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# Potential use of sugar cane bagasse ash as sand replacement for durable concrete

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## Abstract

The increasing urban development, led by concrete, requires a higher availability of materials and energy, and it will be responsible of a high waste generation. To face the exploitation of natural resources, the use of fossil fuels and the reduction of waste disposal new environmental-friendly strategies emerge accomplishing the circular economy principles. In this research, the use of poor reactive agro-industrial ashes as sand replacement in cement-based materials is investigated. Poor reactive sugar cane bagasse ashes (fly and bottom ash -SCB FA and SCB BA, respectively) from a power plant in Dominican Republic have been used in substitution rates of 10%, 20% and 30% of weight of sand. Physico-chemical characteristics of ashes are investigated and correlated to the performance of the bio-concretes. SCB FA showed being an enhancer of durability-related properties of the concrete even with high content of silica in form of quartz, due to the capability of modifying the microstructure of the concrete and an additional binding capacity of chlorides ions. Durability-related tests (open porosity test, electrical resistivity test, capillary absorption test and chloride migration test) have been conducted at 28, 60, 90 and 240days. Direct correlations exist when compared chloride migration resistance against porosity and electrical resistivity in concretes with SCB FA, not so for capillary absorption. This demonstrates the inadequacy of establishing conclusions about durability performance of bio-concretes based on durability tests when run independently. The use of agro-industrial ashes as substitutes of natural aggregates not only reduces the consumption of natural sand but can deliver bio-concretes with potential benefits in terms of compressive strength and durability.

**Keywords:** Building waste materials, sand substitution, bio-ashes, industrial ashes, sugar cane bagasse, circular economy, agricultural waste, bio-concrete, eco-efficiency, sustainability.

## 1. Introduction

World population is predicted to overpass 9 billion people by 2050, the demand in energy will increase by 50-60%, in food by 60% and around 70% of world population will live in cities [1, 2]. This will result in a high generation of waste and high economic, social and environmental impact. The built environment, which is the main consumer of metallic and non-metallic materials and generate 40% of total carbon emissions in the world, must drive a green role in the years ahead. By 2060, world's global extracted materials use will double the actual demand overpassing the 167Gt, Figure 1. Non-metallic minerals, which constitute the main share, is expected to increase 79% and biomass 68% by 2060. Half of share (44Gt) of non-metallic minerals -mainly gravel, sand, clay, limestone and gypsum- were used for construction purposes in 2017. As a direct consequence of the urban population and living standards growth, the consumption of non-metallic minerals for construction will double by 2060 reaching 86Gt[3]. Construction aggregates

(sand, gravel and crushed stone) entail the 70% of share of non-metallic ores and 28.8 Gt are employed in concrete production. By 2060, the global demand of construction aggregates will be driven by BRIICS countries -Brazil, Russia, India, Indonesia, China and South Africa- (39Gt), [3].

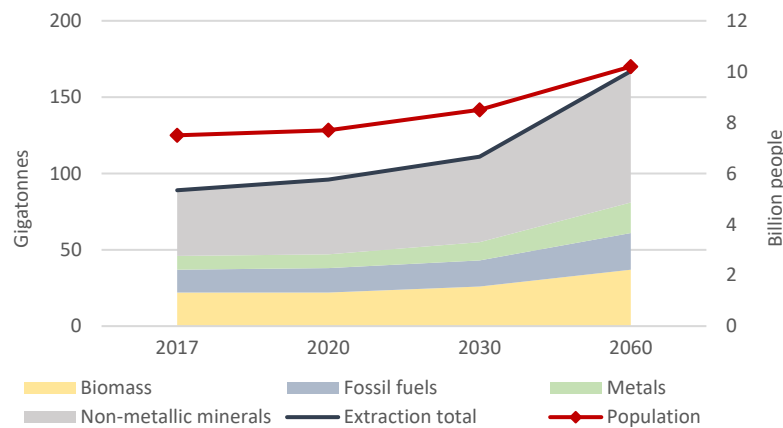


Figure 1 Projections of global materials extraction and population. Data source:[3]

Sand and gravel extraction are responsible of severe habitat deterioration in rivers and sea-beds. Further consequences on human lives have been listed such as premature fail of infrastructures, serious disturbances in cultivable land and drinking water, diseases, and human rights abuses due to illegal markets [4-6].

Concrete is expected to promote most of the urban development covering buildings and infrastructures. Since concrete is the second most used material, after water, and it requires a significant use of extracted materials, concrete production is one of the human activities with a higher environmental impact. Production of cement alone entails the 7% of the world's CO<sub>2</sub> emissions [7]. In this context, finding alternate materials and durable solutions is a priority to face the increasing demand of construction aggregates, minimising the exploitation of natural sand and gravel and the linked consequences.

On the other hand, industry is concerned about the necessity of following more sustainable strategies and practices to reduce the environmental impact of waste [8-10]. Focusing on wastes originated by the increasing agricultural industry, one of the developed strategies is the energy production from agriculture biomass, avoiding landfill diversion and covering the higher demand of energy while minimising the use of fossil energies [2, 11]. During the biomass burning process, bio-ashes are generated as the resulting waste of this process retained on the bottom of the boiler and on the filters of the combustion chambers. These are known as bottom ashes and fly ashes, respectively. Vassilev et al. [12] estimated the global biomass-ash generation in 476 million tonnes per year considering the total burned biomass to be 7 billion tonnes and 6,8% mean ash yield on dry basis. According to the authors, this quantity would be comparable to that of coal ash in 2012 (780 million tonnes), giving an idea of the environmental implications. This, combined with the forecasted pressures on the coal ash market and the pozzolanic capacity of some bio-ashes, make biomass ashes a potential materials source in novel low-carbon concrete formulas [13]. Agricultural bio-ashes management is not only an actual disposal and environmental concern, but an increasing problem for the future. When two of the most pollutant human activities converge, construction and agriculture, green strategies emerge to face with this scenario. Agricultural waste become a new source of construction waste materials, meeting the circular economy principles and ensuring better environmental practices. In this research, the use of agro-industrial ashes resulting from the combustion of the bagasse of the most cultivated crop in the world, sugar cane, is investigated. Sugar cane annual production has being increasing on time until reaching 1,907,024,730 tonnes in 2018, Figure 2, [14]. The entire production is

distributed along tropical and subtropical areas in the world, as shown in Figure 3, where the data are compared with the Gross Net Incoming per capita [14, 15]. The 66% of total sugar cane production is held by BRIICS countries led by Brazil (41%) and followed by India (17%) and China (6%). In small countries, such as Dominican Republic, sugar cane is the most cultivated crop in terms of production, and the second one in terms of harvested area (only overpassed by rice which has a yield 14 times lower than that of sugar cane), Figure 4.

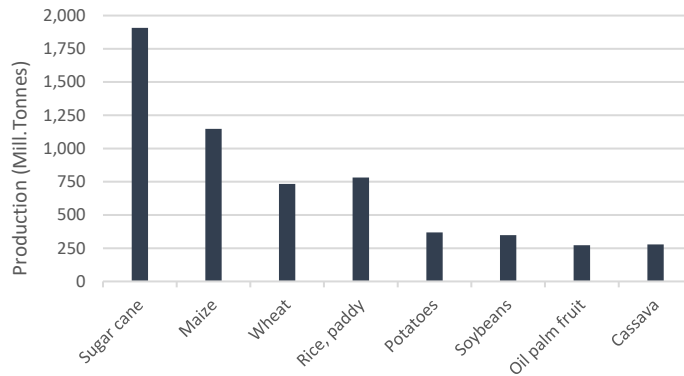


Figure 2 World's most cultivated crops, 2018. Source data: [14]

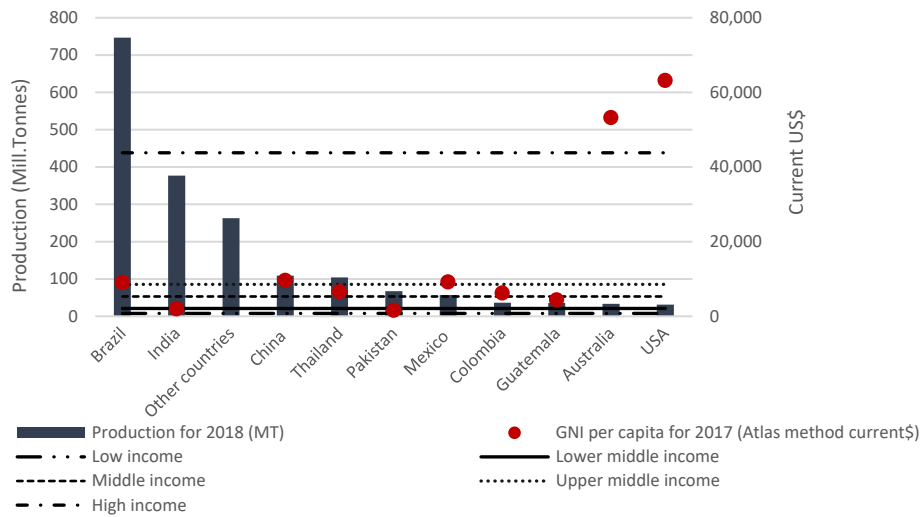


Figure 3 Sugar cane main producer countries in the world in 2018 (Source data: [9], [15]).

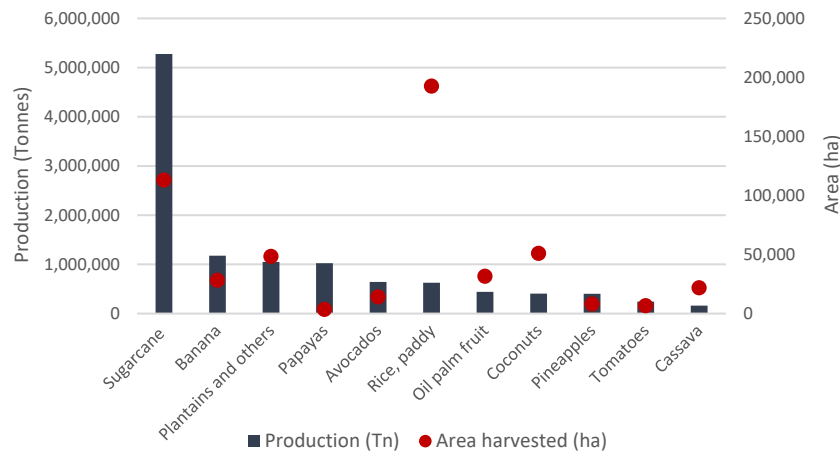


Figure 4 Crops production (tonnes) and harvested area in Dominican Republic, 2018 (Data source: FAOSTAT)

Sugar cane is the main source for obtaining sugar and it is also used in alcohol factory and bioethanol production [16]. Its residues, bagasse, have further uses as bio-product with interesting and potential applications in the industry.

Bagasse is the term for the residues of a plant after the extraction of the juice. These wastes are normally revalorized and used as animal food, fertilizers, cellulosic industry, and energy recovery or conversion to fuel. The sugar cane bagasse accounts up to the 30-34% by mass of collected sugar cane [17]. According to this, almost 600 million of tonnes of sugar cane waste are obtained. The aforementioned results in a high environmental impact if it would be disposed in landfill, due to the methane gas released during the decomposition. Besides, SCB biomass is an interesting biofuel which does not compete with food crop production [16].

Sugar cane bagasse ash (hereafter SCBA) is a secondary by-product obtained from the combustion process of the biomass for energy from waste plants. The bagasse resulting from the principal agricultural process are reused as fuel for heat generation, leaving 8-10% of ashes by mass. Considering the aforementioned data, up to 48-60 million of tonnes of sugar cane bagasse ashes can be obtained per year if all the residues were burnt.

Traditionally, ashes have been treated as waste to be disposed in landfill or accumulated onsite. One of the actual disposing alternatives is the use of ashes as fertilizer for soils due to their contain of mineral fertilizers [18]. Sales and Lima (2010), [19] called into question the nutrient capacity of the SCBA and the real environmental impact due to the capacity of the ashes to retain the agrochemicals in the soil. Zhao et al. (2013) [20] claimed that the use of this type of ashes may be limited by a high presence of harmful poly-aromatic hydrocarbon in ashes with a high content of residual carbon.

In response to the environmental awareness, the efforts are focussed on the possible incorporation of *bio ashes* in the cement-based matrix. In general, during the biomass combustion process two types of residues are generated: bottom ashes (BA) and fly ashes (FA). Bottom ash is made off partial or totally burnt material deposited in the bottom of the boiler and it is commonly mixed with mineral impurities existing in the biomass such as sand, stones and others. Fly ash is composed of particles carried along by the combustion gases out of the combustion chamber that precipitated in filters. The properties of the ashes depend on the material used as a fuel and on the combustion process. Factors such as temperature, time of combustion and intensity will determine the physical and chemical characteristics and some of these can be observed by the appearance of the resulting waste.

The main issue in the use of industrial ashes from energy recovery plants in concrete production is to ensure the quality of the by-product, which can have undesirable physical or chemical characteristics and they are, by definition, heterogeneous materials.

The addition of bio ashes in cement-based materials may enhance the mechanical strength and durability properties due to the pozzolanic activity and/or the filler effect [21-23]. The pozzolanicity depends on the oxide content, the mineralogical structure (pozzolans have amorphous structure) and the fineness. SCBA can have pozzolanic characteristics since they are rich in silica and alumina oxides mainly that react in the presence of calcium hydroxide when they are mixed in water forming additional retarded cementing products. Nevertheless, pozzolans have to be amorphous. Sales and Lima (2010) [19] reported crystalline ashes containing high content of silica (88.2-96.2%). The crystallisation of silica occurs at high temperatures (>800 °C) or prolonged burning times [18]. Some authors have studied the effect of the temperature under controlled calcination process in the ultimate properties of the sugar cane bagasse ash [18, 21, 24]. Cordeiro et al. (2009) [18] observed high pozzolanic activity in the resulting ashes when the SCB biomass is burnt under controlled conditions in the lab. The highest pozzolanicity activity index (PAI) occurred for ashes obtained under two combustion cycles of three hours: the first one

at 350°C and the second one at 600°C after 3 hours. Rajasekar et al. (2018) [21] used ashes obtained under controlled conditions (240 min at 550°C) and treated by grinding (120 min). Deshmukh et al. (2011) [24] concluded that, after a burning process of 12 h at 500°C, high reactive silica can be obtained in RHA (rice husk ash). In industry, there is almost no control in the operational temperature and burning and cooling processes. In addition, temperature varies depending on the humidity content of the biomass overpassing the crystallisation temperature. Thus agro-industrial ashes are prone to have crystallinity structure and unburnt organic matter as a result of uncontrolled burning processes influencing the resulting by-product [19, 25].

Ashes as-received from industrial plants have to be subjected to high energy demanding treatments such as ultra-grinding or re-burning in order to boost the pozzolanic activity of sugar cane bagasse fly ash and minimise the LOI for being used as binders with positive results [16, 18, 21, 26-30]. The optimal substitution rate for ultra-treated ashes in concrete, high performance concrete (HPC), ultra-high performance concrete (UHPC) and recycled aggregate concrete has been declared to be 15-20% (weight of binder) [21, 30, 31], meanwhile for not ultra-treated ashes, the optimum replacement by cement is between 5%-10% in mortars and concretes due to lower pozzolanic reaction or higher carbon content [23, 32, 33]. Arenas-Piedrahita et al. (2016) observed this behaviour at early ages when the substitution rate was above 10%, but highlighted an enhancement after 56 days – nevertheless the optimal rate substitution was 10% (weight of binder). At early ages (28 days) compressive strength enhancements in comparison with the control concrete have been observed when ground SCB FA was used as cement replacement in 10%, 20% and 30% substitution rates due to early pozzolanic reaction of fine particles [34].

The required combustion temperature in industry leads to poor reactive SCBA with high content of quartz (mean compound of natural sand) [19]. On the other hand, the energy needed to ultra-treat the ashes in order to boost the pozzolanicity, when possible, increases the embodied energy of bio-ashes. These limitations open a research field in order to find alternate uses further to that of cement substitute material, already widely investigated. The benefits of using ashes as sand replacement can be: i) addressing the exploitation of natural resources, ii) finding a solution for those ashes that cannot be used as cement-replacement due to physico-chemical requirements, iii) reduction of the disposal cost for bio-energy companies, and iv) provision of enhanced properties to the cement-based solutions when used as an improved material in comparison to sand.

The use of inert or poor reactive SCBA as sand alternate materials has not been widely explored yet. Sales and Lima (2010) [19] assessed the use of agro-industrial SCBA extracted from the boilers or from conveyor belts with high silica content and high crystallinity as sand substitutes in mortars and concretes. A higher compressive strength than the control specimens was observed at 28 days when 20% and 30% of sand was replaced in mortars. The same authors substituted 30% and 50% of sand in concrete mixes with different type of cement. The best performance was in mixes with slag-modified Portland cement (CEM II) with an increase in compressive strength at 28 days of 17.65% and 20.67% when 30% and 50% of sand is replaced by ashes respectively. Modani and Vyawahare (2013) [35] substituted up to 40% of fine aggregates (by volume) by untreated ashes in concretes observing reductions in compressive strength and tensile strength along with the increase of ashes. Macedo et al. (2014) [36] observed the filler effect and concluded that 10% of substitution (weight of sand) showed the highest compressive strength but 3% was the optimal substitution rate when tensile strength is under consideration. Moretti J. P et al. (2016) [37] studied the interaction between SCBA used as sand replacement and waste concrete aggregates in concrete.

Few researchers have addressed the impact of the implementation of ashes as cement replacements in the durability properties of concrete and the transport mechanisms. The results showed that the use of treated SCBA is positive in terms of durability since it reduces the permeability and the chloride penetration and promotes the corrosion resistance [21, 30, 31, 34,

38, 39]. The filler effect of fine particles and the generation of secondary hydrated products have been pointed as the main causes for these due to a modification in the transport stream. Ganessan et al. (2007) [38] reported a twofold and threefold enhancement of the chloride ion penetration resistance in concretes with treated SCBA (up to 20% cement replacement) at 28 and 90 days and a reduction of the corrosion rate. Chusilp et al. (2009) observed a reduction of 50% and 69% of permeability at 28 and 90 days in concretes with 30% of ground SCBA used as cement replacement due to filler effect of pozzolanic reaction. A. Bahurudeen et al. (2015) [34] observed that the use SCBA based blended cement improves the chloride and gas resistance of concretes with increase in ashes replacement and showed higher surface resistivity. Rerkpiboon et al. (2015) [40] that ground SCBA can be used up to 50% to replace OPC and concluded that the chloride resistance improvement is more influential than the compressive strength gain.

Furthermore, to the knowledge of the authors, no research has been published where the durability properties related with the chloride ions penetration are investigated when SCBA are used as sand replacements in concrete.

In this research, the feasibility of using two types of high crystalline agro-industrial SCBA as sand alternate material for concrete is investigated. SCBA were characterised and undesirable particles removed. Mixes with 10%, 20%, 30% of sand substitution rate were casted for each type of ash. In addition, concrete without ashes was produced to comparison. Compacity, fresh and hardened concrete densities, compressive strength, capillary water absorption, open porosity index, surface electrical resistivity and chloride migration resistance tests were conducted. The possible correlations between different durability properties at 28, 60, 90 and 240 days (capillary water absorption, porosity, surface electrical resistivity and chloride diffusion resistance) in bio-concretes were established.

## 2. Materials and Method

### 2.1 Materials

The concrete is made of cement, natural sand, aggregates, two types of bio-ashes and water. Ordinary Portland Cement, (OPC) type CEM I, class of strength 52.5 N, conformed to the Standard BS EN 197-1: 2011 was used [41]. The chemical composition of cement is shown in Table 3. Fine natural dried sand with size under 600  $\mu$ m and 10mm and 20mm aggregates that accords with the British Standard BS EN 12620:2002+A1:2008 [42] have been used. The Particle Size Distributions (PSD) and densities are shown in Figure 11 and Table 3.

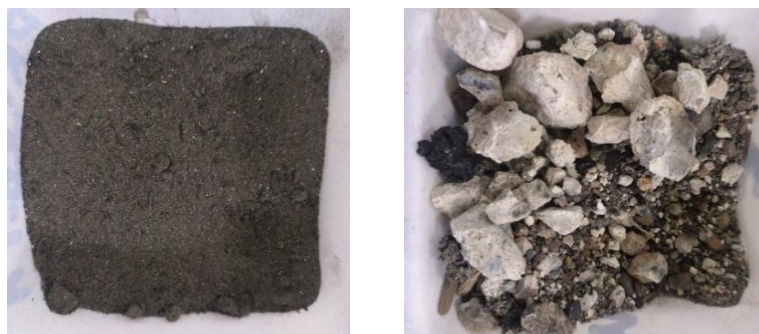


Figure 5 As received ashes: (a) SCB FA, (b) SCB BA

The investigated as-received ashes are shown in Figure 5. The composition and properties of the ashes highly depend on the burning process. This 30 Mw energy plant uses a travelling grate boiler, where, almost the 80% of bagasse is burnt in suspension, meanwhile the rest sets on the bottom mixed with heavier particles from the soil of the yard where the bagasse is accumulated.



Thus, in this case, SCB BA main compound is  $\text{CaCO}_3$  from the stones swept away from the soil, and silica is the second compound. SCB FA composition is characterised by the presence of silica whose origin mainly comes from the silica absorbed by plants from soil during their life. Additionally, some silica grains were observed which origin could be in the harvested field. According to the ash producer, SPBE, the combustion temperature of the gases is not constant, and the average is in the range 750-800°C.

#### *Treatment of ashes*

Ashes were physical-chemically analysed *as-received* and after being *treated*. Based on the particle size distribution and on the chloride and contaminants content, the ashes were subjected to minimal treatments according to their requirements, described below.

SCB FA was sieved and the portion retained in 200  $\mu\text{m}$ , mainly charcoal, was discarded since it reduces the workability. The portion of ashes retained in sieve 150 $\mu\text{m}$ , mix of powder and charcoal, was separated to be partially washed as per Figure 6(a). Charcoal has further utilization in industry (e.g. in briquettes fabrication or as adsorbent materials). SCB BA was completely water-washed to remove contaminants by solubility and floatability, Figure 6(a). The porosity and heterogeneity of the grains of SCB BA would have compromised significantly the concrete soundness and the mechanical properties. For this reason, particles greater than 2.00 mm were grinded for 15 minutes obtaining a well-graded sand, Figure 6(b, c). In both cases a cheap and low-energy system to wash the ashes was used to remove contaminants and organic matter. In both cases, the ashes were dried at  $70\pm 5^\circ\text{C}$  in the oven for 24h after washing.

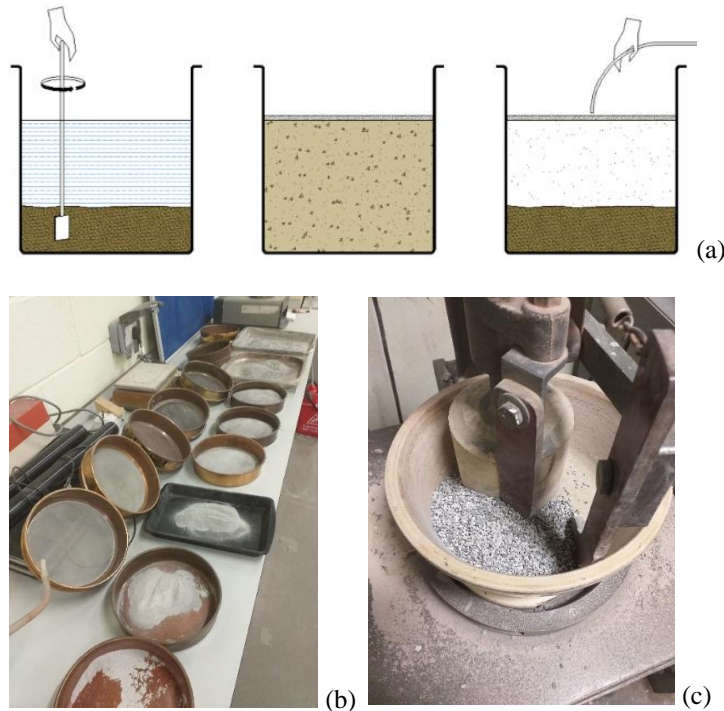


Figure 6 Treatment of SCB BA: (a) contaminants removal by solubility and floatability; (b) sieving; (c) grinding of SCB BA ashes

## 2.2 Methodology

Two different types of ashes from the same energy plant are studied: sugar cane bagasse fly ash (hereafter SCB FA) and sugar cane bagasse bottom ash (hereafter SCB BA). The physico-chemical characterisation of ashes has been conducted and low-energy consumer treatments proposed. The treated ashes were used as fine aggregate to cast different types of bio-concrete and consequently tested according 2.2.2 *Characterisation of concrete. Experimental campaign*. The experimental campaign is divided in three distinct phases:



- i) the analysis and characterisation of *as-received* (ar) and *treated* (t)
  - ii) the preparation of the bio-concrete and
  - iii) the characterisation of the concrete at different ages.
- Constant quantities of cement and w/b ratio (0.45) were used considering *b* as the sum of cement and ashes. Fresh and hardened concrete properties were tested: workability, compressive strength, porosity, capillary, resistivity and chloride migration resistance.

### 2.2.1 Characterisation of *as-received* (ar) and *treated* (t) ashes

Physical-chemical properties of the ashes were analysed. The morphology was observed by means of scanning electron microscope, SEM, using FEI SEM model Inspect S50. The particle size distribution of samples was obtained by dry sieving test as per [43]. Additionally, *SCB FA* was subjected to the laser diffractometry test using the analyser Beckman Coulter LS 13320. It must be highlighted that this method considers particles as spheres and it can make an approximation to non-spherical particles that could work. However, for many particles, the size distribution obtained is only apparent. This will be the case of the elongated charcoal particles presented in the ashes [44].

Bulk density, real density and specific surface based on the Blaine method were obtained according to the standard BS EN 1097-6:2013 [45]. Some authors pointed out the overestimated results of loss on ignition test due to further chemical reactions at different temperatures [20, 46]. Thermogravimetric analyses (TGA) with a TA-Q50 thermogravimetric analyser have been done to have a deeper comprehension of the ashes in the *as-received* and treated forms. Chemical characteristics are obtained by means of XRD and XRF analyses. Soluble chloride content in ashes were additionally analysed with spectrophotometer DR3900 from HATCH for more accurate results.

### 2.2.2 Characterisation of concrete. Experimental campaign.

Durability of concrete depends on the exposure environment and the inherent characteristics of the material. Focussing on the second ones, concrete's durability relies largely on the microstructure of the material: size, distribution and shape of pores and the porous interconnectivity. In general, a reduction in the interconnectivity results in a reduction of permeability into the concrete so the external ions migration is hampered. These properties can be assessed with different techniques; in this research the following tests were conducted: open porosity, surface electrical resistivity, capillary absorption and chloride migration. The results obtained were correlated pursuing a deeper understanding of the durability properties of concrete due to the addition of ashes. Compositions with 0%, 10%, 20% and 30% of ashes were designed. Three cubes of 150x150x150 mm and 6 cylinders of 100 mm of diameter and 200 mm high were casted per composition. To compare the initial data, mixes with both types of ashes were casted considering the water/binder ratio equals 0.45. Due to the XRD and XRF results, no/low reactive reactions were expected. Hence, two families with three different compositions of bio-concrete plus the control one was casted. Fresh and hardened properties were tested according to Table 5.

### Mix design and concrete preparation

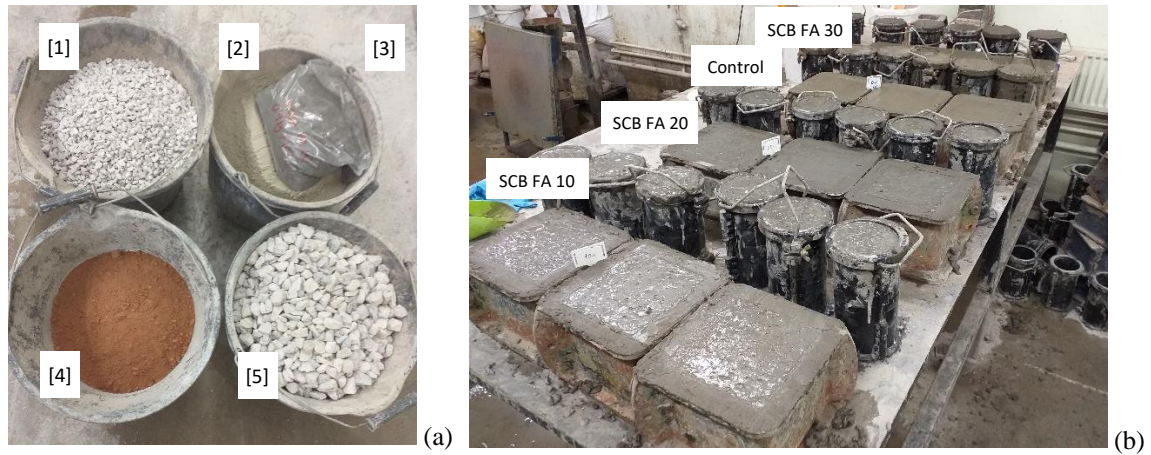
The ashes, *SCB FA* and *SCB BA*, were added as a replacement of sand in percentages of substitution of 10%, 20% and 30% (weight of sand). For all the ashes assessed, the water in the mixes designs was estimated considering the possible binder capacity of the ashes. In these cases, the ratio considered is water-binder ratio (hereafter w/b), where binder is the sum of both, cement and ashes. Based on these considerations, the different mixes were designed as following in the Table 4. After casting, the concrete samples were kept under lab conditions during 24h before

being demoulded and then wet cured in water tanks until the testing date. All samples were oven dried at 60°C until constant mass before capillary absorption, chloride migration and porosity tests.

*Table 1 Concrete mix design.*

	CEM (kg)	Aggregate 20 mm (kg)	Aggregate 10 mm (kg)	Sand (kg)	Ash (kg)	Water (l)	w/b
Control	450	712	610	335	-	202.5	0.45
CEM I + 10 ash(t)	450	712	610	301.5	33.5	202.5	0.45
CEM I + 20 ash(t)	450	712	610	268	67	217.58	0.45
CEM I + 30 ash(t)	450	712	610	234.5	100.5	232.65	0.45

In Figure 7 the materials used and the cubes and cylinders casted are shown during the SCB FA mixes preparation. It is noteworthy the colour change in the fresh concrete when SCB FA are added becoming darker.



*Figure 7 (a) Concrete preparation of SCB FA-10: [1] 10mm aggregates, [2] OPC, [3] SCB FA, [4] Sand, [5] 20mm aggregates; (b) Casted concrete: 0%, 10%, 20% and 30% of replacement*

### *Tests definition*

Table 5 summarises the tests conducted to assess the physical and chemical properties of concrete at different ages and the applied standards.

*Table 2. Tests summary table*

Physical and chemical properties	Tests	Age (days)
Consistency (Slump test)	BS EN 12350-2 [47]	0
Density of fresh concrete	BS EN 12350-6 [48]	0
Density of hardened concrete	BS EN 12390-7 [49]	28
Compressive strength	BS EN 12390-3:2019 [50]	28
Water absorption due to capillary	BS EN 1015-18:2002 [51]	28, 60, 90, 240
Total open porosity	BS EN 1936: 2006 [52]	28, 60, 90, 240
Chloride migration of concrete	NT Build 492 [53]	28, 60, 90, 240
Surface electrical resistivity	Wenner four-probe system	28, 42, 60, 90, 120, 240

Chloride migration coefficient of concrete have been measured according to NT Build 492 [53], a non-steady state migration test at 28, 60, 90 and 240 days. An external potential is applied across a cylindrical specimen, (Ø100mm, h≈50 mm) that forces the chloride ions in the catholyte solution migrate into the specimen. The specimens were prepared in vacuum and submerged in Ca(OH)<sub>2</sub>, later fitted in a rubber sleeve and this filled with an anolyte solution (0.3M NaOH)

where the anode was introduced, Figure 8(a). This was put in a reservoir with a catholyte solution (10%NaCl). All the system was connected to the power supply, Figure 8(b). After 24h, the specimens were split, and the chloride penetration depth assessed with silver nitrate, Figure 8(c).

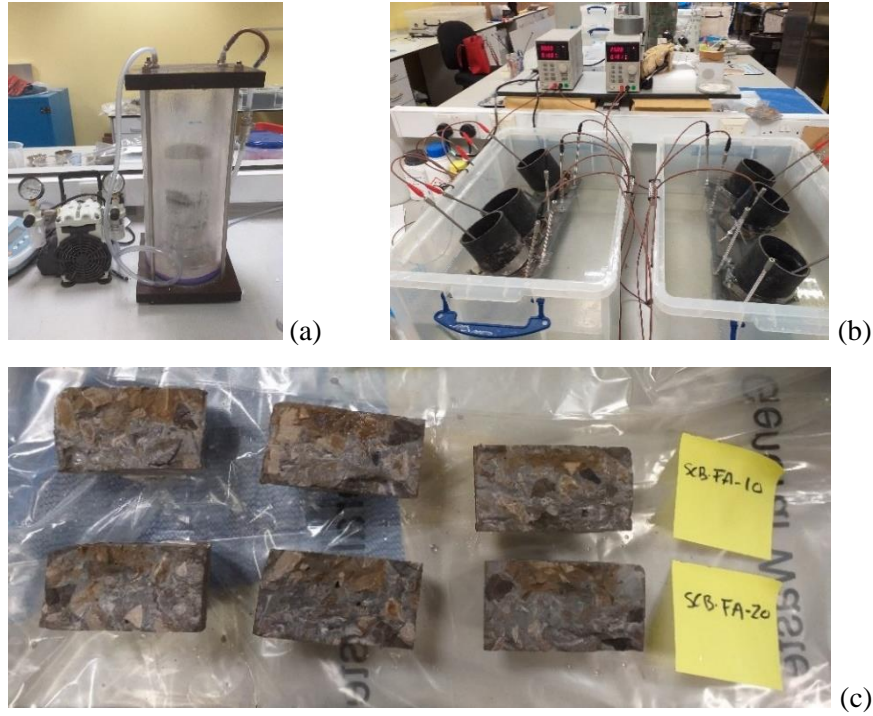


Figure 8 Chloride migration coefficient procedure: (a) vacuum of samples, (b) application of potential, (c) Chloride penetration depth assessed with silver nitrate

Finally, the registered data were worked out according to formula (1) where  $D_{nssm}$  is the non-steady-state migration coefficient ( $\times 10^{-12} \text{ m}^2/\text{s}$ );  $U$  is the absolute value of the applied voltage, (V);  $T$  is the average value of the initial and final temperatures in the anolyte solution, ( $^{\circ}\text{C}$ );  $L$ , thickness of the specimen, (mm);  $x_d$ , average value of the penetration depths, (mm) and  $t$ , test duration, (hour).

$$D_{nssm} = \frac{0.0239(273+T)L}{(U-2)t} \left( x_d - 0.0238 \sqrt{\frac{(273+T)L x_d}{U-2}} \right) \quad (1)$$

The electrical resistivity of concrete is an inherent property of the material and express the opposition that the concrete mass exerts to the transport of charged ions through the material under an external current [54]. It depends on several factors such as the porosity microstructure, the relative humidity, the pore solution content, etc. In this research the Wenner four probe system with a resistivity meter RESIPOD PROCEQ model with 50 mm spacing was used to measure the surface resistivity. Two internal probes measure the potential difference between these and the external ones where a current is applied and carried by ions in the pore solution through the concrete. The limitation of this system is the not semi-infinite depth condition of the cylinders, affecting the value of the cell constant and consequently the accuracy of the reading. Thus, the readings must be treated in a qualitative way in order to have a better comprehension of the evolution of the concrete permeability on time. An increment on the electrical resistivity values can indicate a reduction on the permeability due to a refinement of the pores microstructure due to further hydration, or a reduction of the hydroxyl ions ( $\text{OH}^-$ ) observed when reactive supplementary cementitious materials are used [34, 54].



### 3. Results and discussion

#### 3.1. Characterisation of as-received (ar) and treated (t) ashes

##### Appearance: colour and shape

Visually, SCB FA is a dark-grey/black powder with presence of needled unburnt carbon particles, Figure 9(a). Black colour in ashes indicate uncompleted burning process. SCB BA is a mix of different types of stones with a wide range of densities, colours and sizes and some traces of bagasse, Figure 9(c). SCB BA colour became whitish after the treatment, but no significative chemical reaction was observed under X-ray diffraction, Figure 9(d).

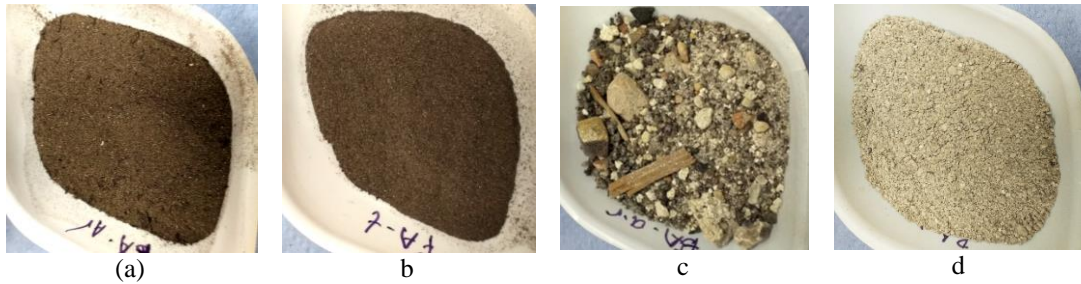


Figure 9 (a) As-received SCB fly ash – SCB FA(ar); (b) Treated SCB fly ash – SCB FA(t); (c) As-received SCB bottom ash – SCB BA(ar); (d) Treated SCB bottom ash – SCB BA(t)

When the samples are analysed under SEM, different types of particles are observed. SCBA FA is made of four main types of particles: prismatic ( $\leq 100\mu\text{m}$ ), spherical ( $\leq 50\mu\text{m}$ ), amorphous particles, unburnt carbonaceous particles ( $\leq 300\mu\text{m}$ ), small particles adhered to the surface of bigger grains ( $\leq 5\mu\text{m}$ ) and bubbles, Figure 10 (a), (b). This is consistent with the observations of Sales and Lima (2010) and Payá et altri (2018) [19]. A complex bimodal distribution pointed by Cordeiro et altri (2008), Codeiro et altri (2009) and Payá et altri (2018), [16, 18, 27], can be slightly observed in Figure 12(b) when the differential volume is analysed. In SCBA BA angular particles, spherical ferric particles and light and porous grains are observed, Figure 10(c),(d).

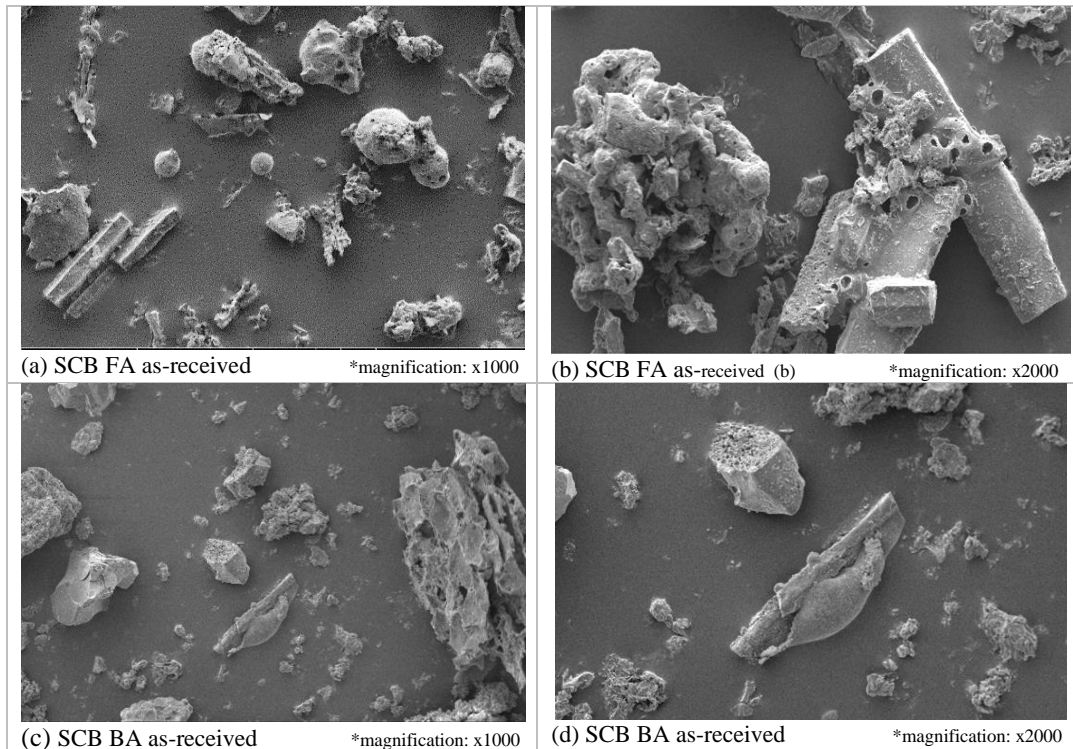


Figure 10 Scanning electron microscopy of ashes

## 1 Particle size distribution

2 For the dry sieving test of the as-received ashes, two single determinations on separate test  
 3 portions for each type, heavier of 100 g, were dried in an oven at  $(105\pm 2)^{\circ}\text{C}$  until the mass was  
 4 stabilised. Depending on the particle sizes, different range of sieves were used:  $63\mu\text{m}$  to  $3.35\text{ mm}$   
 5 for SCB FA, meanwhile, for the SCBA BA a larger range had to be used to cover until  $14\text{ mm}$ .  
 6 The assembled stack of sieves with the testing sample was shaken for 10 minutes, the quantity  
 7 retained in each sieve and the retainer pan was weight, and the percentage passing, D10, and  
 8 finally the coefficients of curvature and uniformity were obtained, Figure 11. It is noteworthy  
 9 that, for SCB FA, above  $200\mu\text{m}$  most of the volume retained is low density char fibrous particles.

Additionally, SCB FA was subjected to the laser diffractometric test using the analyser Beckman  
 Coulter LS 13320, Figure 12. This apparatus determines the particle size distribution suspended  
 in water by measuring the pattern of light scattered by the particles in the sample. It must be  
 noted that this method considers particles as spheres and it makes an approximation to non-  
 spherical particles that could work. However, for many particles, the size distribution obtained  
 is only apparent. This is the case of the elongated charcoal particles presented in the ashes. In  
 addition, due to the small amount of sample tested, the biggest needed particles may drop and  
 not been considered. This will justify the possible discrepancies between both analyses. SSA  
 measurements with laser diffractometer and Blaine method may also differ.

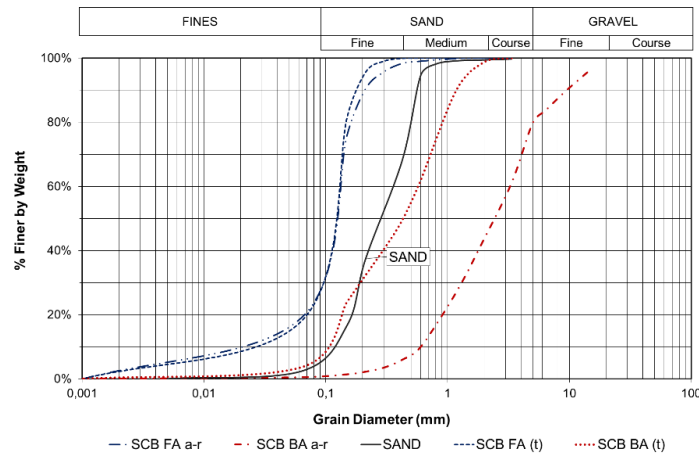


Figure 11 Particle size distribution. As-received and treated ashes.

11 SCB FA particle size distribution is represented by a steep curve with the mean value in  $140\mu$  and  
 12 thinner than the sand used but classified as fine sand. The fineness modulus is 1.06 and 1.05 for *as*  
 13 *received* and *treated*, respectively. Sizes from  $1.18\text{ mm}$  to  $150\mu$  were dominated by the presence  
 14 of unburnt carbon and the content of some white grains - sand from the field. SCB BA (ar) has a  
 15 distribution covering from medium sand to fine gravel with a fineness modulus of 6.95. SCB BA  
 16 (t) is a coarse fine aggregate with a fineness modulus of 3.99 and mean value of  $550\mu$ , Figure 11.

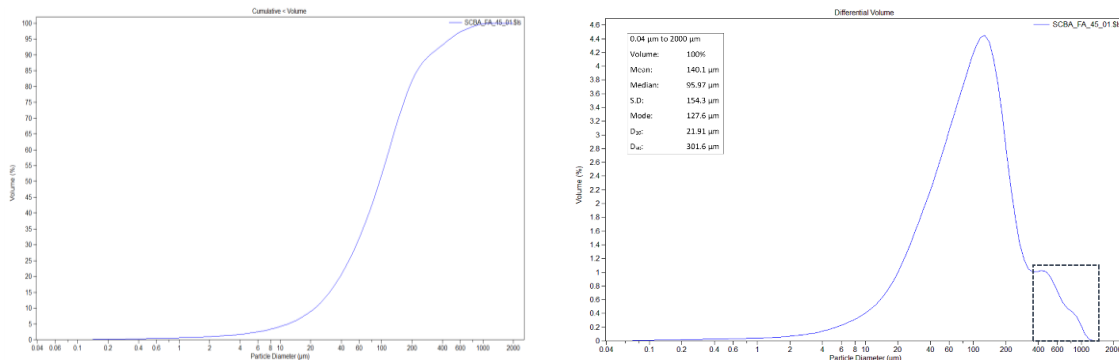


Figure 12 Laser diffractometric analysis of SCB FA(ar). (a) "Less than" cumulative volume (b) Differential volume

## Density and specific surface area (SSA)

Table 1 shows the physical properties of bio-ashes. Bulk density of SCB FA is similar to that of cement and slightly lower than that of sand, and SCBA BA bulk density is close to that reported by Sales and Lima (2010) [19]. Nevertheless, the SCB FA real density is lighter than sand and cement, meanwhile SCB BA real density is comparable to sand. In the case of SCB FA the specific surface area is much bigger than the normal values for fine sand and still bigger than that of cement, meanwhile SCB BA SSA is a quarter of that of SCB FA.

Table 3 Physical properties of bio-ashes

	OPC	Sand	SCB FA		SCB BA	
			<i>As-received</i>	<i>treated</i>	<i>As-received</i>	<i>treated</i>
Real density (kg/m <sup>3</sup> )	3150	2420	1776.6	1820.2	2349.19	2352
Bulk density (kg/m <sup>3</sup> )	1400	1635	1422	1492	2432	2447
Fineness modulus	-	2.84	1.21	1.01	7.65	3.99
Specific Surface area (cm <sup>2</sup> /g)	3000-4500	360	5853	5750	-	1502

## pH of ashes

The alkalinity of ashes is shown in Table 2. The decrease in alkaline elements in SCB FA may be due to the charcoal removal which has a higher pH (12-13). The water-washing did not alter the pH of SCB BA probably because minimal amounts of contaminants were removed but not chemical changes occurred.

Table 4 pH values of as-received and treated ashes

	As-received	Treated
SCB FA	11.92	11.37
SCB BA	12.67	12.68

## Mineralogical and chemical analysis

Major and minor elements of cement, treated and untreated ashes are expressed as oxides in Table 5. The heterogeneity of particles and the mineralogical structure were observed by means of XRD, and are shown in Figure 10 and Figure 13. In Figure 13 it can be observed the crystalline silica that leads the XRD pattern for SCB FA and the presence of silicon and carbon carbonate in SCB BA particles.

Table 5 Chemical properties of ashes. Main oxides

Element, %	OPC	SCB FA		SCB BA	
		<i>As-received</i>	<i>Treated</i>	<i>As-received</i>	<i>Treated</i>
SiO <sub>2</sub>	26.66	53.09	60.92	23.74	21.77
Al <sub>2</sub> O <sub>3</sub>	2.22	6.94	7.62	1.19	0.84
Fe <sub>2</sub> O <sub>3</sub>	2.43	5.55	5.99	2.31	1.99
CaO	64.11	9.60	11.84	65.56	66.40
MgO	1.55	2.36	2.78	0.97	0.90
K <sub>2</sub> O	0.64	2.08	2.25	0.89	0.68
Na <sub>2</sub> O	0.27	1.18	1.24	1.31	1.30
TiO <sub>2</sub>	1.33	0.57	0.58	0.31	0.32
P <sub>2</sub> O <sub>5</sub>	0.87	0.25	0.25	0.25	0.25
MnO	0.15	0.16	0.17	0.04	0.04
Cl- (soluble)	-	0.129	0.10	0.128	0.09



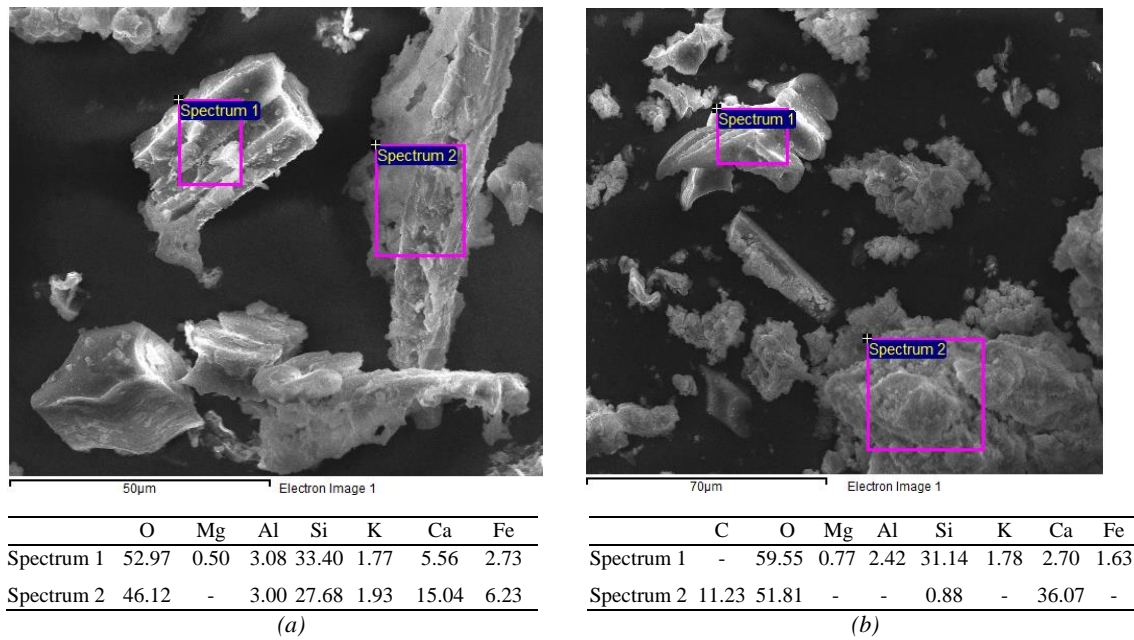


Figure 13 Chemical composition and scanning electron microscopy (SEM) of particles of (a)SCB FA and (b)SCB BA

SCB FA is predominated by  $\text{SiO}_2$  which contents in *as-received* and *treated* ashes (53.09%/60.92%) are lower than the mean value (63.56%/67.90%) reported by Payá et altri, (2018) [16] after having compiled 22 authors data who reported  $\text{SiO}_2$  contents between 31.41% up to 81.20%. Rajasekar, A. et al. (2018) used high silica content SCBA (86.79%) to enhance the properties of UHSC, [21]. The silica content comes from the absorption of the plant from the soil during its life and the content of grain of quartz removed from the field during the harvesting [55]. The amount of silica -as the rest of elements- increase after the sieving due to the removal of charcoal particles, which main element is carbon. The amount of  $\text{Al}_2\text{O}_3$  (6.94%/7.62%) and  $\text{Fe}_2\text{O}_3$  (5.55%/5.99%) are lower than the mean values gathered by Payá et altri (2018): (9.18%/9.80%) and (6,09%/6,50%) respectively. The total amount of main oxides ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ) is 65.58% before sieving and 74.53% after sieving, higher than the minimum content of oxides required for Pozzolans type F: 70% [56]. Silica content is not the only parameter that define the pozzolanic activity of ashes.

The crystalline phase detected is quartz, a non-amorphous phase (inert) with non-binding capacity, that makes SCB FA suitable as aggregates substitutes, Figure 14(a). Cristobalite has not been detected, contrary to Cordeiro et al. (2019) [13] who observed its presence in ashes obtained under controlled combustion at 800°C. This indicates a combustion temperature below 800°C that confirms the declared temperature (750-800°C) by the ash producer, San Pedro BioEnergy. Optimal temperature for pozzolan SCBA have been stablished around 550 °C and 600°C [18, 21]. The baseline in XRD is slightly displaced showing a minor halo with any major outstanding embossments such as that detected by other authors who investigated the use of SCBA as cement replacements [21, 34]. All this, indicates a low activity index.

The separated char has been observed under the X-ray diffraction and amorphous structure and the presence of attached particles of silica was detected, Figure 14(b).

SCB BA is clearly crystalline with no presence of amorphous halo, characterised by the presence of calcium carbonate ( $\text{CaCO}_3$ ) in the mineral phase of calcite, Table 5 and Figure 14(c). The main oxides are CaO (65.56%/66.40%) and  $\text{SiO}_2$  (23.74%/21.77%). The calcium carbonate indicates the presence of stones from the field in the boiler and added together with the biomass. After the treatment, no important chemical reactions are observed in the X-ray diffractogram, but the removal of some contaminants.

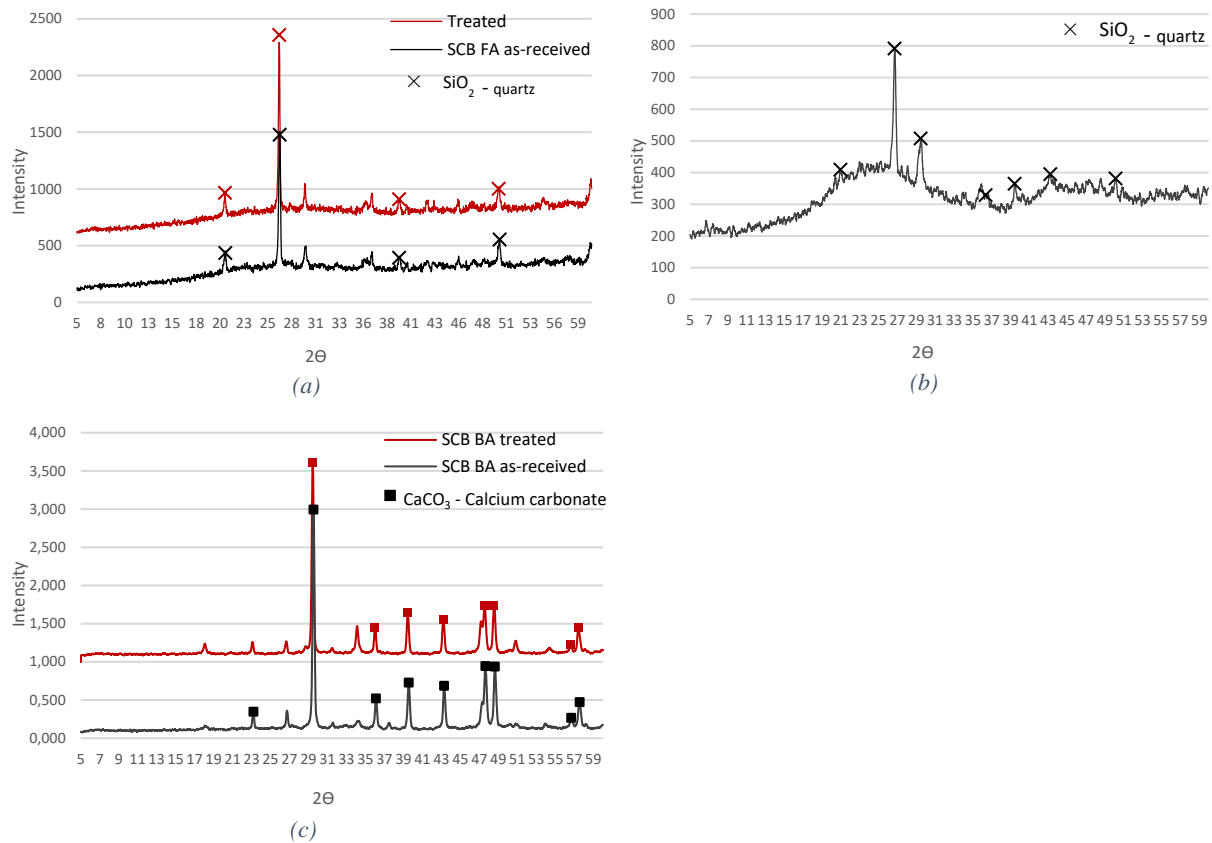


Figure 14 (a) XRD pattern: SCB FA as-received (dark grey), SBA FA treated (garnet); (b) XRD pattern of CHAR COAL removed from SCB FA; (c) XRD pattern: SCB BA as-received (dark grey), SBA BA treated (garnet)

Water-washing reduces the water-soluble chloride content. The reduction depends on the initial content, being higher with higher initial  $\text{Cl}^-$  contents. SCB FA and SCB BA have low soluble-chloride content in the as-received forms but it is still higher than the limit established by the standards for total chloride in cement or PFA ashes for steel reinforced concrete: 0.10% content by mass of cement [57, 58]. The limit for total chloride content in concrete is 0.4% by mass of cement for the sum of all the constituent materials. No limits are established for aggregates, nevertheless, natural aggregates from inland deposits have very low water-soluble chloride ion content (<0.01%) [42].

In Figure 15 the thermogravimetric analysis (TGA) of SCB FA (ar) and SCB FA (t) shows a first loss of mass below 500°C, corresponding to the water removal and the oxidation of residual carbon and organic matter pointed in similar ranges by Zhao et al (2013) [20]. SCB FA (t) showed a higher humidity content derived from environmental circumstances which should be omitted when both ashes are compared. The differential char content between SCB FA(ar) and SCB FA(t) can be observed in the range of 450°C -600°C. Around the 650°C a third mass loss occurs with a new slope likely related with the crystallization of the amorphous silica. At the end of SCB FA TGA curve, around 900 °C, occurs a change that can be related with a change of phase of silica, Figure 15(a).

In the case of SCB BA, Figure 15(b), there is no major mass loss until 425°C, due to the residual carbon oxidation. The decomposition of  $\text{CaCO}_3$  is observed at 780°C where SCB BA(ar) has undergone a greater mass loss. Zhao et al (2013) [20] observed the release of soluble alkali and chlorides between 660-900°C. In this case, due to the low content of soluble elements in SCB FA and SCB BA, the removed parts are more obvious in Table 5.

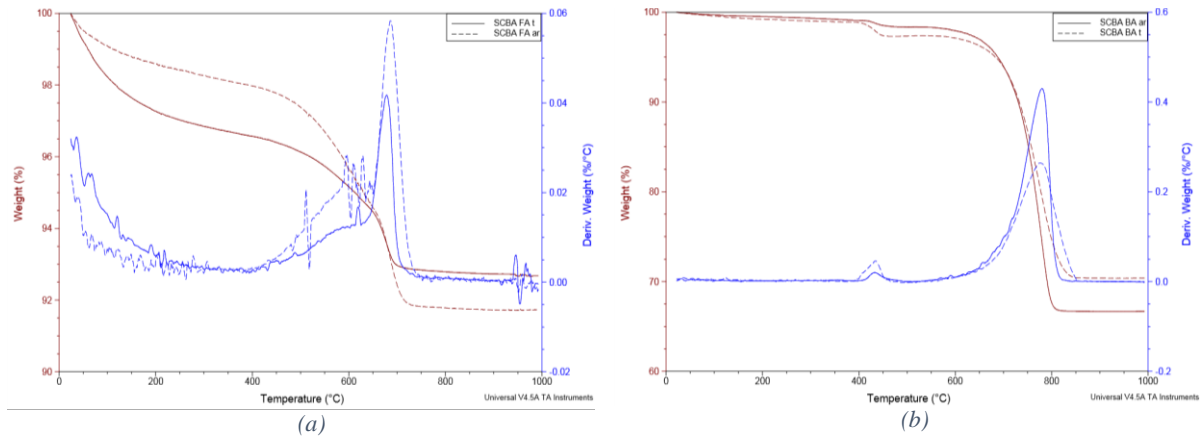


Figure 15 (a) TGA overlayed of SCB FA(ar) and SCB FA(t); (b) TGA overlayed of SCB BA(ar) and SCB BA(t)

From the characterisation stage, it can be concluded that both ashes from the studied energy plant have different nature: SCB FA results from the combustion of the bagasse at a higher temperature than the optimal considered to use as cement substitute. The predominant element is silica in form of quartz (crystalline) what will justify the use as sand replacement. A minimal amorphous halo The presence of light charcoal needled particles is the predominant organic matter. On the other hand, SCB BA ashes are a mixed of stones from field, bagasse and contaminants deposited in the furnace. This concord with the high crystalline structure (XRD), the predominance of  $\text{CaCO}_3$  and the angularity of particles. Both ashes were treated according to the results and characterised again. The properties of ashes such as shape, density, porosity, chemical composition, etc, will affect the bio-concrete properties.

### 3.2. Characterisation of concrete. Experimental campaign.

Important differences were observed between compositions with SCB FA and SCB BA. In the first case, when SCB FA is used as sand substitute, a notable improvement in the durability-related properties can be observed on time. The more ashes are used, the best performance is obtained. On the other hand, SCB BA do not have any significant pozzolanic reaction, leading to concretes with no enhanced durability-related properties. The results of SCB BA will be determine by an excess of water in the mix.

#### Consistency

Slump test values are shown in Figure 16, and fresh density are depicted in Table 5. The addition of SCB FA(t) reduces the workability and the bulk density of concrete.

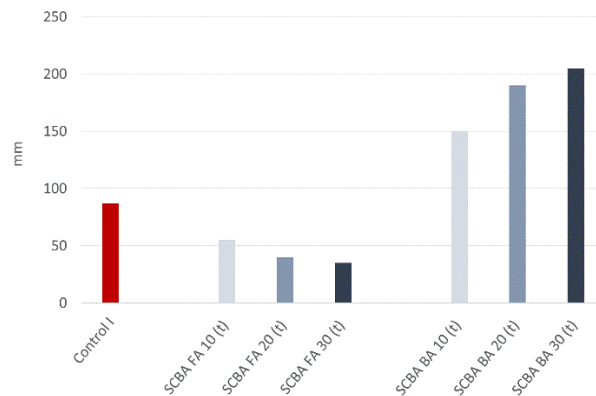


Figure 16 Slump test results for SCB FA and SCB BA, w/b = 0.45

When SCB FA(t) is used as sand substitution in 10%, 20% and 30% of weight, the workability is reduced up to 36.8% (55mm), 54% (40mm) and 59.7% (35mm) when compared to the control concrete (87mm). This is due to a higher SSA, the presence of elongated and irregular particles and the existence of a pozzolanic capacity of ashes that give rise to a higher binding water demand in comparison with the control concrete. The pointed reduction in the workability has been also observed by other authors even with treated ashes [16, 23, 30, 31, 40]. Opposite results, a positive impact in the workability, were declared when the ashes are ultra-grinded [21, 26].

The results obtained in each case correspond to the following specified consistency classes as per The British Standard Institution [59], Table 6: class S1 (0-60mm) for mix SCB FA-10 and class S2 (40-110mm) for mixes SCB FA-20 and SCB FA-30, Figure 17(a). The concrete control slump class is S2-S3. In British Standard Institution [59], the default slump class for housing and foundations is S3 and S2 for sliding formwork construction, floor slabs and pavements. Other standards such as the Indian Standard Institution [60], consider low workability mixes (slump range: 25-75mm) for foundations with light reinforced and roads vibrated by hand operated machines; and medium workability mixes (slump range: 50-100mm) used for normal reinforced sections manually compacted and heavily reinforced sections in vibrated sections in concrete structures). Nevertheless, the use of plasticisers can be considered to enhance the workability according to the desired final use.



Figure 17 Slump test for fresh concrete: (a) SCB FA-20 (40 mm); (b) SCB BA-20 (190 mm)

Table 6 Consistency class

	Slump (mm)	Consistency class [59]
Control	87	S2-S3
SCB FA-10	50	S1-S2
SCB FA-20	40	S1-S2
SCB FA-30	35	S1
SCB BA-10	150	S3-S4
SCB BA-20	190	S4
SCB BA-30	205	S4

The addition of SCB BA(t) leads to more workable concretes than those with SCB FA(t) or only natural sand due to a lower specific surface area and a crystalline structure. In compositions with SCB BA there is no extra water requirement, due to a more crystalline and angular structure of the ashes. Analysing the increasing values for SCB BA slump results when the amount of ashes is increased, it becomes clear that SCB BA do not show any binding capacity in concrete or need any additional water. Based on this, according to the standard BS EN 206-1:2000 [59], mixes with SCB BA yield more flowable concrete than the control one classified as S3-S4 for SCB-BA 10 (150mm) and S4 for SCB-BA 20 (190mm) and SCB-BA 30 (220mm), Figure 17(b). Concretes

with slump class S4 are recommended for trench fill foundations and in-situ piling by BS EN 1936: 2006[59]. According to IS 1199 (1959) [60], concretes with slumps 100-175mm are considered as high workability concrete, suitable for sections with congested reinforcement.

#### Fresh and hardened concrete bulk density

The use of lighter materials as substituents result in lighter concretes [30]. The substitution of natural sand by industrial agro-ashes with a lower real density, such as SCB FA, deliver lighter concrete: the density decreases up to 3.9% in fresh state -even with a higher compacity- and up to 3.5% in hardened state at 28 days when 30% is substituted. This can be clearly observed in Figure 18. This effect should not be confused with the case of bio-concretes with SCB BA, where the density of the ashes is like that of sand, and the lower values in the density of hardened concrete are due to an excess of water and the consequent porosity.

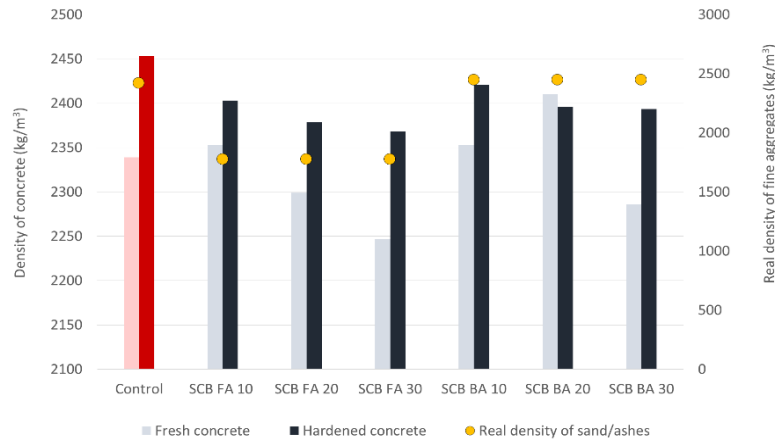


Figure 2 Concrete density vs. fine aggregates density

#### Compressive strength

Compressive strength was tested at 28 days. The results and the corresponding strength class as per BS EN 12390-3:2019 [59] are shown in Table 6. When 10% of sand is replaced by SCB FA, the compressive strength increases up to 4% at 28 days. Nevertheless, when 20% and 30% are replaced, the compressive strength decreases 6.8% and 8.9% respectively.

A linear correlation exists between electrical resistivity and compressive strength for the same mix designs [54]. In these terms, a later improvement in the compressive strength can be expected at 56 days, since a delayed pozzolanic reaction was indirectly observed by means of resistivity tests, Figure 23(b). Under non-accelerated curing conditions an improvement in the mechanical properties can be expected after 56 days due to the reactions between the  $\text{Ca(OH)}_2$  and the existing pozzolans in the presence of water forming secondary hydration products [21]. Early pozzolanic reaction (28d) cannot be expected based on the mean value of SCB FA [31]. Therefore, this should be confirmed with further experimentation.

Table 7 Fresh and hardened concrete density and compressive strength

	Fresh density, (kg/m <sup>3</sup> )	Hardened bulk density, (kg/m <sup>3</sup> )	$\sigma_{c28}$ , (MPa)	CoV $\sigma_{c28}$	Strength class
Control	2339	2453.4	56.33	2.5	C50/55
SCB FA 10	2353	2403	58.58	3.5	C50/55
SCB FA 20	2299	2378.7	52.71	1.5	C45/50
SCB FA 30	2247	2368.2	51.30	2.3	C45/50
SCB BA 10	2353	2420.6	50.63	2.0	C45/50
SCB BA 20	2410	2396	49.71	3.3	C40/45
SCB BA 30	2286	2393.4	46.43	1.5	C40/45



The addition of SCB BA decreased the compressive strength of 10,1%, 11,7% and 17.6% when considering the w/b ratio in comparison to the control concrete. These results must be assessed considering the nature of the ashes and other characteristics of the concrete such as consistency and porosity. The increasing values in the slump test demonstrate that SCB BA are not reactive. This concurs with the previous observations during the chemical characterisation where a clear crystalline structure was observed. Nor does the mixes with SCB BA need extra amount of water due to the physical structure of ashes. In order to get comparable results between SCB FA and SCB BA w/b ratio was used where  $b$  considers the amount of cement plus ashes. The excess of water reduces the compressive strength. By adjusting the w/c ratio, higher compressive strength values, comparable with the control concrete, may be obtained for mixes with SCB BA. To corroborate this, concrete with SCB BA and w/c=0.45, where  $c$  stands for cement, was casted. When 20% of SCBA is substituted and w/c=0.45 considered, the same compressive strength as the control one is achieved for similar slump, Figure 19.

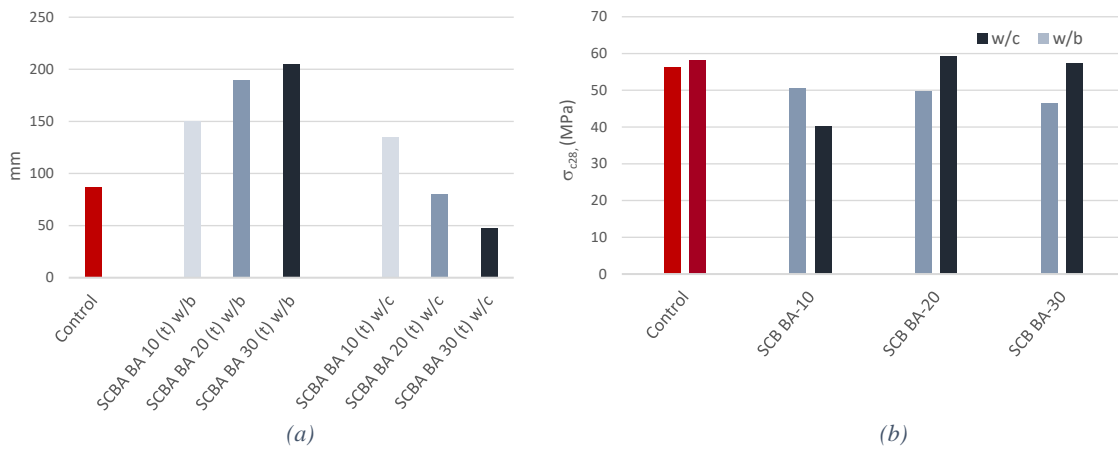


Figure 3 SCB BA with w/b = 0.45 and w/c = 0.45 (a) Slump test results; (b) Compressive strength at 28 days

### Open porosity

Open porosity (OP) measures the fraction of total volume of open pores through which a fluid can penetrate the concrete. This makes OP an important characteristic to assess the durability properties of the concrete: the lower OP values, the higher resistance for the diffusivity of external aggressive ions to penetrate.

The addition of industrial SCB FA increases the open porosity (OP) of the concrete when compared with the control concrete, Figure 20(c). A linear correlation exists between OP and density of hardened bio-concrete after 28d when SCB FA is used, Figure 20(a). The trend line has a R-square value close to 1, Figure 20(a). The more SCB FA is used the higher OP values are obtained at 28 days:  $OP_{10-28d} = \uparrow 29,2\%$ ,  $OP_{20-28d} = \uparrow 35,0\%$ ,  $OP_{30-28d} = \uparrow 45,0\%$ . Nevertheless, this situation reverses after 60 days: between 28d and 240d, SCB FA-10 and SCB FA-20 experience a similar reduction ( $OP_{10-(28d-240d)} = \downarrow 15,8\%$  and  $OP_{20-(28d-240d)} = \downarrow 18,1\%$ ) meanwhile an acute reduction occurs in mixes with 30% of substitution rate, doubling the previous mixes reductions until achieve the control concrete value ( $OP_{30-(28d-240d)} = \downarrow 33\%$ ). This improvement of the initial values on time are due to further cement hydration and/or a later pozzolanic reaction.

Mixes with SCB BA have higher open porosity index in comparison to the control concrete, and like concretes with SCB FA with 20% and 30% of substitution rates up to 60 days, Figure 20(d). Any reliable trend line can be established, Figure 20(b). Nevertheless, the number of samples is limited, and further tests should be conducted in order to corroborate this. In addition, mixes with 10% of replacement are showing an unexpected value, much higher to those with higher substitution rates, this might have the origin in the casting stage. The resulting values when



compared with the control concrete are:  $OP_{10-28d}=\uparrow 56\%$ ,  $OP_{20-28d}=\uparrow 35,7\%$ ,  $OP_{30-28d}=\uparrow 49,7\%$ . All coefficients of variation are lower than 6%. Between 28 and 60 days it can be observed higher gradients with higher substitution rates in all the bio-concretes indicating the possible production of further hydration products.

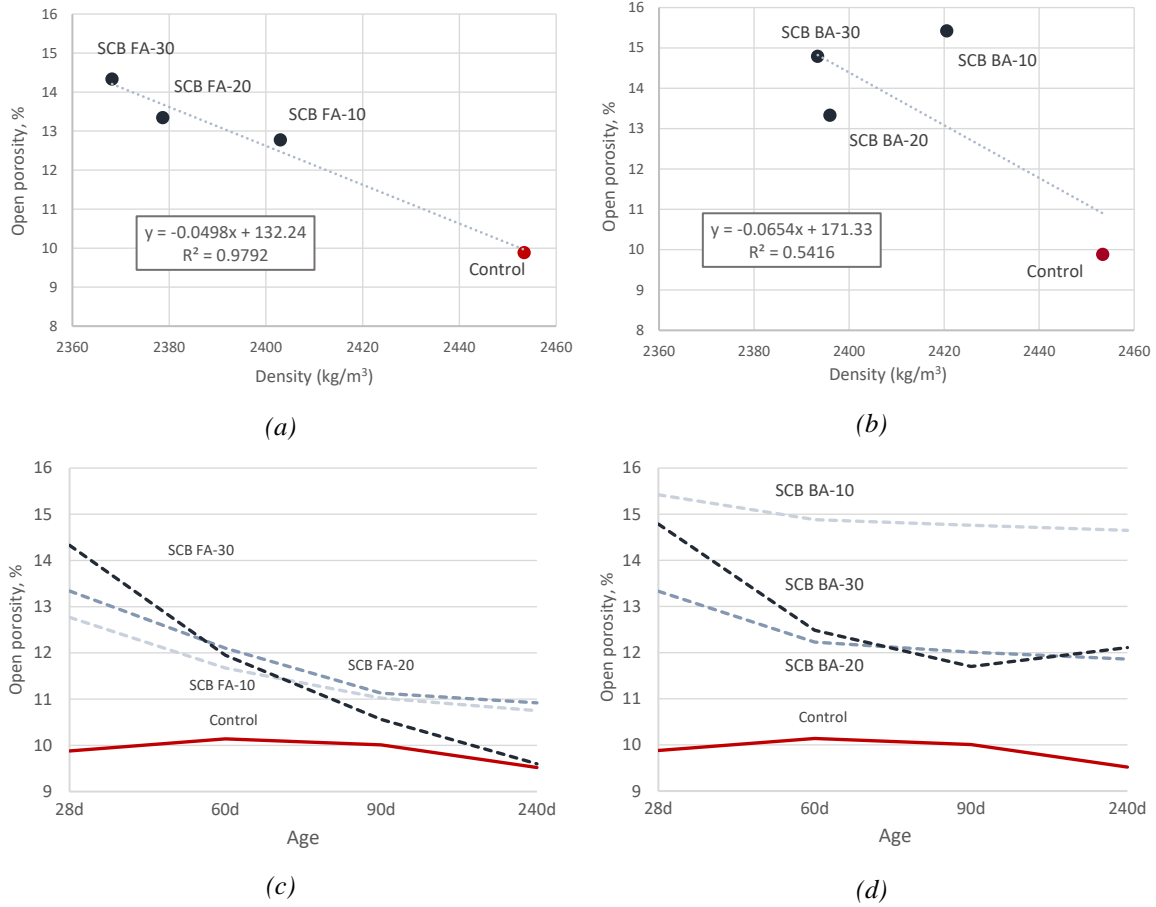


Figure 4 Correlation between open porosity and density of hardened concrete at 28d for (a) SCB FA and (b) SCB BA. Open porosity at 7 28, 60, 90 and 240 days of (c) bio-concretes with SCB FA and (d) bio-concretes with SCB BA

### Capillary absorption

By assessing the capillary absorption, the liquid transportation from the exterior through pores under no applied hydraulic pressure can be assessed. The addition of SCB FA of low reactive SCB FA as sand replacement increased the capillary suction of concrete. This is contrary to the observation made by other authors when high reactive fly ashes are used [21].

Capillary absorption of mixes with SCB FA-10 and SCB FA-30 are comparable with that of the control concrete after 24 hours at 60 days, Figure 21(a). At 240, the absorption decreases for all the compositions between 25.6%-42.6%, Figure 21(c). At this age, SCB FA-10 shows the best performance when compared with the control concrete (+0.41 g/cm²), and no difference is observed between SCB FA-20 and SCB FA-30 (+0.83 g/cm²). The plateau is achieved after 7 days after 60 days of curing and reduces up to 6 days after 240 days of curing.

In the case of SCB BA, the capillary absorption at 60 and 240 days increases up to 13.4% and 35%, 13.9% and 70%, and 36% and 70% when 10%, 20% and 30% of ashes are substituted respectively, Figure 21(b) and Figure 21(d). From 60days to 240 days, the absorption of the mixes decreases between 16.5-42.6%. Mixes with SCB BA arrive to the peak at 3 days in both cases. In both cases, the curves of mixes with SCB FA follow the pattern of the control concrete.

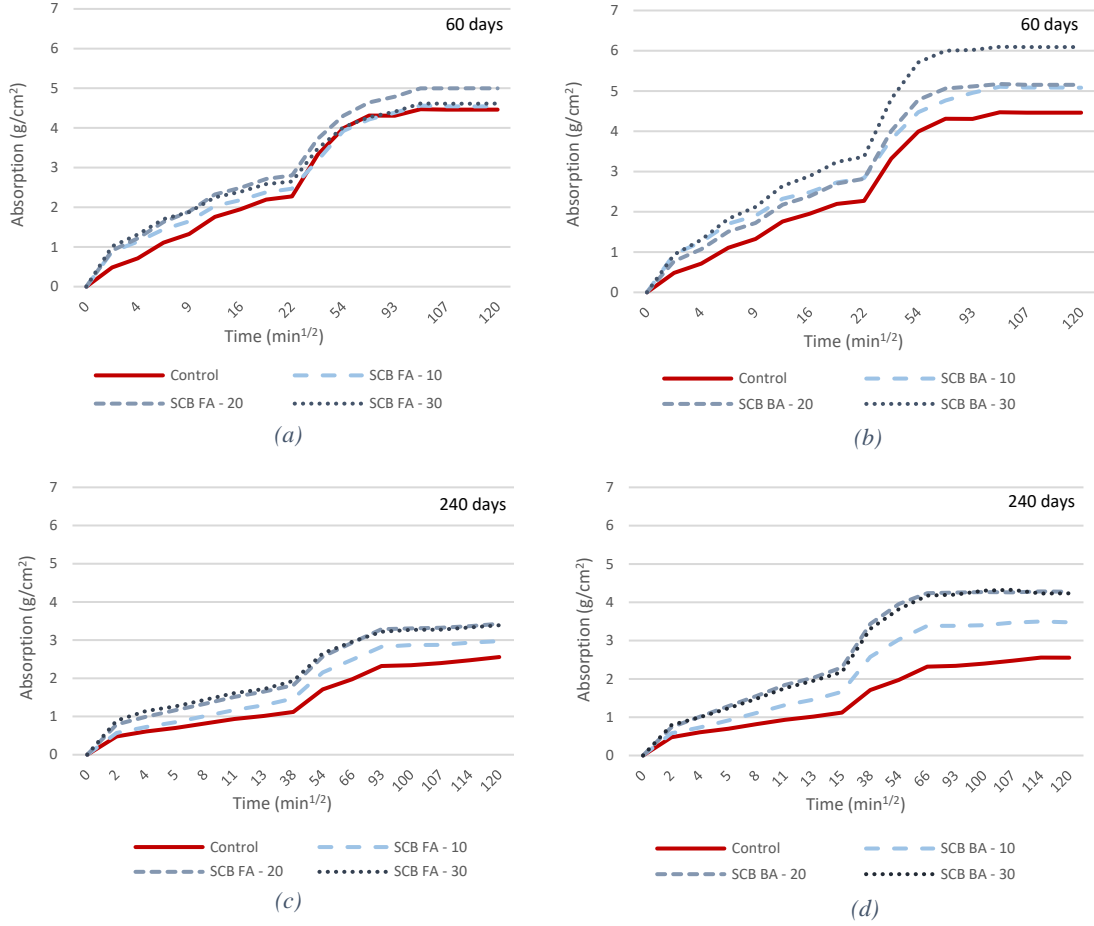


Figure 21 (a) Capillary 60 days. SCB FA w/b; (b) Capillary 60 days. SCB BA w/b; (c) Capillary 240 days. SCB FA w/b; (d) Capillary 240 days. SCB BA w/b

### Chloride migration, surface electrical resistivity and correlations

Figure 22 (a,b) shows that at 28 days bio-concretes with 10% and 20% of SCB FA as sand replacement have similar chloride migration coefficients ( $D_{nssm}$ ) and surface electrical resistivity ( $\Omega$ ) to that of the control concrete. For 30% of SCB FA there is a decrease of the chloride migration and an increase of resistivity ( $D_{nssm,30-28d}=\downarrow 10.9\%$  ;  $\Omega_{30-28d}=\uparrow 9.8\%$ ), in comparison to the control concrete, emphasising that higher amounts of SCB FA show an improvement in the durability properties even before the delayed hydration products are formed.

At 60 and 240 days, further improvements in terms of chloride migration resistance and surface electrical resistivity have been observed when compared to the control concrete for all substitution rates, particularly, those of SCB FA 30. Increments respect the control concrete after 60 and 240 days are:  $D_{nssm,10-60d}=\downarrow 17.2\%$ ,  $\Omega_{10-60d}=\uparrow 10.65\%$ ;  $D_{nssm,20-60d}=\downarrow 16.0\%$ ,  $\Omega_{20-60d}=\uparrow 20.8\%$ ;  $D_{nssm,30-60d}=\downarrow 47.9\%$ ,  $\Omega_{30-60d}=\uparrow 56.5\%$ . After 240 days  $D_{nssm,30-240d}=\downarrow 0.4\%$ ,  $\Omega_{10-240d}=\uparrow 18.6\%$ ;  $D_{nssm,30-240d}=\downarrow 17.4\%$ ,  $\Omega_{10-240d}=\uparrow 44.4\%$ ;  $D_{nssm,30-240d}=\downarrow 36\%$ ,  $\Omega_{10-240d}=\uparrow 104.2\%$ ).

The better performance of the concrete with SCB FA on time can correspond to the presence of a retarded pozzolanic activity [34]. The formation of hydration products due to the reaction of silica with the  $Ca(OH)_2$  block the interconnectivity of pores, thus the ions transportation is affected. The same effect was observed by Arenas J.C et al. (2016) [23, 34] where concrete's resistivity increased twofold and threefold when 10% and 20% of untreated SCB FA was used as cement replacement in mortars at 180 days. The influence of the mineralogical composition and shape of alternate fine aggregates in the resistivity measurements is not clear in this research [54].

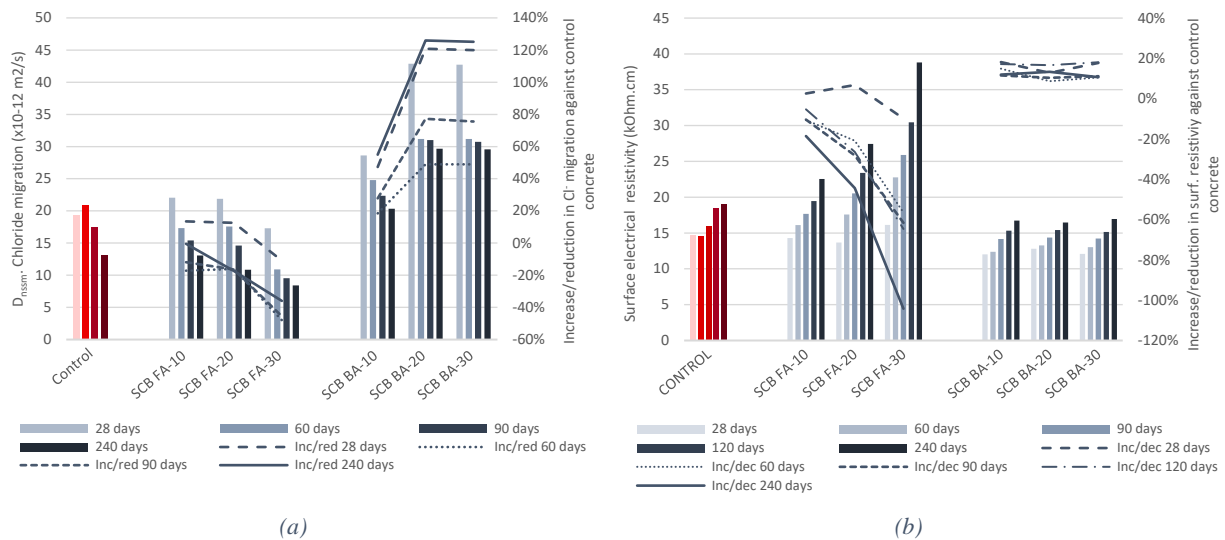
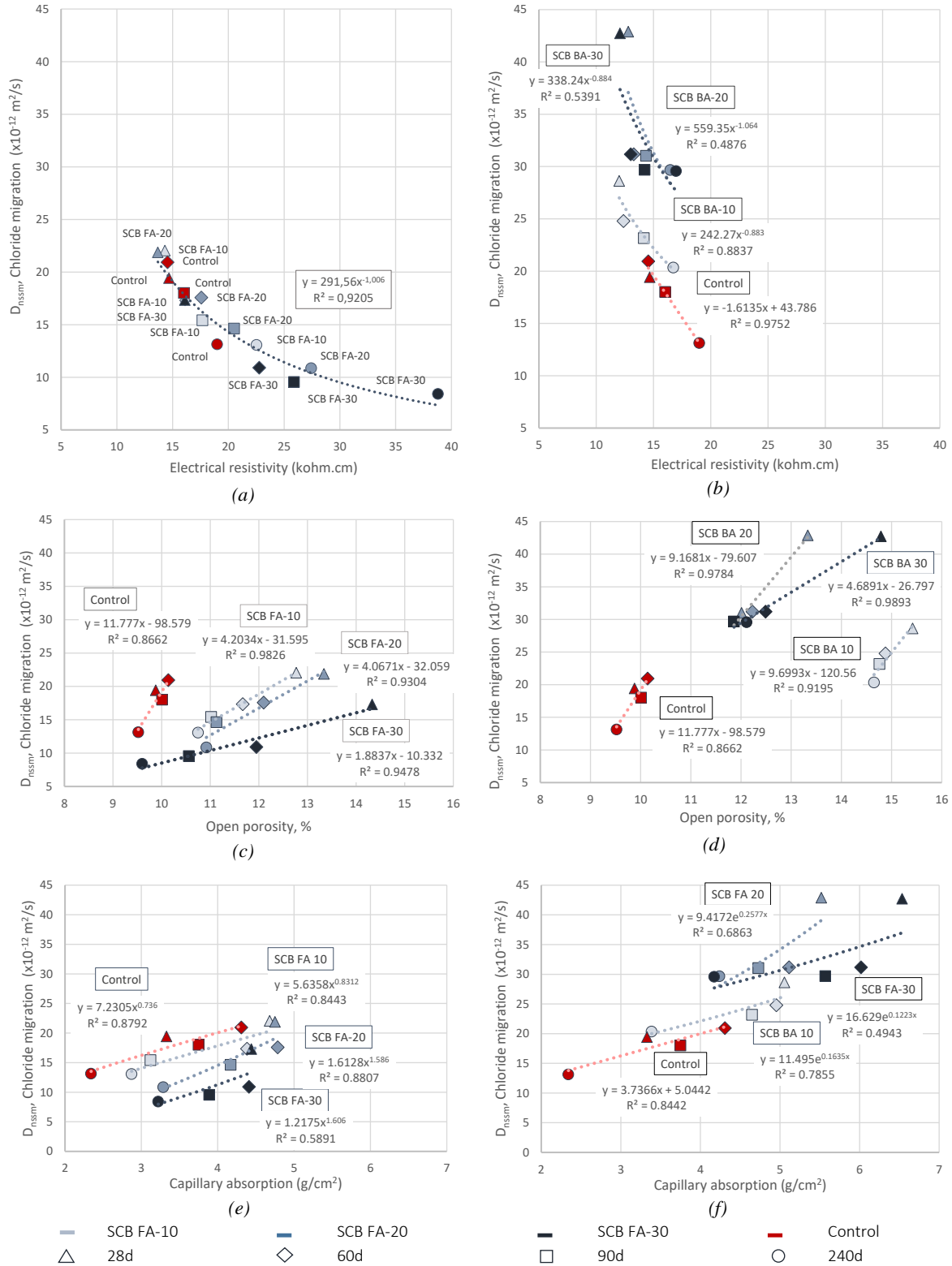


Figure 22 (a) Chloride migration at 28, 60, 90 and 240d; (b) surface electrical resistivity at 28, 60, 90, 120 and 240 d

When the correlation is established between chloride migration resistance and surface electrical resistivity for concretes with SCB FA a relationship can be found Figure 23 (a). This relationship has been also pointed by other authors, with different tendencies of the curves determined by factors such as the type of cement or the w/b ratio [23, 61]. Sengul (2014) [61] established a similar relationship between chloride diffusion coefficients and bulk electrical resistivity but, contrary to the previous ones, stated that all the mixes investigated containing different materials and proportions had a single relationship when diffusivity and resistivity were correlated. The reason of this might be in the fact that the sum of cement+mineral admixture was constant, similar slumps were obtained by means of plasticisers (140-220 mm; mean value 186mm) and the large number of samples may hide any displacement due to the multiple variables.

In the case of SCB-BA, the resistivities and migration coefficients of the different mixes are lower than the control concrete at all ages, Figure 20. At 28 days, the results are:  $D_{nssm,10-28}=\uparrow 47.3\%$ ,  $\Omega_{10-28}=\downarrow 18.2\%$ ;  $D_{nssm,20-28}=\uparrow 120.8\%$ ,  $\Omega_{20-28}=\downarrow 12.8\%$ ;  $D_{nssm,30-28}=\uparrow 120.0\%$ ,  $\Omega_{30-28}=\downarrow 17.7\%$ . Contrary to mixes with SCB FA, in terms of resistivity, no variations are observed between mixes with different ratios of SCB BA. At 60 days, mixes do not show substantial variations in the resistivity ( $\leq 3.75\%$ ) with respect to results at 28 days, Figure 22(b). At 240 days, all mixes with SCB BA experimented a total increase in resistivity of approximately 40%, around 12% lower if compared to the control concrete at same age. This behaviour is apparently comparable to that of the control concrete, but this must be assessed with caution. If completely non-pozzolanic reaction is assumed for SCB BA based in the XRD pattern, the w/b ratio should be recalculated considering only the cement and not the ashes that makes w/b=0.45 equals to w/c=0.48; w/c=0.52 and w/c=0.55 for mixes with 10%, 20% and 30% respectively. In this hypothetical situation, the porosity should increase along with the amount of ashes incorporated due to an excess of water resulting in more conductive concretes, thus, in lower values of resistivities for higher substitution rates. In other words, a reduction in electrical resistivity occur for higher w/c rates [54]. But resistivities are the same for all substitution rates. This can be explained by considering the very low reactivity of SCB BA due to the 23.74% of silica contained in the ashes which would be the responsible of counteracting the effect of the excess of water. This is consistent with the decreases in the open porosity values after 60 days and the reduction of  $D_{nssm}$  for 10% of substitution rate on time. By comparison, the conclusions are not clear for  $D_{nssm}$  in SCB BA 20 and SCB BA 30 that experience a sharp drop after 28 days and a later stabilization between 60 and 90 days with negligible variations. This might occur due to the lack of accuracy of the procedure in the case of concretes with lower resistance to chloride ions migration. A correlation between chloride migration and surface electrical resistivity values on time does not exist for SCB BA mixes as a group, nor for

- 1 type of mix (with same substitution rate) at different ages, Figure 23(b). It seems to exist a
- 2 correlation for similar substitution rates. This confirms that the water binding ratio is a key factor
- 3 in the correlation of transport mechanism in concrete such as  $D_{nssm}$  and  $\Omega$ .



4 Figure 23 Correlations between chloride migration and surface electrical resistivity for (a) SCB FA and (b) SCB BA;  
 5 between chloride migration and open porosity for (c) SCB FA and (d) SCB BA; between chloride migration and  
 6 capillary absorption for (e) SCB FA and (f) SCB BA, at 28d, 60d, 90d and 240d.

A linear correlation exists between the open porosity and the chloride migration capacity of each bio-concrete composition with SCB FA and SCB BA ( $R^2 > 0.92$ ), Figure 23 (c, d). Curves of mixes with SCB FA are less steep than the control concrete curve and below this one, in other words, the addition of SCB FA increase the open porosity meanwhile derive concretes with comparable or enhanced results of chloride migration resistance. Only SCB FA-30 at 240d achieve the OP values of control concrete. The evolution on time leads to think about an interruption in the interconnectivity of porous due to the later hydration of pozzolans and cement. Considering that the addition of SCB FA increase the capillary absorption (Figure 23(e)), there is no option to think about a deposition of the hydrated products from the exterior to the interior. Thus, an additional phenomenon may occur which helps to block the chloride migration: a possible physical or chemical chlorides ions bounding capacity of concrete promoted by the incorporation of ashes with high SSA and charcoal particles.

Capillary water absorption is usually related with the diffusivity of aggressive ions into the concrete through the porous structure [62], consequently it is used as a parameter to assess the adequacy of a mix exposed to a specific environment. In this research it has been observed that the addition of SCB FA increase the capillary absorption when compared with the control concrete but, in contrast, the chloride migration is reduced, and no direct correlation exists, Figure 24(e). This means that capillary absorption is not enough to understand the vulnerability of concrete to external aggressive agents and its diffusion through the concrete mass until corrode the embedded rebars.

In comparison to SCB FA, the chloride migration and open porosity correlations curves of concretes with SCB BA are above of the control concrete curve due to lower chloride migration resistance due to an excess of water and a minimal reactivity (higher in concretes with higher substitutions rates). As with SCB FA mixes, no clear correlations can be established between  $D_{nssm}$  and capillary absorption ( $0.49 < R^2 < 0.78$ ), except that, at 28 days, higher capillary absorption lead to higher  $D_{nssm}$ , Figure 23(f).

#### 4. Conclusions

This study investigates the feasibility of incorporating low-reactive industrial sugar cane bagasse ashes (fly ash -SCB FA-, rich in silica and bottom -SCB BA- rich in  $\text{CaCO}_3$ ), in concrete production as sand alternate materials with low-cost and low-energy consumption treatments, concluding that:

- The specific surface area of ashes directly affects the workability of the bio-concretes: when SCB FA(t) with higher specific surface area is used, the workability decreases, meanwhile with SCB BA increases.
- Concretes with SCB FA achieve the compressive strength of the control concrete when 10% is added at 28 days. Later increases in the compressive strength can be expected due to delayed pozzolanic reaction. SCB BA reduce the compressive strength (between 10-21%) when  $w/b=0.45$  is considered. By adjusting the  $w/b$  ratio higher compressive strengths and better durability properties can be obtained.
- In terms of durability, SCB FA(t) enhances the chloride migration resistance showing the best performance at 30% of substitution rate. At early ages (28 days), SCB FA-10 and SCB FA-20 of replacement provide comparable resistance to the control concrete, and SCB FA-30 improves the control concrete resistance ( $\uparrow 10.9\%$ ). At 60 days, all the mixes show a better performance than the control concrete and enhancements can be still observed after 240 days with an average value of 43.1%. A reduction in the connectivity of microstructure of pores, consistent with later hydration of pozzolans and cement, has been pointed as the main cause of the enhancement in the durability properties.

- The addition of SCB FA promotes the capillary absorption and the open porosity of concretes. The more ashes are used, the higher reductions occur on time. Based on these results, a possible chloride ion binding capacity of ashes has been stated as second cause of the enhancement in chloride migration resistance. Consequently, the open porosity test or capillary absorption test cannot be taken as conclusive test when durability properties want to be assessed, in specific, the corrosion vulnerability.
- The incorporation of SCB BA(t) with w/b=0.45 increases the capillary water absorption and reduces chloride diffusion resistance of the different mixes, promoted by the excess of mixing water. A reduced pozzolanic activity has been indirectly observed.

This research demonstrates that apparent low-reactive SCB FA rich in quarts, can show later pozzolanic activity that makes this waste a potential alternate sand to enhance durability properties of cement-based materials. SCB BA may have potential uses where durability requirements are low, if the amount of mixing water is reduced. This opens a market opportunity for low quality ashes and can be a solution for the increasing housing and material demand in countries with a high urban development where sugar cane is cultivated.

This study focussed in the durability performance. In order to have a thorough comprehension of the performance of an optimised mix design, future works would consider assessing further fresh and mechanical properties (rheology, setting time, compressive strength, tensile strength, flexural strength, elastic modulus) on time. For future studies further electrochemical characterisation is going to be done in order to assess the influence of the ashes in relation to the service life.

The main limitation of this study is the heterogeneity of ashes. The results and conclusions obtained are applicable to the concrete made with ashes from the mentioned company and batches with the specifications described before. However, the interest of this study is that the methodology and findings can be extrapolated to other studies with this type of waste.

The obtention of optimal ashes through a controlled combustion process is out of the scope of this research. Nevertheless, the authors believe that the implementation of new burning and collecting procedures is necessary in industry where the quality of the resulting ashes is taken into consideration.

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