Ordinary Portland Cement composition for the optimization of the synergies of supplementary cementitious materials of ternary binders in hydration processes

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Abstract

The synergistic effects of using several supplementary cementitious materials (SCMs), such as Blast Furnace Slags plus Limestone Filler or Fly Ashes, depend on the OPC composition. When using an OPC which is poor in C₃A and alkalis in ternary formulations, a similar initial strength gain to that of a plain OPC is detected and at longer hydration ages, the formation of monocarboaluminate, hemicarboxonate and hydrotalcite instead of monosulphate can be seen. If an OPC with a higher C₃A content and alkalis is used with SCMs, the higher availability of Al causes the early formation of monocarboaluminate and a lower initial strength gain. At longer hydration times, in ternary blends with both OPCs, the mechanical strengths are higher and the C-S-H gels formed are richer in Al and poorer in C/S ratio with a subsequent lowering of the alkali content in the pore solution when compared to that in plain OPC.

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1. Introduction.

The use of supplementary cementitious materials (SCMs) in suitable proportions and combinations in the fabrication of cementitious materials can have technical, economic and environmental advantages due to a lower consumption of clinker being required and the valorization of industrial byproducts [1-3]. Therefore, the use of multiblends (composed of OPC plus one or more SCM/s) is being standardized following the new trends in cement development.

The most commonly used SCMs in cement production are blast furnace slag (BFS), fly ash (FA), limestone filler (LF), silica fume, natural pozzolan and metakaolin. It is well known that BFS mixed with OPC shows mainly hydraulic but also slightly pozzolanic activity that causes slower reactivity than OPC at early ages, but at longer hydration ages, a greater amount of C-S-H gel with a lower C/S ratio is formed to accommodate the lower overall C/S ratio of the system [4]. Moreover, the high Al content (compared to OPC) facilitates the formation of hydrates such as monocarboaluminate (in the presence of CaCO_3 in OPC) and the incorporation of Al in the C-S-H gels formed. In the case of FA, a similar situation occurs, due to a higher Al content than BFS, but lower reactivity because it only has pozzolanic properties when mixed with OPC. The substitution of OPC for high FA or BFS contents can mean a decrease in the mechanical performance of the cementitious materials obtained, especially at early hydration ages

[5-7], so longer curing times are needed in order to achieve similar strength values [1], although the use of BFS or FA in suitable proportions can show improved mechanical strength after longer hydration times [5]. The use of LF is commonly used as a minor additional constituent (below 5% in mass) of most of the OPC that contributes to filling the fine fraction of aggregates, improving packaging and blocking capillary pores [5]. In addition, it has a certain ability to build nucleation sites for the formation of the first portlandite crystals at early ages and it is also believed to participate in monocarboaluminate formation [4, 8]. In addition, LF can enhance BFS hydration [9]. However the percentage of OPC to be replaced by LF is recommended as being lower than 10-15%, in order to avoid the loss of mechanical strength caused by the dilution effect of hydrated material at advanced hydration ages [3, 5, 10].

The combination of SCMs with synergistic effects caused by the above limitations of binary blends has been proposed. In this context, ternary blends emerge as a sustainable option for improving the performance of binary blends and also that of cements without SCMs. For this reason, there are many recent studies on ternary and even quaternary blends. Some of these studies were carried out in the development of low-pH cementitious materials for high level radioactive waste (HLRW) repositories [11-13], while others are mainly focused on their mechanical and/or durability properties [3, 5, 14, 15] and other studies involve microstructural processes [16-18], including thermodynamic modelling [19]. Nevertheless, some differences can be seen in the papers published and it seems that better mechanical strength gain is obtained in ternary blends at early hydration ages when using an OPC with a low C_3A content and/or alkali content [3, 5, 20, 21], while the initial synergy is lower when the OPC used has a higher content [16, 17, 22-25]. In addition, these results have no apparent relation to other

parameters of the OPCs used, such as their fineness or the content in the rest of the anhydrous phases. Therefore, this suggests that the chemical and mineralogical composition of the OPC used must be a key factor in the mechanical performance of the ternary blends created and, accordingly, the phenomena involved must be related to several changes in the microstructural development of the resulting materials. These changes have not been well identified in previous publications so the goal of this paper is to analyze the modifications caused by the synergistic effects of the different SCMs, depending on the OPC composition (specifically, the C₃A and the alkali contents). This will be done by studying the mechanical properties and evaluating the related changes in the pore solution and the microstructure of the resulting ternary blends.

2. Experimental.

2.1 Initial characterization of raw materials

Ternary blend cement pastes and mortars were manufactured using Ordinary Portland Cement (OPC) plus two SCMs selected from: blast furnace slag (BFS) and class F low calcium fly ash (FA) or limestone filler (LF). Two types of OPC were used: CEM I 42.5 R-SR (identified as OPC-1) and CEM I 42.5 R (identified as OPC-2). Both OPCs contain a calcium carbonate content incorporated as a minor additional constituent according to UNE-EN 197-1:2011 (<5%): 4% in the case of OPC-1 and 3% in OPC-2, determined from TG tests. The chemical compositions of these materials were analyzed by X-ray fluorescence (XRF) and they are detailed in Table 1 (expressed in wt.%).

<Table 1>

The $\text{Na}_2\text{O}_{\text{eq}}$ contents calculated show relevant differences between both OPCs. In fact, the content in OPC-1 is considered as low ($<0.60 \text{ Na}_2\text{O}_{\text{eq}}$). Although there is not a significant difference between the Al_2O_3 content in both OPCs, by applying the Bogue formula [26], with a correction by using a mass balance with the calcium carbonate present in both OPCs, a significant difference is obtained in the C_3A content between both OPCs: 4% in OPC-1 and 10% in OPC-2. The content of the rest of anhydrous phases of clinker are: 50% C_3S , 12% C_2S and 15% C_4AF for OPC-1, and 53%, 16% and 7%, for OPC-2 respectively. SCMs have higher alkali and Al_2O_3 contents than both OPCs. The mineralogical composition of the raw materials was studied by using X-ray diffraction (XRD). The diffractograms of both OPCs show C_3S , C_2S and calcite as major constituents and C_3A , C_4AF and gypsum as minor ones. The C_3A peak is more pronounced in the case of OPC-2. The results show differences in the crystallinity of the SCMs, with BFS as the lowest with only some diffuse peaks of calcite detected. FA shows calcite, quartz, magnesite and mullite and LF shows calcite as a major constituent, as well as traces of quartz, arcanite and dolomite.

The thermal stability of the materials was characterized using thermo-gravimetric analysis (TG). In the case of the OPCs, the peaks seen are associated with the decomposition of gypsum at 90 and 350°C [27], and with the decarbonation of carbonates from filler at around 700°C. For SCMs, the peak was identified at 700°C, although this is very slight in BFS and FA. The low content of carbonates in the LF used ($<70\%$) for ternary blends is due to the geological nature of the parent rock (black limestone) used.

The particle size distribution was characterized by using laser diffraction spectrophotometry. The results are shown in Figure 1. Furthermore, Table 2 shows the pore size distribution parameters. The particle size distribution was similar in both OPC and BFS. The similar particle size distribution of the cements used in this study can rule out this parameter as being responsible for the possible differences detected in the ternary blends [28]. LF showed the lowest mean particle size, while FA had the highest.

<Figure 1>

<Table2>

The water solubility of the alkalis present in the OPCs and SCMs was also analyzed. The solubility test followed was based on mixing each separate component with deionized water in a solid/liquid ratio by weight = 1 [29, 30] and stirring the resulting slurry for 30 min. The suspension was vacuum filtered, and the pH and the ionic composition were determined. The percentage of soluble alkalis and the pH of the filtrate were measured with an electrode in the resulting suspensions of the solubility test, which are shown in Table 3.

<Table 3>

The initial water solubility of the alkalis from both OPCs is much greater than that of the SCMs (two orders of magnitude in the case of K and one in the case of Na), which is expected to cause, at least in the initial stages, less alkalis incorporated into the pore solution of ternary blends, despite the higher $\text{Na}_2\text{O}_{\text{eq}}$ content of the SCMs (Table 1).

2.2. Preparation of ternary blends

Table 4 shows the cement formulations considered in this paper. Prismatic mortar samples (4 cm x 4 cm x 16 cm) with a water/binder ratio (w/b) = 0.5 and binder:sand of 1:3 were manufactured, following the UNE-EN 196-1 standard, to analyze the mechanical performance of the different binder mixes at 1, 7, 28 and 90 days of curing. In addition, cement pastes were manufactured by using a w/b ratio of 0.5. The manufactured samples were demolded after 24 hours and kept in a curing chamber at $21\pm2^{\circ}\text{C}$ and $98\pm2\%$ RH. In this paper, both the mortars and cement pastes were subjected to the same curing conditions in order to better relate the mechanical properties measured in mortars to the microstructure development evaluated in cement pastes. Samples were taken out at different curing ages for the characterization tests required. In the case of the cement pastes, approximately 1 cm depth was removed before each test to minimize any carbonation effect, and the core of the sample was used for characterization.

2.3. Determination of hydration evolution

The hydration of ternary blends was characterized at several curing ages (2, 7, 28, 90, and in some cases, 200 days) by determining the pore solution composition and the evolution of solid phases.

Pore solution extraction was carried out by following the “Pore Fluid Expression” technique [31, 32]. Two samples for each blended cement paste were used for determination of repeatability. The protocol described in [33] was followed. It basically

consists of applying high pressures to a granulated cement paste (particles of approximately 5 mm) to collect the pore solution of the paste. For the extraction of the solution, about 125 grams of granulated material were used. The pH was measured using two procedures: 1) using a pH stable electrode in a high alkaline media and 2) titration of OH^- using HCl 0.01N and with phenolphthalein and methyl orange used as color indicators. The concentration of Na, K, Ca, Si, Al and S were analyzed using a plasma mass spectrometer. The results shown in this paper refer to the mean value of two similar pore expressions of each cement paste sample.

The hydration evolution in solid cement pastes was determined after stopping the hydration processes at different ages, after powdering the samples and removing the free water using ethanol (to stop the hydration) and acetone (to remove the excess ethanol) to minimize leaching of the solid phases (C-S-H gel and portlandite) as considered in [34]. The evolution of the hydrated solid phases was followed using several characterization techniques: 1) XRD patterns were recorded at room temperature in the interval $5^\circ < 2\theta < 60^\circ$, with a step size of $2\theta = 0.01973^\circ$ and 0.5 s per step. 2) DTA/TG data was obtained with a resolution of 0.01 mg. The sample was heated to 1000°C at a heating rate of $10^\circ\text{C}/\text{min}$ using nitrogen as a medium under static conditions. Alumina powder was used as a reference material. 3) FT-MIR measurements were performed with a Thermo Scientific Nicolet 6700 by preparing a pellet with 1 mg of the sample and 300 mg of KBr and compacted under a vacuum, with 64 scans in a range of $40000 - 400 \text{ cm}^{-1}$. 4) BSEM images were obtained using a Hitachi S-4800 scanning electron microscope equipped with a BRUKER 5030 energy dispersive analyzer that allowed the analysis of the chemical composition of the hydration products. The samples were embedded into an epoxy resin, cut, polished and

then coated with carbon. The EDX microanalyses were mainly used to analyze the C-S-H gel composition at different hydration ages.

3. Results and discussion.

3.1. Evolution of mechanical strength

The compressive strength of the ternary blends was evaluated in order to determine the influence of the synergy of the SCMs used on the mechanical strength gain, depending on the OPC composition. Figure 2 shows these results. When comparing each ternary blend with its counterpart with a different OPC, there are no significant differences between the SL samples. However, while at early hydration ages, SF-1 and SF-2 show a similar strength gain, at advanced hydration ages, the compressive strength of SF-1 is 15% higher than that of SF-2. In fact, SF-1 shows the highest long-term compressive strength of the manufactured mortars. Therefore, it is possible that the FA reactivity depends on the OPC used at a higher level than BFS. Regarding the comparison between ternary mortars and their references, it should be highlighted that the mechanical strength evolution of both reference mortars is very different, so this logically influences the comparative results. With the low alkali and low C_3A cement the compressive strength of ternary blends shows a very low mechanical loss with respect to the reference at 1 day of hydration, while with OPC-2, the loss is about 50%. After the first 24 hours of hydration, OPC-2 shows a low strength gain, so the ternary blends based on OPC-2, with a strong increase during this period, are equalling and even improving the long term reference result. The designed ternary blends

1 manufactured with OPC-1 can replace OPC-1, due to their similar mechanical behavior,
2 even in the first day of hydration.
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11 The different mechanical behavior of the references, as well as the modifications seen in
12 the ternary mortars, should, logically, be due to the different precipitation-solubilization
13 processes of the products formed in the hydration reactions of the material. For this
14 reason, the microstructures and the pore solutions of the samples have been analyzed in
15 the following sections.
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26 ***3.2. Evolution of the microstructure and pore solution compositions of the reference*** 27 ***samples*** 28 29 30

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32 In order to evaluate the influence of the OPC composition on the synergistic effects
33 caused by the combination of two SCMs in the microstructural phenomena, the results
34 of the reference pastes are shown first. The composition and pH of the pore solutions
35 vary widely between both references. Table 5 shows the mean value of the 2
36 measurements of the compositions and the pH values of the pore solutions of OPC-1
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56 K is the main species in the pore solution of both references, but OPC-2 has a higher
57 content, especially at advanced ages of hydration caused by a significant decrease in the
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1 K content in OPC-1. The Na content is more or less similar in both samples and the
2 total alkali content ($\text{Na}_2\text{O}_{\text{eq.}}$) calculated is higher in OPC-2. The lower $\text{Na}_2\text{O}_{\text{eq.}}$ content in
3 OPC-1 in relation to the hydration time causes a lower pH value in the pore solution and
4 it is compensated for with a higher Ca content. The Al content is much higher in OPC-2
5 than in OPC-1, and this could be due to the higher C_3A content in OPC-2 than in OPC-
6 1. The Si content is also higher in OPC-2 than in OPC-1 in the first days of hydration,
7 despite the similar Si content in both OPCs. There is a faster dissolution of the C_3S
8 and/or C_2S in OPC-2 than in OPC-1, which explains the higher compressive strength of
9 OPC-2 than that of OPC-1 in the first day of hydration (Figure 2), which would
10 contribute to these differences. Regarding the S content, in OPC-1 there are high values
11 at early hydration ages caused by the fast dissolution of gypsum [35], while in OPC-2
12 this high content is prolonged for a longer period. In the long term, the S content
13 decreases in both samples.

14 In order to analyze the different processes of precipitation-solubilization in the
15 hydration of the material, the microstructure references were characterized by using
16 XRD. The diffractograms (Figures 3 and 4) show differences in terms of the
17 formation/consumption of the crystalline phases of both reference samples. The main
18 hydrated phases identified in both references are portlandite, ettringite and hydrated
19 calcium silicates (C-S-H); although most of the C-S-H has an amorphous formation,
20 there are semi-crystalline forms with a C/S ratio higher than 1.5 that can be identified in
21 these XRD tests. The Si-hydrogarnet detection should also be highlighted, despite being
22 a difficult compound to identify using conventional characterization techniques without
23 pretreatment with a selective SAM (salicylic acid/methanol) solution to remove the
24 main phases of the paste [36]. At 2 days of hydration, C_3A is detected in OPC-2 and in

1 OPC-1, but with less intensity in OPC-1, due to the lower content in OPC-1 than in
2 OPC-2. At 90 days of hydration, the main difference between both references is the
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4 formation of monocarboaluminate in OPC-2 instead of monosulphate in OPC-1, due to
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6 the higher availability of Al in the pore solution of OPC-2, which limits the ettringite
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8 and aluminium reaction.
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14 <Figure 3>
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21 TG analysis was also performed. Figures 5 and 6 show the dTG results of the reference
22 samples at the different hydration times. In OPC-2 a peak in the 110-170°C region is
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24 detected after 7 days and it increases with the hydration time; this peak is associated
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26 with the dehydration of the hemi- or monocarboaluminate, as suggested in [37, 38]. In
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28 both references, slight weight loss is detected at 180-195°C, which could be related to
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30 monosulphate dehydration [39-41]. Both references also show three main peaks: 1) up
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32 to 350°C it is mainly associated with C-S-H gel dehydration, but also with other
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34 products such as ettringite, 2) at 400-500°C it is associated with the portlandite
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36 dehydration and 3) at 650-750°C it is associated with the decomposition of carbonates
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48 <Figure 5>
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51 <Figure 6>
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55 In order to evaluate the C-S-H gel in depth, its chemical composition was studied by
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57 using BSEM-EDX, especially the Al_2O_3 content and C/S ratio. These results are shown
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in Figures 7 and 8 respectively. The results shown refer to the mean value of more than 50 measurements in each sample so the standard deviations are also shown in these figures. The results of the other cement pastes are also shown in order to be discussed in the next sections. A higher Al content is detected in C-S-H gels formed in OPC-2 than those in OPC-1 at 2 and at 90 days of hydration due to the higher availability of this element (Table 5) and the higher C₃A content of OPC-2 than that of OPC-1 (Table 1).

<Figure 7>

<Figure 8>

Once the different microstructural evolution of the reference materials are evaluated, the influence of the OPC composition in the microstructural synergistic effect of each SCM pair (BFS + LF or BFS + FA) in ternary blend is analyzed in depth. This is shown in the following two sections.

3.3. Evolution of the microstructure and pore solution compositions of BFS + LF blends

The pore solutions of SL-1 and SL-2 were analyzed. Their compositions and pH values are shown in Table 6. There are some differences between the SL-1 and SL-2 pore solution compositions. The K content is higher in SL-2 than in SL-1, although in both cases, the values are lower than those of the reference samples (Table 5). Slight differences in pH can be seen in the references with respect to these ternary blends, which are always slightly lower, since the blends have a lower Na₂O_{eq.} content. The Ca content is higher in SL-1 than in SL-2, as occurred between OPC-1 and OPC-2, to

compensate for the lower $\text{Na}_2\text{O}_{\text{eq}}$ content calculated. The Al contents are lower in SL-2 than in OPC-2, but the SL-1 contents are higher than the OPC-1 ones, especially in the short term. The lower initial Al content in SL-2 than in the OPC-2 pore solution can explain the lower mechanical response of this sample at 1 day of hydration (Figure 2). This is because it can promote the formation of compounds like monocarboaluminate or hemicarbonate in SL-2, instead of C-S-H gels as in OPC-2. This is also because this low Al content should be related to a lower C_3A dissolution. As C_3A is the most reactive anhydrous phase, accordingly, its slower reaction causes a lower formation of hydrates during the early ages. In fact, this early formation of monocarboaluminate in SL-2 and the latter formation in SL-1 are detected in the XRD tests (Figures 9 and 10). The Si content is higher in SL-2 than in SL-1, but the values of SL-2 are much lower than in OPC-2, mainly in the first days of hydration, which can be related to the higher formation of C-S-H gels in OPC-2. This agrees with the lower initial strength of SL-2 or with these C-S-H gels incorporating more Si into their composition [16]. The S content is similar in both ternary blends, although it is much lower than the reference values at early hydration ages. This is probably due to the higher S initial reactivity in addition to the lower gypsum content. Figures 9 and 10 show the diffractograms of SL-1 and SL-2.

<Table 6>

<Figure 9>

<Figure 10>

In SL-1, at 90 days of hydration, monocarboaluminate, hemicarbonate and hydrotalcite are detected, instead of the monosulphate detected in OPC-1 (Figure 3), due to the reaction between the calcium carbonate from the LF and the aluminate hydrates [37,

43]. Monosulphate hydrate is not stable in the presence of calcium carbonate, and monocarboaluminate (and/or hemicarbonat) is formed instead. Monocarboaluminate causes the stabilization of ettringite, thus increasing the volume of hydration products, which causes the higher compressive strength measured in SL-1 (Figure 2) [5, 16]. This phenomenon is also corroborated by considering the S/Al evolution ratios of the pore solutions (Tables 5 and 6), as a decrease in this value causes the decomposition of more ettringite after sulphate depletion. In OPC-1, a continuous and significant decrease is detected but not in SL-1. Therefore, the ettringite stabilization is mainly due to the formation of monocarboaluminate in SL-1, and the subsequent increase in the stable volume of hydrates can partially explain the good compressive strength values detected in SL-1 (Figure 2).

In OPC-2, monocarboaluminate was detected by using XRD (Figure 4), but only at 90 days of hydration, while in SL-2 it is already present at 2 days of hydration. These differences compared to SL-1 must also be related to the compressive strength results, possibly because the early formation of monocarboaluminate could limit the role of this hydrate in the ettringite stabilization, thus also reducing the volume of stable hydrates. It should be highlighted that at 90 days of hydration, C₄AF is not detected in the samples based on OPC-2, so their faster liberation to the pore solution can be deduced, thus increasing the monocarboaluminate formation. The presence of monocarboaluminate is also detected by the TG tests. Figures 11 and 12 show the dTG results of SL-1 and SL-2.

<Figure 11>

<Figure 12>

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2 In both cases, the same phases as in OPC-2 (Figure 6) are detected, although in SL-1,
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4 the peak associated with monocarboaluminate/hemicarbonate is only evident at 90 days
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6 of hydration. In addition, in both cement pastes a fifth peak appears just before the
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8 portlandite peak that can be attributed to hydrotalcite and which also increases in
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10 intensity with BFS hydration.
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17 A higher alumina content is detected in the C-S-H gels formed in SL-1 and SL-2 with
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19 respect to their respective references at 2 and 90 days of hydration (Figure 7) caused by
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21 the Al released by the SCMs. These contents are higher in SL-2 than in SL-1 due to the
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23 higher Al content in OPC-2 than in OPC-1. The C/S ratios (Figure 8) are similar in both
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25 blends, but they are lower than their references, even though LF should increase this
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27 ratio in the cases of SL-1 and SL-2 [9]. The C-S-H gel structure was analyzed in the
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29 pastes by using the FT-MIR results at 28 and 200 days of hydration in Figure 13.
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41 In all the cases, the main bands corresponding to C-S-H gels are detected at 973 cm^{-1}
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43 and to a lesser degree at 458 cm^{-1} [44], with the former being assigned to the Si-O
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45 stretching vibrations of the Q^2 tetrahedra of C-S-H gels with high C/S ratios (>1.5).
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47 However, the band at 458 cm^{-1} corresponds to the internal deformation of TO_4
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49 tetrahedra and, at 200 days of hydration, it has a slightly higher intensity in SL-1 than in
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51 OPC-1. This can be related to the presence of certain C-S-H gels with a C/S ratio <1.5 .
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53 This structure means a higher polymerization of silicate chains and a high content of the
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55 less strongly hydrogen-bonded water molecules in the interlayer space [45]. Several
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studies suggest that C-S-H gels with a rich-Al content and a poor C/S ratio retain a higher alkali content in their structure and therefore present a lower alkali content and lower pH values in the pore solution [11, 13, 16, 35, 46-51], although in this study the differences in the C/S ratio (Figure 8) are not very significant. This kind of C-S-H gel is formed by the contribution of SCMs, mainly BFS, in these samples. The hydration products that are being formed around the BFS particles have low C/S ratios and very high Al contents, especially in the areas closest to the unreacted core of the particle. Regarding this, Figure 14 shows a BSEM image focused on a particle of BFS at 90 days of hydration and the EDX analysis points are defined.

<Figure 14>

The points analyzed in the core of the anhydrous particle (squares) have (on average) 14% Al content and a C/S ratio of 1; the points in the cement paste near to the BFS (crosses), 9% Al and a C/S ratio of 1.3; and the C-S-H gel in the triangle point, far from the BFS particle, C/S ratio of 1.5 and 5% Al. Therefore, the BFS reactivity, whose composition is richer in Al and Si and poorer in Ca than the OPCs, (Table 1) is related to the formation of C-S-H which is richer in Al and poorer in C/S ratio in the ternary blends than in the references.

Therefore, according to the results obtained, there are no big differences between the microstructure evolution of SL-1 and SL-2, being the main difference the formation at long hydration ages of hemicarbonate and hydrotalcite in SL-1 and at earlier ages, the formation of monocarboaluminate in SL-2. These slight differences agree with the similar strength gain evolution obtained in SL-1 and SL-2 mortars. However, there are

significant differences between the references and the ternary blends, especially in the initial synergy, with the OPC with low C₃A and alkali content being higher.

3.4. Evolution of the microstructure and pore solution compositions of BFS + FA blends

Although 90% of the raw composition of SF-1 and SF-2 is the same as SL-1 and SL-2 respectively, the microstructures and pore solutions of SF-1 and SF-2 are analyzed in order to study the possible differences between this combination of SCMs and the BFS + LF with both OPCs. The pore solution compositions of SF-1 and SF-2 are very similar to SL-1 and SL-2 (Table 6) respectively, as can be seen in Table 7. Only in the case of SF-2 is a significant decrease in Al content identified at 90 days of hydration, which is probably related to a limited reactivity of FA in SF-2.

<Table 7>

Therefore, the availability of Al is again a key factor, as in SF-2 the formation of compounds like monocarboaluminate is caused in the first days of hydration with a lower initial compressive strength caused by the limitation of the C-S-H gel formation (Figure 2) as in the case of SL-2 (Figure 10), while in SF-1 it is only detected at 90 days of hydration, as in the case of SL-1 (Figure 9). Figure 15 and 16 show the diffractograms of SF-1 and SF-2.

<Figure 15>

<Figure 16>

1 The most significant difference between SL-formulations and SF-formulations is the
2 monosulphate formation in SF-2 at 90 days of hydration, but not in SL-2, and this could
3 be related to a higher volume of stable hydrates in the latter, thus explaining its higher
4 compressive strength. This agrees with the fact that FA reactivity is lower than BFS
5 reactivity and SF-2 also has a lower BFS content than SL-2. In fact, FA causes long
6 term pozzolanic reactions and the calcium aluminate hydrates formed in these reactions
7 can react with the carbonate of the LF and form calcium carboaluminate hydrates.
8 Therefore, the early formation of monocarboaluminate in SF-2 due to the higher Al
9 content in OPC-2 than in OPC-1, can limit the later formation of this hydrate with the
10 alumina released from FA, whose reactivity could be lower with OPC-2, and the one
11 previously released by BFS is not enough. The lower Al content in the pore solution of
12 SF-2 than in SL-2 (Tables 6 and 7) confirms this.

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31 Regarding thermal stability, the same compounds were detected in SF-1 and SF-2
32 (results not shown) as in SL-1 and SL-2. In addition, as occurs in these samples, a
33 higher Al content is detected in the EDX analysis of the C-S-H gels of SF-1 and SF-2
34 than in their respective references and the content is higher in SF-2 than in SF-1 (Figure
35 7) due to the low Al content of OPC-1. The C/S ratios (Figure 8) are similar in both
36 blends and lower than their references.

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48 Therefore, according to the results obtained, the OPC composition has a greater
49 influence on the microstructure development of binders based on BFS plus FA. It is
50 clear that the alumina content is the key parameter that mainly explains the differences
51 seen. FA has a high Al_2O_3 content, so its reactivity must be limited when it is combined
52 with BFS (which also has a high Al_2O_3 content) plus OPC with a medium Al_2O_3 . This

also explains the lower long-term pozzolanic reaction effect detected in the mechanical strength of SF-2.

3.4. Influence of OPC composition on the synergies between SCMs

The synergistic action of the SCMs used in the percentages considered in this study causes different changes in mechanical properties. As demonstrated, these changes are related to changes in the microstructure and pore solution evolution of the resulting materials during hydration. In fact, these changes are different depending on the chemical composition of the OPC used, with a stronger resulting effect when using BFS and FA than when using BFS and LF.

The alkali (especially K) content in ternary blends is lower than in their references, although these differences are more significant at early ages of hydration in the pastes based on OPC-1. As shown in Figure 17, the alkali content (expressed as mg/l of $\text{Na}_2\text{O}_{\text{eq.}}$) is closely linked to the pH of the pore solution, regardless of the age of hydration or the SCMs used in each case.

<Figure 17>

Instead of the higher alkali content of the binder formulations of the ternary blends, the alkali content of the pore solution is always lower (or at least similar) in ternary cement pastes with respect to their references. Some mechanisms that could explain these differences are the composition of C-S-H gels formed in blended cement pastes at longer hydration ages, which are richer in Al and poorer in C/S ratio than the C-S-H

1 gels formed from plain OPC, the lower clinker content and the portlandite consumption
2 in the pozzolanic reactions. García Calvo *et al.* [12] associated the retention of alkalis in
3 these kinds of C-S-H gels with the possible replacement of alkalis by Ca^{2+} in the pore
4 fluid (electro-neutralization of the system) and Lothenbach *et al.* [4] postulated that the
5 higher sorption of alkalis by C-S-H gel with a lower C/S ratio is probably caused by the
6 negative charges from the ionization of silanol groups, the partial substitution of Si^{4+} by
7 Al^{3+} , and the lower Ca content.
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19 However, these mechanisms cannot explain the great differences in alkali contents seen
20 during the first days of hydration in the pore solutions, as at these shorter ages the
21 reactions from SCMs still have not started. Therefore, the slow initial solubility of the
22 alkalis from SCMs (Table 3) can explain the differences in pH value and K content at 2
23 and 7 days of hydration. In the case of Na, the higher content in SCMs is compensated
24 by their lower solubility. The results agree with previous results; Shehata *et al.* [52]
25 asserted that a great quantity of alkalis in FA with low CaO contents (such as the one
26 used in this study) is fixed in crystalline phases. This lower release of alkalis in cements
27 with SCMs was demonstrated in cementitious materials with blends with ultrahigh Si
28 contents [12, 46, 53], and according to the results obtained in this paper, the lower
29 solubility of alkalis from SCMs is maintained even in ternary blends with a pH close to
30 those of conventional OPC materials. Therefore, the combined effect of both
31 phenomena could explain the content modifications of alkalis seen in the pore solutions
32 of ternary blends in this and other papers [16] and even in the leachates of ternary
33 blends [54].
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1 The OPC composition also influences the formation rate of the hydration products and
2 their chemical composition in ternary blends, but mainly in binders with the BFS plus
3 FA combination. The DTA/TG results were used to calculate the portlandite (CH) and
4 bound water (H) contents. The peaks associated with CH were used to quantify the
5 corresponding contents, and the amount of bound water (H) was calculated from the
6 water loss between 40 and 550°C [55], because the C-S-H gel content cannot be
7 measured directly as its dehydration overlaps with that of other compounds. Table 8
8 shows these results. In the case of ternary blends, the CH content has also been related
9 to the OPC content at all ages due to it only coming from OPC, and the H content has
10 also been related to the OPC content, but only at 2 days of hydration, when the
11 hydration of the SCMs can be considered as negligible.

26 <Table 8>

33 The evolution of CH content shows an increase with age in both references, although in
34 OPC-2 it remains practically constant between 28 and 90 days of hydration due to the
35 low level of reactivity of OPC-2 at these hydration ages. In the case of H, the OPC-1
36 content increases with age but the content in OPC-2 is stabilized with age, as also
37 happens with the compressive strength evolution (Figure 2). The evolution of H and CH
38 contents in all the ternary blends are very similar, in fact, they have similar compressive
39 strength results (except for the difference between SF-1 and SF-2 at 90 days of
40 hydration, as can be seen in Figure 2), so the filler contribution also occurs despite the
41 low LF content in SF-1 and SF-2 (only the initial LF which is present in OPCs as a
42 minor constituent). Therefore, the FA and BFS must also contribute to this effect [17,
43 56-58]. The CH content is very constant in the ternary blends due to its formation being

1 compensated for by the slight long-term pozzolanic reactions of BFS and/or FA, and the
2 H content increases with time, unlike what happens in OPC-2. Therefore, SL-2 and SF-
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4 2 have a mechanical strength which is far higher than OPC-2 at advanced hydration
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6 ages. Furthermore, the higher initial formation of CH/OPC and H/OPC in the ternary
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8 blends than in their references confirms the higher initial reactivity of the clinker
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10 through the filler effect of the SCMs [8, 16, 59, 60]. Regarding this issue, the most
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12 important influence of the OPC composition resides in the fact that the initial CH/OPC
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14 formation in ternary blends with respect to the references is much higher in those based
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16 on OPC-1. In this sense, the higher initial influence of SCMs in the reactivity with
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18 OPC-1 can explain the lower differences in the initial mechanical strength in the
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20 samples based on OPC-1, with respect to those detected in the mortars based on OPC-2.
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22 These results are also related to a lower delay of the setting times of the blends based on
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24 OPC-1 compared to the reference and a higher contribution to the initial heat flow of the
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26 SCMs in these blends than in the blends based on OPC-2 [15].
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36 The joint action of the high alkali content in the pore solution and the lower OPC (and
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38 therefore Ca) content in the ternary blends based on OPC-2 can limit the dissolution and
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40 subsequent precipitation of Ca to form portlandite, which explains the lower Ca content
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42 of pore solution in SL-2/SF-2 than in SL-1/SF-1 (Tables 6 and 7). Therefore, these
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44 phenomena could limit the ability of LF to build nucleation sites for the early formation
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46 of portlandite crystals. There is no a significant difference between the effect of the LF
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48 (in SL-1 and SL-2) and the FA (in SF-1 and SF-2) in the CH and H evolution caused by
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50 the poor reactivity of the FA in the period considered (and the low content in the
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52 blends) and caused by the filler effect of the SCMs used.
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Therefore, it seems that the synergistic action of SCMs is affected by the composition of the OPC used at early ages of hydration, but mainly at advanced ages of hydration in SF-blends. In ternary blends based on OPC-2, monocarboaluminate is already present at 2 days of hydration due to the higher Al content of OPC-2, and this early formation could limit the C-S-H gel formation and the ettringite stabilization, and therefore explains the significant loss of initial mechanical strength of the blends based on OPC-2 with respect to the reference. However, with OPC-1, the initial mechanical strength of the reference and the ternary blends are quite similar. In the case of SF-2, the joint action of the higher availability of Al and the slow reactivity of FA cause the early formation of monocarboaluminate, but limit its formation at advanced ages of hydration. Therefore, in these conditions, monosulphate can be more stable with the subsequent loss of mechanical strength with respect to SF-1 caused by the lower volume of hydration products formed. Moreover, the pozzolanic action of FA is also limited when using OPC with a medium Al_2O_3 content. In Table 8 a slight reduction of the CH content with age is detected in SF-1 while in SF-2 the opposite happens. This limitation of the FA pozzolanic reactivity agrees with the compressive strength results. Therefore, the low C_3A content of OPC-1 and its lower alkali content are key parameters when ternary blends, especially those based on BFS plus FA, are developed.

4. Conclusions.

From the experimental results in this work, the main conclusion about the synergistic effect of SCMs in ternary blends is that the OPC composition is a key parameter in the optimization of ternary blends. The specific conclusions are:

- The use of SCMs in OPC with low alkali and aluminate contents hardly punishes the initial mechanical strength of the resulting ternary blends.
- In the ternary blends based on the OPC with low alkali and aluminate contents, monocarboaluminate, hemicarboxylate and hydrotalcite are formed instead of monosulphate at advanced ages of hydration. However, with more C_3A in the OPC composition, monocarboaluminate can be formed at much younger ages in ternary blends, which could reduce mechanical strength growth.
- The initial formation of hydrates, with respect to the OPC content, is higher in the ternary blends than in their respective references, so SCMs, especially LF, stimulate the initial hydration of clinker in both cements.
- The lower initial solubility of alkalis from LF, BFS and FA than from both OPCs causes the lower alkali content and slightly lower pH value of the pore solution of the ternary blends than their respective references at the first days of hydration. At longer ages, the C-S-H gels which are richer in Al and poorer in C/S ratio in the ternary blends than in the references retain more alkalis in their structures and also contribute to these differences in pH value and alkali content at advanced ages of hydration
- The OPC composition mainly influences the synergistic effects of ternary binders when BFS plus FA is used. In this sense, it seems that FA reactivity is especially limited when it is used in combination with raw materials with a significant Al_2O_3 content. In this paper, it has been demonstrated that a similar Al_2O_3 content in the OPC, but different C_3A contents, has a major influence on FA reactivity if a BFS with a high Al_2O_3 content is also used.

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Table 1. Chemical composition of raw materials (wt.%).

Material	Na ₂ O	K ₂ O	Na ₂ Oeq	Al ₂ O ₃	CaO	SiO ₂	Fe ₂ O ₃	MgO	SO ₃
OPC-1	0.18	0.34	0.40	4.68	60.30	17.40	5.08	1.78	3.17
OPC-2	0.08	0.92	0.69	5.49	63.30	19.60	2.40	0.78	3.20
BFS	0.42	0.49	0.74	10.39	45.50	36.57	0.29	7.46	0.05
FA	0.77	4.51	3.74	24.94	3.64	51.97	6.29	1.65	0.15
LF	0.55	2.65	2.30	7.75	26.09	21.39	2.57	5.80	0.05

Table 2. Particle size distribution parameters of raw materials.

% <		10	50	90	Mean size (μm)
Particle diameter (μm)	OPC-1	1.9	14.4	44.5	19.2
	OPC-2	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

Table 3. Solubility (in %) of alkalis in OPC-1, OPC-2, BFS, FA and LF.

	Element solubility (%)		pH
	K	Na	
OPC-1	45.0	17.7	12.5
OPC-2	51.0	49.5	12.8
BFS	0.2	2.9	8.9
FA	0.2	0.7	9.2
LF	0.2	2.2	9.1

Table 4. Cement formulations (wt.%).

Sample	OPC-1	OPC-2	BFS	FA	LF
OPC-1	100	-	-	-	-
OPC-2	-	100	-	-	-
SL-1	64	-	30	-	6
SL-2	-	64	30	-	6
SF-1	64	-	26	10	-
SF-2	-	64	26	10	-

Table 5. K, Na, Ca, Al, Si and S content (mg/l) and pH in pore solutions of the references at 2, 7, 28 and 90 days of hydration.

Days	Sample	mg/l							pH	
		K	Na	Na ₂ O _{eq}	Ca	Al	Si	S	Electrode	Titration
2	OPC-1	10647	1435	10389	313	0.12	0.18	309	13.1	13.2
	OPC-2	12719	1608	12267	184	6.23	6.02	229	13.5	13.6
7	OPC-1	11842	1705	11702	204	0.27	1.71	137	13.2	13.3
	OPC-2	18567	1646	16963	95	8.15	5.86	150	13.5	13.6
28	OPC-1	4947	1369	5773	290	0.37	1.11	38	13.2	13.2
	OPC-2	11992	1456	11486	109	1.99	2.04	449	13.6	13.6
90	OPC-1	2621	729	3063	322	0.39	3.26	20	13.0	13.0
	OPC-2	10448	960	9591	156	1.11	2.66	97	13.6	13.6

Table 6. K, Na, Ca, Al, Si and S content (mg/l) and pH in pore solutions of the SL-binders at 2, 7, 28 and 90 days of hydration.

Days	Sample	mg/l							pH	
		K	Na	Na ₂ O _{eq}	Ca	Al	Si	S	Electrode	Titration
2	SL-1	4541	1152	5158	338	0.22	0.00	23	13.1	13.1
	SL-2	10095	848	9160	156	0.55	1.07	24	13.4	13.3
7	SL-1	5160	1547	6183	349	0.30	0.00	32	13.1	13.2
	SL-2	10992	1135	10259	100	1.09	1.88	45	13.4	13.3
28	SL-1	3107	866	3634	399	0.21	0.74	24	13.0	13.1
	SL-2	9330	1246	9088	194	1.22	1.60	29	13.4	13.3
90	SL-1	2246	792	2851	407	0.40	0.46	36	12.9	13.0
	SL-2	8443	1054	8126	176	1.11	1.56	67	13.4	13.4

Table 7. K, Na, Ca, Al, Si and S content (mg/l) and pH in pore solutions of the SF-binders at 2, 7, 28 and 90 days of hydration.

Days	Sample	mg/l							pH	
		K	Na	Na ₂ O _{eq}	Ca	Al	Si	S	Electrode	Titration
2	SF-1	4496	1165	5140	373	0.23	0.00	38	13.0	13.1
	SF-2	9916	836	9002	198	0.84	2.19	26	13.4	13.3
7	SF-1	3794	1078	4466	321	0.28	0.59	25	13.1	13.1
	SF-2	10579	1122	9915	192	0.97	2.75	40	13.4	13.3
28	SF-1	4567	1347	5442	511	0.57	0.64	29	13.1	13.1
	SF-2	9333	1211	9044	216	0.99	1.51	46	13.4	13.3
90	SF-1	2167	928	2971	236	0.82	2.78	79	12.9	13.0
	SF-2	6549	886	6396	204	0.64	1.18	47	13.4	13.4

Table 8. CH and H calculated from TG analysis for all the samples at 2, 7, 28 and 90 days of hydration.

Sample	Time (days)	CH (%)	CH/OPC (%)	H (%)	H/OPC (%)
OPC-1	2	14.1	14.1	13.8	13.8
	7	15.9	15.9	15.7	-
	28	17.4	17.4	18.8	-
	90	19.5	19.5	21.8	-
OPC-2	2	12.8	12.8	13.8	13.8
	7	15.6	15.6	21.8	-
	28	17.0	17.0	23.4	-
	90	17.3	17.3	22.1	-
SL-1	2	10.9	17.0	11.7	18.3
	7	11.0	17.2	14.8	-
	28	10.8	16.9	15.1	-
	90	11.3	17.7	17.9	-
SL-2	2	8.7	13.6	12.9	20.2
	7	10.7	16.7	16.2	-
	28	9.9	15.5	19.7	-
	90	9.9	15.5	23.5	-
SF-1	2	10.7	16.7	11.6	18.1
	7	11.4	17.8	13.3	-
	28	11.0	17.2	14.9	-
	90	11.2	17.5	18.3	-
SF-2	2	9.2	14.4	13.1	20.5
	7	9.6	15.0	18.9	-
	28	10.4	16.3	18.4	-
	90	10.9	17.0	24.2	-

Figure 1. Particle size accumulated of OPC-1, OPC-2, BFS, FA and LF (in cumulative %).

Figure 2. Compressive strength evolution of the elaborated mortars.

Figure 3. Diffractogram of OPC-1 at 2 and 90 days of hydration.

Figure 4. Diffractogram of OPC-2 at 2 and 90 days of hydration.

Figure 5. dTG of OPC-1 at 2, 7, 28 and 90 days of hydration

Figure 6. dTG of OPC-2 at 2, 7, 28 and 90 days of hydration.

Figure 7. Al_2O_3 content (in %) of C-S-H gels in samples at 2 and 90 days of hydration.

Figure 8. C/S ratio of C-S-H gels in samples at 2 and 90 days of hydration.

Figure 9. Diffractogram of SL-1 sample at 2 and 90 days of hydration.

Figure 10. Diffractogram of SL-2 sample at 2 and 90 days of hydration.

Figure 11. dTG of SL-1 at 2, 7, 28 and 90 days of hydration.

Figure 12. dTG of SL-2 at 2 to 90 days of hydration.

Figure 13. FT-MIR spectra of OPC-1, SL-1 and SF-1 at 28 (top) and 200 (bottom) days of hydration.

Figure 14. BSE image of a particle of BFS in SL-1 at 90 days of hydration.

Figure 15. Diffractogram of SF-1 sample at 2 and 90 days of hydration.

Figure 16. Diffractogram of SF-2 sample at 2 and 90 days of hydration.

Figure 17. Relationship between pH (measured by electrode) and alkali content in pore solution of the cement pastes at all evaluated ages.

Ordinary Portland Cement composition for the optimization of the synergies of supplementary cementitious materials of ternary binders in hydration processes

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Abstract

The synergistic effects of using several supplementary cementitious materials (SCMs), such as Blast Furnace Slags plus Limestone Filler or Fly Ashes, depend on the OPC composition. When using an OPC which is poor in C_3A and alkalis in ternary formulations, a similar initial strength gain to that of a plain OPC is detected and at longer hydration ages, the formation of monocarboaluminate, hemicarbonate and hydrotalcite instead of monosulphate can be seen. If an OPC with a higher C_3A content and alkalis is used with SCMs, the higher availability of Al causes the early formation of monocarboaluminate and a lower initial strength gain. At longer hydration times, in ternary blends with both OPCs, the mechanical strengths are higher and the C-S-H gels formed are richer in Al and poorer in C/S ratio with a subsequent lowering of the alkali content in the pore solution when compared to that in plain OPC.

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1. Introduction.

The use of supplementary cementitious materials (SCMs) in suitable proportions and combinations in the fabrication of cementitious materials can have technical, economic and environmental advantages due to a lower consumption of clinker being required and the valorization of industrial byproducts [1-3]. Therefore, the use of multiblends (composed of OPC plus one or more SCM/s) is being standardized following the new trends in cement development.

The most commonly used SCMs in cement production are blast furnace slag (BFS), fly ash (FA), limestone filler (LF), silica fume, natural pozzolan and metakaolin. It is well known that BFS mixed with OPC shows mainly hydraulic but also slightly pozzolanic activity that causes slower reactivity than OPC at early ages, but at longer hydration ages, a greater amount of C-S-H gel with a lower C/S ratio is formed to accommodate the lower overall C/S ratio of the system [4]. Moreover, the high Al content (compared to OPC) facilitates the formation of hydrates such as monocarboaluminate (in the presence of CaCO_3 in OPC) and the incorporation of Al in the C-S-H gels formed. In the case of FA, a similar situation occurs, due to a higher Al content than BFS, but lower reactivity because it only has pozzolanic properties when mixed with OPC. The substitution of OPC for high FA or BFS contents can mean a decrease in the mechanical performance of the cementitious materials obtained, especially at early hydration ages

[5-7], so longer curing times are needed in order to achieve similar strength values [1], although the use of BFS or FA in suitable proportions can show improved mechanical strength after longer hydration times [5]. The use of LF is commonly used as a minor additional constituent (below 5% in mass) of most of the OPC that contributes to filling the fine fraction of aggregates, improving packaging and blocking capillary pores [5]. In addition, it has a certain ability to build nucleation sites for the formation of the first portlandite crystals at early ages and it is also believed to participate in monocarboaluminate formation [4, 8]. In addition, LF can enhance BFS hydration [9]. However the percentage of OPC to be replaced by LF is recommended as being lower than 10-15%, in order to avoid the loss of mechanical strength caused by the dilution effect of hydrated material at advanced hydration ages [3, 5, 10].

The combination of SCMs with synergistic effects caused by the above limitations of binary blends has been proposed. In this context, ternary blends emerge as a sustainable option for improving the performance of binary blends and also that of cements without SCMs. For this reason, there are many recent studies on ternary and even quaternary blends. Some of these studies were carried out in the development of low-pH cementitious materials for high level radioactive waste (HLRW) repositories [11-13], while others are mainly focused on their mechanical and/or durability properties [3, 5, 14, 15] and other studies involve microstructural processes [16-18], including thermodynamic modelling [19]. Nevertheless, some differences can be seen in the papers published and it seems that better mechanical strength gain is obtained in ternary blends at early hydration ages when using an OPC with a low C_3A content and/or alkali content [3, 5, 20, 21], while the initial synergy is lower when the OPC used has a higher content [16, 17, 22-25]. In addition, these results have no apparent relation to other

parameters of the OPCs used, such as their fineness or the content in the rest of the anhydrous phases. Therefore, this suggests that the chemical and mineralogical composition of the OPC used must be a key factor in the mechanical performance of the ternary blends created and, accordingly, the phenomena involved must be related to several changes in the microstructural development of the resulting materials. These changes have not been well identified in previous publications so the goal of this paper is to analyze the modifications caused by the synergistic effects of the different SCMs, depending on the OPC composition (specifically, the C₃A and the alkali contents). This will be done by studying the mechanical properties and evaluating the related changes in the pore solution and the microstructure of the resulting ternary blends.

2. Experimental.

2.1 Initial characterization of raw materials

Ternary blend cement pastes and mortars were manufactured using Ordinary Portland Cement (OPC) plus two SCMs selected from: blast furnace slag (BFS) and class F low calcium fly ash (FA) or limestone filler (LF). Two types of OPC were used: CEM I 42.5 R-SR (identified as OPC-1) and CEM I 42.5 R (identified as OPC-2). Both OPCs contain a calcium carbonate content incorporated as a minor additional constituent according to UNE-EN 197-1:2011 (<5%): 4% in the case of OPC-1 and 3% in OPC-2, determined from TG tests. The chemical compositions of these materials were analyzed by X-ray fluorescence (XRF) and they are detailed in Table 1 (expressed in wt.%).

<Table 1>

The $\text{Na}_2\text{O}_{\text{eq}}$ contents calculated show relevant differences between both OPCs. In fact, the content in OPC-1 is considered as low ($<0.60 \text{ Na}_2\text{O}_{\text{eq}}$). Although there is not a significant difference between the Al_2O_3 content in both OPCs, by applying the Bogue formula [26], with a correction by using a mass balance with the calcium carbonate present in both OPCs, a significant difference is obtained in the C_3A content between both OPCs: 4% in OPC-1 and 10% in OPC-2. The content of the rest of anhydrous phases of clinker are: 50% C_3S , 12% C_2S and 15% C_4AF for OPC-1, and 53%, 16% and 7%, for OPC-2 respectively. SCMs have higher alkali and Al_2O_3 contents than both OPCs. The mineralogical composition of the raw materials was studied by using X-ray diffraction (XRD). The diffractograms of both OPCs show C_3S , C_2S and calcite as major constituents and C_3A , C_4AF and gypsum as minor ones. The C_3A peak is more pronounced in the case of OPC-2. The results show differences in the crystallinity of the SCMs, with BFS as the lowest with only some diffuse peaks of calcite detected. FA shows calcite, quartz, magnesite and mullite and LF shows calcite as a major constituent, as well as traces of quartz, arcanite and dolomite.

The thermal stability of the materials was characterized using thermo-gravimetric analysis (TG). In the case of the OPCs, the peaks seen are associated with the decomposition of gypsum at 90 and 350°C [27], and with the decarbonation of carbonates from filler at around 700°C. For SCMs, the peak was identified at 700°C, although this is very slight in BFS and FA. The low content of carbonates in the LF used ($<70\%$) for ternary blends is due to the geological nature of the parent rock (black limestone) used.

The particle size distribution was characterized by using laser diffraction spectrophotometry. The results are shown in Figure 1. Furthermore, Table 2 shows the pore size distribution parameters. The particle size distribution was similar in both OPC and BFS. The similar particle size distribution of the cements used in this study can rule out this parameter as being responsible for the possible differences detected in the ternary blends [28]. LF showed the lowest mean particle size, while FA had the highest.

<Figure 1>

<Table2>

The water solubility of the alkalis present in the OPCs and SCMs was also analyzed. The solubility test followed was based on mixing each separate component with deionized water in a solid/liquid ratio by weight = 1 [29, 30] and stirring the resulting slurry for 30 min. The suspension was vacuum filtered, and the pH and the ionic composition were determined. The percentage of soluble alkalis and the pH of the filtrate were measured with an electrode in the resulting suspensions of the solubility test, which are shown in Table 3.

<Table 3>

The initial water solubility of the alkalis from both OPCs is much greater than that of the SCMs (two orders of magnitude in the case of K and one in the case of Na), which is expected to cause, at least in the initial stages, less alkalis incorporated into the pore solution of ternary blends, despite the higher $\text{Na}_2\text{O}_{\text{eq}}$ content of the SCMs (Table 1).

2.2. Preparation of ternary blends

Table 4 shows the cement formulations considered in this paper. Prismatic mortar samples (4 cm x 4 cm x 16 cm) with a water/binder ratio (w/b) = 0.5 and binder:sand of 1:3 were manufactured, following the UNE-EN 196-1 standard, to analyze the mechanical performance of the different binder mixes at 1, 7, 28 and 90 days of curing. In addition, cement pastes were manufactured by using a w/b ratio of 0.5. The manufactured samples were demolded after 24 hours and kept in a curing chamber at $21\pm2^\circ\text{C}$ and $98\pm2\%$ RH. In this paper, both the mortars and cement pastes were subjected to the same curing conditions in order to better relate the mechanical properties measured in mortars to the microstructure development evaluated in cement pastes. Samples were taken out at different curing ages for the characterization tests required. In the case of the cement pastes, approximately 1 cm depth was removed before each test to minimize any carbonation effect, and the core of the sample was used for characterization.

2.3. Determination of hydration evolution

The hydration of ternary blends was characterized at several curing ages (2, 7, 28, 90, and in some cases, 200 days) by determining the pore solution composition and the evolution of solid phases.

Pore solution extraction was carried out by following the “Pore Fluid Expression” technique [31, 32]. Two samples for each blended cement paste were used for determination of repeatability. The protocol described in [33] was followed. It basically

consists of applying high pressures to a granulated cement paste (particles of approximately 5 mm) to collect the pore solution of the paste. For the extraction of the solution, about 125 grams of granulated material were used. The pH was measured using two procedures: 1) using a pH stable electrode in a high alkaline media and 2) titration of OH^- using HCl 0.01N and with phenolphthalein and methyl orange used as color indicators. The concentration of Na, K, Ca, Si, Al and S were analyzed using a plasma mass spectrometer. The results shown in this paper refer to the mean value of two similar pore expressions of each cement paste sample.

The hydration evolution in solid cement pastes was determined after stopping the hydration processes at different ages, after powdering the samples and removing the free water using ethanol (to stop the hydration) and acetone (to remove the excess ethanol) to minimize leaching of the solid phases (C-S-H gel and portlandite) as considered in [34]. The evolution of the hydrated solid phases was followed using several characterization techniques: 1) XRD patterns were recorded at room temperature in the interval $5^\circ < 2\theta < 60^\circ$, with a step size of $2\theta = 0.01973^\circ$ and 0.5 s per step. 2) DTA/TG data was obtained with a resolution of 0.01 mg. The sample was heated to 1000°C at a heating rate of $10^\circ\text{C}/\text{min}$ using nitrogen as a medium under static conditions. Alumina powder was used as a reference material. 3) FT-MIR measurements were performed with a Thermo Scientific Nicolet 6700 by preparing a pellet with 1 mg of the sample and 300 mg of KBr and compacted under a vacuum, with 64 scans in a range of $40000 - 400 \text{ cm}^{-1}$. 4) BSEM images were obtained using a Hitachi S-4800 scanning electron microscope equipped with a BRUKER 5030 energy dispersive analyzer that allowed the analysis of the chemical composition of the hydration products. The samples were embedded into an epoxy resin, cut, polished and

then coated with carbon. The EDX microanalyses were mainly used to analyze the C-S-H gel composition at different hydration ages.

3. Results and discussion.

3.1. Evolution of mechanical strength

The compressive strength of the ternary blends was evaluated in order to determine the influence of the synergy of the SCMs used on the mechanical strength gain, depending on the OPC composition. Figure 2 shows these results. When comparing each ternary blend with its counterpart with a different OPC, there are no significant differences between the SL samples. However, while at early hydration ages, SF-1 and SF-2 show a similar strength gain, at advanced hydration ages, the compressive strength of SF-1 is 15% higher than that of SF-2. In fact, SF-1 shows the highest long-term compressive strength of the manufactured mortars. Therefore, it is possible that the FA reactivity depends on the OPC used at a higher level than BFS. Regarding the comparison between ternary mortars and their references, it should be highlighted that the mechanical strength evolution of both reference mortars is very different, so this logically influences the comparative results. With the low alkali and low C_3A cement the compressive strength of ternary blends shows a very low mechanical loss with respect to the reference at 1 day of hydration, while with OPC-2, the loss is about 50%.

After the first 24 hours of hydration, OPC-2 shows a low strength gain, so the ternary blends based on OPC-2, with a strong increase during this period, are equalling and even improving the long term reference result. The designed ternary blends

1 manufactured with OPC-1 can replace OPC-1, due to their similar mechanical behavior,
2 even in the first day of hydration.
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7 <Figure 2>
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11 The different mechanical behavior of the references, as well as the modifications seen in
12 the ternary mortars, should, logically, be due to the different precipitation-solubilization
13 processes of the products formed in the hydration reactions of the material. For this
14 reason, the microstructures and the pore solutions of the samples have been analyzed in
15 the following sections.
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26 *3.2. Evolution of the microstructure and pore solution compositions of the reference* 27 *samples* 28 29 30

31 In order to evaluate the influence of the OPC composition on the synergistic effects
32 caused by the combination of two SCMs in the microstructural phenomena, the results
33 of the reference pastes are shown first. The composition and pH of the pore solutions
34 vary widely between both references. Table 5 shows the mean value of the 2
35 measurements of the compositions and the pH values of the pore solutions of OPC-1
36 and OPC-2.
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51 <Table 5>
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56 K is the main species in the pore solution of both references, but OPC-2 has a higher
57 content, especially at advanced ages of hydration caused by a significant decrease in the
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1 K content in OPC-1. The Na content is more or less similar in both samples and the
2 total alkali content ($\text{Na}_2\text{O}_{\text{eq.}}$) calculated is higher in OPC-2. The lower $\text{Na}_2\text{O}_{\text{eq.}}$ content in
3 OPC-1 in relation to the hydration time causes a lower pH value in the pore solution and
4 it is compensated for with a higher Ca content. The Al content is much higher in OPC-2
5 than in OPC-1, and this could be due to the higher C_3A content in OPC-2 than in OPC-
6 1. The Si content is also higher in OPC-2 than in OPC-1 in the first days of hydration,
7 despite the similar Si content in both OPCs. There is a faster dissolution of the C_3S
8 and/or C_2S in OPC-2 than in OPC-1, which explains the higher compressive strength of
9 OPC-2 than that of OPC-1 in the first day of hydration (Figure 2), which would
10 contribute to these differences. Regarding the S content, in OPC-1 there are high values
11 at early hydration ages caused by the fast dissolution of gypsum [35], while in OPC-2
12 this high content is prolonged for a longer period. In the long term, the S content
13 decreases in both samples.

34 In order to analyze the different processes of precipitation-solubilization in the
35 hydration of the material, the microstructure references were characterized by using
36 XRD. The diffractograms (Figures 3 and 4) show differences in terms of the
37 formation/consumption of the crystalline phases of both reference samples. The main
38 hydrated phases identified in both references are portlandite, ettringite and hydrated
39 calcium silicates (C-S-H); although most of the C-S-H has an amorphous formation,
40 there are semi-crystalline forms with a C/S ratio higher than 1.5 that can be identified in
41 these XRD tests. The Si-hydrogarnet detection should also be highlighted, despite being
42 a difficult compound to identify using conventional characterization techniques without
43 pretreatment with a selective SAM (salicylic acid/methanol) solution to remove the
44 main phases of the paste [36]. At 2 days of hydration, C_3A is detected in OPC-2 and in

1 OPC-1, but with less intensity in OPC-1, due to the lower content in OPC-1 than in
2 OPC-2. At 90 days of hydration, the main difference between both references is the
3 formation of monocarboaluminate in OPC-2 instead of monosulphate in OPC-1, due to
4 the higher availability of Al in the pore solution of OPC-2, which limits the ettringite
5 and aluminium reaction.
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11 <Figure 3>
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22 TG analysis was also performed. Figures 5 and 6 show the dTG results of the reference
23 samples at the different hydration times. In OPC-2 a peak in the 110-170°C region is
24 detected after 7 days and it increases with the hydration time; this peak is associated
25 with the dehydration of the hemi- or monocarboaluminate, as suggested in [37, 38]. In
26 both references, slight weight loss is detected at 180-195°C, which could be related to
27 monosulphate dehydration [39-41]. Both references also show three main peaks: 1) up
28 to 350°C it is mainly associated with C-S-H gel dehydration, but also with other
29 products such as ettringite, 2) at 400-500°C it is associated with the portlandite
30 dehydration and 3) at 650-750°C it is associated with the decomposition of carbonates
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48 <Figure 5>
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51 <Figure 6>
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56 In order to evaluate the C-S-H gel in depth, its chemical composition was studied by
57 using BSEM-EDX, especially the Al₂O₃ content and C/S ratio. These results are shown
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in Figures 7 and 8 respectively. The results shown refer to the mean value of more than 50 measurements in each sample so the standard deviations are also shown in these figures. The results of the other cement pastes are also shown in order to be discussed in the next sections. A higher Al content is detected in C-S-H gels formed in OPC-2 than those in OPC-1 at 2 and at 90 days of hydration due to the higher availability of this element (Table 5) and the higher C₃A content of OPC-2 than that of OPC-1 (Table 1).

<Figure 7>

<Figure 8>

Once the different microstructural evolution of the reference materials are evaluated, the influence of the OPC composition in the microstructural synergistic effect of each SCM pair (BFS + LF or BFS + FA) in ternary blend is analyzed in depth. This is shown in the following two sections.

3.3. Evolution of the microstructure and pore solution compositions of BFS + LF blends

The pore solutions of SL-1 and SL-2 were analyzed. Their compositions and pH values are shown in Table 6. There are some differences between the SL-1 and SL-2 pore solution compositions. The K content is higher in SL-2 than in SL-1, although in both cases, the values are lower than those of the reference samples (Table 5). Slight differences in pH can be seen in the references with respect to these ternary blends, which are always slightly lower, since the blends have a lower Na₂O_{eq.} content. The Ca content is higher in SL-1 than in SL-2, as occurred between OPC-1 and OPC-2, to

compensate for the lower $\text{Na}_2\text{O}_{\text{eq}}$ content calculated. The Al contents are lower in SL-2 than in OPC-2, but the SL-1 contents are higher than the OPC-1 ones, especially in the short term. The lower initial Al content in SL-2 than in the OPC-2 pore solution can explain the lower mechanical response of this sample at 1 day of hydration (Figure 2). This is because it can promote the formation of compounds like monocarboaluminate or hemicarboaluminate in SL-2, instead of C-S-H gels as in OPC-2. This is also because this low Al content should be related to a lower C_3A dissolution. As C_3A is the most reactive anhydrous phase, accordingly, its slower reaction causes a lower formation of hydrates during the early ages. In fact, this early formation of monocarboaluminate in SL-2 and the latter formation in SL-1 are detected in the XRD tests (Figures 9 and 10). The Si content is higher in SL-2 than in SL-1, but the values of SL-2 are much lower than in OPC-2, mainly in the first days of hydration, which can be related to the higher formation of C-S-H gels in OPC-2. This agrees with the lower initial strength of SL-2 or with these C-S-H gels incorporating more Si into their composition [16]. The S content is similar in both ternary blends, although it is much lower than the reference values at early hydration ages. This is probably due to the higher S initial reactivity in addition to the lower gypsum content. Figures 9 and 10 show the diffractograms of SL-1 and SL-2.

<Table 6>

<Figure 9>

<Figure 10>

In SL-1, at 90 days of hydration, monocarboaluminate, hemicarboaluminate and hydrotalcite are detected, instead of the monosulphate detected in OPC-1 (Figure 3), due to the reaction between the calcium carbonate from the LF and the aluminate hydrates [37,

43]. Monosulphate hydrate is not stable in the presence of calcium carbonate, and monocarboaluminate (and/or hemicarbonat) is formed instead. Monocarboaluminate causes the stabilization of ettringite, thus increasing the volume of hydration products, which causes the higher compressive strength measured in SL-1 (Figure 2) [5, 16]. This phenomenon is also corroborated by considering the S/Al evolution ratios of the pore solutions (Tables 5 and 6), as a decrease in this value causes the decomposition of more ettringite after sulphate depletion. In OPC-1, a continuous and significant decrease is detected but not in SL-1. Therefore, the ettringite stabilization is mainly due to the formation of monocarboaluminate in SL-1, and the subsequent increase in the stable volume of hydrates can partially explain the good compressive strength values detected in SL-1 (Figure 2).

In OPC-2, monocarboaluminate was detected by using XRD (Figure 4), but only at 90 days of hydration, while in SL-2 it is already present at 2 days of hydration. These differences compared to SL-1 must also be related to the compressive strength results, possibly because the early formation of monocarboaluminate could limit the role of this hydrate in the ettringite stabilization, thus also reducing the volume of stable hydrates. It should be highlighted that at 90 days of hydration, C₄AF is not detected in the samples based on OPC-2, so their faster liberation to the pore solution can be deduced, thus increasing the monocarboaluminate formation. The presence of monocarboaluminate is also detected by the TG tests. Figures 11 and 12 show the dTG results of SL-1 and SL-2.

<Figure 11>

<Figure 12>

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2 In both cases, the same phases as in OPC-2 (Figure 6) are detected, although in SL-1,
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4 the peak associated with monocarboaluminate/hemicarbonate is only evident at 90 days
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6 of hydration. In addition, in both cement pastes a fifth peak appears just before the
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8 portlandite peak that can be attributed to hydrotalcite and which also increases in
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10 intensity with BFS hydration.
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17 A higher alumina content is detected in the C-S-H gels formed in SL-1 and SL-2 with
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19 respect to their respective references at 2 and 90 days of hydration (Figure 7) caused by
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21 the Al released by the SCMs. These contents are higher in SL-2 than in SL-1 due to the
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23 higher Al content in OPC-2 than in OPC-1. The C/S ratios (Figure 8) are similar in both
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25 blends, but they are lower than their references, even though LF should increase this
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27 ratio in the cases of SL-1 and SL-2 [9]. The C-S-H gel structure was analyzed in the
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29 pastes by using the FT-MIR results at 28 and 200 days of hydration in Figure 13.
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41 In all the cases, the main bands corresponding to C-S-H gels are detected at 973 cm^{-1}
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43 and to a lesser degree at 458 cm^{-1} [44], with the former being assigned to the Si-O
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45 stretching vibrations of the Q^2 tetrahedra of C-S-H gels with high C/S ratios (>1.5).
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47 However, the band at 458 cm^{-1} corresponds to the internal deformation of TO_4
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49 tetrahedra and, at 200 days of hydration, it has a slightly higher intensity in SL-1 than in
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51 OPC-1. This can be related to the presence of certain C-S-H gels with a C/S ratio <1.5 .
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53 This structure means a higher polymerization of silicate chains and a high content of the
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55 less strongly hydrogen-bonded water molecules in the interlayer space [45]. Several
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1 studies suggest that C-S-H gels with a rich-Al content and a poor C/S ratio retain a
2 higher alkali content in their structure and therefore present a lower alkali content and
3 lower pH values in the pore solution [11, 13, 16, 35, 46-51], although in this study the
4 differences in the C/S ratio (Figure 8) are not very significant. This kind of C-S-H gel is
5 formed by the contribution of SCMs, mainly BFS, in these samples. The hydration
6 products that are being formed around the BFS particles have low C/S ratios and very
7 high Al contents, especially in the areas closest to the unreacted core of the particle.
8 Regarding this, Figure 14 shows a BSEM image focused on a particle of BFS at 90 days
9 of hydration and the EDX analysis points are defined.

10 <Figure 14>

11 The points analyzed in the core of the anhydrous particle (squares) have (on average)
12 14% Al content and a C/S ratio of 1; the points in the cement paste near to the BFS
13 (crosses), 9% Al and a C/S ratio of 1.3; and the C-S-H gel in the triangle point, far from
14 the BFS particle, C/S ratio of 1.5 and 5% Al. Therefore, the BFS reactivity, whose
15 composition is richer in Al and Si and poorer in Ca than the OPCs, (Table 1) is related
16 to the formation of C-S-H which is richer in Al and poorer in C/S ratio in the ternary
17 blends than in the references.

18 Therefore, according to the results obtained, there are no big differences between the
19 microstructure evolution of SL-1 and SL-2, being the main difference the formation at
20 long hydration ages of hemicarboxylate and hydrotalcite in SL-1 and at earlier ages, the
21 formation of monocarboaluminate in SL-2. These slight differences agree with the
22 similar strength gain evolution obtained in SL-1 and SL-2 mortars. However, there are

significant differences between the references and the ternary blends, especially in the initial synergy, with the OPC with low C₃A and alkali content being higher.

3.4. Evolution of the microstructure and pore solution compositions of BFS + FA blends

Although 90% of the raw composition of SF-1 and SF-2 is the same as SL-1 and SL-2 respectively, the microstructures and pore solutions of SF-1 and SF-2 are analyzed in order to study the possible differences between this combination of SCMs and the BFS + LF with both OPCs. The pore solution compositions of SF-1 and SF-2 are very similar to SL-1 and SL-2 (Table 6) respectively, as can be seen in Table 7. Only in the case of SF-2 is a significant decrease in Al content identified at 90 days of hydration, which is probably related to a limited reactivity of FA in SF-2.

<Table 7>

Therefore, the availability of Al is again a key factor, as in SF-2 the formation of compounds like monocarboaluminate is caused in the first days of hydration with a lower initial compressive strength caused by the limitation of the C-S-H gel formation (Figure 2) as in the case of SL-2 (Figure 10), while in SF-1 it is only detected at 90 days of hydration, as in the case of SL-1 (Figure 9). Figure 15 and 16 show the diffractograms of SF-1 and SF-2.

<Figure 15>

<Figure 16>

1 The most significant difference between SL-formulations and SF-formulations is the
2 monosulphate formation in SF-2 at 90 days of hydration, but not in SL-2, and this could
3 be related to a higher volume of stable hydrates in the latter, thus explaining its higher
4 compressive strength. This agrees with the fact that FA reactivity is lower than BFS
5 reactivity and SF-2 also has a lower BFS content than SL-2. In fact, FA causes long
6 term pozzolanic reactions and the calcium aluminate hydrates formed in these reactions
7 can react with the carbonate of the LF and form calcium carboaluminate hydrates.
8 Therefore, the early formation of monocarboaluminate in SF-2 due to the higher Al
9 content in OPC-2 than in OPC-1, can limit the later formation of this hydrate with the
10 alumina released from FA, whose reactivity could be lower with OPC-2, and the one
11 previously released by BFS is not enough. The lower Al content in the pore solution of
12 SF-2 than in SL-2 (Tables 6 and 7) confirms this.

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31 Regarding thermal stability, the same compounds were detected in SF-1 and SF-2
32 (results not shown) as in SL-1 and SL-2. In addition, as occurs in these samples, a
33 higher Al content is detected in the EDX analysis of the C-S-H gels of SF-1 and SF-2
34 than in their respective references and the content is higher in SF-2 than in SF-1 (Figure
35 7) due to the low Al content of OPC-1. The C/S ratios (Figure 8) are similar in both
36 blends and lower than their references.

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48 Therefore, according to the results obtained, the OPC composition has a greater
49 influence on the microstructure development of binders based on BFS plus FA. It is
50 clear that the alumina content is the key parameter that mainly explains the differences
51 seen. FA has a high Al_2O_3 content, so its reactivity must be limited when it is combined
52 with BFS (which also has a high Al_2O_3 content) plus OPC with a medium Al_2O_3 . This

also explains the lower long-term pozzolanic reaction effect detected in the mechanical strength of SF-2.

3.4. Influence of OPC composition on the synergies between SCMs

The synergistic action of the SCMs used in the percentages considered in this study causes different changes in mechanical properties. As demonstrated, these changes are related to changes in the microstructure and pore solution evolution of the resulting materials during hydration. In fact, these changes are different depending on the chemical composition of the OPC used, with a stronger resulting effect when using BFS and FA than when using BFS and LF.

The alkali (especially K) content in ternary blends is lower than in their references, although these differences are more significant at early ages of hydration in the pastes based on OPC-1. As shown in Figure 17, the alkali content (expressed as mg/l of $\text{Na}_2\text{O}_{\text{eq.}}$) is closely linked to the pH of the pore solution, regardless of the age of hydration or the SCMs used in each case.

<Figure 17>

Instead of the higher alkali content of the binder formulations of the ternary blends, the alkali content of the pore solution is always lower (or at least similar) in ternary cement pastes with respect to their references. Some mechanisms that could explain these differences are the composition of C-S-H gels formed in blended cement pastes at longer hydration ages, which are richer in Al and poorer in C/S ratio than the C-S-H

1 gels formed from plain OPC, the lower clinker content and the portlandite consumption
2 in the pozzolanic reactions. García Calvo *et al.* [12] associated the retention of alkalis in
3 these kinds of C-S-H gels with the possible replacement of alkalis by Ca^{2+} in the pore
4 fluid (electro-neutralization of the system) and Lothenbach *et al.* [4] postulated that the
5 higher sorption of alkalis by C-S-H gel with a lower C/S ratio is probably caused by the
6 negative charges from the ionization of silanol groups, the partial substitution of Si^{4+} by
7 Al^{3+} , and the lower Ca content.
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19 However, these mechanisms cannot explain the great differences in alkali contents seen
20 during the first days of hydration in the pore solutions, as at these shorter ages the
21 reactions from SCMs still have not started. Therefore, the slow initial solubility of the
22 alkalis from SCMs (Table 3) can explain the differences in pH value and K content at 2
23 and 7 days of hydration. In the case of Na, the higher content in SCMs is compensated
24 by their lower solubility. The results agree with previous results; Shehata *et al.* [52]
25 asserted that a great quantity of alkalis in FA with low CaO contents (such as the one
26 used in this study) is fixed in crystalline phases. This lower release of alkalis in cements
27 with SCMs was demonstrated in cementitious materials with blends with ultrahigh Si
28 contents [12, 46, 53], and according to the results obtained in this paper, the lower
29 solubility of alkalis from SCMs is maintained even in ternary blends with a pH close to
30 those of conventional OPC materials. Therefore, the combined effect of both
31 phenomena could explain the content modifications of alkalis seen in the pore solutions
32 of ternary blends in this and other papers [16] and even in the leachates of ternary
33 blends [54].
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The OPC composition also influences the formation rate of the hydration products and their chemical composition in ternary blends, but mainly in binders with the BFS plus FA combination. The DTA/TG results were used to calculate the portlandite (CH) and bound water (H) contents. The peaks associated with CH were used to quantify the corresponding contents, and the amount of bound water (H) was calculated from the water loss between 40 and 550°C [55], because the C-S-H gel content cannot be measured directly as its dehydration overlaps with that of other compounds. Table 8 shows these results. In the case of ternary blends, the CH content has also been related to the OPC content at all ages due to it only coming from OPC, and the H content has also been related to the OPC content, but only at 2 days of hydration, when the hydration of the SCMs can be considered as negligible.

<Table 8>

The evolution of CH content shows an increase with age in both references, although in OPC-2 it remains practically constant between 28 and 90 days of hydration due to the low level of reactivity of OPC-2 at these hydration ages. In the case of H, the OPC-1 content increases with age but the content in OPC-2 is stabilized with age, as also happens with the compressive strength evolution (Figure 2). The evolution of H and CH contents in all the ternary blends are very similar, in fact, they have similar compressive strength results (except for the difference between SF-1 and SF-2 at 90 days of hydration, as can be seen in Figure 2), so the filler contribution also occurs despite the low LF content in SF-1 and SF-2 (only the initial LF which is present in OPCs as a minor constituent). Therefore, the FA and BFS must also contribute to this effect [17, 56-58]. The CH content is very constant in the ternary blends due to its formation being

1 compensated for by the slight long-term pozzolanic reactions of BFS and/or FA, and the
2 H content increases with time, unlike what happens in OPC-2. Therefore, SL-2 and SF-
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4 2 have a mechanical strength which is far higher than OPC-2 at advanced hydration
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6 ages. Furthermore, the higher initial formation of CH/OPC and H/OPC in the ternary
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8 blends than in their references confirms the higher initial reactivity of the clinker
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10 through the filler effect of the SCMs [8, 16, 59, 60]. Regarding this issue, the most
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12 important influence of the OPC composition resides in the fact that the initial CH/OPC
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14 formation in ternary blends with respect to the references is much higher in those based
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16 on OPC-1. In this sense, the higher initial influence of SCMs in the reactivity with
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18 OPC-1 can explain the lower differences in the initial mechanical strength in the
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20 samples based on OPC-1, with respect to those detected in the mortars based on OPC-2.
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22 These results are also related to a lower delay of the setting times of the blends based on
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24 OPC-1 compared to the reference and a higher contribution to the initial heat flow of the
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26 SCMs in these blends than in the blends based on OPC-2 [15].
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36 The joint action of the high alkali content in the pore solution and the lower OPC (and
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38 therefore Ca) content in the ternary blends based on OPC-2 can limit the dissolution and
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40 subsequent precipitation of Ca to form portlandite, which explains the lower Ca content
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42 of pore solution in SL-2/SF-2 than in SL-1/SF-1 (Tables 6 and 7). Therefore, these
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44 phenomena could limit the ability of LF to build nucleation sites for the early formation
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46 of portlandite crystals. There is no a significant difference between the effect of the LF
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48 (in SL-1 and SL-2) and the FA (in SF-1 and SF-2) in the CH and H evolution caused by
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50 the poor reactivity of the FA in the period considered (and the low content in the
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52 blends) and caused by the filler effect of the SCMs used.
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Therefore, it seems that the synergistic action of SCMs is affected by the composition of the OPC used at early ages of hydration, but mainly at advanced ages of hydration in SF-blends. In ternary blends based on OPC-2, monocarboaluminate is already present at 2 days of hydration due to the higher Al content of OPC-2, and this early formation could limit the C-S-H gel formation and the ettringite stabilization, and therefore explains the significant loss of initial mechanical strength of the blends based on OPC-2 with respect to the reference. However, with OPC-1, the initial mechanical strength of the reference and the ternary blends are quite similar. In the case of SF-2, the joint action of the higher availability of Al and the slow reactivity of FA cause the early formation of monocarboaluminate, but limit its formation at advanced ages of hydration. Therefore, in these conditions, monosulphate can be more stable with the subsequent loss of mechanical strength with respect to SF-1 caused by the lower volume of hydration products formed. Moreover, the pozzolanic action of FA is also limited when using OPC with a medium Al_2O_3 content. In Table 8 a slight reduction of the CH content with age is detected in SF-1 while in SF-2 the opposite happens. This limitation of the FA pozzolanic reactivity agrees with the compressive strength results. Therefore, the low C_3A content of OPC-1 and its lower alkali content are key parameters when ternary blends, especially those based on BFS plus FA, are developed.

4. Conclusions.

From the experimental results in this work, the main conclusion about the synergistic effect of SCMs in ternary blends is that the OPC composition is a key parameter in the optimization of ternary blends. The specific conclusions are:

- The use of SCMs in OPC with low alkali and aluminate contents hardly punishes the initial mechanical strength of the resulting ternary blends.
- In the ternary blends based on the OPC with low alkali and aluminate contents, monocarboaluminate, hemicarboxylate and hydrotalcite are formed instead of monosulphate at advanced ages of hydration. However, with more C_3A in the OPC composition, monocarboaluminate can be formed at much younger ages in ternary blends, which could reduce mechanical strength growth.
- The initial formation of hydrates, with respect to the OPC content, is higher in the ternary blends than in their respective references, so SCMs, especially LF, stimulate the initial hydration of clinker in both cements.
- The lower initial solubility of alkalis from LF, BFS and FA than from both OPCs causes the lower alkali content and slightly lower pH value of the pore solution of the ternary blends than their respective references at the first days of hydration. At longer ages, the C-S-H gels which are richer in Al and poorer in C/S ratio in the ternary blends than in the references retain more alkalis in their structures and also contribute to these differences in pH value and alkali content at advanced ages of hydration
- The OPC composition mainly influences the synergistic effects of ternary binders when BFS plus FA is used. In this sense, it seems that FA reactivity is especially limited when it is used in combination with raw materials with a significant Al_2O_3 content. In this paper, it has been demonstrated that a similar Al_2O_3 content in the OPC, but different C_3A contents, has a major influence on FA reactivity if a BFS with a high Al_2O_3 content is also used.

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