Baeza-Brotons, F.; Garces, P.; Paya, J.; Saval, JM.; Paya Bernabeu, JJ. (2014). Portland cement systems with addition of sewage sludge ash. Application in concretes for the manufacture of blocks. Journal of Cleaner Production. 82:112-124. doi:10.1016/j.jclepro.2014.06.072.

PORTLAND CEMENT SYSTEMS WITH ADDITION OF SEWAGE SLUDGE ASH. APPLICATION IN CONCRETES FOR THE MANUFACTURE OF BLOCKS

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Abstract:

This study analyzes the viability of using sewage sludge ash (SSA) as a raw material in the composition of concrete, with a similar dosage to when it is used to manufacture blocks, therefore, with dry consistency given the type of the industrial process of these precast. These ashes are a serious problem, so their valorization in a sector like construction, with a high demand of resources, would be a great advantage from an economic and environmental perspective. A scale with the percentages of addition of ash in relation to cement (5, 10, 15 and 20 %) was designed and the replacement of sand by this material, as well as the addition of an inert material such as marble dust. For a better understanding about how these mixtures behave in other cementitious systems, thermogravimetric analysis were performed on pastes with curing ages of 7, 28 and 90 d, and physical and mechanical tests on mortars cured for 28 and 90 d. It was proved that the addition of SSA in concrete used for manufacturing blocks cured for 28 d provided densities and resistances similar to the control sample (without SSA) and significantly reduces the water absorption. The replacement of sand by the mineral addition significantly improves the parameters mentioned above.

Key words: waste valorization, precast concrete block, block performance, paste, thermogravimetry, mortar.

INTRODUCTION

The construction industry is a great consumer of resources and materials, which makes it a sector with an enormous potential for the use of waste materials generated by its own activities and those from other sectors. The use of such waste materials allows decrease the energy consumption, to preserve non-renewable natural resources, and to reduce the high amount of material that goes to landfills (CEDEX, 2014). However, in the cement industry, which has always been among the largest CO2 emission sources, technical, economic and legal challenges still play as remarkable obstacles against the widespread implementation of procedures to help mitigate this situation (Benhelal et al., 2013).

Although industrial wastes can be incorporated in cementitious materials by various traditional methods, the substitution ratio of industrial wastes in cementitious materials is relatively low to avoid unacceptable performance loss. Novel methods, such as improving hydraulic activities of metallurgical slags by adding composition adjusting material at high temperature, improving surface cementitious properties of fly ashes by dehydration and rehydration treatment, and arranging cement clinker and industrial wastes in the particle size and distribution of blended cements according to their hydraulic activities, are reviewed. These methods provide more effective approach to prepare high performance blended cements with larger amount of industrial wastes, leading to a very significant role in CO2 emissions reducing, resources and energy conservation of the cement industry (Tidåker et al., 2006).

Mineral additions are defined as inorganic materials, pozzolanic materials or latent hydraulic materials that finely divided can be added to concrete and/or to Portland cement based mortars, in order to improve some of their properties or confer special characteristics (Hewlett, 1998). This paper focuses on the study of the viability of using sewage sludge ash (SSA), a mineral addition, as an additive to Portland cement in the dosage of concretes for the manufacture of concrete blocks. It was also used to lesser extent another mineral addition such as marble dust (MD), generated from the cut of large pieces of marble rocks by numerous companies within the province of Alicante, Spain.

The amount of sewage sludge produced in Spain was approximately 1.06 Mt of dry material (European Commission, 2010). According to the source consulted, there is wide variation in the destination of the percentage distribution of this residue, but the figures allow an approach to the current situation: 65 % as fertilizer, 20 % in controlled landfill and 10 % is incinerated to reduce its volume, but the trend is to increase this amount to 20-25 %, which is the average percentage of sewage sludge incinerated in Europe (European Commission, 2010); or 80 % as fertilizer, 8 % in controlled landfill and 4 % is incinerated (Ministerio de Agricultura, Alimentación y Medio Ambiente, 2013). Approximately, 1.7 Mt of such incinerated waste are being produced worldwide (Donatello and Cheeseman, 2013). The problem with these residues after incineration, which justifies an intensive search for alternatives to its landfill, is the presence of heavy metals in its composition, which turns it into a potential pollutant. In the last two decades, different recycling and recovery options have been developed (Donatello and Cheeseman, 2013): manufacturing of ceramic tiles and bricks, synthesis of lightweight materials, production cementitious inorganic binders and phosphate recovery. Also, the use of

sewage sludge as an alternative fuel was proposed in the clinkerization process in Portland cement industry (Husillos et al., 2013).

The leaching behavior of systems containing SSA is also an important topic and has been analyzed by several authors: It was shown that the leaching behavior of mortars containing SSA was of the same order of magnitude as the reference mortar without residue (Cyr et al., 2007). Results obtained from the leaching of ashes in their powdery form revealed that among the potential contaminants followed, only Mo and Se were leached at concentrations above the threshold limits considered. The leaching tests conducted on concrete monoliths showed, however, that none of the contaminants monitored, including Mo and Se, were leached above the threshold limits, according to the Building Materials Decree of Netherlands (Maozhe et al., 2013). Another study evaluated alternatives to render inert waste in cement-based materials by combining the reduction of waste content with the immobilization properties of metakaolin. In particular, the use of metakaolin led to a significant decrease of soluble fractions and heavy metals released from the binder matrix, especially in the case of crushed mortars. (Cyr et al., 2012). Also, ash from incineration of sewage sludge has been compacted and fired at different temperatures to produce a range of sintered ceramics, reducing the leaching of metals for all metals analyzed (Cheeseman et al., 2003).

Although MD is not a contaminant residue (98 % calcium carbonate), its uncontrolled dumping represents a problem in local scale, as it can cause environmental damages, primarily for visual impact and water pollution. Currently, the province of Alicante produces and exports 70 % of domestic marble, being Spain the 2nd European producer and the 7th worldwide, which generates near 500,000 t of sludge in the region where the industry is concentrated, as a result of the cutting and polishing of natural stones (Marble Association of Alicante, 2013).

It is known the effect of these wastes as cement substitutes in matrices with conventional binders. For example, previous work has shown that mortars fabricated with 10 % of replacement by SSA meet the mechanical requirements of the European standard in terms of early age compressive strength and nominal compressive strength (Garcés et al. 2008), and mixtures containing 30 % of SSA as cement replacement showed a higher compressive strength at the age of 7d compared to the reference mixture, and a similar strength at 28d (Fontes et al., 2004). On the other hand, the compressive strength of SSA mortar increased with the increase of SSA fineness: 15 % replacement of portland cement by SSA with particle sizes of 80, 40 and 20 μm (Monzó et al., 1996), or 20 % replacement with Blaine fineness of 500–1000 m2/kg (Pan et al., 2003). The improvement is due to the pozzolanic activity of the SSA (Donatello et al., 2010), although SSA presented a limited content of SiO_2 and Al_2O_3, which are the two oxides responsible for the pozzolanic activity in cement-based materials. Moreover, a fraction of these oxides were in a crystallized form, thus limiting the pozzolanic activity of SSA compared to other classical mineral admixtures (Cyr et al., 2007). Furthermore, it must be noted also a reduction in workability due to the irregular shape of the particles, which prevents its behavior as a solid lubricant, and the water absorption on the surface of the ash particles (Monzó et al, 2003), however, the use of FA as a second replacement material in mortars containing water demanding pozzolans is an appropriate procedure for enhancing the workability of the mixtures. The contribution to strength development due to the presence of

FA in association with other pozzolanic such as SSA becomes important, especially for long curing times (28 d - 90 d) (Payá et al., 2002).

Several researches show that the addition of MD in cementitious composites is effective to improve the cohesion of mixtures. It can replace up to 10 % of sand without affecting the compressive strength, with a better mechanical performance compared to the same limestone filler content (Corinaldesi et al., 2010). In concrete with a 15 % replacement of sand, a good workability is obtained; the abrasion resistance is comparable to that of conventional concrete; and provides a lower water permeability. (Binici et al., 2007). In self-compacting concrete, where although the plastic viscosity of the concrete increased with the addition of sludge, and was corrected by adding specific superplasticizers, the concretes obtained are consistent with the stated requirements and their mechanical properties have improved, as a consequence of the increase of packaging, due to the incorporation of fine particles (Valdez et al., 2010). Additionally, waste marble dust was used for preparing Portland cement by intergrinding of Portland cement clinker and 10 % of waste (Aruntaş et al., 2010).

No research was found about the application of the wastes proposed as concrete components for the manufacture of concrete blocks, however, previous studies have proposed to use construction and demolition waste in the manufacture of blocks (Sabai et al., 2013), and the results showed that the blocks produced with 100 % of recycled aggregates were weaker than those made with natural aggregates. Nevertheless, the results also showed that there is a possibility for recycling these wastes because the 85 % of the samples tested achieved compression strengths equals to or greater than the minimums required by the standards.

This study aims to determine the effect of the addition of SSA to Portland cement regarding the properties of concretes for the manufacture of precast blocks, therefore with particular characteristics due to the manufacturing process. To a lesser extent, it will also be considered the addition of an inert residue, as it is the MD. Previously, and in a complementary manner, the behavior of these additions on two completely different cementitious matrices, such as pastes and standardized mortars, will be studied to expand the knowledge about the use of these mineral wastes.

Although the results obtained in this study with cubic concrete specimens would not be directly comparable to the results obtained with precast concrete blocks, as they differ in size, configuration, and in the manufacturing process, as it will be seen in the experimental procedure. However, since the same dosage was used, this work could be a previous step to the pilot manufacturing of precast blocks with those additions, showing a better technical answer in the laboratory. It is known that the European Conformity mark on building materials is an essential requirement to commercialize a product, and does not imply the compliance of some specific and minimal requirements, but the manufacturers must establish and guarantee the features of their products. This means that although some of the additions studied provide unsuitable qualities for a particular use could be suitable for another quality or different use.

EXPERIMENTAL

Materials

Mineral additions used in this work have the following origins: a) Sewage sludge ash (SSA) has been supplied in bulk by the incinerator of the wastewater treatment plant of Pinedo in Valencia, where it was obtained from the discharge of a fluidized bed incinerator with a maximum temperature applied of 800 ºC, b) Marble dust (MD) was obtained from a landfill located in the town of Novelda in the province of Alicante-Spain, which collects the waste produced by many local industries.

Components of pastes and mortars: in both cases was used Portland cement type CEM II/BL-32.5R, supplied by Cementval in bags of 25 kg. According to the instruction for cement reception (RC-08), this type corresponds to a Portland limestone cement, with strength class 32.5 N/mm2 and high early strength, with the following percentage composition by mass: clinker between 65-79 %, limestone between 21-35 %, and other minor components between 0-5 %. For the fabrication of mortars reference sand CEN EN 196-1 (Normensand GMBH Beckum/Germany) was used, it was served in bags of 1350 g, according to the standardized dosage.

Concrete components: the Portland cement used for concrete was CEM II BM (S-LL)-42.5R (Cemex), the same as that used in local plant for manufacturing concrete blocks. In this case it was supplied in bags of 25 kg. It is therefore a mixed cement, strength class 42.5 N/mm2 and high early strength, with the following percentage composition by mass: clinker between 65-79 %, blast furnace slag and limestone between 21-35 % and other minor components between 0-5 %, according to the Spanish instruction for cement reception (RC-08). The crushed limestone aggregates were obtained from the concrete blocks manufacturing plant cited above, and correspond to the fractions sizes designated as F1: 0/4-TC and F2: 2/8-TC, according to the Spanish Instruction on Structural Concrete (EHE-08). Data on physical and chemical characterization of aggregates, provided by the supplier, are as follows: Los Angeles Coefficient = 23 (≤ 40-50); Water absorption: F1 = 1.8 %, F2 = 0.5 % (< 5 %); Chloride content: F1 = 0.001 %, F2 = 0 % (< 0.03-0.05 %); Soluble sulfates content (SO3): F1 = 0.02 %, F2 = 0.04 % (< 0.8 %); Total sulfur compounds (S): F1 = 0.01 %, F2 = 0.01 % (< 1 %); No presence of organic matter was detected. These limitations are according to the European Conformity mark and the Spanish EHE-08.

Dosage

Dosages for three cementitious matrices were designed: pastes, mortars and concretes. All of them with additions of 5, 10, 15 and 20 % of SSA relative to cement in dry basis (referenced in the tables as Sample "1" to "4" or A5, A10, A15 and A20); a mixture with 15 % addition of MD (Sample "5" or A15 (MD)); another with a 10 % of sand replacement by SSA in mortars and concretes (labeled as "6" or Ss10), and a reference sample (identified as "0" or C).

Table 1 shows the dosages used to prepare the samples of pastes and mortars. For the mortar's reference sample the dosage used is specified in UNE-EN 196-1, composed by 3 parts of sand, 1 part of cement and 0.5 of water. In all the samples, the water/binder ratio remained constant, or said in a different way, the water/(cement + mineral addition) ratio was equal to 0.5. No plasticizing additives were used.

Insert Table 1.

Regarding the dosage of concrete, shown in Table 2 in kg per m3, the reference sample proposed has a similar dosage to that used in the manufacturing plant of concrete blocks, with dry consistency (Abram's cone slump equal to zero). This consistency is essential in the process of manufacturing these precast, since the concrete is poured into molds and it is removed from them immediately to be cured (see Figure 1).

Insert Table 2.

Insert Figure 1

The water/binder ratio equal to 0.68 remained constant in all the mixtures. As shown in Table 2, the absolute amounts of water and cement are lower than for a conventional concrete, joint to a high proportion of fine aggregate (F-0/4), which is associated to a higher absorption of water, the result is a fresh concrete with a very dry consistency, as required by the particular application for which the concretes studied would be used.

Experimental program

Prior to the fabrication of the specimens, the following tests were performed in order to characterize the starting materials: a) Particle size and distribution of the two fractions of the aggregate used for the manufacture of concrete and Sand Equivalent test of the fine fraction; b) X-Ray Fluorescence analysis of the mineral additions used (SSA and MD).

In the case of pastes, thermogravimetry tests were carried out in order to study their hydration. For this purpose, 3 paste samples of each mixture were made, one for each curing age (7, 28 and 90 d).

Each mortar sample was represented by six specimens: three for each of the two curing ages (28 and 90 d). The tests performed were flexural strength and compressive strength for the two curing ages; ultrasonic pulse velocity, dry mass density and water absorption in specimens cured for 90 d.

Each concrete sample was represented by six specimens: three for physical tests and three for mechanical tests, with a curing age of 28 d. The test program carried out on these samples was the following: obtaining a dry mass density, water absorption, capillary water absorption, and compressive strength. The choice of these tests was motivated by the fact that they are included in the list of initial tests set by the European standard EN 771-3 for precast concrete blocks.

Procedure

Previous tests

The test for the particle size and distribution performed following the reference standards UNE-EN 933-1 and UNE-EN 933-1/A1, separated through a series of sieves with 9 screens with opening sizes between 63 mm and 63 µm. The Sand Equivalent Test of the fraction 0/2mm was performed according to the reference standard UNE-EN 933-8.

In order to provide information about the chemical composition of the mineral additions the X-ray fluorescence technique was applied. The equipment used to carry out the technique was a sequential X-ray spectrometer (Philips Magix Pro) equipped with rhodium tube and beryllium window.

Pastes – Thermogravimetry

PVC moulds with circular section, diameter of 3 cm and thickness of 1cm were used to fabricate de specimens. The components were dry mixed as a previous step to manual mixing. Each set of samples was held in the mould over a porcelain surface, covered with plastic wrap and stored in a moisture room (20 °C and 90 % RH) until the tests were carried out.

After reaching the age of curing required for each case, half of the sample was separated and conditioned following the next procedure: 1) grinding in agate mortar, 2) acetone washing with suction by a vacuum pump to remove all liquids, 3) sieving in a standardized 100µm mesh, 4) drying in an oven at 50 °C for 20 min. To carry out the test, a Netzsch-TG-209F3 thermobalance with an open ceramic crucible of 85µL was used. The test was conducted in a dry nitrogen atmosphere at 75mL/min, with a heating rate of 10 K/min in the temperature range between 35 and 600 °C.

Insert Figure 2

The analyzed results were obtained from the TG curves and their corresponding derivative curves (DTG or weight loss rate over time). In almost all of them it can be observed, with greater or lesser clarity, several peaks attributed to various hydration products in two different regions, as shown in Figure 2.

First region: between 75-200 °C. One peak (104 ºC) corresponding to the dehydration of the calcium-silicate-hydrates (C-S-H) and ettringite (AFt); and close to 150 ºC, a smaller peak corresponding to the dehydration of calcium-aluminates-hydrates (CAH) and calcium-aluminosilicate-hydrates (CASH). An overlapping of the different thermogravimetric events can be observed in this region.

Second region 400 ºC-500 ºC. The peak (453 ºC) due to dehydroxylation of portlandite (CH) formed during cement hydration can be observed.

The results section regarding the TG test was focused on the analysis of the second region (CH), which helped to determine the pozzolanic activity of the mineral additions. The parameters included in the tables of the section mentioned above are the following:

Weight loss related to portlandite (WCH) obtained from TG curve;

Percentage of portlandite (CH) obtained according to the expression:

Equation 1: % CH=(W_CH (%) * 74)/18

which is produced according to the reaction: Ca(OH)_2 → CaO+ H_2 O

The percentage of fixed portlandite by the mineral addition. This percentage is affected by the proportion of cement and it is calculated using the following equation (Payá et al., 2003):

Equation 1: % FP=([〖(CH)〗_(c)* C] - 〖(CH)〗_i)/[〖(CH)〗_(c)* C] *100

Where, for the same curing age (CH)c is the percentage of portlandite in the control paste; (CH)i is the percentage of portlandite in each paste and C is the proportion per unit of cement in the admixtures.

If we were considering a cement replacement instead of an addition in relation to binder, C would take the value Cs = 1-S in the expression above, being S the proportion per unit of the mineral residue that replaces the cement, so considering the corresponding reduction of CH in the assessment.

In our case, since the only components involved in pastes are, besides water, the cement and the mineral residue, it can be considered the addition of residue in relation to Portland cement as a replacement of the binder in the system formed by cement + residue. In this way, the C value of the equation above could be replaced by the value CA (Equation 3), where A is the proportion per unit of the mineral residue added in relation to cement. Thereby, the additions in relation to cement of 5, 10, 15 and 20 % involve substitutions in this system of 4.76, 9.09, 13.04 and 16.67 %.

Equation 1: C_A=1-(A/(1+A))

Mortars.

The samples were mechanically mixed and then compacted. After the curing time, both flexural and compression strength tests were performed. All the procedure was carried out in accordance to the Spanish Standard UNE-EN 196-1, with the exception that all the samples were kept in a moisture room (20 °C and 90 % RH) after being demoulded and until the tests were performed. A multi-test Suzpecar MEM-101-10A was the equipment used for mechanical tests.

The ultrasonic pulse velocity (UPV) was measured with a Steinkamp BP-5 instrument, using the direct measurement method (on the longitudinal axis of the prismatic specimen).

The two undamaged sides of the samples resulting from the compression strength tests were reserved to be used for the density and absorption tests, according to UNE-EN 1015-10, and so obtaining the following parameters: 1) dry mass by oven drying to constant mass; 2) saturated mass in water to constant mass; 3) mass in hydrostatic weighing. For this procedure, a Mettler-Toledo XS 4035 weighing scale was used.

Concrete

Fabrication of the concrete specimens

Prior to the manufacture of the concrete specimens in the laboratory, it was observed the procedure followed in the local plant taken as a reference for the production of concrete blocks: after the mixture, the concrete reaches the equipment (Figure 1-a1) where after a single blow of compaction-vibration the molds are removed and the blocks are ready (Figure 1-a2) to be cured at room temperature for at least 28 d before commercialization.

Given the difficulty of handling a concrete with the mentioned characteristics, very dry consistency and the purpose of simulating in the laboratory the industrial process used in the plant to manufacture the precast concrete blocks, it was taken as starting point the reference standard UNE EN 12390-2 with the specifications listed below:

Cubic samples with nominal dimension of 150 mm, made from PVC molds according to standard UNE-EN 12390-1 were used (Figure 1-b1). Such molds were sprayed with release agent and covered with thin sheets of plastic material to facilitate the subsequent extraction; otherwise, the dry mixture makes it an impossible task.

To prepare the samples, the humidity of the components was reduced from the dosage water. Cement and additives were dry mixed as a previous step to mechanical mix with water and aggregates. The filling of the molds was made in a single layer and was compacted for 30 seconds at low speed with a pneumatic hammer (Milwaukee Kango-900) over a stand (Figures 1-b2 and 1-b3). After 24 hours in the moisture room, the samples were extracted using compressed air (Figure 1-b4) and were stored in the environment provided until the tests were carried out.

To keep constant the storage conditions during curing (20 ºC and RH ≥ 90 %), the concrete specimens were stored in a moisture room from their fabrication day until the test date. However, other storage conditions were foreseen, so one of the blends was doubled to compare the results with its counterpart cured in the moisture room. Specifically, this sample was referenced as 3'-A15_Air, therefore with an addition of 15 % SSA, and was kept in the laboratory's ambient air. It was intended to simulate the conditions of conservation of the blocks made in plant, which are also air-cured, but with variations in humidity and temperature conditions for being in the outdoor.

Tests on concrete specimens.

To determine the density and the absorption the standard UNE-EN 12390-7 was followed, finding volume by the water displacement method (Saturated and immersed mass).

The capillary water absorption was obtained according to the standard UNE-83982, using the cubic specimens with measurements for 4 h at intervals of 5, 10, 15, 30, 60, 120, 180 and 240 min. The expression used to obtain the capillary absorption was:

Equation 4: $Cap=((Q_f-Q_0)*10)/(A*\sqrt{t})$

Where the coefficient Cap is expressed in kg/m2min0.5; Q_f is the mass of the specimen after 4 hours of testing (expressed in grams); Q_0 is the initial mass of the specimen (expressed in grams) before starting the test and after drying to constant mass in oven and cooled in a desiccator to room temperature; A is the section of the specimen (in cm2), and t is the duration of the test (240 min).

The mass increase (Q) in relation to the initial mass, which is used in the graphic representations of this parameter against time, was obtained from the following expression:

Equation 5: $Q= 100*(Q_t/Q_0 -1)$

where Q is expressed in percentage; Q_t is the mass of the specimen during the t time of the test (expressed in grams); Q_0 is the initial mass of the specimen (expressed in grams) before starting the test and after drying to constant mass in oven and cooled in a desiccator to room temperature.

The compressive strength test was performed with a Suzpecar CMP-150 t press, following the standard UNE-EN 12390-3 and the load was applied in the direction where the specimen was filled during its manufacture.

Procedure of statistical analysis

A multivariate statistical analysis was performed. It includes the results of all the representative specimens of the samples analyzed with the three curing ages (7, 28 and 90 d) and the three cementitious systems (paste, mortar and concrete). Only in this section, for the coding of the variables it is used the following format: fixed portlandite (FP), dry mass density (Dmd), water absorption (Abs), capillary water absorption (Cap), Flexural and Compressive strength (Rf and Rc) and ultrasonic pulse velocity (Upv).

In section 3.5.1 the first two tables collect measures of central tendency, variability and form. As shown in the row labeled count, the results of each specimen were initially considered: 6 in pastes, 21 in mortars (3 per 7 samples tested), and 24 in concretes (3 per 8 samples tested). Of particular interest are the measures that can be used to determine if the sample comes from a normal distribution (bell curve). Shows that variables with values of bias (degree of symmetry) and standardized kurtosis (degree of sharpness or flatness) out of the range of -2 to +2, which indicates that there are significant deviations from normality.

In the table of correlation matrix, where each pair of variables is related, each cell displays two settings: a) the upper part of the cell indicates the Pearson's product-moment correlation between each pair of variables. The range of these correlation coefficients goes from -1 to +1 and measures the strength of the linear relationship between variables, being greater as the coefficients are closer to these values; b) the second is a P-value from the ANOVA analysis

(analysis of variance), which tests the statistical significance of the estimated correlations. P-values below 0.05 indicate correlations significantly different from zero, with a confidence level of 95.0 % (shaded cells in the table). Based on these results, the analysis of the simple regression models included in the corresponding section is completed.

Finally, an analysis of variance (ANOVA) was performed in section 3.5.2 to determine statistically significant differences between the mixtures. If the P-value of the F-factor is less than 0.05, we can say that there is a statistically significant difference between the mean of the parameters studied and the different types of mixtures, with a confidence level of 95 %. To determine which means are significantly different from one another, each pair of samples is compared by Multiple Range test; it is used for the least significant difference method (LSD) Fisher, with a confidence level of 95 %. The most relevant results will be discussed in the corresponding section. All the statistical analysis was obtained by applying SPSS.

RESULTS AND DISCUSSION

Previous tests

Characterization of aggregates

The information about the particle size distribution of the aggregates was shown in Table 3, and these aggregates may be designated according to EHE-08 as Fraction F1: 0/4-T-C and Fraction F2: 2/8-T-C.

Insert Table 3.

Regarding to the Sand Equivalent index (SE), the fine aggregate used had an average SE index of 68.4 %, very close to the permissible limit by the EHE-08 (≥ 70) for structures subjected to general exposure class I, IIa or IIb, and not subjected to any specific kind of exposure.

X-ray fluorescence analysis on mineral additions

Table 4 shows the results obtained by X-ray fluorescence analysis about oxides concentration of the two mineral additions used. It can be observed that the SSA has a considerable content of SiO_2 (17.27 %) and Al_2O_3 (9.64 %), which generates good expectations about using it as an active mineral addition on Portland cement based composites. The content of CaO, SO_3, P_2O_5 and Fe_2O_3 are also noticeable. Regarding to MD, it is essentially made of CaO (64.25 %) as calcium carbonate; therefore, it is expected to behave as an inert mineral residue.

Insert Table 4.

Thermogravimetry

It is possible to assess the amount of portlandite generated in the hydration of Portland cement with the control samples (C-7, C-28 and C-90 at ages 7, 28 and 90 d). It can be seen in Table 5 that the percentage of CH was very high at early ages (9.78 % at 7 d), and it increased moderately for longer curing times. In mixtures that involve pozzolanic mineral additions, which can be considered as mixtures with partial replacement of Portland cement in the system conformed by cement + residue addition (see 2.4.2 section), the quantity of the available portlandite decreases proportionately. Therefore, when the percentages of addition-substitution are higher, the percentages of CH available for the pozzolanic reaction are lower, which coincides with lower contents of Portland cement. Consequently, when the estimated percentage of fixed portlandite (FP) is positive, it means that the pozzolanic reaction was significant, whereas if the percentage of FP is negative or zero, it means that the pozzolanic reaction did not occur.

Insert Table 5.

In the tests performed (see Table 5), when increasing the percentage of addition of SSA (samples "1" to "4"), indeed the available CH decreased due to lower cement content. This also occurs, to a lesser extent, in sample "5" (with 15 % MD), which may be due to a dilution effect in the cement+residue system, since it is an inert material. The percentages of FP on samples 1 to 4 were positive and were higher as the percentage of SSA and the curing time increased, which suggests that the pozzolanic effect progresses. For example, for 90 d of curing ages: 7.18 % (A5), 12.00 % (A10), 29.62 % (A15) and 33.28 % (A20). In some cases, the positive values of FP are observed at early ages, as shown by the numbers taken at 7 d. In the case of mixture ”5”, it is confirmed again the inert nature of the residue for obtaining a value close to zero for this parameter at 90 d of curing age.

Studies on mortars.

Density and water absorption in mortars.

Table 6 shows the average values of density and water absorption for each mortar sample, cured for 90 d. Regarding to density, the results of the ANOVA analysis (section 3.5.2) showed that there is a significant difference between the values, reaching a 95.7 % of the control sample with the smallest relative value of the series, consisting on the samples "1" to "4" (Addition of SSA). A downward trend is observed in the density value when the amount of SSA increases in the series mentioned above, which may be due to the low density of the residue and the great amount of hollows. The density is closely linked to absorption, this last one with trend to increase as the amount of SSA increases.

Samples "3" and "5" had a similar behavior and did not show a significant difference (section 3.5.2), because in both cases the percentage of addition was the same and the specific gravity for SSA and MD are similar (2.6 and 2.7). Sample “6” behaved as expected, considering what

occurred in the previous: it contained the highest amount of SSA of all the samples analyzed and showed the lowest density and the greatest absorption when comparing to the others.

Insert Table 6.

Insert Figure 3.

The quantification of the degree of relationship between both parameters is confirmed in the statistical analysis (section 3.5.1) and Figure 3, where the statistically significant linear regression (-0.99) is represented, and it demonstrates a relatively strong relationship between the variables shown. The statistical R-Squared indicates that the fitted model explains 97.37 % of the variability in the Abs.

Mechanical strength and Ultrasonic Pulse Velocity.

Table 7 shows the mean values of flexural and compressive strengths, and ultrasonic pulse velocity for mortar specimens cured for 28 and 90 d. Regarding to flexural strength, it can be seen in all cases that the values are positively increased with the curing time, but are always below the control sample (between 71 and 85 % of the reference value), highlighting the mixture "5 (with MD) which shows the lowest flexural strength. This means that the pozzolanic reaction in mortars with SSA positively influences the increase of flexural strength, although higher absorption values are associated with a higher porosity and a relative lowering of the flexural strength compared to control sample.

Insert Table 7.

As for compressive strength, Table 7 shows similar results to those of the flexural strength: in all mixtures it increases positively with curing time, but it is always below control sample, with approximate values between 90 and 81 % from the reference value in series "1" to "4" cured for 90 d, with a downward trend when increasing the addition of SSA. However, series "6", with a higher amount of SSA but replacing the sand, provides an interesting result with a relative value of 88.3 % at 90 d of curing. It is also a very positive fact that all the specimens with an age of 28 d, except for series "5" (with MD), approximate or exceed the strength class of the cement used (32.5 MPa). Again, the difference between series "5" and the remaining series show the pozzolanic contribution of SSA to the compressive strength.

There is a significant difference between the values of the ultrasonic pulse velocity (Table 7 and section 3.5.2), except between samples 2 and 3, with a downward trend for mortars containing high amounts of SSA.

Studies on concretes

Density and water absorption

Table 8 shows the mean values of absorption and dry mass density on concrete mixtures cured for 28 d. The results of the ANOVA analysis (section 3.5.2) showed that there is a significant difference between the values, and all of them reach or exceed the control sample density, with an increasing trend as the amount of SSA increases. This behavior was probably due to the effect produced by the fine particles occupying the gaps between coarse aggregates, which compensated its low relative density. Sample “6” (10 % substitution of sand by SSA) is distinguished for containing the highest amount of SSA of all samples.

Mixture “3” (15 % of SSA, air-cured), which intended to simulate the curing of the concrete blocks in the precast plant, showed lower density than its counterpart cured in a moisture room, and was the mixture with the lowest density and the highest absorption of all. It may be because the hydration of cement is not equally effective in these conditions, so the porosity of the system increases, and thus a stronger process of carbonation occurs. As for mixture "5" (15 % MD), unlike mortars, it reached a slightly higher density than the others (except for mixture "6"), so it could be concluded that in this porous cementitious matrix the effect produced by the fine particles when filling gaps acquires more importance than the pozzolanic activity of SSA, although the fine particles are inert as the MD.

Regarding to water absorption, there is a tendency to decrease when the amount of SSA increases. Based on correlation matrix (section 3.5.1) it can be stated that there is a statistically significant relationship between absorption and dry mass density; it is a linear and moderately strong relationship between the two variables (coefficient -0.87).

Insert Table 8.

Capillary water absorption

Table 9 shows the mean values obtained after four hours of testing on concrete specimens with 28 d of curing age. It is noticed a significant decrease in capillary absorption when increasing the addition of SSA. For mixture "4", with a 20 % addition of SSA in relation to cement, the reduction was a 38 % compared to the control sample; and for mixture "6 ", with a 10 % substitution of sand by SSA, therefore with the highest proportion of SSA of all the mixtures studied, the reduction reached a 57 %. The counterpart mixtures to mixture "3" (3'-air-cured and 5-with MD) showed higher capillarity than mixture “4”, reaching almost to duplicate in the case of air-cured, which means that both the presence of inert materials and the incomplete hydration of the system, result in materials with higher capacity for capillary absorption.

Figure 4a shows the lines of average mass gain by capillary water absorption (Q) of concrete samples against time, during the four hours of testing on concrete samples cured for 28 d. It

can be noticed that lines are approximately parallel to each other, which evidences a similar behavior of the mixtures throughout the testing. The water did not reached its upper surface in none of the samples (state 2 in Figure 4b, which is demonstrated by the slopes of the lines still rising at the end of testing, so that the time √(t_n) was not obtained, and according to Fagerlund (AENOR, 2008), water filling occurred by absorption through the capillary pores.

Insert Table 9.

Insert Figure 4

Based on the statistical analysis (correlation matrix-section 3.5.1) and Figure 5 (fitted model), it can be affirmed that there is a statistically significant relationship between capillary absorption and absorption. It is a linear relationship labeled as relatively strong (coefficient 0.96), where the fitted model explains the 92.07 % of variability in capillary absorption.

Insert Figure 5.

Compressive strength.

Table 10 shows the average values of the representative specimens of each mixture cured for 28 d. The mechanical strength values were low, due to the high porosity of concretes for this kind of precast. The control sample reached strength of 7 MPa; exceeded only by the mixture with 5 % addition of SSA. In all other cases of addition (samples "1" to "5"), a lower mechanical strength is noticed, while mixture 3-A15 exceeds the 90 % of the control sample strength. It is evident that the curing process significantly affects the development of strengths: if samples "3" and "3' " are compared, a decrease in strengths can be identified, from 6.5 to 4.3 MPa. Although it may seem that the SSA has no influence on the development of strengths, it is not so. When comparing sample "3" (SSA) and sample "5 " (with MD), there is a clearly identified difference in their behavior: 6.5 MPa for sample 3 and 4.0 MPa for sample 5. In the case of sample 6, with substitution of sand, an improved performance was observed in terms of density, absorption and capillarity. Evidently in this case, due to the increase of fine particles, a matrix that fills the gaps in a better way was obtained, and its mechanical evolution is above the control sample.

Insert Table 10.

Statistical analysis

Correlation matrix

Table 11 shows a statistical summary of all the variables analyzed. In the variables "compressive strength" and "dry mass density" in concretes with 28d of curing age, the observed values of bias and standardized kurtosis, which are out of the range of -2 to +2, indicate that there are significant deviations from normality, as shown in Figure 6 (box and whisker plot). These results are caused by sample 6-Ss10 (10 % substitution of sand by SSA), because its three specimens are situated far from the others. This actually indicates it is a different cementitious matrix, not a wrong result, as saw in the dosage section and throughout the document with distant results to the remaining samples. In any case, since in the three results of Rc for sample 6-Ss10 the P-value for the Grubbs test is less than 0.05, it can be stated to be a significant value with a significance level of 5.0 %, assuming that the others values follow a normal distribution, so it was decided not to include that sample in the correlation matrix.

Insert Table 11.

Insert Figure 6.

As a result of the mentioned above, a new statistical summary is reported in Table 12, in which all the results regarding to sample 6-Ss10 in pastes, mortars and concretes disappear. Now all the variables meet the restrictions of bias and kurtosis, so all the comments can be considered as belonging to the same population.

Insert Table 12.

Table 13 shows the correlation matrix of all the variables analyzed. This matrix highlights the strong relationship between density, absorption and capillarity in mortars and concretes, and between ultrasonic pulse velocity and compressive strength in mortars, in addition to the correlation coefficients between the same variables at different ages.

Insert Table 13.

Analysis of variance

Table 14 shows the results of the analysis of variance (ANOVA) of all the independent variables analyzed by comparing sample pairs. Since the P-value is less than 0.05 in all cases, it can be stated there is a statistically significant difference between the mean of the parameters studied and the different types of mixtures; it is to say that the characteristics of the blends studied are influenced by the addition of SSA and MD.

Insert Table 14.

Economic and environmental benefits

This section aims to compare the standard sample (C) with those containing addition, determining quantitatively the potential environmental and economic benefits. Of the three cementitious systems analyzed we focus on concretes, as it is the final application of this study.

The samples selected to compare with the reference concrete are the following: the first is called A15, which contains a 15 % addition of SSA. The reason for this choice is to compare C with a mixture with the most similar technical features as possible. If taken as a reference value the compressive strength, both mixtures provide similar values (7 MPa for C and 6.5 MPa for A15).

The density and absorption values of C are modified by the addition, which could be an advantage in some uses. The second sample chosen is SS10, with a 10 % replacement of sand by SSA. In this case, the characteristics of both samples are totally different, with a clear advantage of SS10 compared to C and the rest of the samples studied. Therefore, it is interesting to see if this technical advantage translates into economic and environmental advantage.

To resolve the issue, a scheme of the reference concrete's life-cycle is shown in Figure 7, which corresponds to a generic concrete, as well as the processes related to the SSA. With the life-cycle is pretended to assess the environmental aspects and potential impacts associated to a product, through: inventory of relevant inputs and outputs of a system; assessment of potential environmental impacts associated with those inputs and outputs; and interpretation of the results in the phase of analysis and impact assessment in accordance with the objectives of the study (AENOR, 2006). It can be observed that the addition of the residue would fundamentally affect the process called "Materials", which includes the design of concrete (dosage), and the collection and processing of the materials. The rest of processes, until the end of concrete's life, would be joint in both cases (with or without addition). For this reason, the differential of environmental and economic benefits obtained in the "Materials" process may be considered as the differential of all life-cycle processes for concretes made with or without addition.

Insert Figure 7.

The concept eco-costs or ecological cost are used to assess the environmental aspects of the product and prevent the ecological impact of its use. These costs are virtual since they are not

yet integrated into the real life costs of the current production chains. Eco-costs encompass three types of impacts: emissions + energy and transport + depletion of materials (Vogtländer, 2001). Table 15 collects the dosages of materials in kg to obtain a ton of concrete and the eco-cost indicator in euros. A database updated in 2014 and submitted by Delft University of Technology (Vogtländer, 2014), with information given in € / kg is used to calculate this indicator. Note that the eco-cost of the SSA addition in concrete has been considered negative for two reasons: first, the SSA is a residue obtained from urban waste water treatment plants, as it do not belong to the concrete manufacturing system no eco-costs are added; secondly, their final destination would be their transportation to the landfill, so if some of this material is rescued and reassessed as an addition in concrete, the economic cost of their disposal as hazardous waste in landfill must be deducted in the new system. Also, the eco-cost of the residues transportation to landfill should be subtracted, but in this case the benefit would be zero or nearly zero because it offset the eco-cost of the transportation to the concrete manufacturing plant.

Table 15 also includes a column labeled "Price", which gives the value of the product on the market, including the cost of the materials placed in concrete plant, marketing, profit, etc., with data provided by local concrete plants consulted. Note that the current value of SSA is 0.00 €, as it is a residue whose final destination is the landfill.

Insert Table 15.

Based on the results obtained, it can be affirmed that it is possible to achieve savings in eco-costs with the addition of 15 % of SSA, compared to the reference concrete, with similar technical performance. These savings are of 1.08 € (7,7 %) per ton of concrete. Regarding to the market value, the saving is less noticeable and is about 0.15 € / t. In the case of concrete SS10, with technical performance superior to other mixtures, the benefits are higher due to the high percentage of addition of SSA: the eco-costs are reduced by almost half compared to the reference due to the high percentage of reuse of residue, and the market value is reduced by about 1 € / t due to the saving of sand, which has a price of cost similar to cement in the area of study. Therefore, the benefits are obvious in terms of the use and reassessment of a product that previously had no value and supposed a cost for disposal. Besides, the use of nonrenewable natural resources and disposal of hazardous materials to landfill are reduced.

4. CONCLUSIONS

From the analysis of the results of this research, the following conclusions can be established:

The addition of SSA in concrete for the manufacture of blocks with very dry consistency provides densities and mechanical strengths similar to the control sample (without SSA), while the water absorption suffers a considerable decrease. It is important to highlight the behavior of the sample with a 10 % replacement of sand by SSA, which shows the best performance in

terms of density, absorption and capillarity. In this case, a matrix that fills the gaps in a better way is obtained, due to the increment of fine particles, and its mechanical evolution is far superior to the control sample and the other samples analyzed in this study. The use of this mixture could also represent significant environmental and economic benefits.

Note that there is a high correlation between density, absorption and capillary absorption in mortars and concretes (when dry mass density decreases, water absorption and capillary absorption increase); and between compressive strength and ultrasonic pulse velocity in mortars.

In conclusion, the results can be attributed to the combination of two features of the SSA. On one side, the fine materials that occupy the gaps between the coarse aggregate particles, with an increase in density. On the other side, it is a pozzolanic material with an identifiable reactivity, even at early ages, which effect is reflected in the different tests performed.

ACKNOWLEDGEMENTS

This research was financed by the University of Alicante through Projects VIGROB-256 and GRE10-28 and by Generalitat Valenciana through project GV/2012/113

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Table 1. Dosages for pastes and mortars, expressed in grams, by mixture type and percentages of additions.

Reference		*Pastes*				*Mortars*				
Sample		*Cement*	*Mineral addition*		*Water*	*Sand*	*Cement*	*Mineral addition*		*Water*
0	C	100	-	-	50.0	1350	450	-	-	225.0
1	A5	100	5	5%	52.5	1350	450	22.5	5%	236.3
2	A10	100	10	10%	55.0	1350	450	45	10%	247.5
3	A15	100	15	15%	57.5	1350	450	67.5	15%	258.8
4	A20	100	20	20%	60.0	1350	450	90.0	20%	270.0
5	A15 (*MD*)	100	15	15%	57.5	1350	450	67.5	15%	258.8
6	Ss10	100	-	-	-	1215	450	135	10%	292.5

Table 2. Dosages for concretes, expressed in kg per m^3 of concrete, and percentages of additions.

Reference		*Aggregates*		*Cement*	*Mineral addition*		*Water*
Sample		*F-0/4*	*F-2/8*				
0	C	1227	571	125.6	--	--	85.6
1	A5	1227	571	125.6	6.3	5%	89.6
2	A10	1227	571	125.6	12.6	10%	93.9

Reference Sample		*Aggregates*		*Cement*	*Mineral addition*		*Water*
		F-0/4	*F-2/8*				
3	A15	1227	571	125.6	18.8	15%	98.2
4	A20	1227	571	125.6	25.1	20%	102.5
5	A15 (*MD*)	1227	571	125.6	18.8	15%	98.2
6	Ss10	1104	571	125.6	122.7	10%	168.8

Table 3. Particle size and distribution of the two fractions of aggregate used in the study (*PR*: Partially retained, *CR*: Cumulative Retained, *F1* and *F2*: fractions 1 and 2).

SIEVE (mm)	*PR* (g)		*CR* (g)		*CR* (%)		*PASSING* (%)	
	F1	*F2*	*F1*	*F2*	*F1*	*F2*	*F1*	*F2*
63	0	0	0	0	0	0	100	100
31.5	0	0	0	0	0	0	100	100
16	0	0	0	0	0	0	100	100
8	0	18.9	0	18.9	0	1.4	100	98.6
4	0	1020.0	0	1038.9	0	78.3	100	21.7
2	84.1	187.8	84.1	1226.7	26.9	92.5	73.1	7.5
1	80.9	31.2	165.0	1257.9	52.7	94.9	47.3	5.1
0.5	47.5	13.2	212.5	1271.1	67.9	95.9	32.1	4.1

0.25	29.2	7.9	241.7	1279.0	77.2	96.5	22.8	3.5
0.125	18.0	5.7	259.7	1284.7	83.0	96.9	17.0	3.1
0.063	10.4	4.8	270.1	1289.5	86.3	97.2	13.7	2.8
Receiver	42.9	36.5	313.0	1326.0	100	100	0	0

Total (without fines)	270.1	1289.5
Total (with fines)	313.0	1326.0
% fines	13.71	2.75

Designation		
d	0	2
D	4	8

Table 4. Oxides concentration (%) in the mineral additions used.

Oxide	*SSA*	*MD*	*Oxide*	*SSA*	*MD*	*Oxide*	*SSA*	*MD*
Na_2O	0.94	0.39	TiO_2	0.92	-	Rb_2O	0.01	-
MgO	3.22	6.90	Cr_2O_3	0.17	-	SrO	0.25	0.04
Al_2O_3	9.64	1.39	MnO	0.07	-	SnO_2	0.03	-
SiO_2	17.27	3.77	Fe_2O_3	8.52	0.35	BaO	0.14	-
P_2O_5	14.25	0.09	NiO	0.03	-	PbO	0.04	-
SO_3	8.95	1.27	CuO	0.18	-	Cl	0.15	0.13
K_2O	1.28	0.30	ZnO	0.32	-			
CaO	30.24	64.25	As_2O_3	0.00	-			

Table 5. TG results for mixtures with curing ages of 7, 28 and 90 days (n.a.: not applicable).

Reference sample	W_{CH} (%)	*CH* (%)	*FP* (%)	*Reference sample*	W_{CH} (%)	*CH* (%)	*FP* (%)
C-70	2.38	9.78	n.a.	A15-73	1.68	6.91	18.82
C-28	2.43	9.99	n.a.	A15-28	1.73	7.11	18.13

	C-90	2.50	10.28	n.a.		A15-90	1.53	6.29	29.62
	A5-7	2.15	8.84	5.15		A20-7	1,54	6,33	22,35
1	A5-28	2.06	8.47	10.99	4	A20-28	1,40	5,76	30,86
	A5-90	2.21	9.09	7.18		A20-90	1,39	5,71	33,28
	A10-7	1.94	7.98	10.34		A15(*MD*)-7	2.18	8.96	-5.34
2	A10-28	1.91	7.85	13.54	5	A15(*MD*)-28	2.31	9.50	-9.32
	A10-90	2.00	8.22	12.00		A15(*MD*)-90	2.20	9.04	-1.20

Table 6. Dry mass density (*Dmd*) and water absoprtion (*Abs*) on mortar specimens cured for 90 days (σ: Standard deviation, *cv*: coefficient of variation, *rel*: relative value compared to control sample).

	Reference sample	*Dmd* (kg/m³)	*σ* (kg/m³)	*cv* (%)	*rel* (%)	*Abs* (%)	*σ* (%)	*cv* (%)	*rel* (%)
0	C	2094	10	0.5	100	8.3	0.13	1.6	100
1	A5	2067	9	0.4	98.7	9.1	0.15	1.7	110.1
2	A10	2034	5	0.2	97.1	9.7	0.01	0.1	117.7
3	A15	2027	7	0.3	96.8	10.2	0.11	1.1	123.7
4	A20	2003	2	0.1	95.7	10.8	0.10	0.9	130.1
5	A15(*MD*)	2020	10	0.5	96.5	10.3	0.10	1.0	124.2
6	Ss10	1923	5	0.3	91.8	13.2	0.20	1.5	160.0

Table 7. Mechanical strengths (*Rf* and *Rc*) and ultrasonic pulse velocity (UPV) in mortar specimens cured for 28 and 90 days (σ: standard deviation, *cv:* coefficient of variation, *rel:* relative value compared to the standard sample of the same age).

	Reference Sample	*Rf* (MPa)	σ (MPa)	*cv* (%)	*rel* (%)	*Rc* (MPa)	σ (MPa)	*cv* (%)	*rel* (%)	*Upv* (km/s)	σ (km/s)	*cv* (%)	*rel* (%)
0	C-28	7.3	0.1	2.0	100	38.0	1.2	3.2	100	-	-	-	-
	C-90	8.3	0.7	7.9	100	41.1	1.4	3.5	100	4.25	0.03	0.7	100
1	A5-28	5.9	0.4	7.3	80.0	32.4	2.4	7.4	85.3	-	-	-	-
	A5-90	6.6	0.5	7.6	79.7	36.9	2.4	6.4	89.6	4.02	0.03	0.8	94.6
2	A10-28	6.0	0.4	6.8	81.2	34.1	1.7	5.1	89.7	-	-	-	-
	A10-90	7.1	0.1	1.7	85.3	35.8	1.5	4.1	87.1	3.97	0.02	0.4	93.5
3	A15-28	5.9	0.0	0.8	80.5	34.0	1.2	3.4	89.5	-	-	-	-
	A15-90	6.7	0.7	10.7	81.0	34.9	1.7	4.9	84.8	3.97	0.01	0.3	93.5
4	A20-28	5.4	0.6	11.1	73.6	32.1	0.9	2.7	84.5	-	-	-	-
	A20-90	6.3	0.3	5.6	76.0	33.3	1.3	3.9	80.9	3.93	0.01	0.1	92.5
5	A15(*MD*)-28	5.2	0.1	2.7	71.3	28.6	0.6	2.3	75.2	-	-	-	-
	A15(*MD*)-90	5.9	0.3	5.0	71.3	29.2	1.1	3.9	70.9	3.84	0.02	0.6	90.3
6	Ss10-28	5.6	0.2	3.7	76.9	32.4	2.3	7.0	85.2	-	-	-	-
	Ss10-90	7.0	0.5	7.0	84.6	36.3	0.6	1.8	88.3	3.76	0.02	0.5	88.4

Table 8. Dry mass density (*Dmd*) and water absorption (*Abs*) on concrete specimens cured for 28 days (σ: standard deviation, *cv*: coefficient of variation, *rel*: relative value compared to control sample).

	Reference sample	*Dmd* (kg/m^3)	σ (kg/m^3)	*cv* (%)	*rel* (%)	*Abs* (%)	σ (%)	*cv* (%)	*rel* (%)
0	C	2058	1	0.0	100	8.7	0.05	0.6	100
1	A5	2059	13	0.6	100	8.9	0.31	3.5	102.5
2	A10	2087	11	0.5	101.4	7.9	0.38	4.8	91.3
3	A15	2096	4	0.2	101.8	7.3	0.20	2.8	83.8
3'	A15_Air	2055	13	0.7	99.8	9.6	0.09	1.0	110.4
4	A20	2101	6	0.3	102.1	7.3	0.03	0.4	84.1
5	A15(*MD*)	2103	7	0.3	102.2	8.1	0.08	1.0	93.7
6	Ss10	2204	15	0.7	107.1	6.0	0.08	1.3	69.8

Table 9. Capillary water absorption (*Cap*) after four hours of testing on concrete specimens cured for 28 days (σ: standard deviation, *cv:* coefficient of variation, *rel:* relative value compared to control sample).

	Reference sample	*Cap* (kg/m²min$^{0.5}$)	*σ* (kg/m²min$^{0.5}$)	*cv* (%)	*rel* (%)
0	C	0.61	0.02	3.1	100
1	A5	0.65	0.01	1.9	105.5
2	A10	0.48	0.01	2.1	78.2
3	A15	0.41	0.02	5.5	67.0
3'	A15_Air	0.75	0.07	8.7	123.0
4	A20	0.38	0.01	2.3	61.7
5	A15 (*MD*)	0.55	0.03	5.4	90.1
6	Ss10	0.26	0.03	10.9	42.9

Table 10. Average compressive strength (*Rc*) of concrete specimens cured for 28 days (σ: standard deviation, *cv:* coefficient of variation, *rel:* relative value compared to control sample).

	Reference sample	*Rc* (MPa)	*σ* (MPa)	*cv* (%)	*rel* (%)
0	C	7.0	0.2	2.7	100
1	A5	7.1	1.0	14.7	101.8

	Reference	*Rc*	*σ*	*cv*	*rel*
	sample	(MPa)	(MPa)	(%)	(%)
2	A10	6.8	0.4	6.6	98.1
3	A15	6.5	0.2	3.6	93.9
3’	A15_Air	4.3	0.8	18.5	62.5
4	A20	5.5	0.2	2.8	79.2
5	A15(*MD*)	4.0	0.8	19.4	58.1
6	Ss10	14.4	2.4	16.7	207.8

Table 11. Statistical summary of all the variables analyzed, including all the representative specimens of each sample with 28 and 90 days of curing (P: paste, M: mortar, C: concrete).

Statistical	*P_CF* *7*	*P_CF* *28*	*P_CF* *90*	*C_Dmd* *28*	*C_Abs* *28*	*C_Cap* *28*	*C_Rc* *28*
Count	6	6	6	24	24	24	24
Percentage	8.6	10.7	13.5	2095.2	8.0	0.5	7.0
Standard deviation	10.7	14.0	14.8	46.6	1.1	0.2	3.2
Coefficient of Variation (%)	125.6	131.2	109.6	2.2	13.4	30.2	46.5
Minimum	-5.3	-9.3	-1.2	2044.4	6.0	0.2	3.4
Maximum	22.4	30.9	33.3	2217.5	9.6	0.8	16.6
Range	27.7	40.2	34.5	173.1	3.6	0.6	13.2
Standardized bias	0.1	-0.1	0.6	3.2	-0.6	-0.1	3.9
Standardized Kurtosis	-0.8	0.0	-0.9	2.1	-0.6	-0.8	3.8

Statistical	*M_Dmd* *90*	*M_Abs* *90*	*M_Rf* *28*	*M_Rf* *90*	*M_Rc* *28*	*M_Rc* *90*	*M_Upv* *90*
Count	21	21	21	21	21	21	21
Percentage	2024.1	10.2	5.9	6.8	33.1	35.3	4.0
Standard deviation	51.7	1.5	0.7	0.7	2.9	3.5	0.1
Coefficient of Variation (%)	2.6	14.5	11.9	10.5	8.7	10.0	3.7
Minimum	1918	8.2	4.9	5.6	28.0	28.8	3.7
Maximum	2104	13.5	7.5	8.3	39.4	41.7	4.3
Range	186.3	5.3	2.6	2.7	11.4	12.9	0.5
Standardized bias	-1.4	1.7	1.9	0.6	0.4	-0.3	1.3
Standardized Kurtosis	0.3	0.6	0.5	-0.5	0.1	0.1	0.3

Table 12. Statistical summary for all the variables analyzed, including all the representative specimens of each sample, except 6-Ss10, with 28 and 90 days of curing age (*P*: paste, *M*: mortar, *C*: concrete).

Statistical	*P_CF*	*P_CF*	*P_CF*	*C_Dmd*	*C_Abs*	*C_Cap*	*C_Rc*
	7	*28*	*90*	*28*	*28*	*28*	*28*
Count	6	6	6	21	21	21	21
Percentage	8.6	10.7	13.5	2079.7	8.2	0.5	5.9
Standard deviation	10.7	14.0	14.8	21.6	0.8	0.1	1.3
Coefficient of Variation (%)	125.6	131.2	109.6	1.0	10.0	23.6	22.4
Minimum	-5.3	-9.3	-1.2	2044.4	7.1	0.4	3.4
Maximum	22.4	30.9	33.3	2107.5	9.6	0.8	8.3
Range	27.7	40.2	34.5	63.1	2.6	0.4	4.9
Standardized bias	0.1	-0.1	0.6	-0.5	0.4	0.4	-0.9
Standardized Kurtosis	-0.8	0.0	-0.9	-1.4	-1.0	-0.9	-0.4
Statistical	*M_Dmd*	*M_Abs*	*M_Rf*	*M_Rf*	*M_Rc*	*M_Rc*	*M_Upv*
	90	*90*	*28*	*90*	*28*	*90*	*90*
Count	18	18	18	18	18	18	18
Percentage	2040.9	9.7	6.0	6.8	33.2	35.2	4.0
Standard deviation	32.1	0.9	0.7	0.7	3.1	3.8	0.1
Coefficient of Variation (%)	1.6%	8.8%	12.5%	11.0%	9.2%	10.8%	3.3%
Minimum	2001	8.2	4.9	5.6	28.0	28.8	3.8
Maximum	2104	10.9	7.5	8.3	39.4	41.7	4.3
Range	103.9	2.7	2.6	2.7	11.4	12.9	0.5
Standardized bias	1.1	-1.1	1.4	0.8	0.2	-0.1	1.9
Standardized Kurtosis	-0.6	-0.6	0.1	-0.5	-0.2	-0.3	0.6

Table 13. Correlation matrix of all the variables analyzed, including all the representative specimens of each sample with 28 and 90 days of curing age, except those belonging to the sample 6-Ss (P: paste, M: mortar, C: concrete).

	P_CF 28	P_CF 90	M_Dmd 90	M_Abs 90	M_Rf 28	M_Rf 90	M_Rc 28	M_Rc 90	M_Upv 90	C_Dmd 28	C_Abs 28	C_Cap 28	C_Rc 28
P_CF 7	0.9661 0.0017	0.9792 0.0006	-0.5244 0.2855	0.5327 0.2766	-0.3648 0.477	-0.0683 0.8977	0.2793 0.5919	0.0794 0.8812	-0.2336 0.6559	0.4362 0.3872	-0.6751 0.1412	-0.8917 0.0169	0.1925 0.7148
P_CF 28		0.9173 0.0100	-0.4613 0.3571	0.4583 0.3607	-0.4074 0.4227	-0.0734 0.8901	0.2088 0.6914	0.1173 0.8248	-0.1975 0.7077	0.2973 0.5671	-0.5401 0.2687	-0.8047 0.0535	0.3083 0.5522
P_CF 90			-0.614 0.1947	0.6448 0.1669	-0.4337 0.3903	-0.1727 0.7435	0.195 0.7112	-0.048 0.9281	-0.3309 0.5217	0.5169 0.2937	-0.708 0.1154	-0.9218 0.0089	0.0451 0.9324
M_Dmd 90				-0.9868 0.0000	0.7774 0.0001	0.6795 0.0019	0.6304 0.005	0.8036 0.0001	0.8603 0.0000	-0.8973 0.0000	0.7926 0.0001	0.7917 0.0001	0.5807 0.0115
M_Abs 90					-0.8017 0.0001	-0.708 0.0010	-0.6463 0.0038	-0.8124 0.0000	-0.8647 0.0000	0.8882 0.0000	-0.8017 0.0001	-0.7966 0.0001	-0.5736 0.0128
M_Rf 28						0.8133 0.0000	0.8048 0.0001	0.8076 0.0001	0.9224 0.0000	-0.6259 0.0055	0.4022 0.0980	0.4083 0.0925	0.5306 0.0235
M_Rf 90							0.8221 0.0000	0.7998 0.0001	0.8442 0.0000	-0.5762 0.0123	0.3171 0.1998	0.2949 0.2349	0.5325 0.0229
M_Rc 28								0.8888 0.0000	0.8643 0.0000	-0.5334 0.0226	0.1677 0.5058	0.1241 0.6238	0.5987 0.0087
M_Rc									0.9265	-0.7989	0.4605	0.3934	0.7745

90									0.0000	0.0001	0.0545	0.1063	0.0002
M_Upv 90										-0.7578 0.0003	0.4717 0.0481	0.4607 0.0543	0.6154 0.0066
H_Dmd 28											-0.8669 0.0000	-0.8055 0.0000	-0.252 0.2704
H_Abs 28												0.9595 0.0000	-0.1284 0.579
H_Cap 28													-0.2372 0.3005

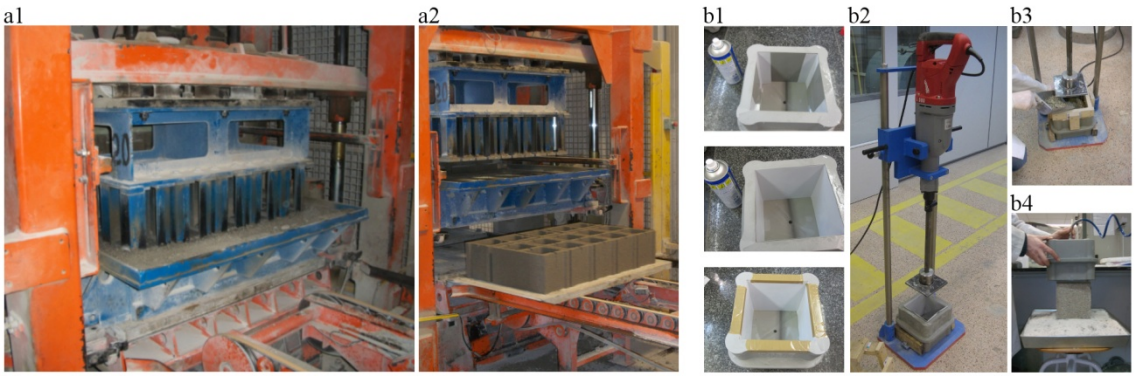
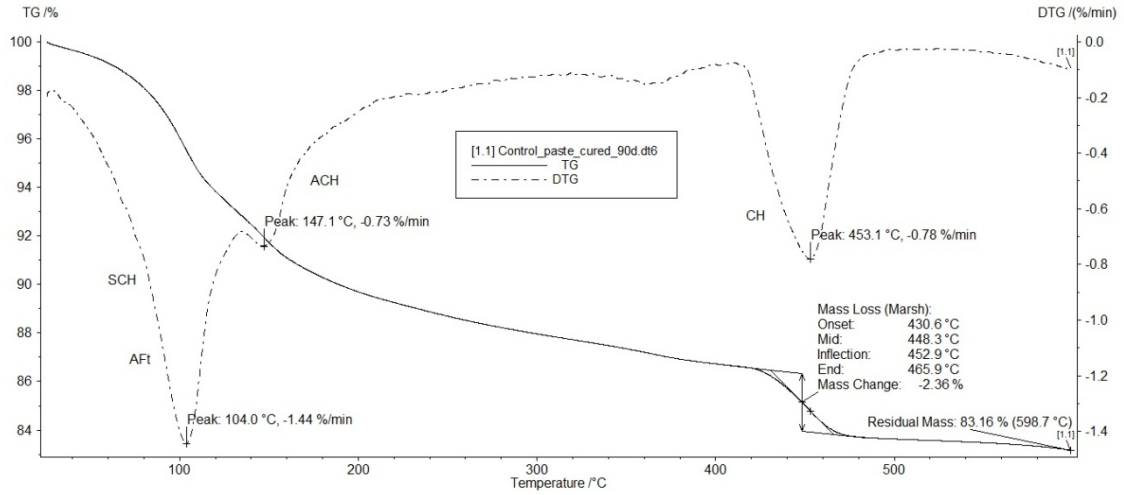

a1
a2
b1
b2
b3
b4

Fig. 1


TG /%
DTG /(%/min)
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TG
DTG
ACH
CH
SCH
AFt
Peak: 147.1 °C, -0.73 %/min
Peak: 453.1 °C, -0.78 %/min
Peak: 104.0 °C, -1.44 %/min
Mass Loss (Marsh):
Onset: 430.6 °C
Mid: 448.3 °C
Inflection: 452.9 °C
End: 465.9 °C
Mass Change: -2.36 %
Residual Mass: 83.16 % (598.7 °C)
Temperature /°C

Fig 2

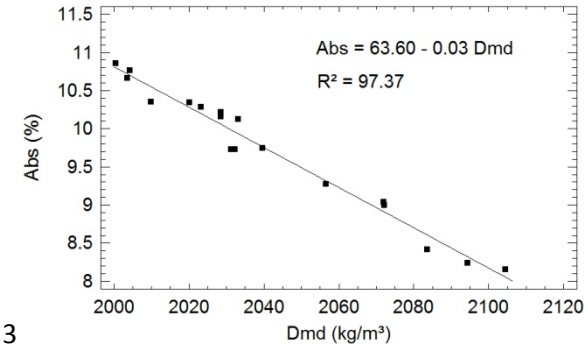

Fig 3

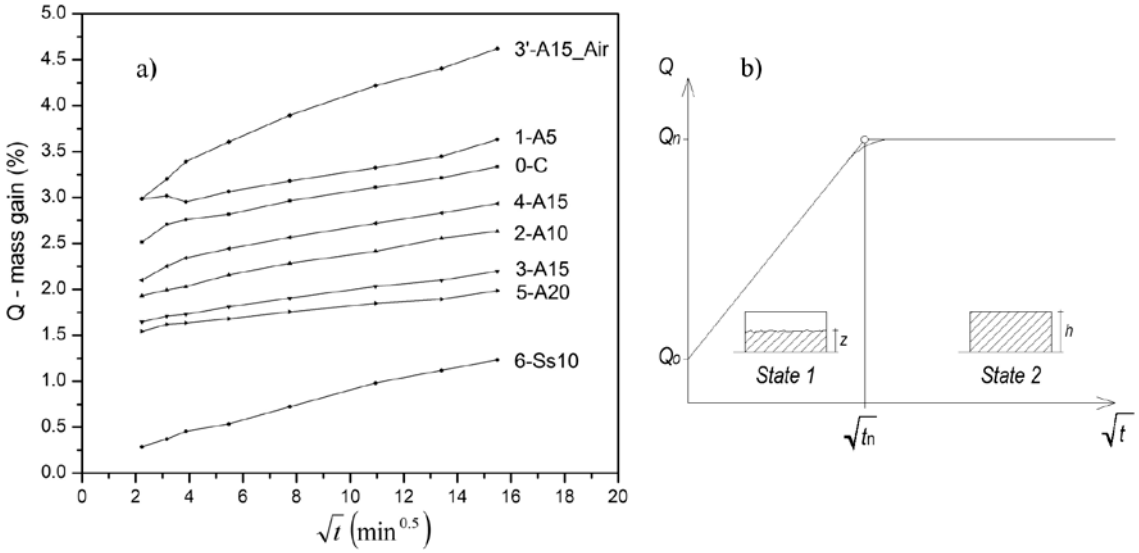

Fig 4.

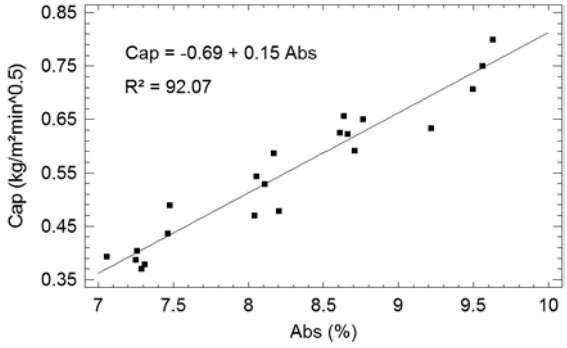

Fig 5

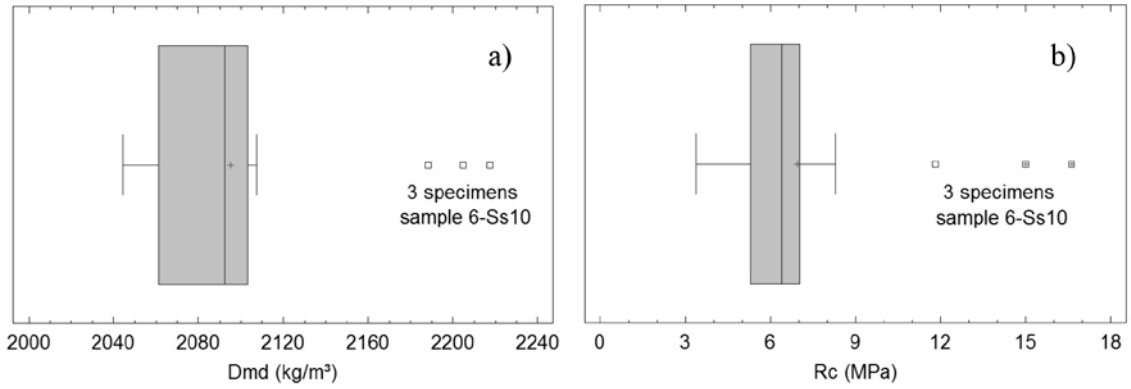
a)
3 specimens
sample 6-Ss10
2000
2040
2080
2120
2160
2200
2240
Dmd (kg/m³)
b)
3 specimens
sample 6-Ss10
0
3
6
9
12
15
18
Rc (MPa)

Fig 6