content, determined from

TABLE 1. Chemical and mineralogical composition and $CaCO_3$ content (wt. %) of the raw materials

%	PC_L	PC_H	LF	BFS	FA
Na_2O	0.2	0.1	0.6	0.4	0.8
K_2O	0.3	0.9	2.7	0.5	4.5
Na_2O_{eq}	0.4	0.7	2.3	0.7	3.7
CaO	60.3	63.3	26.1	45.5	3.6
SiO_2	17.4	19.6	21.4	36.6	52.0
Al_2O_3	4.7	5.5	7.8	10.4	24.9
Fe_2O_3	5.1	2.4	2.6	0.3	6.3
MgO	1.8	0.8	5.8	7.5	1.7
SO_3	3.2	3.2	0.1	0.1	0.2
LoI	4.2	2.5	30.1	NA	NA
C_3S	50	53	-	-	-
C_2S	12	16	-	-	-
C_3A	4	10	-	-	-
C_4AF	15	7	-	-	-
$CaCO_3$	4	3	61	< 1	< 1

LoI: Lost of Ignition, NA: Not Analyzed

TG/DTA tests, (4% in CEM I 42.5 R-SR and 3% in CEM I 42.5 R). The most notable difference between the two PCs is the alkali and C_3A contents. CEM I 42.5 R-SR had low alkali content (0.4% Na_2O_{eq}.) while CEM I 42.5 R had 0.7%. The C_3A content was estimated through Bogue equations (27), after correction taking into account $CaCO_3$ content, the obtained values were 4% for R-SR and 10% for R CEM I. The C_4AF of both PC was also different, 15% for CEM I R-SR and 7% in CEM I R. To differentiate both PCs, PC_L and PC_H nomenclatures are used, where L indicates low alkali and low C_3A contents (PC CEM I R-SR) and H higher alkali and C_3A contents (PC CEM I R).

The chemical compositions of the mineral additions employed to prepare the mixes are also included in Table 1. All of them are commercial products. LF containing 61% $CaCO_3$ was used. The low content of the carbonates in the LF is due to the geological nature of the base rock (black limestone) used. FA with low calcium content and BFS were also employed as mineral additions for ternary binders. The three mineral additions had higher alkali and Al_2O_3 and lower SO_3 contents than the PCs.

Binary and ternary blends were prepared using PC_L or PC_H plus one or two mineral additions, combining BFS, FA and LF in different proportions, as shown in Table 2. Both PCs were mixed in 100, 94 and 64% content. The content of BFS was varied from 26 to 36 wt.%, 10 wt.% for the FA and 6 wt.% for the LF. Additionally mixes with 36% of quartz (Q) as inert addition were prepared. $PC_L30BFS6LF$ and $PC_H30BFS6LF$ are classified as CEM II/C-M (S-L) according to the new cement standard EN 197-1 (9). $PC_L26BFS10FA$ and $PC_H26BFS10FA$ are classified as CEM II/C-M (S-V) according to the same standard. These ternary binders have been chosen in accordance with new EN 197-1 (9) and the experience from literature review (11, 15, 24), and binary ones have been chosen to be compared with the ternary binders with BFS and LF.

Table 3 summarizes the particle size distribution of the raw materials with the mean size value and some percentiles. The mean particle sizes and the particle size distribution of PC_L and PC_H were similar. Thus, the differences between the two types of PC can be only related to their chemical and mineralogical compositions; BFS also shows similar particle size as the PCs. The highest particle size is observed for the FA and the lowest for the LF.

Cement pastes using a w/b ratio 0.5 were prepared. Setting time was determined with a Vicat needle,

TABLE 2. Composition (in % by weight) of blended mixes

Sample identification	PC_L	PC_H	BFS	FA	LF	Q
				%		
PC_L	100	-	-	-	-	-
PC_H	-	100	-	-	-	-
PC_L6LF	94	-	-	-	6	-
PC_H6LF	-	94	-	-	6	-
PC_L36BFS	64	-	36	-	-	-
PC_H36BFS	-	64	36	-	-	-
PC_L36Q	64	-	-	-	-	36
PC_H36Q	-	64	-	-	-	36
PC_L30BFS6LF	64	-	30	-	6	-
PC_H30BFS6LF	-	64	30	-	6	-
PC_L26BFS10FA	64	-	26	10	-	-
PC_H26BFS10FA	-	64	26	10	-	-

TABLE 3. Particle size distribution of the raw materials

		10%	50%	90%	Diameter Mean Size (μm)
Particle Size (μm)	**PC_L**	1.9	14.4	44.5	19.2
	PC_H	1.8	13.4	41.3	17.8
	BFS	1.6	11.9	38.9	16.4
	FA	3.8	20.0	99.3	37.6
	LF	1.1	5.5	23.0	9.5

following recommendations of EN 196-3 standard. All tests were performed at constant temperature using a thermostatic bath at 25 °C for immersion of the cement paste mix during setting test.

Calorimetry tests were performed for both PCs, in binary and in ternary mixes to evaluate the initial contribution of the mineral additions, also PC incorporating 36% quartz was evaluated in this case. For calorimetry tests a Thermometric TAM AIR calorimeter was used. The samples were prepared with 6 grams of binder and 3 grams of water. The tests lasted 7 days at 20 °C. The pastes were introduced in the calorimeter immediately after being mixed and shaken during 60 seconds.

Mortars were prepared to study mechanical and porosity changes. 4x4x16 cm prismatic samples were fabricated with a w/b = 0.5 and binder/sand = 1/3. These samples were demolded after 24 hours and kept in a curing chamber at 21 ± 2 °C and 98 ± 2% RH until testing. The evolution of the mechanical and the pore size properties of the mortars were determined after 1, 7, 28 and 90 days of hydration. The mechanical strength results refer to mean values of two and four measurements of flexural and compressive strength, respectively.

The pore size distribution and total porosity values were also obtained using mercury intrusion porosimetry at 1, 7, 28 and 90 days of hydration. A piece of mortar with approximately 1 cm^3 was used (2.5 times higher than the maximum particle size of the sand) in order to guarantee the representativeness of the sample. This piece was obtained from the core of an additional prismatic sample. The hydration process was then stopped at each specific curing age by removing the free water with ethanol and acetone.

3. RESULTS AND DISCUSSION

3.1. Ternary blends contribution to the early cement hydration

The incorporation of mineral additions changes the early hydration, as also found by other authors (28–31). One of the properties modified is the setting time. Table 4 compares the initial and final

setting times of the binary and ternary blends, and the reference samples (PC$_L$ and PC$_H$).

The chemical composition of the plain PC clearly affects the setting time. PC$_H$ showed initial setting after 1.7 hours while PC$_L$ set only after 3.3 hours. In this sense, setting time depends on the initial particle size (which is similar for the two cements) and the composition of the binders (32, 33). PC$_H$ had some higher content of alite and aluminate than PC$_L$ consistent with the faster setting of PC$_H$. The higher initial content of alkalis in PC$_H$ contributed to accelerate the setting too, as also found in (16).

The incorporation of 36% BFS retarded the setting times compared to PC$_L$ by 18%, in accordance with (34, 35). However, with ternary blends the retardation in setting caused by the introduction of BFS was significantly reduced with the incorporation of LF (12%). Different causes can be contributing to this fact, the LF at early ages favors higher effective water/PC ratio for reaction and provides additional sites for the nucleation of hydration products (30, 31). Besides, the BFS also contributes to accelerate the clinker hydration (19), but its role depends on the PC composition as found in (21). In fact, higher portlandite content was detected at early ages of hydration with PC$_L$30BFS6LF but lower content in Al and Si in the pore solution with respect to PC$_H$30BFS6LF. These phenomena can explain the differences in initial reactivity of anhydrous phases in both PCs in presence of synergic mineral additions.

Similar trends are observed for ternary blends containing BFS + FA; the relative delay in setting was again more significant for PC$_H$, although the absolute setting times were shorter for PC$_H$. The presence of FA resulted in later setting than in the presence of LF. These results agree with the higher setting times reported for ternary blends formed by PC with low alkali content, FA and LF, with respect to the setting times obtained in binary blends without LF (20).

The delay observed in setting time in the presence of mineral additions should be closely related to the heat flow measured by calorimetry. Figures 1 and 2 show the heat flow measured for PCs and the blends

TABLE 4. Initial and final setting times

Samples Identification	Initial setting (h)	%Δ delay relative to PC	Final Setting (h)	%Δ delay relative to PC
PC$_L$	3.3	-	4.3	-
PC$_H$	1.7	-	2.4	-
PC$_L$36BFS	3.9	18	5.2	21
PC$_L$ 30BFS6LF	3.7	12	4.8	12
PC$_H$ 30BFS6LF	2.0	18	2.8	17
PC$_L$ 26BFS10FA	4.0	21	4.9	14
PC$_H$ 26BFS10FA	2.2	29	3.2	33

during the first 50 hours of hydration. Heat flow results were normalized to 100% of PC in order to allow comparison and facilitate the detection of the contribution of the mineral additions on the cement hydration.

All mixes showed a very early reaction (dissolution), the initial period (I) followed by an induction period (II), with a low heat flow during first hours. The length of induction period varied with the type of PC used to prepare the blend, but is only very little affected by the presence of mineral additions. This indicates that the early reaction was dominated by PC due to the C_3S dissolution and hydration and the formation of C-S-H and portlandite as noticed in (36–38), which caused a sharp increase in heat flow after the induction period, the acceleration period (III). The onset of period III was faster for PC_H than for PC_L, and the heat flow per gram of PC at the maximum of the exothermic heat peak was higher in the presence of the mineral additions. This fact can

be related to the higher effective water to PC ratio of the ternary mixes during the initial hydration. As no or little of quartz, BFS, FA or LF reacted during the first hours of mixed, more water was available per g of Portland cement, which leaded to a faster reaction of the PC as also found in (31). Generally setting took place within this period. A shoulder at around 20 hours for PC_L and 15 hours for PC_H was observed. Minerals additions had little effect on the appearance of the first shoulder. This shoulder has been attributed to the heat released in the C_3A dissolution and the precipitation of ettringite (38) from the PC that had been also identified by XRD in similar ternary mixes after 2 days of hydration (21).

A second shoulder between 25 to 35 hours was clearly observed in blends containing PC_H. Its appearance and duration depended on the mineral addition employed as can be seen in Figure 1-right and Figure 2. This shoulder was not clear in PC_L mixes, but it had been observed in blends based on
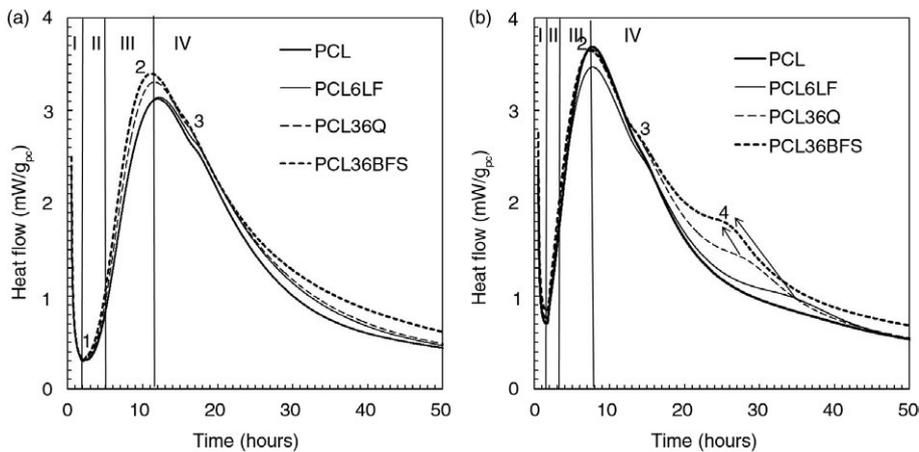

FIGURE 1. Heat flow per gram of PC during the first 50 hours of hydration. Left) PC_L and binary blends based on PC_L. Right) PC_H and binary blends based on PC_H.
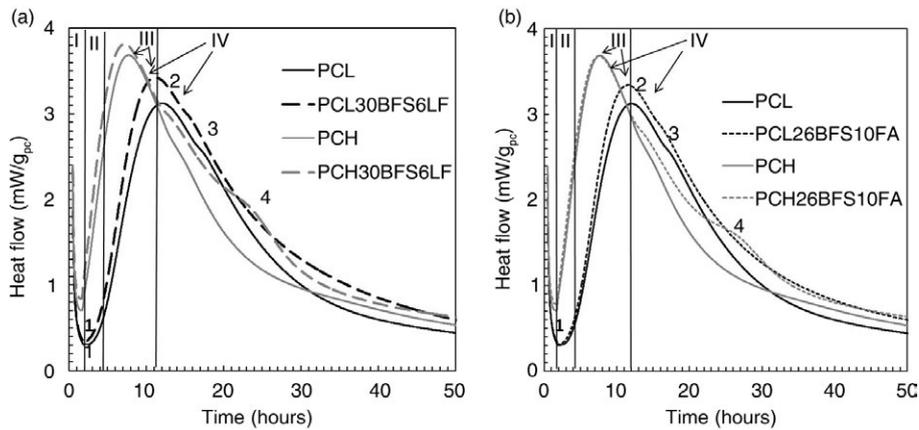

FIGURE 2. Heat flow per gram of PC during the first 50 hours of hydration. Left) PC_L and PC_H and ternary blends with 30BFS + 6LF. Right) PC_L and PC_H and ternary blends with 26%BFS + 10%FA.

PC with low alkali content and high replacement of BFS (39). The second shoulder had been attributed to a faster reaction of the C_4AF from the PC in blends containing BFS (19). In present case, the C_4AF content in PC_L was higher (15%) than in PC_H (7%); however, other factors as the higher pH in PC_H can influence the intensity of the shoulder in the ternary binders with this PC.

The two shoulders appeared in the last period (retardation period: IV) of hydration, which was a progressive deceleration resulting in a continuous decrease of heat flow. Table 5 summarizes the time period and the heat flow associated to each binder composition in the singular points (1–4) identified in Figures 1 and 2.

The influence and differences with the PC type can be clearly identified. PC_L mixes showed a similar exothermic heat flow in T1 but lower than PC_H mixes. In fact, PC_H mixes with mineral additions showed a certain increase in this parameter. In period T2 the maximum of the heat flow was more similar for binders using the two PC, although some higher with PC_H, what justifies the higher activity at early hydration with PC_H. At longer time, in period T3 the response was very similar whatever the type of PC, but clear differences were observed again at period T4 in PC_H showing higher heat flow.

After 24 hours of hydration, the formation of a rigid and hardened cement paste is obtained. The physical-mechanical properties at 24 hours in mortar still reflect the history of processes occurring during the first hours of hydration. Thus, the mortars showed differences in total porosity, average pore diameter, pore structure and mechanical strength as compiled in Table 6 and Figures 3 and 4.

There were several differences in pore size structure between the mixes depending on the PC composition. The PC_H showed a more refined pore structure in all mixes, especially in the region of small pores (< 1µm), probably due to a higher degree of reaction as observed in the higher heat flow (Figure 2, Table 5). The total porosity of the mixes with PC_H was also lower (Table 6). In agreement with the slower reaction of PC_L, bigger pores were observed except for PC_L30BFS6LF. PC_L30BFS6LF blend had a clearly refined pore structure, particularly fewer capillary pores (1 to 10µm). The result of the refinement of PC_L30BFS6LF explains its good

TABLE 5.   Time period (T) and corresponding heat flow (HF) in function of binder composition

Samples Identification	T 1 (h)	HF 1 (mW/gPC)	T 2 (h)	HF 2 (mW/gPC)	T 3 (h)	HF 3 (mW/gPC)	T 4 (h)	HF 4 (mW/gPC)
PC_L	1.9	0.3	12.0	3.1	16.7	2.6	-	-
PC_L6LF	2.1	0.3	12.1	3.1	17.0	2.6	-	-
PC_L36Q	2.1	0.3	11.6	3.6	15.7	2.9	-	-
PC_L36BFS	2.1	0.3	11.2	3.4	15.1	3.0	-	-
PC_L30BFS6LF	2.1	0.3	11.2	3.4	15.1	3.0	-	-
PC_L26BFS10FA	2.2	0.3	11.5	3.3	15.3	2.9	-	-
PC_H	1.5	0.7	7.7	3.7	13.6	2.7	-	-
PC_H6LF	1.7	0.8	7.7	3.5	14.0	2.5	34.0	1.0
PC_H36Q	1.6	0.7	7.6	3.7	13.6	2.7	27.5	1.4
PC_H36BFS	1.5	0.8	7.5	3.6	13.7	2.7	24.8	1.8
PC_H30BFS6LF	1.6	0.8	7.2	3.8	12.3	3.0	21.6	2.0
PC_H26BFS10FA	1.5	0.8	7.6	3.7	13.3	2.8	24.5	1.7

TABLE 6.   Total porosity and average pore diameter at 24 hours of hydration of PCs, binary and ternary blends

| Samples Identification | Total Porosity (%)/Average Pore Diameter (µm) | | | |
	1 day	7 days	28 days	90 days
PC_L	17.0/0.15	13.7/0.12	15.8/0.09	15.3/0.07
PC_L36BFS	16.0/0.10	12.0/0.07	12.7/0.06	9.8/0.07
PC_L30BFS6LF	15.8/0.09	14.8/0.07	12.0/0.04	10.3/0.04
PC_L26BFS10FA	14.9/0.08	12.6/0.07	11.3/0.05	9.5/0.04
PC_H	13.2/0.15	13.0/0.18	13.6/0.15	12.3/0.13
PC_H30BFS6LF	12.9/0.08	11.6/0.07	9.9/0.06	10.9/0.06
PC_H26BFS10FA	14.4/0.10	14.6/0.09	12.9/0.06	14.6/0.07
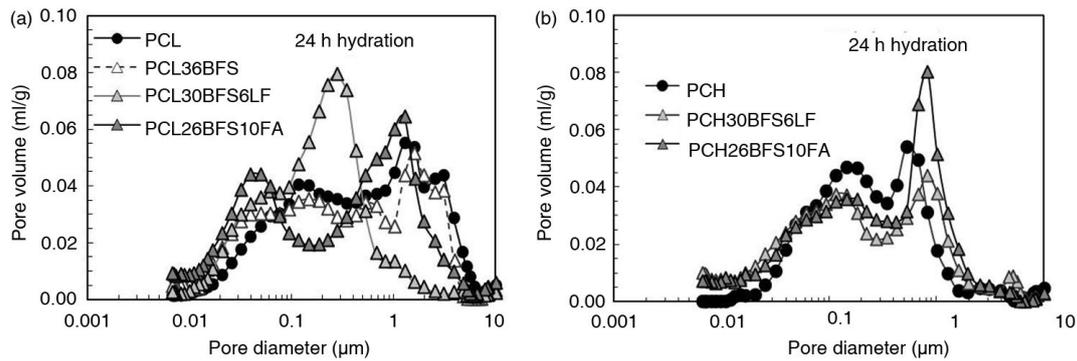
FIGURE 3.   Pore size distribution at 24 hours of hydration of PCs, binary and ternary blends.
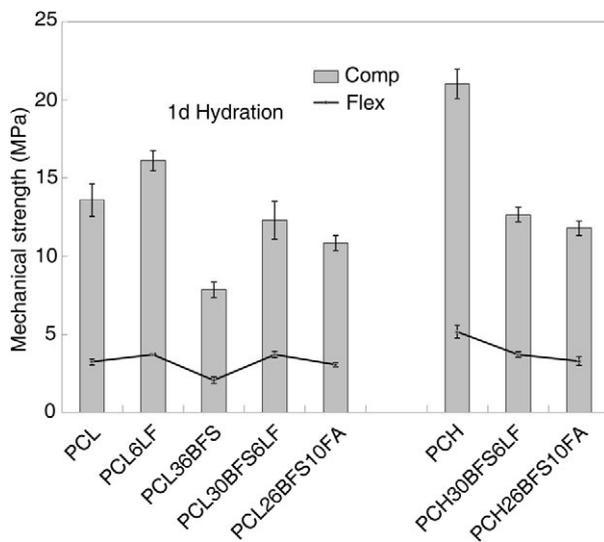

FIGURE 4.   Mechanical properties at 24 hours of hydration of PCs, binary and ternary blends.

mechanical properties shown in Figure 4 in comparison to its reference without mineral additions.

The binary mix with BFS reached lower compressive strength than PC_L. While the ternary mixes with PC_L and plain PC_L mortar exhibited similar compressive strength, the incorporation of LF (6%) in a binary mix increased compressive strength. This is related to synergistic contribution of mineral addition with the PC type, in this case the lower particle size of LF and the good ability of limestone to act as nucleation sites for C-S-H accelerating the initial hydration of PC_L must be contributing, as also suggested in (30, 31, 40).

After 1 day of hydration, the PC_H had higher mechanical strength than PC_L, in accordance with the setting times (Table 4) and calorimetric data (Figures 1 and 2). However, in contrast to PC_L, the ternary blends of PC_H had much less strength than the plain PC_H. In PC_L30BFS6LF mix the slower reaction of BFS than PC as suggested in (16) was compensated by the acceleration induced by the LF

in accordance with (40). The beneficial effect in ternary blends with BFS and FA can be also associated with the acceleration of the initial clinker hydration as suggested in (19, 22, 41), although this effect is expected to be less effective than for LF. In fact, in present study the compressive strength after 1 day of hydration was slightly lower in ternary binders with BFS + FA as also the setting time was slightly slower (Table 4).

In summary, ternary blends with PC_L minimized the loss in mechanical properties at early hydration ages (24 h), while in blends with PC_H, which exhibited a higher initial hydration, the incorporation of combined mineral additions further decreased the compressive and flexural strength.

3.2. Contribution of blends to the built-up of the microstructure and the mechanical properties

After the early hydration (24 h), which was dominated by the reaction of the Portland cement, the contribution of the mineral additions slowly became more important. The cumulative heat flow summarized in Table 7 shows a slightly higher total heat flow after two days in the presence of inert quartz, but no significant contribution of the quartz after this time. The slightly higher heat flow measured was related to the higher effective water to Portland cement ratio, which leaded to the availability of more water and thus a higher hydration degree of the Portland cement as also found in (31). The blends with LF showed some more heat flow after 48 hours in both cements, as a part of the LF could react with the aluminates to form monocarbonate thus preventing the destabilization of ettringite and it also accelerated the PC reactions (5, 22). The participation of BFS and FA was clearly observed after 48 hours, both in binary and ternary mixes. The contribution was more pronounced in the case of BFS, due to its higher hydraulic reactivity (16), while FA reacted slowly (13, 26, 42). This explains the higher total heat flow of $PC_{L/H}$30BFS6LF than that of $PC_{L/H}$26BFS10FA.

TABLE 7. Cumulative heat flow (HF) and relative increase as a function of mineral additions

Samples Identification	Cumulated H-F 1d Hydr. (mW/gPC)	% increase relative to PC	Cumulated H-F 2d Hydr. (mW/gPC)	% increase relative to PC	Cumulated H-F 7d Hydr. (mW/gPC)	% increase relative to PC
PC_L	170	-	239	-	314	-
PC_L36Q	174	2	252	5	328	4
PC_L6LF	181	7	262	9	340	8
PC_L36BFS	187	10	278	16	392	25
PC_L30BFS6LF	189	11	281	17	392	25
PC_L26BFS10FA	183	8	273	14	379	21
PC_H	197	-	268	-	357	-
PC_H36Q	194	0	272	2	367	3
PC_H6LF	206	5	291	9	385	8
PC_H36BFS	213	8	310	16	449	26
PC_H30BFS6LF	223	14	309	15	439	23
PC_H26BFS10FA	211	7	300	12	427	20
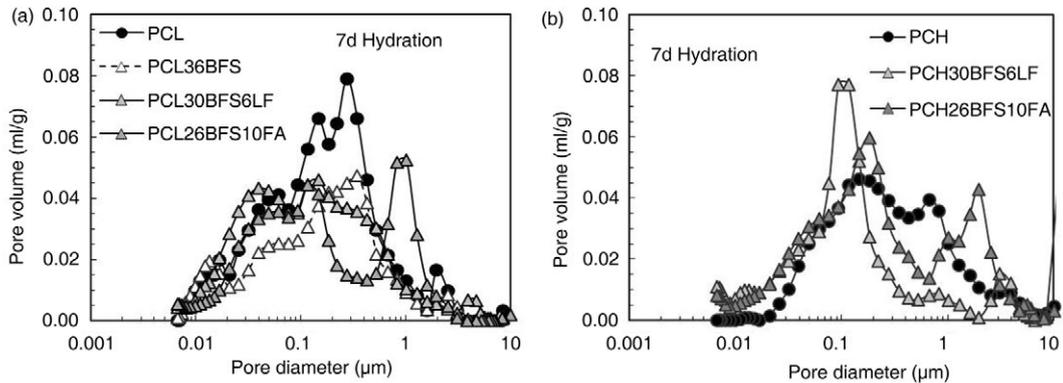
FIGURE 5. Pore size distribution at 7 days of hydration of PCs, binary and ternary blends.
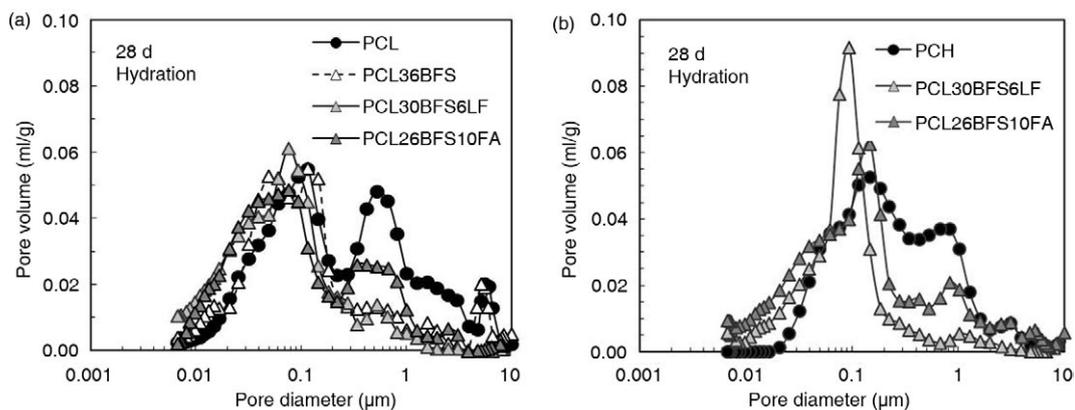
FIGURE 6. Pore size evolution at 28 days of hydration of PCs, binary and ternary blends.

The porosity or rather fraction of space occupied by unreacted solids and hydrates determines the mechanical properties for the mortars. Thus a refinement of the pore structure is expected to increase mechanical strength. Mineral additions refined significantly the pore structure compared to the plain PCs and also reduced the total porosity, especially in blends based on PC_L after 90 days of
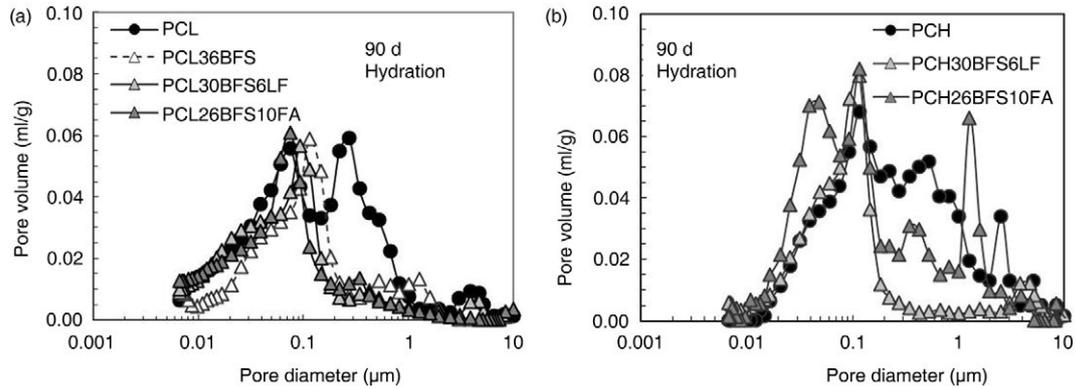
FIGURE 7. Pore size evolution at 90 days of hydration of PCs, binary and ternary blends.
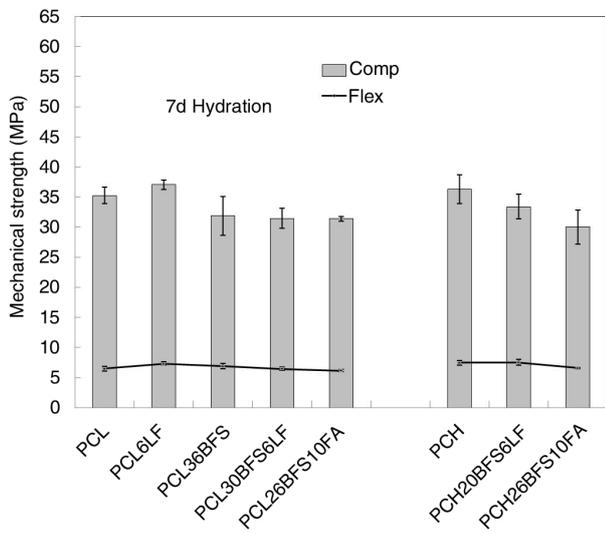

FIGURE 8. Mechanical properties at 7 days of hydration of PCs, binary and ternary blends.
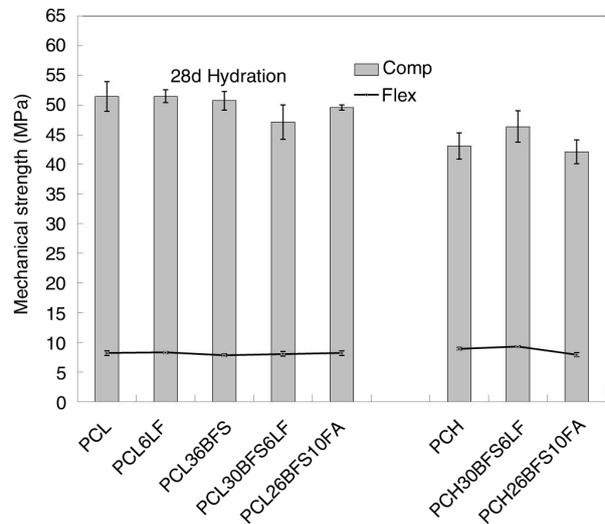

FIGURE 9. Mechanical properties at 28 days of hydration of PCs, binary and ternary blends.

hydration. Figures 5 to 7 compile the pore size distribution and the Table 6 shows the total porosity at 7, 28 and 90 days of hydration.

The contribution of the hydration of FA and in particular of BFS, as observed from heat flow, was mirrored in the refined pore structure both for binary and ternary blends. The refinement of the pores was less distinct in ternary blends containing FA due to its lower reactivity. This refinement of the pores was in agreement with the higher bound water content of BFS + LF compared to BFS + FA ternary blends observed in the first week of hydration as found in a previous work (21). In all cases, the blends showed fewer capillary pores at 90 days of hydration than the plain PC_L.

In summary, regardless of the type of PC and additions combined, the inclusion of a mix of BFS and FA or limestone up to 36% refined the pore microstructure. In addition, it did not penalize the mechanical strength compared to plain PC after 28 days and longer (Figures 8-10).
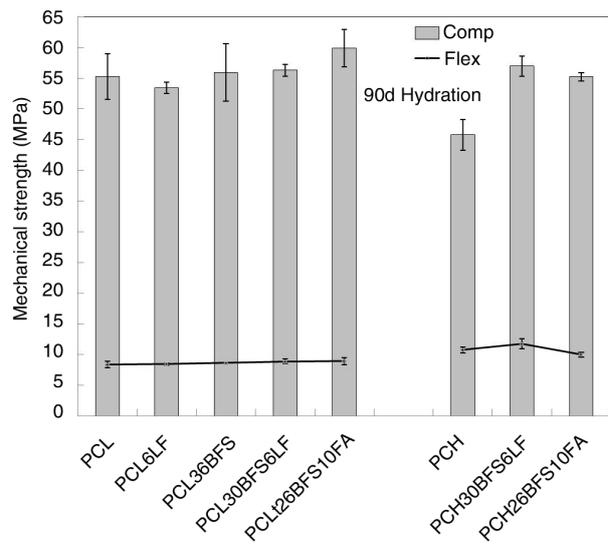

FIGURE 10. Mechanical properties at 90 days of hydration of PCs, binary and ternary blends.
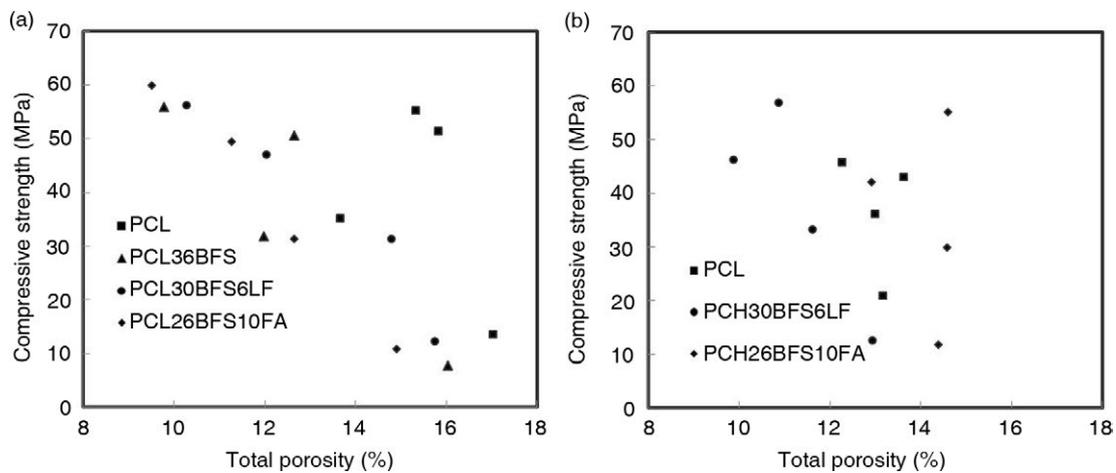
FIGURE 11.   Compressive strength against porosity at 1, 7, 28 and 90 days of hydration of PCs, binary and ternary blends.

After 90 days of hydration the $PC_L26BFS10FA$ blend had a somewhat higher compressive strength than $PC_L30BFS6LF$ as consequence of the pozzolanic reactions of the FA. Although FA reacted slower than the clinker (43) or BFS (13), its reaction could generate additional hydration products and thus a higher compressive strength after long hydration times. In fact, only 20 to 25% of FA will have reacted in such blends (44–46) after 90 days of hydration. It is remarkable that there were not significant differences in the compressive strength between the same blends with different PC. However, the values of $PC_L26BFS10FA$ were higher than $PC_H26BFS10FA$, indicating that the reactivity of the FA varies with the type of PC. For the plain PC_H, which had shown a fast initial hydration and high early strength, slight refinement of the pore structure and slight increase of compressive strength was observed after 28 days, such that after 90 days PC_H had the lowest compressive strength of the evaluated samples. This also agrees with the increase in the bound water content measured after 28 days detected in ternary blends (based on both PCs) and PC_L pastes but not in PC_H one (21).

This mechanical response correlates with the porosity. In fact, a good correlation between the compressive strength and the total porosity was found, especially in ternary blends based on PC_L, as can be seen in Figure 11.

In general, samples based on PC_L had a better correlation between both parameters, especially the blends. In this sense, the PC_L sample at 28 and 90 days of hydration had higher total porosity values than expected considering the compressive strength values. By contrast, the results of the samples based on PC_H had more dispersion. These results also agree with the loss of effectiveness of the mineral additions when they were used with PC_H, mainly in the early ages.

4. CONCLUSIONS

The chemical and mineralogical composition of the PC is a key parameter in the hydration kinetics and in the synergy between PC and mineral additions.
–   Low alkali and low C_3A Portland (PC_L) cement exhibit a slower hydration initiation, that results in later setting time, lower initial heat flow, lower early strength generation and less pore structure refinement than higher alkali and higher C_3A content cement (PC_H). However, in the long term, PC_L has a more refined pore structure and a higher compressive strength than PC_H.
–   The PC type used in ternary blends influences the generation of properties at early ages of hydration. At long hydration times, however, higher compressive strengths were observed in all ternary blends regardless the PC type.
–   For higher alkali and higher C_3A cement (PC_H), the blending with two mineral additions (in the contents and compositions evaluated in this paper) significantly reduces the initial heat flow of the hydration, delays the setting, causes poorer initial mechanical strength and coarser pore structure with respect to the reference PC without additions. In the long term, however, the reaction of the mineral additions results in a more refined pore structure and higher compressive strength of the ternary blends studied than that of plain PC_H.
–   For low alkali and low C_3A cement (PC_L), the presence of mineral additions had little delay in the initial heat flow and setting times, resulting in similar early mechanical strength and porosity than for plain PC. These good mechanical properties of the ternary blends are maintained and even improved at longer ages of hydration, also in the pore structure refinement.
–   Ternary blends containing FA show significant dependence of the PC composition used.

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