

Extended Abstract

Incorporating supplementary cementitious materials in mortars produced with recycled cement

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1. Introduction

Nowadays, global warming due to mass pollution is a major concern to the general population. Governments all over the world are making great efforts to promote the reduction of large emissions of greenhouse gases (GHG), specially carbon dioxide (CO₂). This is the most noxious gas and represents 90 % of the total GHG's emissions. Simultaneously, the building materials sector is responsible for about 10 % of the total anthropogenic CO₂ emissions, 85 % of which are directly linked to the cement production [1]. In cement plants, limestone is burnt at 1450 °C and one of the results of it, besides obtaining the clinker, is the release of 0,92 tons of CO₂ per ton of clinker that is processed [1].

Recently, many investigation studies have been conducted to find the better solution to reduce CO₂ in the cement industry, such as low-carbon thermal activated cements [2]. Moreover, such investigations could give an answer to all the wasted construction and demolition residues. This study emerges as a contribution for a better understanding on the effect of pozzolanic supplementary cementitious materials (SCM) when used as an admixture to reactivated cementitious materials (RCM), as some authors already explored [3, 4]. In order to improve hydraulic properties, this type of SCM were selected for its capacity of reaction with the remnant calcium hydroxide (CH) found in RCM's portlandite [4]. To study this, further investigations on characterizing mortars with recycled binders

are necessary. There is clear evidence that a more sustainable path can be followed.

2. Materials and methodology

The recycled cement used as the mortars' main binder was obtained from a source cement paste produced for that purpose. In order to find the perfect dehydration temperature for the paste, the material was analyzed before and after the heating process.

2.1. Recycled cement – production and characteristics

The original cement paste used in the experimental part of this work was prepared by mixing ordinary Portland cement (OPC), type I 42,5 R and water, in a water/cement (w/c) ratio of 0,40. The fresh mixture was casted in cubes (150x150 mm), demolded after 24 h. The hardened cubes were cured for approximately 120 days in a water spraying chamber (25 °C and 95 % of relative humidity), then crushed in two different sized jaws crushers and ground in a grinding ball mill.

The resulting powder was collected after sieving between the square mesh sieves of 125 and 45 µm and sent to the furnace in order to dehydrate it. The choice of the dehydration temperature and length of exposure was based on previous work by a former investigation colleague [5]. It was optimized and confirmed by subjecting a powder sample to a thermal weight variation test and a thermal analysis, with thermogravimetry (TG) and differential scanning

calorimetry (DSC) tests. The sieved powder was submitted to a stepped controlled heating regime with a rate of 20 °C/min and it was kept under 100 °C for 1 h, 350 °C for 2 h and 700 °C for 5 h. The cooling was inside the furnace to the room's temperature. Due to a 3-months break between the dehydration and the mortar's preparation, in which the recycled cement (RC) lost some reactivity, the same batch of ground cement paste went for a second heating in order to promote a better dehydration. This time however, a different equipment was used – a rotary kiln, specifically designed for the purposed of producing cement. The powder was heated to a rate of 10 °C/min, reaching a maximum exposure of 700 °C for 3 h and cooled to the room temperature with the kiln's door closed. The RC was immediately collected and stored in sealed plastic bags due to its sensibility to react with any kind of humidity. This product was analyzed in a laboratory of the quality department of SECIL, a Portuguese cement producer. The results can be found in Table 1.

Table 1 – Physical and chemical properties of RC

| Chemical properties | |
|--------------------------------|-------------------------|
| Loss on ignition (950 °C) | 7,68 % |
| CaO | 59,58 % |
| SiO ₂ | 18,23 % |
| Al ₂ O ₃ | 4,88 % |
| Fe ₂ O ₃ | 2,99 % |
| SO ₃ | 2,97 % |
| MgO | 1,57 % |
| Physical properties | |
| Specific gravity | 2650 kg/m ³ |
| Blaine surface area | 4390 cm ² /g |
| Fraction > 45 µm | 32,70 % |
| Fraction between 3 and 32 µm | 41,70 % |

2.2. Pozzolanic supplementary cementitious materials

Since this work was developed in Portugal, the chosen SCM were two products commercialized in this country: fly ash (FA) and silica fume (SF).

Fly Ash

The FA used is a by-product of power plant's coal-burning, consisting of small spherical shaped and soft textured particles, with an average size of 10 µm. This batch of FA was mainly composed by silica (50,16 %), alumina (25,62 %) and iron oxide (7,14 %). Scanning Electron Microscopy (SEM) images of this FA show a presence of non-burnt carbon, which could jeopardize its flowability and reactivity with CH. Moreover, the activity index of this product was found to be lower than the standard limit of 75 %, established by the norm NP EN 450-1, reaching a value of only 59 % at the age of 28 days.

Silica Fume

The used SF was supplied in a densified form and is mostly composed by silica (< 90 %). The product supplier assures at least a 100 % activity index, at 28 days of age. SEM images show that the SF came agglomerated in irregular particles with an average size of 10 µm and with traces of non-burnt carbon, which could also compromise its flowability and reactivity with CH.

2.3. Mortar's production

To produce the mortars, besides the referred RC and SCM, two different sands were used (one coarser and one finer), in a weight proportion of 1:3 regarding the amounts of binder and sand (according to the reference composition described in NP EN 196-3, for cement mortars). In order to get a proper analysis of the effect of these pozzolanic SCM on recycled cements, different percentages of each SCM were used in the binder's composition and then the same amount of mortar mixtures was replicated with OPC, instead of RC. The chosen w/b (water-binder ratio) was 0,67 for all mortars. Using the same ratio across mortars eases the direct comparison of the influence of each SCM. The compositions of the mortar's binders used for the experimental part of the work are described in Table 2.

Table 2 – Compositions of the mortar's binders

| SCM | Cement | FA (%) | SF (%) | OPC (%) | RC (%) |
|-----|--------|--------|--------|---------|--------|
| FA | RC | 15 | | | 85 |
| | RC | 30 | | | 70 |
| | RC | 50 | | | 50 |
| SF | RC | | 10 | | 90 |
| | RC | | | | 100 |
| FA | OPC | 15 | | 85 | |
| | OPC | 30 | | 70 | |
| | OPC | 50 | | 50 | |
| SF | OPC | | 10 | 90 | |
| | OPC | | | 100 | |

All mixtures produced were casted in steel prismatic molds (40x40x160 mm). They were demolded after 24 to 48 h, depending on each specimen hardened state and placed in a water spraying chamber (at 25 °C and 95 % of relative humidity), to cure until the testing ages were reached (3, 7, 28 or 90 days).

2.4. RC characterization

Every mixture produced was evaluated according to its fresh properties, such as bulk density, flowability, water requirement for standard consistency, initial and final setting time.

Water requirement for standard consistency, initial and final setting

These properties were assessed in accordance with NP EN 196-3, using a Vicat apparatus with the adequate needles and rigs. The main goal was to find the right amount of water required by the binder (w/b), that makes the Vicat's rig reach a standard depth in the mix. This standard consistency mix was later used to determine and evaluate the initial and final setting times of the binder, using the Vicat apparatus as well. The time was measured in minutes, since the mixer was turned on. For a more complete observation on the influence of SCM on these properties, OPC, RC, RC with SF (10 %) and RC with FA (30 %) were included in the analysis.

Flowability

This property was evaluated for every mortar in order to analyze its applicability in a construction site. The procedures were applied in accordance with NP EN 1015-3.

Bulk density

This property was determined according to what is described in NP EN 1015-6 and consisted in weighting (using a scale) a known volume bucket full of mortar. The result is obtained in kg/m³.

2.5. Compressive and flexural strength

The specimens, previously manufactured and described (2.3), were tested after 3, 7, 28 and 90 days of age for every composition. The exceptions were the 100 % RC and OPC, only tested at the age of 3 and 28 days. The compressive and flexural strengths were tested in accordance with NP EN 1015-11, in a hydraulic machine for compressing small mortar prisms. Even though they follow the same trend, the main property to evaluate would be the compressive strength, since the flexural strength is comparably very low.

3. Results and discussion

3.1. Thermal exposure effect

After the grinding and sieving procedures, the resulting powder was subjected to a thermal analysis (TG and DSC) in which three weight losses regions were highlighted: 100-150 °C; 430-550 °C; and 700-800 °C. The first region (100-150 °C) is associated with the initial stage of dehydration with free and bound-water removal and decomposition of low temperature phases (such as sulfoaluminates). The second region (430-550 °C) corresponds to the dihydroxylation of CH. The decarbonation of carbonated products starts slightly above 550 °C, though it only gets significant expression in the third region (700-800 °C). This process of decarbonation is responsible for the main weight loss, as shown by the TG. Also, in this last region, there still is a loss of CSH (calcium silicate hydrate) molecules' bound-water that progressively gives origin to

calcium silicates. Similar weight losses and dehydration stages were identified by other authors [6].

Based on the TG curve, it was possible to determine the initial hydration level of the cement paste powder. A level of 82 % was reached, implying a great initial hydration, thus proving an accurate simulation of an old hydrate cement paste. It was also possible to estimate that 15,7 % of CaO (calcium oxide) would be generated at 700 °C. This prediction does not count with the possibility of low temperatures carbonation inside the furnace, as noticed by some authors [7].

The results obtained by DSC, regarding the heat flow (HF) and the differential heat flow (dHF) analysis, enable the identification of non-weight loss occurrences.

By analyzing the dHF curve, exothermic peaks are identifiable around 140 °C and 185 °C, possibly corresponding to gypsum's decomposition [2]. At 120 °C, the peak may be associated with ettringite's (calcium sulfoaluminate) decomposition [2]. Between 200 and 230 °C a low intensity peak can be identified, that may be related to bound-water removal from the hydrated particles [6]. These results seem to prove an efficient dehydration of RC's hydration products. Around 450 °C, an endothermic reaction from portlandite's dehydration stands out, followed by a high intensity peak at 500 °C, product of a strong exothermic reaction, which can be related to a partial lime's carbonation caused by the dehydration of portlandite. Low temperature conditions inside the furnace are propitious to carbonation [7]. This could be the reason why a lower-than-expected amount of CaO (15,7 %) was generated for the RC. The decarbonation of the previously formed calcite occurs between 750 and 775 °C. Based on the thermal analysis, is correct to affirm that 700 °C is an efficient dehydration temperature, as shown by other authors as well [2, 5].

3.2. Phase analysis

In order to get a better comprehension of the crystalline phases created during the thermal activation, the produced RC was subjected to X-rays diffraction (XRD) analysis. An analysis that includes samples of: OPC; non-treated cement paste powder; and a 3 days aged cement paste produced with the RC, allowed a more efficient comparison. The results of the analysis are shown in Fig 1.

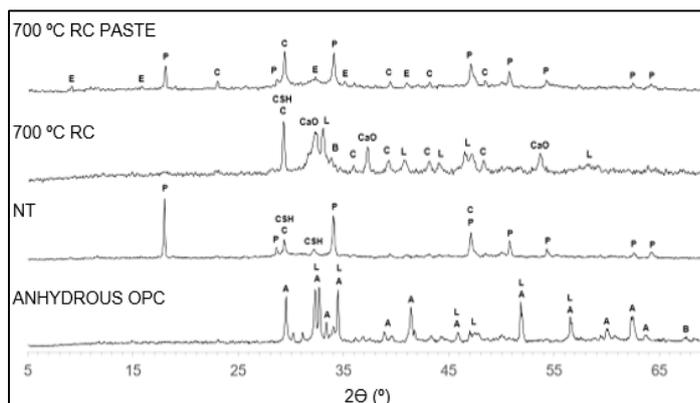


Fig. 1 – X-ray diffraction analysis of the produced RC (700 °C RC), anhydrous OPC, non-treated cement paste powder (NT) and a 3 days aged cement paste produced with the RC (700 °C RC PASTE). E – Ettringite, P – Portlandite, C – Calcite, CSH – Calcium silicate hydrate, CaO – Calcium oxide, L – Larnite (C₂S), B – Brownmillerite (C₄AF), A – Alite (C₃S). Some minor phases are not indicated.

The curve regarding anhydrous OPC shows clearly clinker's major compounds, in which the presence of alite (C₃S) stands out. This compound cannot be generated with a thermal treatment of RC. The narrow and well-defined peaks demonstrate how crystalline larnite and alite can be, as its intensity suggests a strong presence of such compounds. Gypsum was originally added to OPC to delay the hydration reaction of calcium aluminate, and its presence is confirmed (particularly, between 11 and 12 °, and 66 °).

In the non-treated cement powder's case (NT), the most relevant crystalline phases are portlandite, ettringite and calcite. However,

ettringite is not represented due to the low expression of its numerous isolated peaks. Since hydrated cement has several hydrated phases of an amorphous or partially crystalline nature, its identification becomes difficult in XRD graphs (especially regarding CSH). The diffractogram line's elevation from the base line (between 30 and 40 °) proves the presence of low crystalline material. The high and well-defined peaks from portlandite demonstrate how the cement paste was well hydrated, as previously shown by thermogravimetry's results. Other authors have also identified ettringite and portlandite as main phases of hydrated cement powders [6, 8].

As it can be observed in Fig. 1, there is a relevant amount of calcite in non-treated cement powder. This contradicts studies in which similar curing processes were applied [3, 9], suggesting some carbonation occurrence during the grinding and sieving processes and the powder's storage.

Regarding the RC treated at 700 °C, portlandite was found to be eliminated, probably consumed to generate CaO and some calcite, as it has been noticed to increase with the treatment temperature rising to 750 °C [6]. Unexpectedly, the amount of CaO generated is not correspondent to the reduction of portlandite, meaning that some of the CaO formed could be transformed in calcite, as noticed in previous studies [7]. Since XRD is a qualitative analysis, it does not allow for a rigorous confirmation of this occurrence. In fact, the high content of calcite in this kind of cements, proves the low-temperatures carbonation phenomenon inside the furnace. There were some diffraction peaks detected regarding the crystalline phases of the dicalcium silicates (C₂S), which demonstrates CSH's dehydration. Despite being named larnite, its presence refers to a component with similar stoichiometry. While some previous studies reveal the formation of β-C₂S (a less reactive form of C₂S), caused by thermal activation at high temperatures [7, 10], other studies reveal a more reactive form (α-C₂S) than OPC's, when

dehydrating cement paste between 660 and 800 °C [4, 6].

Based on the results obtained in the thermal and diffraction analysis, it is accurate to affirm the possibility of producing RC without a relevant release of CO₂, as also concluded by some studies in this field [2, 5].

Besides the phases of RC already identified in Fig. 1, traces of more complex phases were detected, but yet less common, such as cowlesite (CaAl₂Si₃O₁₀.6H₂O) and calcium hemicarboaluminates (Ca₄Al₂O₆(CO₃)_{0,5}(OH).11,5H₂O), as it has been identified by other authors as well [7]. Such authors then suggested the quick reaction between anhydrous product's calcite and aluminates to be the origin of this compounds, contributing to RC's initial reactivity. For OPC, bassanite (CaSO₄.0.5H₂O) and tilleyite (Ca₅Si₂O₇(CO₃)₂) were also identified, though they are not represented in Fig. 1.

It is of great importance to mention that, despite the resulting product from thermal activation of hydrated cement pastes having great rehydration potential, its composition is quite different from OPC, in which calcium silicate phases are formed with distinct chemical and morphological characteristics.

3.3. Binder's characterization

Water requirement for standard consistency, initial and final setting

As it was expected, binders incorporating RC demand a larger amount of water than OPC, as it has been observed in several studies [2, 5, 11], due to the increase of porosity and specific surface area, and to the high level of CaO found in these cements. The water demand obtained, in this study, for RC is higher than the referred studies - 74 % - probably given the coarser particles used in this experimental campaign. Despite the particles being coarser and resulting in a smaller specific surface area, the porosity increases, leading to a higher water consumption. Moreover, it is possible that some particles were

agglomerated, increasing the water demand as well.

Contrarily to what was expected and mentioned by a few authors [8, 11] the initial and final setting times of the recycled binders were not reduced. It tended to increase considerably. One study [10] suggested that the decrease of setting times of RC takes place in the CaO reaction with water. A false setting occurs, while the real setting is a slower reaction. In Table 3 it is easily observed the effect of incorporating SCM in the binders, regarding water demand and setting times.

Table 3 – Different binder's water demand and setting times

| 100 % OPC | | 100 % RC | |
|-----------------------|------|-----------------------|------|
| Water demand | 0,27 | Water demand | 0,74 |
| w/c | 0,27 | w/c | 0,74 |
| Initial setting (min) | 120 | Initial setting (min) | 300 |
| Final setting (min) | 200 | Final setting (min) | 330 |
| 90 % RC + 10 % SF | | 70 % RC + 30 % FA | |
| Water demand | 0,78 | Water demand | 0,64 |
| w/c | 0,87 | w/c | 0,91 |
| Initial setting (min) | 590 | Initial setting (min) | 660 |
| Final setting (min) | 640 | Final setting (min) | 710 |

Regarding SCM: in one hand, FA incorporation led to a lower water demand due to the spherical form of the particles that induce a lubricant effect in mixtures. In the other hand, SF tend to jeopardize flowability due to its agglomerated and irregular particles. The SCM incorporation led to an increase of setting times. This could be justified by the initial inert behavior these products have before starting to develop hydration reactions.

Flowability

As it was expected, the flowability of recycled binders was seriously worse than OPC binders. Moreover, for both types of binders, incorporating

FA led to more fluid mixtures, while SF jeopardized mixtures' flowability, making them dryer, as observed in previous studies [3, 4].

Bulk density

The higher values for bulk density (ρ) were obtained in OPC mixtures, since this cement has a higher ρ itself (3080 kg/m³) than RC (2650 kg/m³). The incorporation of SCM in OPC mixtures led to lower ρ values, reaching the lowest when adding SF. However, in recycled mixtures incorporating FA the ρ tended to increase with increasing FA level. Its lubricant property led to a denser mixture, since FA's ρ (2320 kg/m³) is close to RC's. Adding SF to RC led to a lower value, due to obtaining a worst flowability mixture and poorly compacted specimens, since SF's ρ (2200 kg/m³) is close to RC's

Mechanical Resistance

Immediately after obtaining the RC, two mortars were produced – one using 100 % RC as binder and the other using 100 % of OPC. The results were quite satisfactory as the recycled mortar specimens reached, at 28 days of age, 23 MPa, while the OPC specimens reached 44,2 MPa. Despite being a considerable resistance reduction, this shows the capacity of reaching values applicable in construction situations, without massive GHG emissions implied in OPC's production [2]. The strength development in the specimens was slower in the first 7 days of age, showing a low initial reactivity, contrarily to what was observed in other studies [2, 8, 10].

3.4. RC's reactivity loss

During the development of the experimental work it was noticed a slight reactivity loss, most likely due to the 3-months break between the thermal activation phase and the RC's characterization phase, in which a slight hydration may occurred. Small signs, such as weaker heat release during the mortars production and extended setting time, exposed this phenomenon. As time went by, it became harder to produce new OPC cement pastes to grind, sieve and activate, before the

appointed deadlines. Hence, it was decided to make another thermal treatment to the material, as it was referred previously (2.1). In order to confirm this occurrence and find its origin, the RC was subjected to XRD analysis and two cement pastes were produced with the RC subjected to two treatments and some remaining non-treated powder, now treated for the first time. The results in 28 days of age specimens, were quite conclusive since it was detected a 26 and 47 % resistance reduction, respectively. The second thermal treatment was not the responsible for the reactivity loss.

Regarding the XRD analysis, three samples were analyzed – the non-treated powder still stored, the two-times treated RC and a sample of the original activated RC, now subjected to 900 °C. The results show an increase of calcite's level in non-treated RC, though the most noticeable increase was detected in the two-times treated RC (at 700 °C), compatible with a strong low-temperature carbonation inside the furnace, as it was already suspected. Moreover, in the two-times treated RC (at 700 °C), CaO disappeared and C₂S became less present and its peaks not as clearly defined, by decalcification of calcium silicates, contributing to the reactivity loss. Also, a

clearer appearance of C₃S was noticed, which contributes to an initial resistance development but almost irrelevant to the long-term resistance. The poor kiln's exhaustion of the water vapor generated in the dehydration phase, is the main cause of the phenomenon, since the 900 °C was supposed to fully decarbonate the material, which did not happen. Despite all calcite was eliminated to form CaO, another carbonated compound was generated and became very present in this cement – spurrite (Ca₅(SiO₄)₂CO₃). Some paste specimens were produced using this cement, but no reactivity was noticed within the following month. This was a key factor to correct the kiln's defect and ensuring low carbonation, enabling the production of high resistance RC. Moreover, the carbonation occurred in non-treated powder shows how sensitive these materials can be to the storage conditions.

3.5. Mechanical Resistance

In Table 4 are presented the results of compression and flexural strength tests. To ease the values interpretation, especially for SCM effect analysis, the water/binder (w/b) and water/cement (w/c) ratios are indicated, as well.

Table 4 – Mechanical resistances of the produced specimens

| Compositions | w/b | w/c | Specimens' ages | | | | | | | |
|---------------------------|------|------|-----------------|------|--------|------|---------|------|---------|------|
| | | | 3 days | | 7 days | | 28 days | | 90 days | |
| | | | fctm | fcm | fctm | fcm | fctm | fcm | fctm | fcm |
| 85 % OPC + 15 % FA | 0,67 | 0,79 | 2,9 | 13,0 | 3,6 | 16,9 | 4,9 | 27,7 | 7,0 | 37,1 |
| 70 % OPC + 30 % FA | 0,67 | 0,96 | 2,0 | 8,3 | 3,4 | 15,1 | 3,5 | 18,2 | 6,2 | 29,4 |
| 50 % OPC + 50 % FA | 0,67 | 1,34 | 1,6 | 6,6 | 2,0 | 8,0 | 2,9 | 12,2 | 4,7 | 20,9 |
| 90 % OPC + 10 % SF | 0,67 | 0,74 | 2,5 | 11,8 | 3,6 | 17,6 | 5,1 | 27,0 | 6,4 | 36,3 |
| 100 % OPC | 0,67 | 0,67 | 4,4 | 20,0 | 5,4 | 27,0 | 8,7 | 44,2 | | |
| 85 % RC + 15 % FA | 0,67 | 0,79 | 1,4 | 6,0 | 2,5 | 9,8 | 3,1 | 13,8 | 4,6 | 17,3 |
| 70 % RC + 30 % FA | 0,67 | 0,96 | 0,8 | 2,9 | 1,7 | 5,8 | 2,9 | 11,1 | 4,5 | 15,0 |
| 50 % RC + 50 % FA | 0,67 | 1,34 | 0,3 | 1,4 | 0,8 | 2,7 | 1,5 | 6,3 | 4,0 | 11,8 |
| 90 % RC + 10 % SF | 0,67 | 0,74 | 1,6 | 5,5 | 2,6 | 10,4 | 4,1 | 18,0 | 4,9 | 20,2 |
| 100 % RC | 0,67 | 0,67 | 1,8 | 6,6 | | | 3,6 | 17,0 | | |

All compositions were tested at the ages of 3, 7, 28 and 90 days, except for 100 % RC and 100 % OPC, that were only tested at 3 and 28 days of age and 3, 7 and 28 days of age, respectively. Reactivity loss (3.5) was analyzed to check the good conditions and properties of OPC. Regarding the reference compositions, incorporating both SCMs led to unexpected abnormally low resistances. Substituting 15 and 30 % of OPC by FA caused resistance reductions rounding 37 and 59 %, respectively. These results cannot only be justified by FA's low activity index (2.2), therefore the excessive flowability of these mortars (that led to a slight exudation and segregation) is also a strong possibility. However, SF and OPC specimens' results were unexpectedly low as well (39 % loss), in which the dry consistency and low bulk density of the mixture led to poorly compacted prisms with excessive inner air bubbles. For both SCM, the major developments in mechanical resistances were noticed between 28 and 90 days of age, leading to results in better accordance with the activity indexes (2.2), indicating a probable delay in their reactivity. This may seem regular in FA, but it is quite unusual in SF. The irregular SF particles agglomeration makes the dispersion harder to happen in the mixer, most probably causing its reactivity delay. For the mentioned reasons, in this study OPC mixtures will be less emphasized.

Regarding the RC mortars, the unexpected reactivity loss made the SCM's pozzolanic reaction less enhanced and effective, which should be taken in account when analyzing results. When FA was incorporated, the specimen's resistance tended to decrease as its incorporation increases. However, when SF was added the resistance slightly increased, reaching a better value than 100 % RC, at 28 days of age. The phenomenon occurred with FA was also verified by other authors [4, 12], who obtained worse results in their specimens' resistance, by adding FA to RC, at least at early ages (<60 days). As it is known, FA demands long

curing periods before getting effective [13]. Moreover, the chosen powder's granulometry used by the referred authors (< 75 μm) is quite finer than the one used in this study (45-125 μm), which potentiates the binders' reactivity. In addition to this, some of those authors reported increases of resistance when adding SF to RC [4]. Although they used a quite higher substitution percentage (40 and 50 %), they concluded that RC has a great capacity of promoting SF's reactivity.

For 10 % substitution (as it was considered for this study), they predicted a 25 % increment in resistance. However, this was not verified in the present results, probably because their SF had greater particles' dispersion and fineness.

Overall, it can be observed that no matter what SCM is used, the greater resistances' development in RC mixtures happened within the first 28 days of age, then slowing a bit between 28 and 90 days of age. It can also be observed, that adding FA or SF to RC, led to smaller resistance losses than 100 % RC mixtures, when compared to the reference specimens. This confirms the improvement of the effect of pozzolanic SCM in the presence of RC, as suggested in previous studies [4, 12]. Moreover, there was a better resistance development over time in RC and SF mixtures, than in OPC and SF mixtures, highlighting the better synergetic effect of RC and SF, when compared to OPC and SF. This phenomenon was also suggested in a previous study [4], in which the authors obtained quite similar resistance values in mortars with RC treated at 700 °C, incorporating 10 % of SF, confirming a probable reaction by SF.

SEM images of some specimens were collected in order to compare the microstructural effects of FA and SF in both cements (RC and OPC). All images regarding RC mixtures show a massive development of hydration products in the spaces between particles, proving RC's reactivity, as confirmed by XRD analysis (3.2) and resistance tests (3.5), and as verified in a previous study [5]. Images collected of OPC and FA (30 %) mortar,

show how denser its microstructure is, but how less ettringite is formed than in RC and FA (30 %) mortar. Since ettringite's presence is a sign for more porous constitution, this goes in line with the results presented in Table 4. For this occurrence, the reactivity loss may have been a key-factor. However, both mixtures were fairly more porous at 28 days of age, than it was supposed, leading to weak reactivity. In fact, it is possible to observe several unreacted FA particles and very few hydration products in both mixtures, most probably due to the low activity index of this SMC (2.2). Those identified hydration products were generated in FA particles' surface (CSH), confirming its reactivity.

Regarding the admixture of SF, SEM images were collected as well. In general, some of the aspects referred for FA and RC mortars can also be applied to RC and SF mixtures, namely the greater presence of ettringite and less dense microstructure. However, given the reduced zoom of the images, the irregular form of the particles and the advanced age of test (28 days) it was not possible to observe non-hydrated SF particles. In both cases, FA and SF, it was observed the development of external hydration products in RC particles with great distribution of hydration nucleus, but with small hydration products volume between nucleus, suggesting a delay on the RC's microstructural development and bonding between the cementitious matrix compounds.

4. Conclusions

This essay reports a study on the effect of pozzolanic SCM on RC mortars. The most important conclusions have been drawn:

- It is possible to thermally reactivate hydrated cement without a significant release of CO₂, though the final products' composition is quite different from OPC.
- Recycled binders demand a larger amount of water than OPC. By adding FA, the water

demand decreases; and by adding SF, the water demand increases.

- Recycled binders' setting time increased, when compared to OPC's. Moreover, SCM incorporation increased binders' setting time even more.
- The mortars produced immediately after reactivation reached 23 MPa at the age of 28 days, though always being inferior to OPC's strength development. This proves that the RC's strength development is construction-fit. However, RC's production does not imply an environmental impact as heavy as OPC's.
- Hydrated cement paste powder proved to be highly sensitive to poor storage conditions, carbonating easily.
- Non-perfect exhaustion conditions of reactivation furnaces easily induce strong carbonation in RC, leading to major reactivity loss.
- Regarding RC mortars, the cement's loss of reactivity led to less effective pozzolanic reactions with both SCM, though they tend to become more effective in RC's presence than in OPC's.
- Incorporating FA in recycled mortars led to a decrease of specimens' resistance, as much as the percentage of FA increased, due to its low activity and the short curing period.
- FA and RC mortars demand long curing periods in order to become effective and develop higher resistances.
- Incorporating 10 % of SF in recycled mortars led to a slight improvement of the specimens' resistance, showing evidences of a pozzolanic reaction.
- SEM images show massive hydration products between RC particles' spaces. However, the strong presence of ettringites and the less dense microstructure indicate higher porosity of the mixtures, contributing to the lack of reactivity of these recycled binders.

- SEM images of both cements' FA mortars show unreacted particles of FA and very few hydration products, most probably due to the low activity index of this SMC. These identified hydration products were generated in FA particles' surface (CSH), confirming its reactivity.

5. References

- [1] Habert, G., Billard, C., Rossi, P., Chen, C. & Roussel, N., *Cement Production Technology Improvement Compared to Factor 4 Objectives*, Cement and Concrete Research, 40, 820-826, 2010
- [2] Bogas, J. A., Carriço, A. & Pereira, M. F. C., *Mechanical Characterization of Thermal Activated Low-Carbon Recycled Cement Mortars*, Journal of Cleaner Production, 377-389, 2019
- [3] Shui, Z., Xuan, D., Wan, H. & Cao, B., *Rehydration Reactivity of Recycled Mortar from Concrete Waste Experienced to Thermal Treatment*, Construction and Building Materials, 22, 1723-1729, 2008
- [4] Serpell, R. & Lopez, M., *Properties of Mortars Produced with Reactivated Cementitious Materials*, Cement and Concrete Composites, 64, 16-26, 2015
- [5] Neto, G. C., *Dissertação – Argamassas com Resíduos de Matérias Cimentícias de Diferentes Finuras*, Instituto Superior Técnico – Universidade de Lisboa, Portugal, 2019
- [6] Alonso, C. & Fernandez, L., *Dehydration and Rehydration Processes of Cement Paste Exposed to High Temperature Environments*, Journal of Materials Science, 39, 3015-3024, 2004
- [7] Wang, J., Mu, M. & Liu, Y., *Recycled Cement*, Construction and Building Materials, 190, 1124-1132, 2018
- [8] Shui, Z., Xuan, D., Chen, W., Yu, R. & Zhang, R., *Cementitious Characteristics of Hydrated Cement Paste Subjected to Various Dehydration Temperatures*, Construction and Building Materials, 23, 531-537, 2009
- [9] Chromá, M., Rovnaník, P., Vorechovská, D., Bayer, P. & Rovnaníková, P., *Concrete Rehydration after Heating Temperatures of up to 1200 °C*, XII International Conference on Durability of Building Materials and Components, 2011
- [10] Serpell, R. & Lopez, M., *Reactivated Cementitious Materials from Hydrated Cement Pastes Wastes*, Cement & Concrete Composites, 39, 104-114, 2013
- [11] Xuan, D. X. & Shui, Z. H., *Rehydration Activity of Hydrated Cement Paste Exposed to High Temperature*, Fire and Materials, 35, 481-490, 2011
- [12] Linnu, L., Yongjia, H. & Shuguang, H., *Binding Materials of Dehydration Phases of Waste Hardened Cement Paste and Pozzolan Admixture*, Journal of Wuhan University of Technology-Mater, 24, 140-144, 2009
- [13] Naik, T.R., Singh, S. S. & Hossain, M. M., *Properties of High-Performance Concrete Systems Incorporating Large Amounts of High-Lime Fly Ash*, Construction and Building Materials, 9, 195-204, 1995
- NP EN 450-1 (2012): *Fly ash for concrete – Part 1: Definition, specifications and conformity criteria*
- EN 1015-6 (2006): *Determination of bulk density of fresh mortar*
- EN 1015-3 (2006): *Determination of consistence of fresh mortars (by flow table)*
- EN 196-3 (2005): *Methods of testing cement. Determination of setting times and soundness*
- EN 1015-11 (2006): *Determination of flexural and compressive strength of hardened mortar*