

# Ternary mixes with high mineral additions contents and corrosion related properties

*Dedicated to Professor Bernhard Elsener on the occasion of his 60th birthday*

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The choice of blended cements and materials with cementitious properties in concrete is currently seen as a choice that increases the environmental sustainability of the construction industry. The developments with non-traditional binders (such as the simultaneous incorporation of several types of supplementary cementitious materials) have highlighted new challenges to be researched. In the present paper ternary binders were prepared by mixing ordinary Portland cement (OPC) plus two blended components: low calcium fly ash, blast furnace slag, and/or limestone filler. Several physical and mechanical properties of ternary blend systems have been analyzed in mortar form at several curing ages: 2, 7, 28, and 90 days. Additionally preliminary tests of corrosion performance of reinforcement in these types of mixes have been considered. The results indicate that the use of appropriate content components in ternary blends will allow binders to fulfill the specified mechanical requirements. The best results are obtained when two additions with antagonist properties are mixed, as fly ashes and slags or slags and filler limestone. Besides, certain influence of the effect on durability performance is detected, in particular associated with the stability of the passive state and corrosion of reinforcements in presence of chlorides.

## 1 Introduction

Sustainable construction requires that the construction industry reconsiders the design and construction standards, codes, and operational performance in order to reduce the environmental effect of materials and products used nowadays, e. g., energy consumption and CO<sub>2</sub> generation. These reasons can partially explain the worldwide gradual decrease in the use of ordinary Portland cement (OPC). In fact, the cement sales in Europe from 1998–2008 show that the blended cement type CEM II is the main used one. The choice of blended cements and materials with cementitious properties at the concrete mixer is

currently seen as a choice that increases the initial environmental sustainability of concrete construction.

However, the opportunities in sustainable construction for blended cements need to be evaluated in the light of the standards. This has been the reason that has moved the European a-doc group WG6 CEN TC/51 to develop pre-normative research works to accurately know the performance of new additions or proportions, as the ternary blended binders (CEM X), comparing to those used at present, also evaluating their influence on the durability properties.

The developments in non-traditional binders (such as various types of pozzolanic materials) have highlighted further challenges to be researched. Recently blended cements containing several supplementary cementitious materials (SCM) are increasingly being considered, particular interest remains in the use of fly ash or blast furnace slag with limestone filler or mixes of both [1–7]. The synergetic action of two SCM will modify the microstructure of concretes [3, 5, 6, 8] and, as a consequence, their technological and durable performances [8–11]. However, lack of knowledge exists concerning their influencing parameters on the durability of reinforcement, such as pore solution pH and ionic composition. In this matter, important issues to be

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evaluated would be the pH influence on passivation of reinforcement, resistance against penetration of CO<sub>2</sub> and chlorides, the chloride binding capacity or the chloride threshold at the onset of corrosion, the water resistance aggression, etc., all of them affecting the long-term performance of the concrete structures.

This paper deals with the development of cementitious materials based on CEM X formulations, firstly proving their good mechanical performance, comparing to a conventional cementitious material, and secondly evaluating their influence in the material behavior against corrosion, also showing the pore solution pH evolution of these special cements due to its importance in corrosion risk.

## 2 Experimental procedure

Ternary binders were prepared by mixing OPC (OPC-52.5R) plus two blended components from following types: (i) low calcium fly ash (F), (ii) blast furnace slag (S), and (iii) limestone filler (L). The chemical compositions of the mineral additions and OPC are shown in Table 1.

The OPC selected was sulfate resistant with low C<sub>3</sub>A content (3.4%) and also low alkali content (Na<sub>2</sub>O<sub>eq</sub> = 0.7%), that implies the obtaining of a pore solution pH in a cement paste ( $w/c = 0.5$ ) ranging from 13 to 13.2 at 28 curing days (pore solution pH measured using the pore fluid expression method described in Refs. [12, 13]).

Three blended families were prepared varying the % of each SCM, identified as: FL (with fly ash and limestone filler), SL (with slags and limestone filler), and SF (with slags and fly ash). The ternary mixes dosages of type OPC-S-L were selected based on limit recommendations of the European CEM X a-doc group WG6 CEN TC/51. The ternary mixes OPC-F-L and OPC-S-F were prepared following equivalent criteria and taking into account previous studies in literature [4–7]. Finally nine different ternary

blends plus a reference one (100% OPC) were fabricated. Table 2 shows the composition of each ternary mix formulation, also showing their total % of blended SCM addition and their SiO<sub>2</sub> and CaO contents (%).

For each binder formulation, standard mortars with a  $w/b = 0.5$  and binder/sand ( $d_{max} = 4$  mm) 1:3 were fabricated. In the fresh state the consistency was measured in order to evaluate the water demand. The mortars were cured in  $100 \pm 5\%$  RH chamber and  $21 \pm 2$  °C. Two types of samples were employed:

- (i) Prismatic mortar samples 4 cm × 4 cm × 16 cm in size: several physical and mechanical properties of ternary blended mortars have been analyzed in fresh and hardened state: workability, compressive and flexural strengths, porosity, and pore size distribution; all these properties were analyzed at several curing ages: 2, 7, 28, and 90 days of curing. Additionally the pore solution pH was determined.
- (ii) Cylindrical samples of 5 cm × 8 cm in size: for corrosion performance of reinforcement, each sample had 1 rib rebar of 6 mm diameter embedded. The rebars were previously cleaned from any residue of oxide. Three replicates were prepared for each condition in order to obtain mean values. Passivity and chloride induced corrosion were studied by adding during mixing 0, 0.5, and 1.2% of chloride as NaCl by weight of binder.

Although the workability is influenced by the synergetic action of the two additions used in each case, in general, in fresh state the addition of L and mainly F in the blend increases the workability, while the additions of S have shown the contrary effect. The workability increase due to the limestone filler introduction is well known, and the one promoted by the F is due to the spherical shape of its particles, its smooth glassy texture, and its finer particle size distribution or the so-called “ball-bearing effect” [14].

**Table 1.** Chemical composition of binder components (%)

	Na <sub>2</sub> O	K <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MgO	SO <sub>3</sub>	Loss Ign.
OPC	0.33	0.59	4.16	67.48	4.57	19.68	0.83	3.25	–
Limestone filler (L)	0.55	2.65	7.75	26.09	2.57	21.39	5.80	0.05	30.07
Blast furnace slag (S)	0.42	0.49	10.39	45.50	0.29	36.57	7.46	0.05	–
Fly ash (F)	0.77	4.51	24.94	3.64	6.29	51.97	1.65	0.15	–

**Table 2.** Composition (in % by weight) of ternary mixes, % of SCM, % SiO<sub>2</sub> and %CaO in blend

Name	%OPC	%F	%L	%S	% of SCM	%SiO <sub>2</sub>	%CaO
OPC 100%	100	0	0	0	0	19.68	67.48
FL1	65	25	10	0	35	26.02	29.07
FL2	65	10	25	0	35	18.59	16.11
FL3	40	40	20	0	60	29.14	40.98
SL1	64	0	6	30	35	23.71	18.83
SL2	42	0	18	40	58	23.32	21.70
SL3	20	0	30	50	80	22.94	24.57
SF1	65	25	0	10	35	29.44	32.87
SF2	65	10	0	25	35	27.13	25.62
SF3	40	30	0	30	60	34.43	43.74

For porosity determination, mercury intrusion porosimetry (MIP) was used. A piece of mortar with approximately 1 cm<sup>3</sup> was used (i.e., 2.5 times higher than the max. particle size of the sand to guarantee the representativity of the sample). For preconditioning the samples the process of hydration was interrupted at each specific age by stopping the cement hydration adding ethanol and acetone to a piece of sample before MIP determination.

The pore solution pH was measured following the methodology described in Ref. [15]. This method is an ex situ leaching pH measurement one specially developed for low-pH cementitious materials that are prepared with high volume of blended additions in the binder composition developed, used for radioactive waste storage concrete facilities, but also allows to obtain good results in conventional cementitious materials. In fact, this method has been calibrated with the reference one (pore fluid expression) by means of a round robin test and the differences between the pore fluid pH values determined using each method were never higher than 0.3 pH units in conventional cementitious materials [15, 16]. In this pH measurement method the mortar samples were finely powdered to a particle size <80 μm. Suspensions are made by mixing 10 g of powdered sample with 10 mL of CO<sub>2</sub>-free deionized water (solid/liquid = 1 by weight). The suspension is continuously and vigorously stirred for 5 min. The pH of the suspension is measured using a pH electrode for suspensions specific use. The tests were performed under a nitrogen atmosphere to avoid carbonation from the atmosphere and stirring was maintained during the pH measurement. The procedure is repeated for two more powdered samples of the same mortar, giving a total of three measured pH values at each specified age (2, 7, 28, and 90 days).

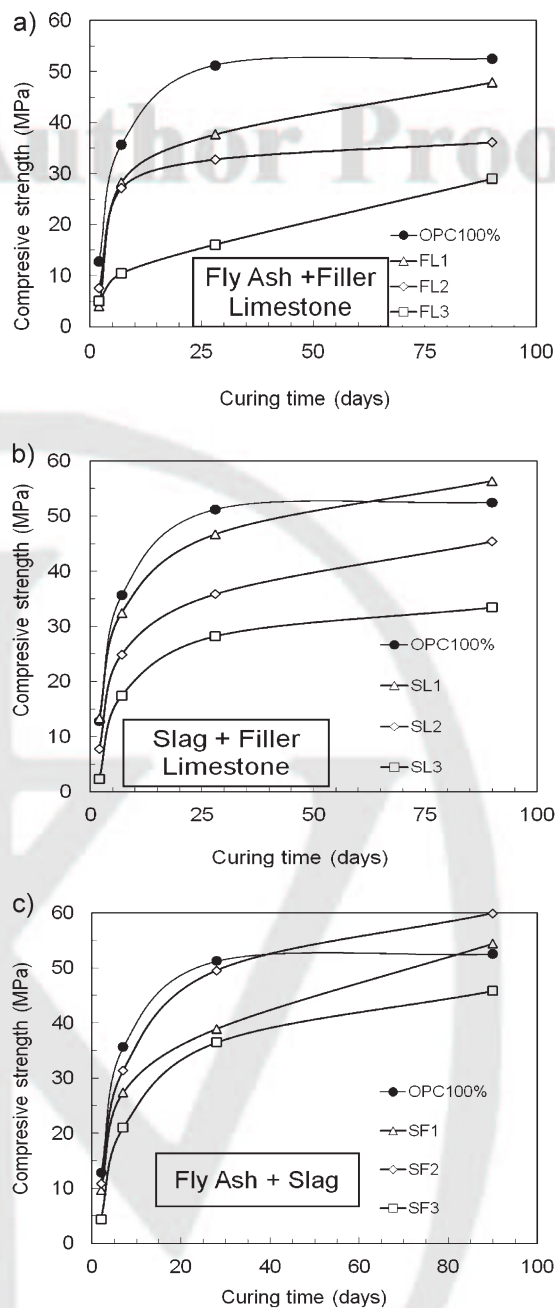
For corrosion performance of reinforcement electrochemical techniques were employed: the  $E_{\text{corr}}$  using a reference electrode of Ag/AgCl [in the present paper the values are given versus saturated calomel electrode (SCE)], the  $i_{\text{corr}}$ , determined through polarization resistance ( $R_p$ ), and the impedance spectroscopy (EIS) for passivating process analyses (not included in the present paper). The corrosion tests extend from 9 to 40 days, respectively.

### 3 Results and discussion

#### 3.1 Strength development behavior in blend ternary binders

The first aim was to identify the variability in mechanical properties due to the use of high percentages and types of ternary blended mixes,  $\geq 35\%$  from Table 2. It was also interesting to detect if ternary binders were able to reach the mechanical requirements, compressive strength, obtained using the reference mortar (100% OPC mortar, strength class 52.5 MPa at 28 days) without significant delay in the strength gain at early ages.

The compressive strengths of the fabricated mortars were measured at 2, 7, 28, and 90 days of curing and Fig. 1 compiles the obtained results. The reference mortar clearly fulfills the characteristic values required in standards for this type of cement. When mineral additions are mixed with the clinker, it is well known that the incorporation of increasing contents of blended



**Figure 1.** Evolution of the compressive strength of the ternary blend mortars. (a) Fly ash + limestone filler, (b) slag + limestone filler, (c) fly ash + slag

components in standardized binary cements (types II–V), delays the mechanical strength gain according to the type and percentage of blended component used, and this same phenomenon occurs in the ternary mixes. Therefore, it is important to define the technical properties of these special cements at 90 days instead of the 28 days commonly used in standardized cementitious materials, because the mechanical properties can even overpass those of OPC as occurs in the present study with some ternary blend systems (SL1, SF1, SF2).

Observing the graphs of Fig. 1 it is evident that it is possible to reach mechanical properties similar to those of plain OPC

mortars even at early ages of hydration, using ternary blends in optimized proportions, although the performance varies according to the ternary blend combination used, being the mortars fabricated using OPC + S + L (as SL2) and OPC + S + F (as SF2) the ones having best results in the whole hydration region considered. In the mortars with limestone filler it is possible to obtain strengths similar to those measured in the reference mortar, provided a 65% of cement content and low limestone filler contents (<15%).

It was also observed that the differences between the values obtained in the reference mortar and the mortars based on CEM X formulations are lower in the flexural strength measurements (results not shown). In fact, with the exception of the FL3 sample, all the others have higher flexural strength than the 100%OPC (Ref. sample) at 90 days of curing, whereas only three formulations show a higher compressive strength at the same age. Therefore, it seems that the inclusion of the SCM used in this study, in adequate proportions, do not penalize the long-term mechanical strength values but can improve them, while at early ages the expected strength reduction can be minimized using an appropriate mix of blended components.

The compressive strength development behavior observed in these mortars agree with other results already published [17–26] although, in general, the SCM contents used are lower than the ones of this study.

### 3.1.1 Ternary mixes of SF type

It is well known that, except for early ages, mixtures containing slag cement have higher compressive strengths than OPC mixtures at 7 days of age and later [17]. This increase in compressive strength is due to the hydraulic reaction of the slag cement with the calcium hydroxide (CH) and available high alkalis to form an additional CSH. This reaction improves the density of the concrete paste matrix thereby improving the strength [17].

Moreover, when slag is used together with the fly ash, better mechanical results can be usually achieved [18]. In fact, high performance concrete with the principal characteristics of strength, dimensional stability, permeability, and high workability has been produced using this ternary blended type [19], although at early age the compressive strength values are lower, as in the present paper.

Wang and Chen [20] have determined that, in ternary blended cements with F and S, the compressive strengths of mortars ( $w/b = 0.44$ ) at 7 days are almost proportional to the proportions of Portland cement, which agrees with the lower strengths of the ternary mixes in mortars of the present study at 2 and 7 days of curing. However, in these mixes with fly ash and slag, it seems that the contribution of S on the strength gain from 7 to 28 days is the largest, and the one of F is the smallest, and the contribution of S on the strength gain from 28 to 90 days is the largest, and the one of OPC is the smallest, which explains the higher long-term compressive strength of the SF mortars with appropriate formulation (SF2 and SF1).

### 3.1.2 Ternary mixes containing limestone filler

With respect to the mortars with limestone filler in their composition (L), it is already known that low contents (around

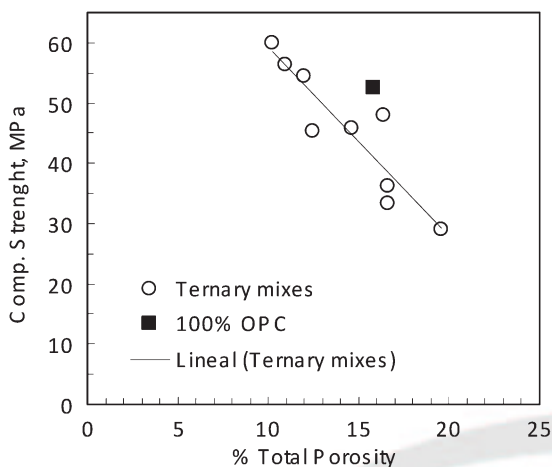
5%) of limestone powder can have a beneficial effect on early compressive strength of OPC materials [21], this beneficial effect being even more pronounced at long-term with its inclusion in fly ash or blast furnace slag blended cements [2, 5]. Limestone filler completes the fine fraction in the granulometric curve of cement without relevant increment on water demand, improves the cement packing and blocks the capillary pores. It also constitutes nucleation sites of CH crystals and CSH at early hydration ages [22, 23], accelerating the hydration of clinker particles especially the  $C_3S$  [24, 25]. This phenomenon can explain the high early strength in SL1, similar to the reference mix (100% OPC), even though the high % of SCM used (35%). In addition, L promotes the formation of mono- or hemicarboaluminate hydrates instead of monosulfoaluminate hydrate that stabilizes thereby the ettringite (when limestone filler is used in combination with fly ash or blast furnace slag, these additions can provide additional aluminates which will lower the sulfate/aluminate ratio and thereby amplify the impact of the limestone). Consequently, the use of limestone filler in appropriate proportion can improve the early strength although this SCM does not have pozzolanic properties so it does not contribute to produce additional CSH [26].

Furthermore, an associated effect of limestone addition is the reduction of potential cementing material, commonly called dilution, causing a reduction of later strength [2] or even at early ages when high percentages are used, as in some of the mortars of the present study. Thus the combination of limestone filler (but in low percentages) and S or F in a ternary blended cement can also achieve the obtaining of a cement formulation with adequate development of strength, because limestone filler contributes to the early strength and the S to the long-term strength. In the evaluated samples the FL mortars have lower strength values than the SL ones due to the higher early reactivity of the slag comparing to the fly ash, because slag is not only pozzolanic but is also hydraulic, meaning that the slag will also hydrate in alkaline environment when mixed with water, but at a much slower rate than Portland cement.

Thus, the technological properties of these special cement formulations are interesting and acceptable and the synergistic effects of different blends used in adequate proportions can allow developing competitive binder systems, even using high volume of SCM, so that their use in the building industry seems to be viable and promising. The fit of composition of the ternary mixes can allow developing the mechanical properties according with the requirements of the structure.

### 3.1.3 Pore structure development with ternary blends

The strength development behavior in ternary binder systems is closely interconnected with the refinement in pore structure during hydration of blends as has been already postulated in Refs. [27, 28]. In Fig. 2 a linear relationship can be deduced between compressive strength and total porosity after 90 days of hydration of ternary mixes. Clearly there are some blends that show higher strength than the limit of the plain OPC mortar and this can be associated to an increase in the volume of hydrates in blends that increase the density of the hydrated products generating a subsequent decrease in porosity [6]. But to obtain an appropriate total porosity value the type and proportion of each

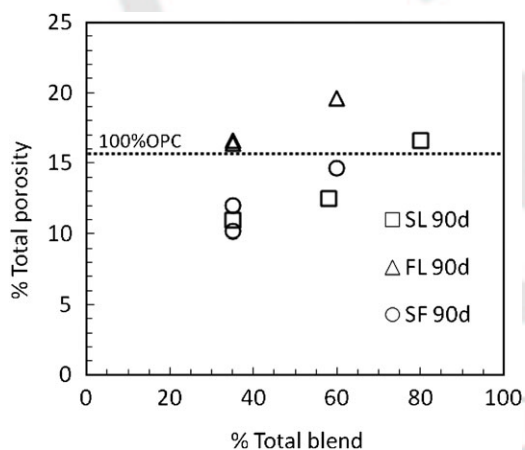


**Figure 2.** % total porosity versus compressive strength of ternary blends after 90 days of hydration

blended material influence, as can be deduced from Fig. 3. The contribution of each SCM to hydration and the synergistic effect between the different types of blends in the ternary system is relevant to reach mechanical requirement. As commented above, the contribution of limestone filler (L) will be more relevant at early ages, S will contribute both in the mean and the long-term, whereas the F effect will be higher at the long-term. As described in Ref. [6] limestone powder will contribute to increase the total hydration products volume with respect to the plain OPC one at early ages.

However, provided a lower total porosity comparing to the reference mortar, this does not always result in a sufficient strength to reach the mechanical performance shown by conventional OPC samples, being very important for the pore size distribution that clearly depends on the content and type of SCM used, as shown in Fig. 4. Besides, the transport of aggressive species is affected by the pore size distribution.

In Fig. 4 the pore structure evolution of OPC 100% and SF2 ternary mix is shown, as both mortars showed similar mechanical compressive strength evolution at early and long hydration ages.



**Figure 3.** % total blend versus % total porosity of ternary mixes after 90 days of hydration

The pore structure of SF2 has more small pores ( $<0.1 \mu\text{m}$ ) at early ages of hydration,  $<28$  days. The region of porosity from  $0.1$  to  $10 \mu\text{m}$  shows significant differences between both materials at every curing age, indicating a different microstructural evolution in each case. In fact, the OPC mean pore size decreases less with hydration than that of SF2. These changes can be associated to the hydration of blended material and the deposition of new CSH within this region of pores. Although at early hydration the coarse pore content is higher for SF system, as also found in Refs. [6], at longer ages of hydration ( $>28$  days) the coarse pores are significantly reduced with respect to OPC which justifies the higher compressive strength reached after 90 days of curing in the SF2 ternary mix. Similar response in the evolution of the pore size distribution with hydration age was obtained for SL1 sample that also gave similar strength evolution than 100% OPC mortar in the early ages ( $<28$  days).

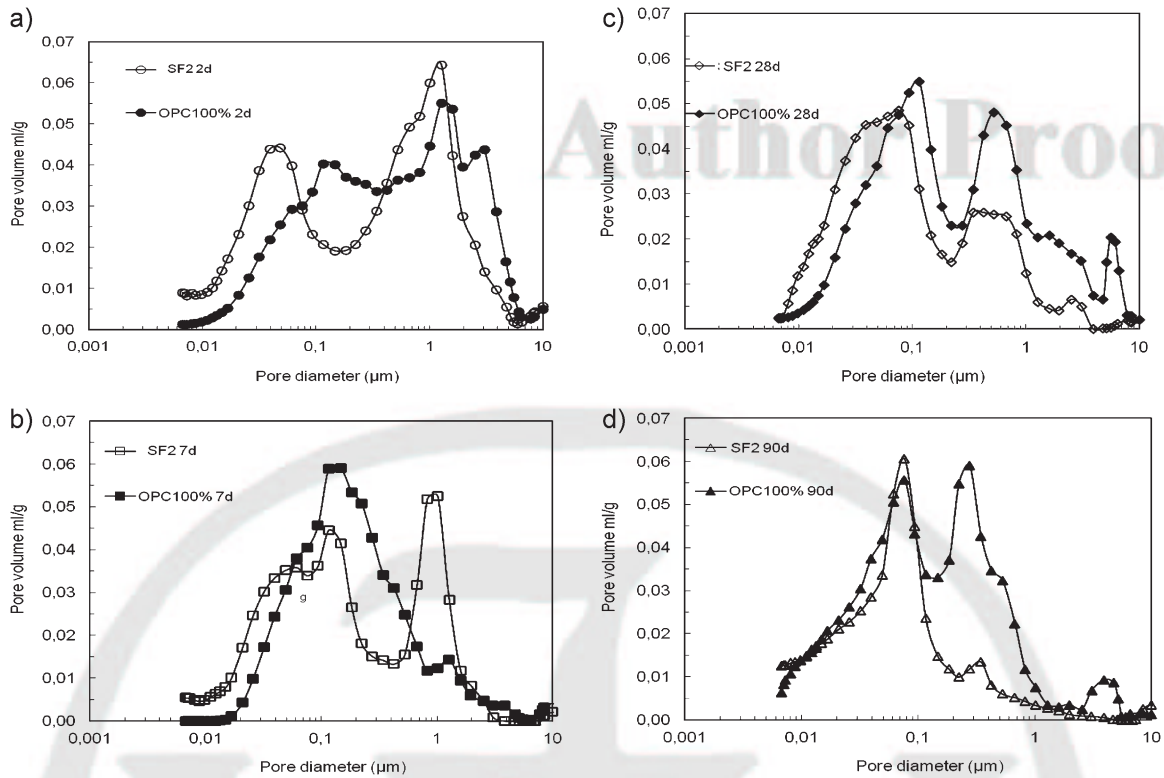
The refinement in pore structure, shown in Fig. 4, would have a favorable consequence in the durability performance derived from the retardation of the transport of aggressives (e.g.,  $\text{CO}_2$ , chlorides, or water). If an optimized ternary blended cement is used the pore structure refinement can contribute to enlarge the initiation stage in case of corrosion of reinforcement, compensating the less portlandite content to resist from carbonation or sum up to the binding action of chloride typically accepted when using some SCM such as F or S.

### 3.2 Changes in pore solution pH of ternary blends mortars

The use of binders containing mineral additions as those used in the present work reduces the amount of OPC in the mix and as a consequence the main source of portlandite as it comes from the hydration of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$ . Besides, the pozzolanic materials need the portlandite for their own hydration with the subsequent formation of additional CSH [29]. Both processes induce changes in the pore solution chemistry of cement pastes that, although they have no consequences in mechanical properties development, they can have consequences in durability performance, as in corrosion of reinforcements. It must be taken into account that the pore fluid pH is a parameter that will be affected by the content and the hydration of the blended materials used.

Figure 5 represents the pore solution pH changes due to the advance of hydration of ternary blended mortars. While the pH value of the 100% OPC sample remains practically unchanged since early hydration ages, a pH decrease is observed with the ternary mortars developed in this study. Similar trend was also observed after 140 days in similar FL mortars but using a higher alkaline OPC [6], indicating that hydration of blended materials as F or S is still developing at these long curing ages.

Different effects can be deduced from the type of binder and age of hydration. Previous results from a 100% OPC mortar and a low pH-cement mortar containing 60% OPC + 40% silica fume [16] are also shown in Fig. 5 for comparison purposes. The 100% OPC shows high alkaline pH ( $>12.8$ ) with low variations along hydration time, while the low pH mortar follows a clear decrease in pore fluid pH from the initial stage of hydration, being more than one pH unit lower after 90 days [16]. The pore solution pH of ternary blended mortars clearly evolves between both limits. The



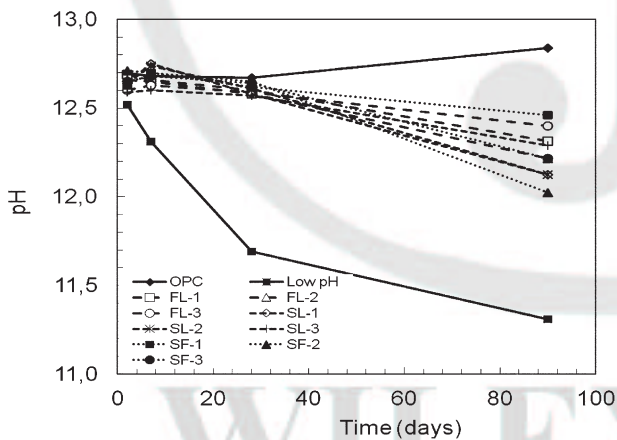
**Figure 4.** Pore size evolution in OPC 100% and ternary binder SF2. (a) 2 days, (b) 7 days, (c) 28 days, (d) 90 days

pore solution pH values measured in the reference OPC mortar are between 12.7 and 12.8 during all the test period. These values are slightly lower than those usually measured in conventional OPC materials. This can be explained considering that the OPC used is a low-alkaline one, but also considering some possible limitations related to the used pH measurement method that could be decreasing the obtained pH value (although it has been demonstrated that these possible decreases are never higher than 0.3 pH units [15, 16]): (i) in materials with high portlandite contents some corrections considering the Ca content of the solution are possibly needed due to the leaching effect of

precipitated portlandite; (ii) in the suspension measured, the powdered cement paste content is lower than the powdered sand content and this can generate a “dilution effect” in the obtained pH value.

The pH of the concrete pore solution depends on the binder type as well as the cement content in the mix. In the case of CEM I cementitious materials, the pH is above 13 in many cases depending on the alkaline content of the OPC and the cement content in the dosage. It is well known that the pozzolanic reaction consumes CH formed during the hydration of clinker phases, and thereby reduces the pore fluid pH [16] but, besides, in low-pH cementitious materials (high blended content) alkalis are removed from the pore solution being bound in CSH structure [16]. In these special cementitious materials the pore solution pH decreases progressively with time as the pozzolanic reaction advances when significant amount ( $\geq 40\%$ ) of OPC is replaced by effective pozzolanic additions such as silica fume, alone or in combination with fly ash [16]. The progressive evolution of pozzolanic reaction reduces the portlandite content ( $\text{OH}^-$  source) and the alkali content of the pore solution is also limited as they are bound in the C–S–H gels formed, thus the pore solution pH is strongly decreased.

In the evaluated ternary mixes, at early ages of hydration the pH approaches to the OPC mortar, although lower pH values in mixes with high content of blended material are observed. On the contrary, there are some mixes, with higher cement content (SL-1 and SF-1) that show a slight increase in the pore solution pH at early ages. The suggested influence of limestone filler in nucleating sites of CH crystals and CSH at early hydration ages



**Figure 5.** Evolution of pore pH during hydration of ternary cement binders

[22, 23] with the subsequent acceleration of the hydration of clinker particles (especially the  $C_3S$ ) [24, 25] might explain this phenomenon.

In the evaluated ternary mixes, at longer ages of hydration the pore fluid pH slightly decreases as the hydration of the blended material advances, although, provided this lower pore solution pH at longer ages comparing to the reference mortar, it is difficult to explain the slight differences observed in the pH values measured in each mix of a same ternary type family and further studies at longer ages are needed to accurately evaluate this parameter. However, if the portlandite is completely consumed due to the pozzolanic reaction between this CH and the silica of the mineral addition, as occurs in the shown low-pH mortar included for comparison in Fig. 5, the pore fluid pH strongly decays to values below 12 [16]. So, it would be interesting to analyze the long-term pore fluid pH evolution of the evaluated ternary mixes as, due to the lower and slower pozzolanic reaction of blast furnace slag and fly ash comparing to silica fume.

### 3.3 Consequences of ternary blends in corrosion performance of reinforcement

If reinforcements are employed with ternary blended cements two aspects have to be taken into account: (i) the effect in the passivation process and (ii) the corrosion consequences if chlorides reach the reinforcement.

#### 3.3.1 Influence in passivation process

It is well known that due to the high alkaline environment of the pore solution in ordinary Portland cementitious materials ( $pH > 12.5$ ), the reinforcements reach a passive state and remain unaltered if no aggressive species penetrate the cementitious system. In the present study the passivation process has been analyzed in reinforcements embedded in ternary blended mortars.

The  $E_{corr}$  evolution, as shown in Fig. 6, does not show clear differences between the different ternary blends probably due to the pore fluid pH values measured are also similar. In fact, as observed in the pore fluid pH results, comparing the  $E_{corr}$  values with those measured in materials showing extreme

changes in pH as 100% OPC and low-pH mortars with higher and lower pH values, respectively, the measured  $E_{corr}$  values in the ternary mixes are between both limits. Although a more anodic  $E_{corr}$  is detected in low-pH mortar up to 90 days, at longer hydration ages  $E_{corr}$  decay to more negative values occurs that suggests increase of corrosion activity [30].

Concerning the kinetic of passivation process, represented in Fig. 7 as  $i_{corr}$  although the passivation process is possible in all ternary mixes, some differences are observed comparing to 100% OPC mortar (that has higher pH; see Fig. 5), allowing thinking to lower corrosion rates after passivation in ternary mortars. This response can be a consequence of changes in the passive layer structure and composition due to changes induced by the observed decreases in the pore solution pH and also the higher resistivity of these binders.

However, the interpretation of this different response of passive layer with the pH of the environment is not clearly understood as some authors consider that higher current densities after passivation of a passive film are representative of lower quality and less protection [31], while others suggest that these differences in current density are a consequence of the type of oxides forming the passive film [32, 33]. The surface film is considered to have a three-dimensional structure with a non-stoichiometric structure of oxides, in which the inner part remains  $Fe_3O_4$  and the outer part appears oxidized to  $Fe_2O_3$ . Changes in the  $Fe^{II}/Fe^{III}$  ratio as function of aging and pH will allow the formation of passive layers with different conductivity ( $Fe^{III}$ -oxides are less conducting compared with the magnetite structure) [34, 35] that would justify the different current densities measured in different pH conditions as those shown in the present study using mortar of ternary binders. However, the protective character of the passive film cannot be directly deduced from these higher current densities as in the literature it is accepted that the chloride threshold for corrosion onset increases with the pH of the environment. Passive films formed in a lower pH could result in less protection but further studies are needed in presence of aggressive species to check this phenomenon in ternary blended mixes [36, 37].

Another aspect derived from Fig. 7 is the response of low-pH material, that shows corrosion rates during passivation process

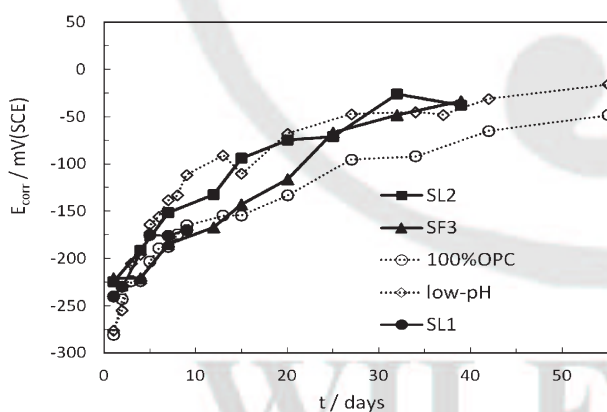


Figure 6. Evolution of  $E_{corr}$  in reinforcement during passivation process of ternary mixes

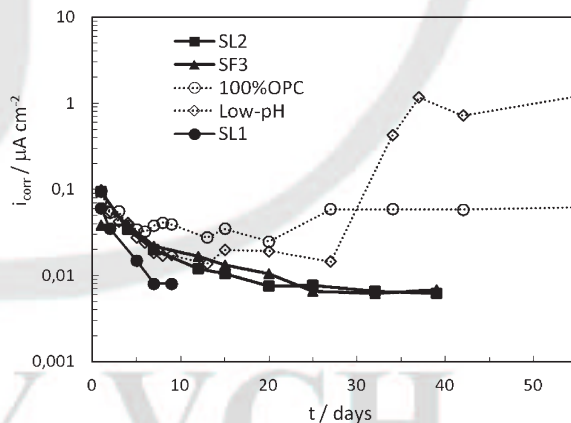
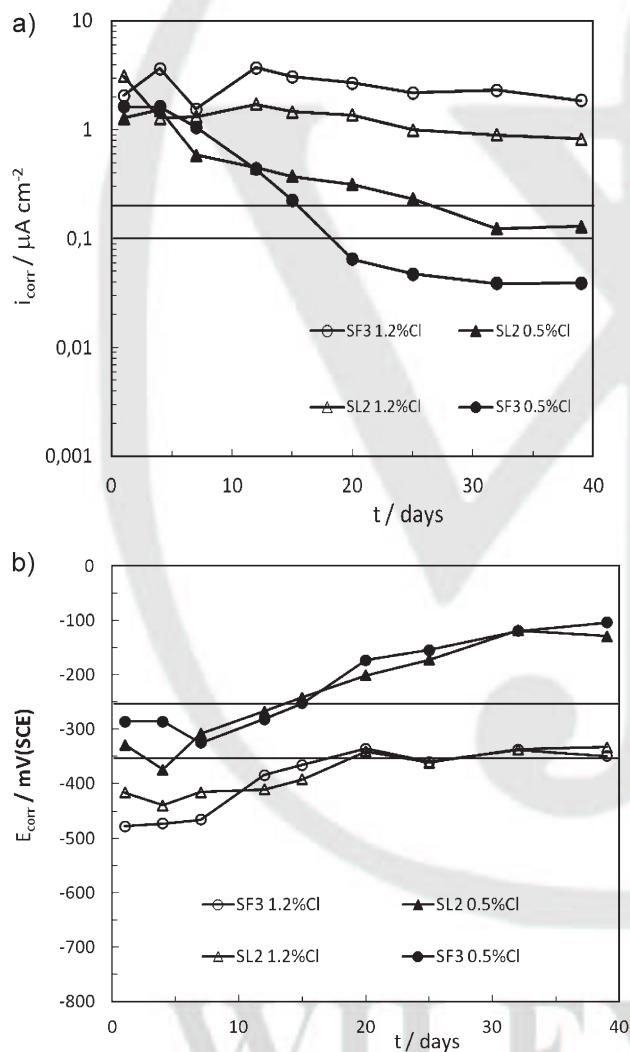


Figure 7. Evolution of  $i_{corr}$  in reinforcements during passivation process of ternary mixes

similar to those measured in ternary mixes, but after 15 days curing the  $i_{\text{corr}}$  of low-pH mortar slowly increases and after 28 days a sharp increase of corrosion rate is detected, reaching values above the limit considered for passivation ( $0.2 \mu\text{A}/\text{cm}^2$ ). The reason of this depassivation of reinforcements in the low-pH mortar is attributed to the pH decrease that has reached a level below 11.5 (see Fig. 5). At this pH the portlandite has been completely consumed due to the pozzolanic reaction [16]. So although passivation of reinforcements is allowed in ternary mixes if the pH decreases with future hydration evolution and reaches a critical level, a risk of corrosion onset can remain. In fact, local corrosion attack was detected in reinforcements embedded in low-pH mortars [30], but if the pore solution pH of the evaluated ternary mixes remains above this limit the passive state is expected to be maintained.

### 3.3.2 Corrosion of reinforcements in ternary blended cements in the presence of chloride

In Fig. 8 an initial attempt of corrosion of reinforcements in ternary blended mixes containing limestone filler + slag (SL2)



**Figure 8.** Corrosion activity of ternary blended cements in presence of chlorides. (a)  $i_{\text{corr}}$  (b)  $E_{\text{corr}}$

and fly ash + slag (SF3) polluted with chlorides is considered. Although the addition of chloride during mixing is a exposure condition scarcely occurring in practice as in more cases chlorides penetrate from outside, this study will allow to characterize what happens if corrosion of reinforcement is initiated (propagation) and also to evaluate the chloride binding capacity of the ternary binder to characterize the consequence in initiation stage and in corrosion of reinforcement.

The results of the present work are compared with those published in [38] for OPC mortar and they indicate a higher activity in the initial period, probably due to lower pore solution pH with similar chloride content for the ternary cement mixes. However, at longer ages of hydration, the high binding chloride capacity of the blend is responsible for the corrosion rate decrease if the free chloride (in water) at the rebar surface remains on a low level. In the ternary blended mixes studied the free chlorides contents were between 0.2 and 0.3% lower than the free chloride content threshold defined in literature to initiate corrosion in OPC materials [36, 37]. The progressive decrease of  $i_{\text{corr}}$  in mixes with the inclusion of 0.5% of total chlorides point out the beneficial effect of the use of ternary blends due to the binding capacity ability of slag and fly ash.

The above corrosion response of ternary blends can also be associated with the changes introduced in the interfacial zone reinforcement/cementitious material. In 100% OPC this interphase is usually rich in portlandite, serving as a reserve to maintain the alkalinity of the interfacial zone in a safety level [39]. Moreover, when the formation of this CH-rich layer is hindered, the chloride threshold decreases [40]. In the ternary mortars fabricated, with high content of blended additions, the CH content can be significantly reduced in the interfacial zone and also be the reason for the chloride threshold decay given in literature with high volume of mineral additions in concretes [36], but further research is needed to confirm the response with high ternary blend content in the cementitious materials.

## 4 Conclusions

The use of optimized content components in ternary blends results in binders able to fulfill interesting requirements with respect to mechanical strength, namely similar to those obtained in conventional cementitious materials. The best results are obtained when two additives with antagonist properties are combined, as fly ashes and slags or the last with limestone filler, in optimized proportions. It would be relevant to study more accurately the hydration process to better understand how the reactions and the modifications taking place give a cementitious material its properties.

More studies concerning the influence of ternary blended type and the synergistic effects on hydrated solid phases/pore solution chemistry, would inform more precisely on their effect on the durability performances, in particular those associated with corrosion of reinforcements.

The effects associated with time-dependences due to the slower reaction velocity of the SCM used in this study that implies a slower mechanical gain strength evolution and the corrosion performance response, can be relevant if no sufficient maturity of



the cementitious material is reached. In the present work curing ages of 90 days has demonstrated to be acceptable.

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