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Additional Information

Assessment of sugar cane straw ash (SCSA) as pozzolanic material in blended Portland cement: microstructural characterization of pastes and mechanical strength of mortars

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Abstract

Portland cement is one of the most used material in the world. Due the environmental problems related to its use, such as CO₂ emission and use of non-renewable raw materials, new materials are being researched. In this context, an alternative is the use of pozzolanic materials replacing partially the Portland cement. Wastes from agroindustry are being studied as pozzolanic materials, and this paper try to analyze the potential use of the sugar cane straw ash (SCSA) as replacement product. This material was obtained from the autocombustion of sugar cane straw. The aim of this paper is to assess SCSA reactivity and the mechanical properties of SCSA containing systems. Characterization of SCSA (XRD, chemical composition, particle size and microscopy) and reactivity studies on hydrated lime/SCSA and Portland cement/SCSA pastes through infrared spectroscopy, thermogravimetry and microscopy tests demonstrated the high pozzolanic activity point of view. This reactivity let to reach good mechanical properties for mortars in which 15-30% of cement was replaced by SCSA. Compressive strength of mortars containing SCSA reached similar values than those found for control mortars in the 3-90 days curing period. The results from microstructural and mechanical properties showed that SCSA can replace partially the cement Portland.

Keywords: sugar cane straw ash, autocombustion, Portland cement, microstructural characterization, mechanical properties, pozzolanic reactivity, lime paste, cement paste, mortar

1. Introduction

Portland cement is widely used in the world nowadays, with a global consumption about of 3.7 billion tons [1]. In addition, Portland cement production represents 5-8% of total CO₂ emission in the world [2], and, to produce 1 ton of the binder, 2.8 tons of raw materials are necessary [3]. These information shows how important is to reduce cement Portland consumption due the environmental problems caused by its production. Hence, alternative materials are being researched to diminish these problems, where one of the solutions is the use of pozzolanic materials replacing partially the Portland cement.

A long time ago, pozzolanic materials were used firstly in Roman Empire, when natural pozzolans were mixed with lime to create a strength and durable material in civil building [4-6]. Nowadays, the use of pozzolans is not only for ecological reasons, but also technological, because this material increases the mechanical strength and improve the durability of blended Portland cements [5-17]. There are two main types of pozzolanic materials: natural and artificial. Natural pozzolans are related to the residues from volcanic activities or deposits of diatomaceous earth, whereas artificial pozzolans are related to products (e.g.: metakaolin), byproducts or waste from industry and agroindustry [4].

Examples of byproducts from industry that are widely known as pozzolanic materials are silica fume and fly ash [18-20]. Many byproducts made from commodity crops are cheap, plenty, worldwide distributed and renewable resources that are suitable for the production of pozzolans: rice husks, sugar cane bagasse palm oil wastes, wheat straw, eucalyptus waste, bamboo leaves among others [21, 22]. In this way, these agroindustry wastes can be converted into ashes (with or without energy recovery), and researches on them are taking part due to good results replacing partially Portland cement [21-26]. In this context, this paper presents another agroindustry waste from sugar cane production: the sugar cane straw ash (SCSA).

The problem related to SCSA starts with the production of sugar cane, which is increasing in Brazil due the production of sugar, alcohol and energy. In 2003/2004, the sugar cane production in Brazil was 358.7

million tons and, in 2013/2014, the production expanded to 653.4 million tons [28], which represents an increment of 82.2% in the production of sugar cane in only 10 years. The part of the plant that is removed during the sugar cane collecting is called sugar cane straw, and it is composed of leaves and the top of the plant [29]. According to the Center of Strategic Studies Management (CGEE), 1000 kg of sugar cane generates 140 kg of sugar cane straw [30]. Since this byproduct is mostly left in the field after the harvest, there are researches about new techniques to collect the sugar cane straw in order to generate energy [31]. The calorific value of sugar cane straw is in the range of 13-19 kJ/ton [31-33] and can be compared to the sugar cane bagasse [34], becoming attractive to generate energy through a burning process.

After the sugar cane straw burning, a waste is generated: the sugar cane straw ash. Studies showed around 3-5.5 kg of ash are obtained from burning 100 kg of sugar cane straw [33, 35]. Knowing the problems of disposal and the high volume of the residue, an appropriate final destination for this ash would be the building construction sector as a pozzolanic material, replacing partially the Portland cement.

Some authors previously studied the pozzolanic activity of SCSA and highlighted it is a very reactive pozzolan [35-40]. Comparisons among SCSA and other pozzolanic materials from agroindustry have been carried out; Martirena et al. [36] compared SCSA and sugar cane bagasse ash (SCBA) in hydrated lime-pozzolan pastes. The authors concluded that the SCSA is more reactivity than SCBA at earlier curing times through microstructural analysis, and mortars containing SCSA presented higher compressive strength after 28 days of curing. In addition, in terms of comparisons, Villar-Cociña et al. compared SCSA and rice husk ash (RHA) by a kinetic-diffusive model to evaluate their reactivity. In this comparison, authors established SCSA presented better reactivity [37].

It is well known that the temperature of calcination influences on the pozzolanic properties of ashes. Then, some authors studied different preparations of the SCSA. Martirena et al. [38] studied a rudimentary incinerator to burn the straw to obtain the SCSA, and compared it to a straw burnt in open-air. The temperature of burning in the incinerator was 600°C for 1-3 hours, and the remaining ash was cooled for 2 hrs. TG, XRD, SEM analysis and compressive strength of pastes let to conclude there are no significant differences by using open-air burnt or incinerator, due the long-time in the incinerator and slow cooling process. Frías et al. [35] studied two different temperatures of straw calcination during 20

minutes: 800°C and 1000°C. Both SCSA obtained were characterized and assessed through lime fixation, and authors concluded that both ashes presented similar activity. Guzmán et al. [40] assessed three procedures to obtain SCSA: burning at 590°C, at 700°C and combined methods with pre-combustion and burning at 700°C. The third method presented the highest amorphous silica content, and the corresponding ash was assessed in mortars replacing partially the Portland cement. Authors concluded the best content of SCSA in terms of mechanical development was between 10 and 20% of substitution. Additional research was carried out on the preparation of pozzolans by calcinations of a mixture of sugar cane straw and clay (20-30%): SCSA had a high pozzolanic activity but its reactivity decreased with increasing the clay content and calcination temperature [41].

This interesting field of the reusing of agrowastes in the production of binders requires more research related to the reactivity and microstructure of SCSA containing binders. Moreover, easier obtaining methods for SCSA are necessary in order to have sufficient amount for preparing different types of mixtures. In this work, the main objective is to assess the sugar cane straw ash (SCSA) obtained from an autocombustion process as pozzolanic material in blended Portland cement. SCSA was chemically and physically characterized, and its pozzolanic reactivity was assessed in pastes of hydrated lime/SCSA and Portland cement/SCSA. Finally, compressive strength of mortars with Portland cement/SCSA proportions of 100:0, 85:15, 80:20, 75:25 and 70:30 in mass was evaluated for several curing times.

2. Materials and Methods

2.1. Materials

Sugar cane straw was obtained from sugar cane plantations near the city of Ilha Solteira (São Paulo, Brazil), and was burned in a furnace by autocombustion without temperature control for 6 hours. The maximum reached temperature into the furnace was 700°C, that is very appropriate for removing organic matter and stabilize the amorphous phases of the SCSA. Afterwards, the SCSA obtained was passed through sieves to remove some unburned material, and the passing fraction was milled for 50 minutes to reduce the particle size in order to increase pozzolanic activity [24]. After these procedures, SCSA was characterized and assessed in pastes and mortars.

Hydrated lime ($\text{Ca}(\text{OH})_2$) used has high purity ($> 95\%$ of calcium hydroxide) and was mixed in pastes with SCSA in order to evaluate the pozzolanic reactivity. Portland cement used in pastes and mortars was the Brazilian Portland Cement CPV ARI, which is composed by more than 95% of clinker and it do not contain pozzolans (appropriate for avoiding interferences with with the pozzolanic reaction of SCSA). Sand was obtained from Castilho (São Paulo, Brazil) city, and presents a fineness modulus of 2.05 and specific gravity of 2667 kg/m^3 .

2.2. Methods

2.2.1 Chemical and physical characterization of SCSA

Chemical composition of sugar cane straw ash was obtained through X-Ray Fluorescence by means of XRF Philips Magix Pro. This test was performed to evaluate percentages of the SiO_2 and Al_2O_3 , important oxides in the pozzolanic reactivity [4]. To assess mineralogical properties of the sugar cane straw ash, X-Ray Diffraction test was carried out. Equipment used was XR Diffractometer Seifert TT, using $\text{Cu-K}\alpha$ radiation and a Ni filter, with a voltage of 40 kV and current intensity of 20 mA. The test was performed in the 2θ range $5\text{--}60^\circ$ with a step of 0.02° and step time of 2 s/step. Particle size of sugar cane straw ash before and after milling was obtained by means of Malvern Instruments Mastersizer 2000: mean particle diameter (D_{med}) and median particle diameter (D_{50}) were measured for evaluating the efficiency of the milling process. SEM micrographs were taken in a JEOL JSM-6300 scanning electron microscope.

2.2.2. Preparation and characterization of hydrated lime/SCSA and Portland cement/SCSA pastes

Hydrated lime/SCSA pastes (CH/SCSA) were prepared using the hydrated lime:pozzolan:water 3:7:8 ratio (by weight), and cured at 20°C with relative humidity (RH) higher than 95%. In Portland

cement/SCSA mixtures (OPC/SCSA), a proportion of water/cementitious material 0.5 was selected (being the cementitious material the sum of OPC and SCSA), and the proportions of OPC/SCSA assessed were 100/0 (control) and 85/15, both also cured at 20° with RH higher than 95%.

Microstructure of pastes were characterized by three instrumental techniques: Fourier transform infrared spectroscopy (FTIR, Bruker TENSOR 27 model, wavenumber spectrum between 4000 cm^{-1} and 400 cm^{-1}), scanning electron microscopy (SEM, JEOL JSM-6300) and thermogravimetric analysis (TG, TGA 850 Mettler-Toledo model). Thermogravimetry tests were performed in 100 μL sealed pin-holed aluminium crucibles at a heating rate of 10°C min^{-1} , from 35°C to 600°C, in an N_2 atmosphere (75 $\text{mL}\cdot\text{min}^{-1}$ gas flow).

Both type of paste systems, CH/SCSA and OPC/SCSA, were analyzed after 3, 7, 28 and 90 days of curing through FTIR and TG, and after 28 days of curing for SEM. About samples preparations for FTIR and TG analysis, pastes were ground with acetone, filtered and put in a laboratory oven at 60°C for 30 minutes. In samples preparation for SEM analysis, small fractured pieces of paste were submerged in acetone for 1 hour, and put in laboratory oven at 60°C for 30 minutes.

2.2.3. Compressive strength of mortars

Compressive strengths of the mortars were measured through an EMIC Universal Machine with a 2000 kN limit of load. For this test, prismatic specimens 40x40x160 mm^3 were molded. Previously to compressive strength measurement, three specimens were broken in flexural mode for obtaining two half parts for specimen. The compressive strength was an average of six values. The proportion of water/cementitious material was 0.50, and the proportion cementitious material:sand was 1:2.5. The replacement of Portland cement by SCSA was 0% (control), 15%, 20%, 25% and 30% by weight. Specimens were cured at 25°C with RH higher than 95% until the compressive strength test, which was performed after 3, 7, 28 and 90 days of curing. **3. Results and discussions**

3.1 Chemical and physical characterization of SCSA

Chemical composition for SCSA measured by XRF is shown in Table 1. The material presents a low quantity of SiO₂ (36.5%) if compared with traditional siliceous pozzolans (e.g. silica fume or rice husk ash). It is noticeable the presence of CaO (16.4%), but SCSA has not hydraulic characteristics: mixtures of this ash with alkaline medium did not harden after 24 hours. The third element in percentage is potassium (K₂O, 7.9%), which is typical of some ashes from biomass [42]. There is also presence of others significant elements, such as Al₂O₃, Fe₂O₃, MgO, SO₃ and P₂O₅. A considerable LOI value (15.5%) was obtained, which was attributed to the presence of organic matter and/or carbon of unburned sugar cane straw. Thus, thermogravimetric analysis and differential thermal analysis of SCSA showed that the main mass loss was produced in the 250-625°C range, which are the typical volatilization/oxidation temperatures of organic matter and carbon [43]. A small mass loss above 650°C (0.34%) was observed, indicating that the presence of calcium carbonate was very low.

X-Ray diffraction (XRD) pattern of SCSA is shown in Figure 1. It is of SCSA presented a deviation of the baseline between $2\theta = 15^\circ$ and $2\theta = 35^\circ$, which is a characteristic of amorphous material. In addition, quartz (SiO₂, PDF Card #331161), calcite (CaCO₃, PDF Card #050586) and diopside (MgCaSi₂O₆, PDF Card #011-0654) as impurities in the SCSA were identified. Probably these impurities were from the soil retained during the sugarcane harvesting. An XRD was carried out on a sample of SCSA obtained from washed straw (without soil impurities): in this X-Ray diffractogram only some saline compounds were found, such as silvite (KCl, PDF Card #411476), halite (NaCl, PDF Card #050628), arkanite (K₂SO₄, PDF Card #050613) and hydroxylapatite (Ca₅(PO₄)₃(OH), PDF Card #090432). These salts were formed, in the calcination process, from selected elements contained in the straw: sodium, chloride, potassium, calcium, sulphur and phosphorus.

Particle size distribution is show in Figure 2. The calculated mean particle diameter (d_{med}) of SCSA was 20.18 μm , and median particle diameter D_{50} was 10.85 μm . Figure 3 shows SEM micrographs for comparison between the SCSA before the milling process and after 50 minutes of milling. In Figure 3a, SCSA before the milling process presents large and irregular particles and, in Figure 3b, SCSA after 50 minutes milling presents smaller and more regular particles compared to SCSA without milling.

Table 1 – Chemical composition of SCSA (in percentage)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	P ₂ O ₅	Cl	Others	LOI
36.5	2.8	3.4	16.4	7.3	0.2	7.9	4.4	4.0	0.4	1.2	15.5

Figure 1 – X-Ray Diffraction pattern of SCSA

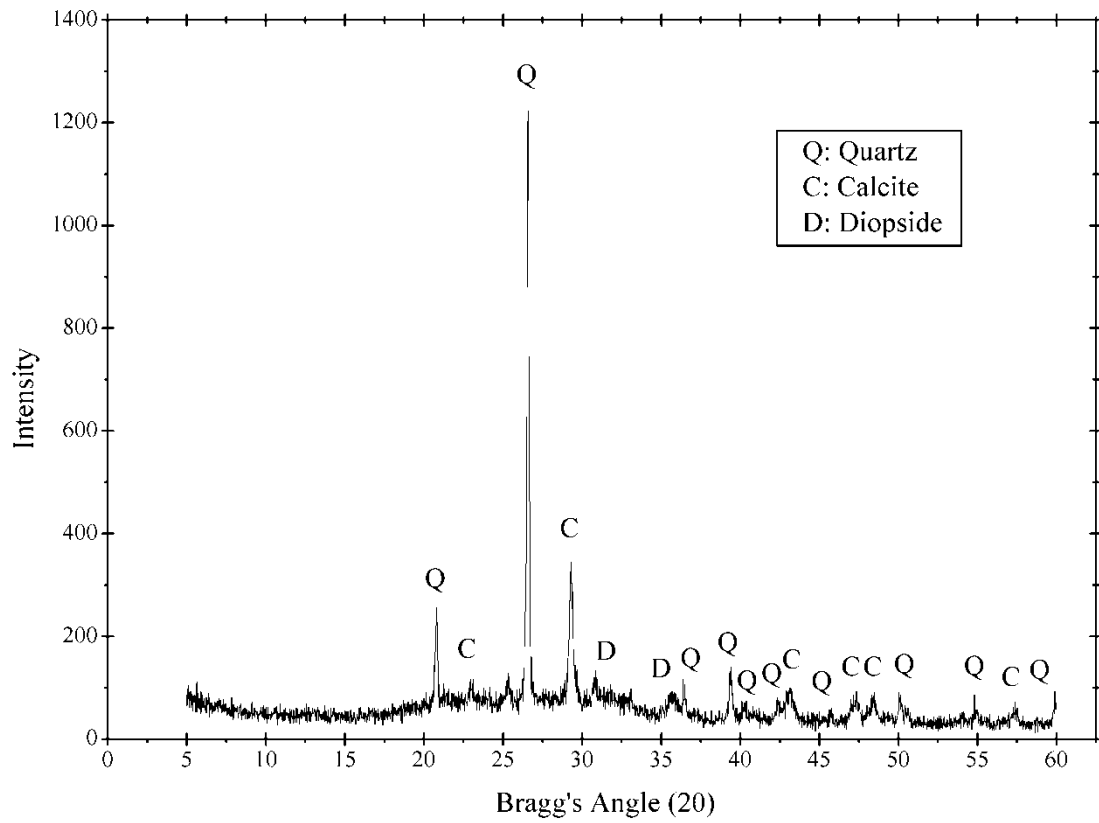


Figure 2 – Particle size distribution of SCSA (Dashed line: cumulative curve; solid line: derivative curve)

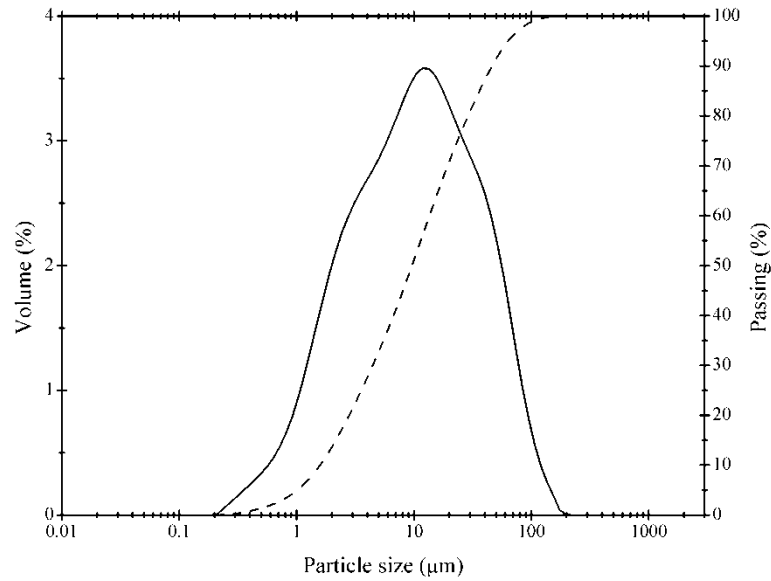
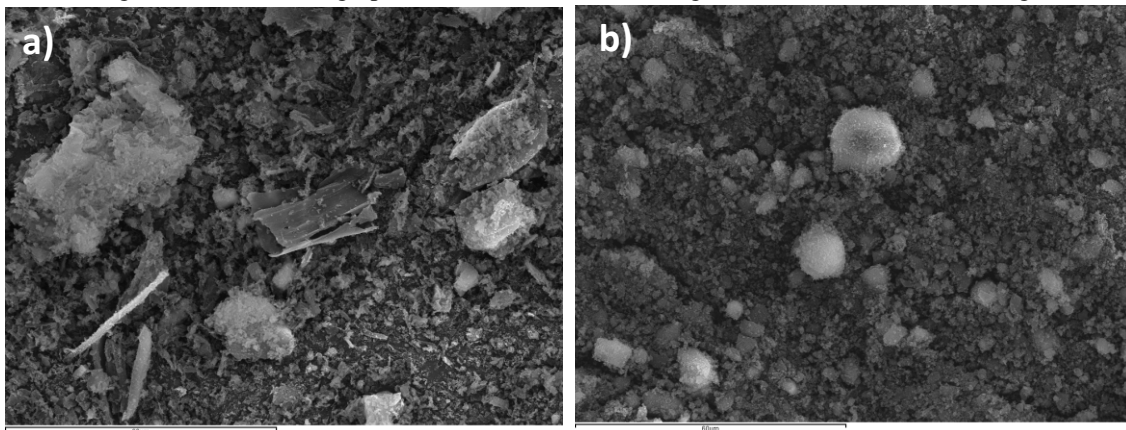


Figure 3 – SEM micrographs of SCSA: a) before milling; b) after 50 minutes of milling



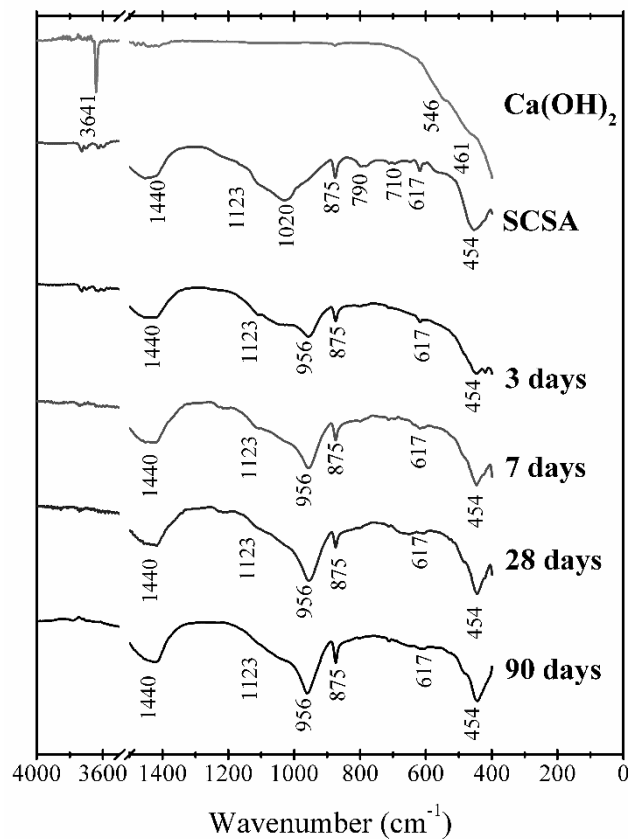
3.2. Microstructural studies of CH/SCSA pastes

CH/SCSA pastes with 3:7 ratio, cured at 20°C were characterized by FTIR, TG and SEM.

FTIR spectra for hydrated lime ($\text{Ca}(\text{OH})_2$), SCSA and CH/SCSA pastes are shown in Figure 4. The bands of vibration for $\text{Ca}(\text{OH})_2$ are 3641 cm^{-1} (strong, O-H vibration) and very small peaks below 600 cm^{-1} , emphasizing the peaks at 546 cm^{-1} and 461 cm^{-1} . For SCSA, main bands of vibrations were: associated to Si-O vibrations 1123 cm^{-1} , 1020 cm^{-1} , 790 cm^{-1} , 710 cm^{-1} , 617 cm^{-1} , 454 cm^{-1} , and associated to O-C-O vibrations 1440 cm^{-1} and 875 cm^{-1} [44].

After 3 days of curing, the main bands of vibration in the paste are 1123 cm^{-1} , 956 cm^{-1} , 617 cm^{-1} , 454 cm^{-1} (Si-O vibration), 1440 cm^{-1} and 875 cm^{-1} (O-C-O vibration). Firstly, it is noticed the hydrated lime was completely reacted, because the characteristic bands of vibration (3641 cm^{-1} and below 600 cm^{-1}) are not present in FTIR spectrum. The bands of vibration 1123 cm^{-1} and 454 cm^{-1} are attributed to quartz present in SCSA, because these peaks are maintained in the FTIR spectrum after the pozzolanic reaction. On the other hand, the new band of vibration at 956 cm^{-1} is related to the pozzolanic reaction products, since it was not present in the hydrated lime neither in the SCSA spectra. This band can be attributed to the C-S-H product formed in the pozzolanic reaction. Its intensity is increased with curing time, suggesting that despite the complete consumption of CH in the CH/SCSA mixture, C-S-H evolved with curing time, and polymerization of SiO_2 units took place. Finally, the bands of vibration at 1440 cm^{-1} and 875 cm^{-1} did not change with the pozzolanic reaction, indicating that carbonates are not involved in the process.

Figure 4 – FTIR spectra for CH/SCSA pastes



DTG curves from TG analysis are shown in Figure 5. Dehydration of compounds formed through pozzolanic reaction, mainly C-S-H, took place, in the TG conditions used [45], at the temperature range of 100-180°C, and mass loss of the Ca(OH)₂ dehydration was at temperature range of 520-560°C. In this analysis, there was no mass loss at 520-560°C for all curing ages, that is, SCSA consumed all the Ca(OH)₂ present in the paste. This result matches with FTIR analysis.

Table 2 summarizes the mass loss related to the dehydration of compounds from pozzolanic reaction (P_{PZ}), from Ca(OH)₂ dehydration (P_{CH}) and lime fixation for all curing ages of CH/SCSA pastes. Since there was no peak in DTG curves in 520°C-560°C, the lime fixation yielded 100%, i.e., the SCSA consumed all the Ca(OH)₂ added to the paste. The mass loss related to the compounds formed through pozzolanic reaction are increasing with curing time due the change in composition of these compounds: initially formed C-S-H gel (with the typical formula (CaO)_x(SiO₂)_y (H₂O)_n) had a high Ca/Si ratio (x/y),. With curing time, the x/y ratio diminishes because more silica from SCSA react and it is bonded to C-S-H gel [45]. Thus, the amount of C-S-H gel increases, and then the released water when heating becomes greater.

Table 2 – Mass loss due to dehydration of compounds from pozzolanic reaction (P_{PZ}), from Ca(OH)₂ dehydration (P_{CH}) and lime fixation

Curing time (days)	P _{PZ} (%)	P _{CH} (%)	Lime fixation (%)
3	13.42	0	100
7	15.34	0	100
28	17.00	0	100
90	17.54	0	100

Figure 6 shows SEM micrographs from CH/SCSA paste after 28 days of curing. As expected taking into account TG and FTIR assessments, there is an amorphous gel formed due the pozzolanic reaction, a dense structure is obtained and the presence of hydrated lime is not noticed. Some C-S-H gel appeared in the form of needle-like products.

Figure 5 – DTG curves for CH/SCSA pastes

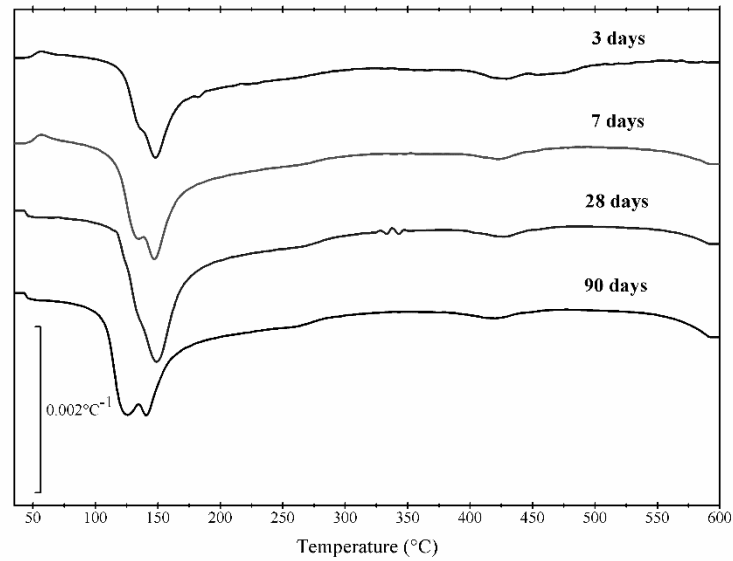
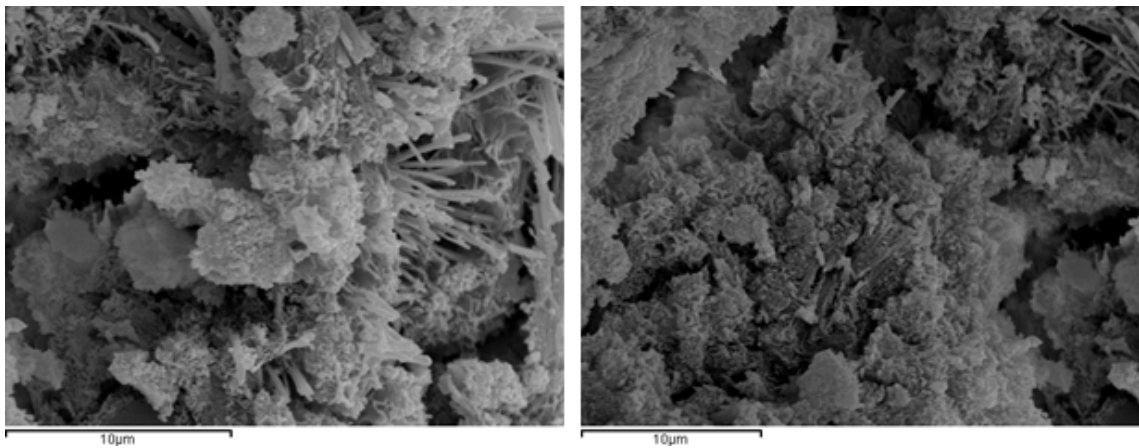


Figure 6 – SEM images of CH/SCSA paste after 28 days of curing

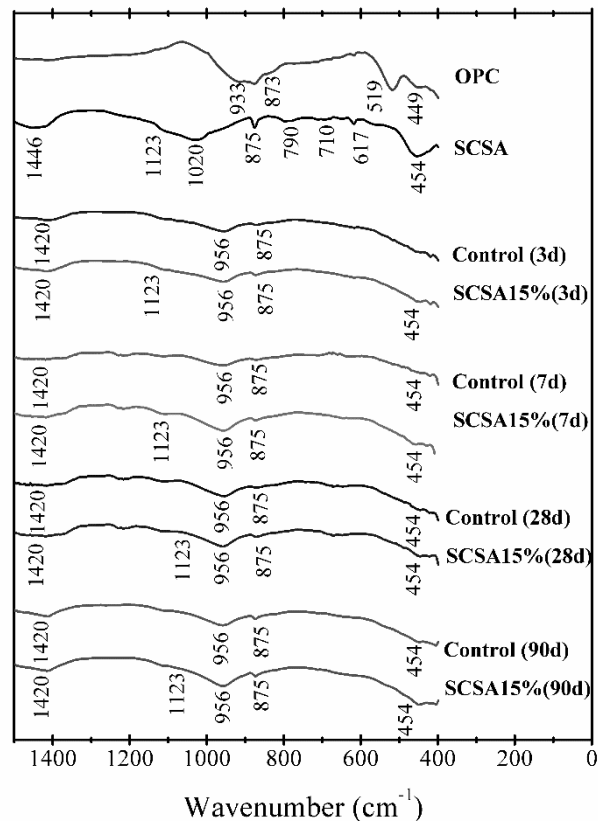


3.3. Microstructural studies of OPC/SCSA pastes

OPC/SCSA pastes with 85:15 ratio, cured at 20°C, were characterized by FTIR, TG and SEM. Also, control OPC pastes were prepared for comparison. Figure 7 shows the FTIR spectra for anhydrous OPC, SCOSA, OPC pastes and OPC/SCSA pastes. The bands of vibration for unhydrated OPC related to Si-O vibrations are: 933 cm^{-1} , 873 cm^{-1} , 519 cm^{-1} and 449 cm^{-1} . After 3 days of curing, the OPC pastes showed a main Si-O type vibration band at 956 cm^{-1} (due to the stretching Si-O in polymeric SiO_4 units produced in the hydration of calcium silicates; and another two O-C-O bands at 1420 cm^{-1} and 873 cm^{-1} were observed. The paste containing SCOSA also presented a peak at 1123 cm^{-1} (Si-O vibration) which was also

found in the original SCSA. Firstly, it is noticed that the band of vibration at 956 cm^{-1} of OPC/SCSA pastes is similar that those found in CH/SCSA pastes (Figure 4), which means the products of the pozzolanic reaction (C-S-H) are similar to those obtained by the OPC hydration. The broadness of this main vibration band for OPC/SCSA hydrated sample was due to the SCSA (the ash presented a band at 1020 cm^{-1}), indicating that this material did react completely in the conditions of the hydration of cement. Finally, the band of vibration at 1123 cm^{-1} (which not appeared in OPC paste) is related to the quartz present in SCSA: this mineral did not react in the studied conditions. After 7, 28 and 90 days of curing, pastes did not show significantly changes compared to 3 days of curing: it may be noticed the band intensity increase for 956 cm^{-1} signal (related to the higher amount of C-S-H gel). The diminution of its shoulder at higher wavenumber in OPC/SCSA pastes suggested the reaction of SCSA and the dissolution/transformation of this material due to pozzolanic process.

Figure 7 – FTIR spectra for anhydrous OPC, SCSA, OPC pastes and OPC/SCSA pastes



DTG curves for OPC/SCSA pastes are shown in Figure 8. Similar hydration products were found for both OPC and OPC/SCSA pastes. In all curing times, the peak presented at 550°C is smaller in the SCSA

containing paste compared to control one. This behavior is due to two effects: on one hand, the dilution effect when SCSA replaced OPC, because less portlandite in the hydration of cement is formed; on the other hand, due to the consumption of the Portlandite by reaction towards SCSA.

Mass loss related to the dehydration of compounds from OPC and pozzolanic reaction (P_{OPC+PZ}), $Ca(OH)_2$ dehydration (P_{CH}) and lime fixation for OPC and OPC/SCSA pastes at all curing ages are summarized in Table 3. It is noticed that the P_{OPC+PZ} value increases with curing age for both pastes, but the paste with SCSA presents higher values compared to the control at first curing times (3 and 7 days). This behavior showed that the pozzolanic material is very reactive. Additionally, the presence of SCSA particles acts as nucleation sites for hydration products from OPC and the hydration reaction rate was enhanced. This reactivity was quantified by means of lime fixation. At 3 days of curing, 19.61% of Portlandite released in the hydration of OPC in OPC/SCSA paste was consumed: this behavior indicated that the pozzolanic reactivity was important at earlier curing ages. The pozzolanic reactivity increased with curing time, and percentage of lime fixation reached 41.18% after 90 days.

Figure 8 – DTG curves for OPC and OPC/SCSA (15% replacement) pastes for different curing times

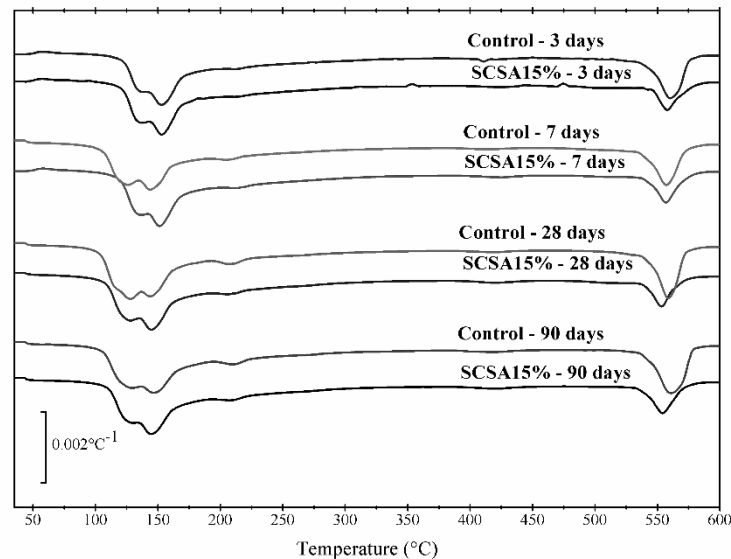


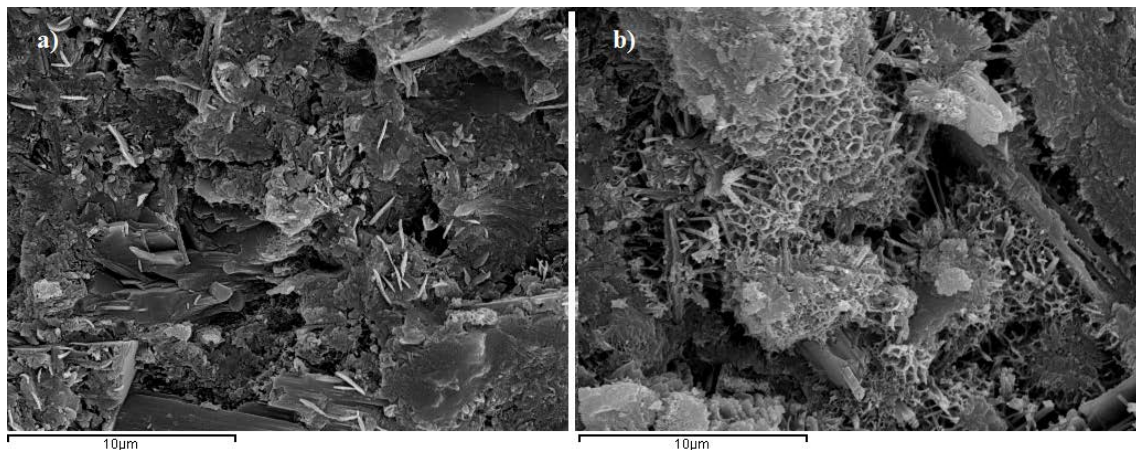
Table 3 – Mass loss in the dehydration of compounds from OPC hydration/pozzolanic reaction (P_{OPC+PZ}), $Ca(OH)_2$ dehydration (P_{CH}) and lime fixation for OPC and OPC/SCSA (15% replacement) pastes

Curing time	P_{OPC+PZ} (%)	P_{CH} (%)	Lime
-------------	------------------	--------------	------

(days)					fixation (%)
	OPC	OPC/SCSA	OPC	OPC/SCSA	
3	13.79	15.09	2.40	1.64	19.61
7	15.47	16.00	2.51	1.68	21.26
28	17.43	17.36	2.92	1.53	38.36
90	17.53	17.49	3.20	1.60	41.18

Figure 9 shows SEM micrographs of OPC and OPC/SCSA pastes. In both figures, there is a dense and amorphous structure, but the control OPC paste (Fig. 9a) presents more portlandite compared to the OPC/SCSA paste (Fig.9b). This is in agreement to thermogravimetric results.

Figure 9 – SEM images of pastes after 28 days of curing: a) control OPC; b) OPC/SCSA (15% replacement)



3.4 Compressive strength of mortars

Five sets of mortars were prepared: control mortar (only OPC as cementitious compound) and four OPC replaced mortars in which 15-30% of OPC was replaced by SCSA in mass: SCSA mortar nomenclature was SCSA-XX% where XX is the replacement percentage (15, 20, 25 and 30%). Compressive strengths and their standard deviation values of mortars are listed in Table 4. All mortars showed a continuous increasing in the compressive strength with curing time as expected. Interestingly, after 3 days of curing, all mortars containing SCSA presented very similar compressive strength than that obtained for control one. This fact is related to the high reactivity of the ash, which agree to the behavior described in the

paste studies. This trend also was observed for 7-90 days curing period. In this case, the consumption of Portlandite by SCSA (observed by TG analysis) for longer curing times did not make evident an enhancement in the compressive strength development.

Table 4 – Compressive strength values (MPa) of mortars and their standard deviation

Specimen/Curing Age	3 days	7 days	28 days	90 days
Control	32.93 ± 1.13	36.06 ± 1.94	41.56 ± 1.70	44.01 ± 2.25
SCSA-15%	32.27 ± 1.30	34.53 ± 0.12	40.55 ± 1.27	44.33 ± 2.55
SCSA-20%	31.08 ± 1.41	36.56 ± 1.11	42.82 ± 1.41	44.42 ± 2.38
SCSA-25%	30.55 ± 0.98	33.97 ± 1.87	42.51 ± 1.51	43.99 ± 1.82
SCSA-30%	31.83 ± 0.16	34.73 ± 0.56	40.28 ± 1.41	40.99 ± 1.11

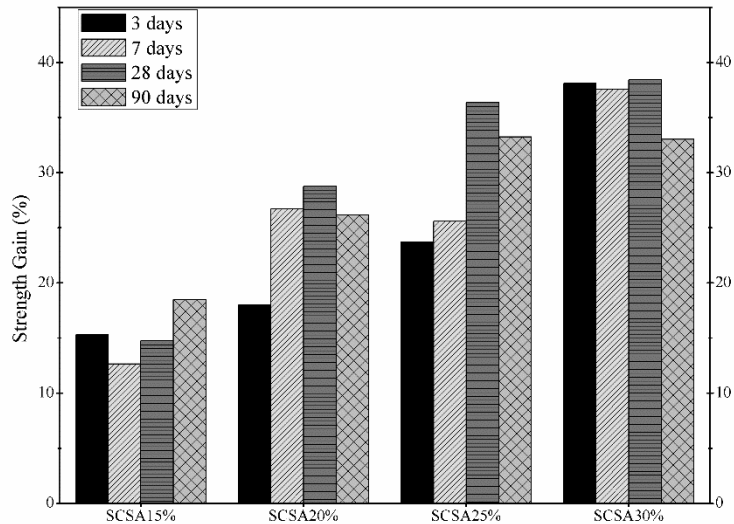
In general terms, from the strength development point of view, and taking into account the important replacement levels achieved in this study, it can be established that there is an important strength gain for replaced mortars.

Figure 10 shows the compressive strength gain (SG) [46] of SCSA mortars. This SG was calculated taking into account the replacement percentage of OPC by the pozzolan; the compressive strength of OPC/SCSA mortar (R_i) was compared with the strength of the OPC mortar (R_o), which was corrected by means of the ratio between OPC mass (w_{cem}) and the binder mass (sum of OPC and pozzolan, $w_{cem}+w_{puz}$). In this case, relative values in percentage were calculated as follows:

$$SG = \frac{R_i - \left[R_o * \frac{w_{cem}}{w_{cem} + w_{puz}} \right]}{\left[R_o * \frac{w_{cem}}{w_{cem} + w_{puz}} \right]} * 100 \quad Eq. 1$$

All SG values calculated according to Eq. 1 were positive values, indicating the high effectivity of SCSA in cement mixtures. Calculated SG values are depicted in Figure 10. SG values were increasing with the replacing percentage. It is noticed that SCSA30% presented the highest strength gain since earlier curing ages. This behavior means that good strengths would be obtained for higher replacing percentages.

Figure 10 – Strength gain (SG) for SCSA containing mortar at 3, 7, 28 and 90 days of curing.



Conclusions

Sugar cane straw ash (SCSA) was chemically and physically characterized: the material presented a relatively low content of SiO_2 (36%) and high unburned fraction (LOI = 15.5%). A baseline deviation in XRD between 15 and 35° showed the presence of amorphous fraction, probably reactive from the pozzolanic point of view. Pozzolanic reactivity was confirmed by means of thermogravimetric studies (TG) on hydrated lime and ordinary Portland cement pastes.

In hydrated lime/SCSA pastes, TG analysis showed that pozzolanic material consumed completely available calcium hydroxide after 3 days of curing. In cement pastes, replaced 15% by SCSA, more than 40% of Portlandite was fixed, and SEM images showed a lower presence of Portlandite crystals

Finally, from the study of mortars, SCSA presented an important contribution on the development of compressive strength when Portland cement was replaced in the 15-30% by weight. Pozzolanic activity was observed after 3 days of curing, and all mortars showed compressive strength close to control. In strength gain analysis, SCSA replacement of 30% showed the best result, since there is less Portland cement and the compressive strength still is similar to other mortars. This study showed that Portland cement can be replaced until 30% by SCSA and the mechanical properties were maintained.

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References

- [1] FICEM - Inter-American Cement Federation. Statistical Report 2013. http://www.ficem.org/estadisticas/statisal_report_2013.pdf. (11/03/2014).
- [2] Sharp JH, Gartner EM, Macphee DE. Novel cement system (sustainability). Session 2 of the Fred Glasser cement science symposium. *Adv Cem Res* 2010; 22(4): 195–202.
- [3] Guo X, Shi H, Dick WA. Compressive strength and microstructural characteristics of class C fly ash geopolymer. *Cem Concr Compos* 2010; 32:142–147.
- [4] Hewlett, P. C. *Lea's Chemistry of Cement and Concrete*. ELSEVIER, Fourth Edition, 2008.
- [5] Vejmelková E, Keppert M, Rovnaníková P, Keršner Z, Cerny R. Application of burnt clay shale as pozzolan addition to lime mortar. *Cem Concr Compos* 2012; 34:486-492.
- [6] Sánchez-Moral S, Luque L, Cañaveras JC, Soler V, Garcia-Guinea J, Aparicio A. Lime pozzolana mortars in Roman catacombs: composition, structures and restoration. *Cem Concr Res* 2004; 35:1555-1565.
- [7] Ghrici M, Kenai S, Meziane E. Mechanical and durability properties of cement mortar with Algerian natural pozzolana. *J Mater Sci* 2006; 41:6965-6972.
- [8] Ramezani pour AA, Jovein HB. Influence of metakaolin as supplementary cementing material on strength and durability of concretes. *Constr Build Mater* 2012; 30:470-479.
- [9] Abd-El-Aleem S, Abd-El-Aziz MA, El-Didamony H. Calcined Carbonaceous Shale Pozzolanic Portland cement. *Egypt J Chem* 2002; 45(3):501-517.
- [10] El-Didamony H, Abd-El-Aleem S. Calcination and Hydration Characteristics of Carbonaceous Shale - Limestone Mixes. *Sil Ind* 2002; 67(11-12):123-128. [11] Senhadji Y, Escadeillas G, Mouli M, Khelafi H, Benosman. Influence of natural pozzolan, silica fume and limestone fine on strength, acid resistance and microstructure of mortar. *Powder Technol* 2014; 254:314-323.
- [12] Ghiasvand E, Ramezani pur AA, Ramezani pur A. M. Effect of grinding method and particle size distribution on the properties of Portland-pozzolan cement. *Constr Build Mater* 2014; 53:547-554.

- [13] Celik, K, Meral C, Mancio M, Mehta PK, Monteiro PJ. M. A comparative study of self-consolidating concretes incorporating high-volume natural pozzolan or high-volume fly ash. *Constr Build Mater* 2014; 67:14-19.
- [14] Peng G, Ma Q, Hu H, Gao R, Yao Q, Liu Y. The effects of air entrainment and pozzolans on frost resistance of 50–60 MPa grade concrete. *Constr Build Mater* 2007; 21:1034-1039
- [15] Kaid N, Cyr M, Julien S, Khelafi H. Durability of concrete containing a natural pozzolan as defined by a performance-based approach. *Constr Build Mater* 2009; 23:3457-3467.
- [16] Nili M, Salehi AM. Assessing the effectiveness of pozzolans in massive high-strength concrete. *Constr Build Mater* 2010; 24:2108-2116.
- [17] Sata V, Jaturapitakkul C, Kiattikomol K. Influence of pozzolan from various by-product materials on mechanical properties of high-strength concrete. *Constr Build Mater* 2007; 21:1589-1598.
- [18] Giner VT, Ivorra S, Baeza FJ, Zornoza E, Ferrer B. Silica fume admixture effect on the dynamic properties of concrete. *Constr Build Mater* 2011; 25:3272-3277.
- [19] Belén G, Fernando M, Isabel M, Javier E. Structural shear behaviour of recycled concrete with silica fume. *Constr Build Mater* 2009; 23:3406-3410.
- [20] Supit SWM, Shaikh FUA, Sarker, PK. Effect of ultrafine fly ash on mechanical properties of high volume fly ash mortar. *Constr Build Mater* 2014; 51:278-286.
- [21] Payá J, Monzó J, Borrachero MV. Outstanding aspects on the use of rice husk ash and similar agrowastes in the preparation of binders. In *Proceedings of the First Pro-Africa conference: Non conventional building materials based on agroindustrial wastes*. Pirassununga 18th-19th October 2010, São Paulo (Brazil).
- [22] Asha P, Salman A, Kumar RA. Experimental study on concrete with bamboo leaf ash. *Int J Eng Adv Technol* 2014; 3:46-51.
- [23] Payá J, Monzó J, Borrachero MV, Peris-Mora E, Ordóñez LM. Studies on crystalline rice husk ashes and the activation of their pozzolanic properties. *Waste Manage* 2000; 1:493-503.
- [24] Cordeiro GC, Toledo Filho RD, Tavares LM, Fairbairn EMR. Ultrafine grinding of sugar cane bagasse ash for application as pozzolanic admixture in concrete. *Cem Concr Res* 2009; 39:110-115.
- [25] Cordeiro GC, Toledo Filho RD, Fairbairn EMR. Effect of calcination temperature on the pozzolanic activity of sugar cane bagasse ash. *Constr Build Mater* 2009; 23:3301-3303.

- [26] Aprianti E, Shafiq P, Bahri S, Farahani JN. Supplementary cementitious materials origin from agricultural wastes – A review. *Constr Build Mater* 2015; 74:176–187.
- [27] Demis S, Tapali JG, Papadakis VG. An investigation of the effectiveness of the utilization of biomass ashes as pozzolanic materials. *Constr Build Mater* 2014; 68:291–300
- [28] Unica - União da Indústria de Cana-de-Açúcar. Produção de cana-de-açúcar, 2003/2014 - 2013/2014. <http://www.unicadata.com.br>. Accessed 18 September 2014.
- [29] Costa SM, Mazzola PG, Silva JCAR, Pahl R, Pessoa Jr A, Costa SA. Use of sugar cane straw as a source of cellulose for textile fiber production. *Ind Crop Prod* 2013; 42:189–194.
- [30] BNDES and CGEE - Centro de Gestão e Estudos Estratégicos. Sugarcane-Based Bioethanol: Energy for Sustainable Development, 1st ed., Rio de Janeiro (Brazil), 2008.
- [31] Ripoli MLC, Gamero CA. Palhiço de cana-de-açúcar: ensaio padronizado de recolhimento por enfardamento cilíndrico. *Energia na Agricultura (Brazil)* 2007; 22(1):75-93.
- [32] Hoi LWS, Martincigh BS. Sugar cane plant fibres: Separation and characterization. *Ind Crop Prod* 2013; 47:1-12.
- [33] Deepchand K. Characteristics, Present Use and Potential of Sugar Cane Tops and Leaves. *Agr Wastes* 1986; 15:139-148.
- [34] Hugot E, 1986. *Handbook of Cane Sugar Engineering*, 3rd ed. Elsevier Science Publishers, Amsterdam.
- [35] Frías M, Villar-Cociña E, Valencia-Moraes E. Characterization of sugar cane straw waste as pozzolanic material for construction: Calcining temperature and kinetic parameters. *Waste Manage* 2007; 27:533-538.
- [36] Martirena JF, Middendorf B, Gehrke M, Budelmann H. Use of wastes of the sugar industry as pozzolana in lime-pozzolana binders: study of the reaction. *Cem Concr Res* 1998; 28(11):1525-1536.
- [37] Villar-Cociña E, Moraes EV, Rodríguez RG, Ruíns JH. Kinetics of the pozzolanic reaction between lime and sugar cane straw ash by electrical conductivity measurement: A kinetic–diffusive model. *Cem Concr Res* 2003; 33:517-524.
- [38] Martirena JF, Middendorf B, Day RL, Gehrke M, Roque P, Martínez L, Betancourt S. Rudimentary, low tech incinerators as a means to produce reactive pozzolan out of sugar cane straw. *Cem Concr Res* 1998; 36:1056-1061.

- [39] Guzmán A, Gutiérrez C, Amigó V, Mejía de Gutiérrez R, Delvasto S. Pozzolanic evaluation of the sugar cane leaf. *Mater Construcc* 2011; 61:213-225.
- [40] Morales EV, Villar-Cociña E, Frías M, Santos SF, Savastano Jr. H. Effects of calcining conditions on the microstructure of sugar cane waste ashes (SCWA): Influence in the pozzolanic activation. *Cem Concr Comp* 2009; 31:22-28.
- [41] Villar-Cociña E, Frías, M, Moraes EV, Rojas, MIS. An evaluation of different kinetic models for determining the kinetic coefficients in sugar cane straw–clay ash/lime system. *Adv Cem Res* 2006; 18(1):17-26.
- [42] Demis S, Tapali JG, Papadakis VG. An investigation of the effectiveness of the utilization of biomass ashes as pozzolanic materials. *Cons Build Mat* 2014; 68:291-300.
- [43] Payá J, Monzó J, Borrachero MV, Díaz-Pinzón L, Ordóñez LM. Sugar-cane bagasse ash (SCBA): studies on its properties for reusing in concrete production. *J Chem Technol Biot* 2002; 77:321-325.
- [44] Allahverdi A, Shaverdi B, Kani E. Influence of sodium oxide on properties of fresh and hardened paste of alkali-activated blast-furnace slag. *Int J Civ Eng* 2010; 8:304–314.
- [45] Pereira CL, Savastano Jr. H, Payá J, Santos SF, Borrachero MV, Monzó J. Use of highly reactive rice husk ash in the production of cement matrix reinforced with green coconut fiber. *Ind Crop Prod* 2013; 49:88-96.
- [46] Payá J, Monzó J, Borrachero MV. Physical, Chemical and Mechanical properties of Fluid Catalytic Cracking Catalyst Residue (FC3R) Blended cements. *Cem Concr Res* 2001; 31:57-61.