

Document downloaded from:

<http://hdl.handle.net/10251/83431>

This paper must be cited as:

Moraes, J.; Melges, JLP.; Akasaki, JL.; Tashima, MM.; Soriano Martinez, L.; Monzó Balbuena, JM.; Borrachero Rosado, MV.... (2016). Pozzolanitic reactivity studies on a miomass-derived waste from sugar cane production: sugar cane straw ash (SCSA). *ACS Sustainable Chemistry and Engineering*. 4(8):4273-4279.
doi:10.1021/acssuschemeng.6b00770.



The final publication is available at

<http://dx.doi.org/10.1021/acssuschemeng.6b00770>

Copyright American Chemical Society

Additional Information

"This document is the Accepted Manuscript version of a Published Work that appeared in final form in *ACS Sustainable Chemistry & Engineering*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <http://pubs.acs.org/doi/abs/10.1021%2Facssuschemeng.6b00770>."

Pozzolanic reactivity studies on a biomass-derived waste from sugar cane production: sugar cane straw ash (SCSA)

João Claudio B. Moraes, José Luiz P. Melges, Jorge Luis Akasaki, Mauro Mitsuchi Tashima, Lourdes Soriano, José Monzo, María Victoria Borrachero, and Jordi Payá

ACS Sustainable Chem. Eng., **Just Accepted Manuscript** • DOI: 10.1021/acssuschemeng.6b00770 • Publication Date (Web): 28 Jun 2016

Downloaded from <http://pubs.acs.org> on June 28, 2016

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.



1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Pozzolanic reactivity studies on a biomass-derived waste from sugar cane production: sugar cane straw ash (SCSA)

João C. B. Moraes[†], José L. P. Melges[†], Jorge L. Akasaki[†], Mauro M. Tashima[†], Lourdes Soriano[‡], José Monzó[‡], María V. Borrachero[‡], Jordi Payá^{‡}.*

[†]UNESP – Univ Estadual Paulista, Grupo de pesquisa MAC – Materiais Alternativos de Construção, Campus de Ilha Solteira, Alameda Bahia, nº 550, 15385-000; Ilha Solteira – SP, Brazil.

[‡]ICITECH – Instituto de Ciencia y Tecnología del Hormigón (GIQUIMA group), Universitat Politècnica de Valencia, Av. dels Tarongers, 4F, 46022; València, Valencia, Spain.

KEYWORDS: agroindustry residue, pozzolan, hydrated lime, Fourier-transformed infrared spectroscopy, thermogravimetric analysis, electrical conductivity measurement, scanning electron microscopy,

ABSTRACT

Biomass has gained in importance as an energy source in recent years. One of the crops that presents interesting opportunities with regard to biomass is sugar cane. In Brazil, sugar cane production is increasing for alcohol and sugar manufacture. Some by-products, such as sugar cane straw, also are obtained during harvesting. Due the calorific value of the sugar cane straw, its use as biomass is increasing. After the straw is burned to produce energy, an ash is obtained: sugar cane straw ash (SCSA). This waste needs an appropriate destination and, since the recent publication of successful studies using biomass derived-ashes as pozzolanic material, the present study aimed to assess the pozzolanic reactivity of sugar cane straw ash. The pozzolanic activity was assessed using a new and simple recently proposed method: evaluation of the electrical conductivity of calcium hydroxide (CH) and pozzolan suspensions, in which solid CH is initially present. These results were compared to those of two other well-established techniques: Fourier transformed infrared spectroscopy and thermogravimetric analysis. The evaluation by all three techniques is similar and shows that sugar cane straw ash is a good pozzolanic material: high lime fixation values for CH:SCSA mixes were determined by thermogravimetric analysis and unsaturation respect to CH in 3.5:6.5 CH:SCSA suspension was achieved at 60°C. According to this behaviour, a bright future for SCSA as a replacement for Portland cement is expected.

INTRODUCTION

Biomass has become an interesting source of energy in the last years. In the early 21st century, concern about the availability of non-renewable resources and CO₂ emissions motivated an increase in research about biomass as an alternative energy source¹. The transformation of

1
2
3 biomass into energy also allows the production of new inorganic materials for different
4 applications²⁻⁴. In some cases, advanced materials based on porous silica nanoparticles have been
5 obtained^{5,6}. One agricultural product that supplies biomass is the sugar cane. In Brazil, the sugar
6 cane crop has increased in recent years for the manufacture of alcohol and sugar, making Brazil
7 the largest producer worldwide⁷. In numbers, the harvest of sugar cane in Brazil was 632 million
8 tons in 2014/2015, which represents an increase of 64% in the last ten years⁸. Formerly, the
9 sugar cane harvest was performed using a burning process in the cultivation area; however, an
10 Agro-Environmental Protocol⁹ was created in order to end this procedure. As a consequence,
11 mechanized harvesting gained in importance. In the mechanized process, a by-product composed
12 of green and dry leaves is generated — sugar cane straw — of which about 140 kg is obtained
13 per ton of sugar cane produced^{9,10}. Initially, the straw was left on the field, but some authors
14 recognized that the calorific value of the sugar cane straw could be used as biomass, in the same
15 way as the sugar cane bagasse that is obtained from alcohol/sugar production^{9,11}. Recent studies
16 have assessed the collection of this by-product from the field^{9,12} and new practices for burning it
17 to produce energy¹³. However, after obtaining energy from the sugar cane straw by burning,
18 waste is generated: sugar cane straw ash (SCSA). There is currently no mechanism for the
19 valorization of this residue and, due to expected increases in sugar cane production and studies
20 on the use the straw as an energy source, the production of SCSA will likely increase in the
21 coming years.

22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53 A good valorization method for this biomass-derived waste could be the partial replacement of
54 Portland cement as a pozzolanic material. Some biomass-derived ashes have been successfully
55 tested in cement and concrete as pozzolanic materials: rice husk ash¹⁴ and sugar cane bagasse
56
57
58
59
60

1
2
3 ash¹⁵. A pozzolan is an amorphous silica or alumina/silica material that reacts with calcium
4
5 hydroxide (portlandite generated from Portland cement hydration) in an aqueous medium, and
6
7 generates cementing gels similar to those found for Portland cement¹⁶. The advantages of using
8
9 biomass wastes such as pozzolans to partially replace Portland cement are technological
10
11 (improving compressive strength and durability) and ecological (reducing both Portland cement
12
13 consumption and the disposal of ashes in landfills)¹⁷.
14
15
16
17
18
19
20
21

22 The pozzolanic reactivity of a material can be assessed via studies of calcium hydroxide
23
24 consumption using several techniques. Previously, reports on the reactivity of SCSA studied the
25
26 behavior of Portland cement blends¹⁸ and kinetic parameters¹⁹. In this paper, the pozzolanic
27
28 activity of SCSA obtained from an auto-combustion process was assessed by means of electrical
29
30 conductivity measurements as proposed by Tashima et al.²⁰. This method consists of monitoring
31
32 the electrical conductivity of suspensions composed of calcium hydroxide/pozzolan for seven
33
34 days.
35
36
37
38
39
40
41
42

43 The SCSA reactivity results obtained by electrical conductivity measurements of suspensions
44
45 were compared to those from other well-established techniques: Fourier transformed infrared
46
47 spectroscopy (FTIR) and thermogravimetric analysis (TGA). The main advantage of electrical
48
49 conductivity measurement is the easy preparation and relatively low cost of the test compared to
50
51 the two other techniques for evaluating the pozzolanic potential of a material. In addition, SEM
52
53 images were obtained in order to show the pozzolanic reaction products between SCSA and
54
55 calcium hydroxide. This study aimed to assess the pozzolanic activity of SCSA and valorize this
56
57
58
59
60

1
2
3 biomass waste, as well as to compare the results of a recently proposed and simple technique to
4
5 those from other well-established methods.
6
7
8
9

10 11 12 **MATERIALS AND METHODS** 13 14 15 16 17 18

19 **Materials.** Sugar cane straw was obtained from a sugar cane plantation near to Ilha Solteira (Sao
20 Paulo, Brazil). The straw was burned in an auto-combustion process with a maximum
21 temperature of 700°C. In this process, the sugarcane straw is initially ignited, and then the
22 combustion heat maintains the process without any fuel added. The temperature was measured in
23 different points and at several times. After burning, the SCSA was collected from the bottom of
24 the furnace, and passed through sieves in order to remove unburned particles. Finally, it was
25 milled for 30 minutes in a planetary ball mill to reduce the particle diameter. Calcium hydroxide
26 of high purity (>95% purity), supplied by Panreac S.A, was used for all pozzolanic reactivity
27 tests.
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44

45 **Equipment.** Electrical conductivity measurements were carried out using a Crison micro
46 CM2201 instrument. pH measurements were obtained using a Crison micro PH2001 pH meter.
47 In order to maintain the test temperature, a Julabo SW22 shaking water bath was used.
48 Thermogravimetric analysis was performed using a Mettler Toledo TGA850 instrument, in a
49 temperature range of 35–600°C at a heating rate of 10°C.min⁻¹ in an N₂ atmosphere (75 mL.min⁻¹
50 gas flow), where the samples were tested in sealed 100 µL pin-holed aluminum crucibles.
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Fourier transformed infrared spectroscopy was performed using a Bruker TENSOR 27 in the wavenumber range between 400 and 4000 cm^{-1} . SEM images of the calcium hydroxide/SCSA pastes were obtained using a JEOL JSM-6300 microscope. The chemical composition of SCSA was obtained through X-ray fluorescence (XRF) by means of a Philips Magix Pro XRF instrument.

Methods. Electrical conductivity measurements were performed as proposed by Tashima et al.²⁰. This followed method differs from others previously reported²¹⁻²⁴: the main difference is related to the presence or not of solid calcium hydroxide in the tested suspensions. Some techniques²¹⁻²³ are based in the preparation of a saturated solution in $\text{Ca}(\text{OH})_2$, and the decreasing in electrical conductivity is measured when pozzolan is added. Other technique²⁴ is based in the same type of measurement, however, the initial $\text{Ca}(\text{OH})_2$ solution is unsaturated. In the test used in the actual study, there is an amount of undissolved $\text{Ca}(\text{OH})_2$ in the initial suspension. In this way, two simultaneous processes take place: the consumption of dissolved $\text{Ca}(\text{OH})_2$ and the dissolution of solid $\text{Ca}(\text{OH})_2$.

In tests according to Tashima's method, 1g of solid (the mixture of calcium hydroxide (CH) and pozzolan) and 50 mL of deionized water were combined in an Erlenmeyer flask. The CH:SCSA suspensions (also named "systems" in the manuscript) were assessed at 40, 50 and 60°C for seven days in six different proportions: 2:8, 2.5:7.5, 3:7, 3.5:6.5, 4:6 and 4.5:5.5 (by mass). In addition, suspensions at 30°C were also studied, where the relative amount of calcium hydroxide was decreased compared to the tests at higher temperature. At this temperature the following

1
2
3 proportions were evaluated: 0.5:9.5, 1:9, 1.5:8.5, 2:8, 2.5:7.5 and 3:7. The results of the loss of
4
5 electrical conductivity (Lc) tests are presented as the percentage decrease in electrical
6
7 conductivity, as reported by Tashima et al.²⁰. This parameter clarifies the electrical conductivity
8
9 results and also takes in account the influence of the ions released by the pozzolan. The pH of the
10
11 suspensions was measured before the addition of the SCSA and at the end of the test (7 days). At
12
13 the end of the test, the suspensions evaluated at 40°C were filtered, and the solid part retained on
14
15 the filter was analyzed by TG.

16
17
18
19
20
21
22
23
24 TG and FTIR studies were carried out for two CH:SCSA pastes with proportions by mass of 3:7
25
26 and 5:5 at a constant water/binder rate of 0.80. The CH:SCSA pastes were assessed after 1, 3, 7
27
28 and 28 days of curing at a temperature of 40°C with relative humidity higher than 95%. At each
29
30 curing time point, the pastes were milled in an agate mortar and mixed with acetone in order to
31
32 stop the hydration process. They were then filtered and dried in a laboratory incubator for 30 min
33
34 at 60°C. SEM images of the fractured surface of the 3:7 paste were obtained after 28 days of
35
36 curing at 40°C. After each curing age the SEM pastes were prepared by breaking samples and
37
38 taking regular fracture images. They were the placed in acetone for one hour and, finally, dried
39
40 for 30 minutes in a laboratory incubator at 60°C.

41 42 43 44 45 46 47 48 49 50 **RESULTS AND DISCUSSION**

51
52
53 **Sugar cane straw ash characterization.** The chemical composition of SCSA obtained from
54
55 XRF analysis is shown in Table 1. SCSA presents a SiO₂ content of 36.5%, which is lower than
56
57
58
59
60

1
2
3 published values for sugar cane bagasse ash¹⁵. Al₂O₃ and Fe₂O₃, other oxides that are important
4
5 in the pozzolanic reaction²⁵, are found in minor amounts: 2.8% and 3.4%, respectively. The CaO
6
7 content is 16.4%, percentage much lower than that found for blast furnace slag or class C fly
8
9 ash¹⁶. SCSA does not harden when mixed with water, suggesting that its hydraulic behavior
10
11 could be negligible.. The total alkali content (K₂O plus Na₂O) was 8.1%, which is considered
12
13 high. However, such high values are very common in ashes produced by burning biomass²⁶. C-S-
14
15 H gel formed in the Portland cement hydration or in the pozzolanic reaction has the ability to
16
17 incorporate alkali ions (Na⁺ or K⁺)²⁷. However, in the presence of reactive aggregates, alkali-
18
19 silica expansion could take place when alkali-rich pozzolanic additions are used²⁸. Finally, the
20
21 amount of LOI is relatively high (15.5%), due to the presence of organic matter — the
22
23 combustion was incomplete and some cellulosic compounds remained. Regarding the phases
24
25 present in SCSA, the XRD pattern showed the presence of an amorphous phase, and crystalline
26
27 phases mainly composed of quartz (SiO₂) and calcite (CaCO₃), which probably originate from
28
29 the soil where the sugar cane straw was collected. It is therefore likely that the SiO₂ and CaO are
30
31 present as crystals in the SCSA and do not take part in the pozzolanic reaction. Studies to
32
33 determine the percentage of insoluble SCSA residue by acid and base treatment presented a
34
35 value of 16.5%, which means that the SiO₂-crystalline phase in the pozzolan represents about
36
37 45% of the total SiO₂. The mean particle diameter (D_{med}), median particle diameter (D₅₀) and
38
39 90% passing particle diameter (D₉₀) of the SCSA were 14.7, 7.0 and 38.8 μm, respectively.
40
41
42
43
44
45
46
47
48 Specific surface area was 0.595 m²/g and specific gravity was 2.25.
49
50
51
52
53
54

55 **Table 1.** Chemical composition of SCSA by percentage
56
57
58
59
60

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

Electrical Conductivity Measurements. The principle of this test is based on the limited solubility of calcium hydroxide (CH) in water. Calcium hydroxide yields a saturated water solution if the quantity of dissolved hydroxide is lower than the amount of added hydroxide. Under these conditions, the concentration of Ca⁺² and OH⁻ remains constant at a given temperature. Thus, the electrical conductivity of the suspension has a high value. If a pozzolan is added to the suspension, a reaction between Ca⁺²/OH⁻ ions and the reactive fraction of the pozzolan takes place. This reaction decreases the concentration of ions and, consequently, the electrical conductivity tends to diminish. However, the dissolution of solid calcium hydroxide present in the suspension maintains a constant concentration of Ca⁺² and OH⁻. While the solution remains saturated due to the dissolution of calcium hydroxide the electrical conductivity remains constant. When the solid calcium hydroxide is exhausted, the solution becomes unsaturated and the electrical conductivity starts to decrease. The time taken to achieve an unsaturated state depends on the CH/pozzolan proportion and the pozzolan reactivity. Highly reactive pozzolans reach the unsaturated state more quickly.

The results of the loss of electrical conductivity (Lc) tests for suspensions studied at 30, 40, 50 and 60°C over seven days are shown in Figure 1. Two types of curves can be seen in the graphics. In one case CH remains in the saturated state, and the Lc value is static during the 4–168 hours testing period. In the other, an increase in the Lc value during the testing period is

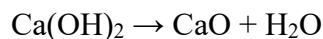
1
2
3 seen. This occurs when unsaturation is achieved because the pozzolanic reaction fixed the entire
4 solid CH phase. The Lc value increases, for all systems, in the first 4 hours due to the addition
5 of SCSA addition to the suspension when adsorption of dissolved ions onto SCSA particles takes
6 place. For the suspensions studied at 60°C (Figure 1a), the 2:8 system presented a Lc value of
7 over 70% after only 24 hours, which represents a rapid consumption of the solid CH. For the
8 2.5:7.5 system, the Lc value is lower than the 2:8 system after 24 hours (almost 40%), however,
9 the suspension is also shown to be unsaturated. The 3:7 suspension presented an increase in the
10 Lc value after 48 hours, whereas the 3.5:6.5 and 4:6 systems only showed a rise in the Lc value
11 after 96 and 168 hours, respectively. The 4.5:5.5 system did not show any increase in Lc at this
12 temperature, which means that the pozzolan could not consume all of the solid calcium
13 hydroxide and the unsaturated state was not achieved. It is well-known that chemical reactions
14 (e.g. pozzolanic reaction) usually are slower when the temperature decreases. Thus, as expected,
15 the loss in the conductivity of suspensions studied at 50°C (Figure 1b) showed a slower
16 unsaturation process than the suspensions tested at 60°C. The 2:8 system presented an Lc value
17 of 40% in the first 24 hours. The 2.5:7.5 and 3:7 systems presented an increase in the Lc value
18 after 48 and 72 hours, respectively, whereas the final three suspensions (3.5:6.5, 4:6, 4.5:5.5) did
19 not show any loss of conductivity. For the suspensions tested at 40°C (Figure 1c), only the 2:8
20 system presented an increase in the Lc value after 48 hours, taking a much longer time to reach
21 the unsaturated state than at the higher temperatures. The 2.5:7.5 and 3:7 systems also showed an
22 increase in the Lc value, after 72 and 120 hours, respectively. As in the test at 50°C, 3.5:6.5, 4:6,
23 and 4.5:5.5 suspensions remained saturated until the end of the test. According to the criteria
24 proposed by Tashima et al.²⁰, SCSA can be classified as a pozzolan with medium reactivity. This
25 behavior is similar to that found for low densified silica fume (DSF-H). For testing at 30°C
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 (Figure 1d), considering that CH:SCSA suspensions of 3.5:6.5 did not reach unsaturation at 40°C
4
5 or 50°C, lower CH:SCSA systems were tested (0.5:9.5, 1:9 and 1.5:8.5). For these suspensions
6
7 tested at 30°C, an increase in the Lc value was found for 0.5:9.5 (4 hours), 1:9 (4 hours), 1.5:8.5
8
9 (48 hours), 2:8 (72 hours) and 2.5:7.5 (144 hours). However, the 3:7 suspension did not show
10
11 any increase in the Lc value, meaning that SCSA could not consume enough calcium hydroxide
12
13 to turn the suspension unsaturated at this temperature.
14
15
16
17
18
19
20
21

22 Additionally, pH measurements were carried out in order to assess the change in the
23
24 concentration of OH⁻. Thus, the pH of calcium hydroxide suspensions before the addition of
25
26 SCSA and the pH of the suspension at the end of the test were measured. In general terms, a
27
28 significant decrease in pH was observed from the testing time at which unsaturation was reached,
29
30 indicating that the OH⁻ concentration diminished. For samples in the saturated state, only minor
31
32 changes in pH were observed, suggesting that the OH⁻ concentration remained constant. Figure 2
33
34 shows these variations in pH (Δ pH). It can be observed that for a given CH:SCSA proportion, a
35
36 higher testing temperature results in a higher Δ pH. A straight line is shown for Δ pH = 0.2
37
38 meaning that below this value the suspension remained saturated. As an exception, the Δ pH of
39
40 the 4:6 CH:SCSA sample at 60°C was below this value: in this case, the Lc value was at the limit
41
42 of unsaturation (see Fig. 1a), and consequently, the change in pH value was also at the limit.
43
44
45
46
47
48
49
50
51

52 Figure 3 shows the DTG curves of the solid residue obtained by filtration of the suspensions after
53
54 the end of electrical conductivity measurements at 40°C. The main peak in the range 125–150°C
55
56 is from the dehydration of pozzolanic reaction products (mainly calcium silicate hydrates, C-S-

1
2
3 H). The aim of this test is to assess the peak in the range 500–600°C, which results from the
4
5 dehydroxylation of the calcium hydroxide, according to the following equation
6
7



8
9
10
11
12 If this peak appears in the DTG curve, it means there is calcium hydroxide remaining in the solid
13
14 residue after filtration, meaning that SCSA could not achieve an unsaturated suspension. From
15
16 these results, it can be seen that only the 3.5:6.5 and 4:6 suspensions presented a peak at 500–
17
18 600°C, where the SCSA could not react with enough calcium hydroxide to result in an
19
20 unsaturated suspension, confirming the results of the electrical conductivity measurements
21
22 (Figure 1c). The suspensions 2.5:7.5 and 3:7 did not show calcium hydroxide in their DTG
23
24
25
26
27 curves, also in good agreement with the electrical conductivity measurements.
28
29
30
31
32

33 **Fourier transformed infrared spectroscopy.** FTIR spectra of the 3:7 and 5:5 ratio CH:SCSA
34
35 pastes after 1, 3, 7 and 28 days curing at a temperature of 40°C are shown in Figure 4. The main
36
37 vibration bands detected in this test were at 3641 (O-H vibration), 1030, 956 and 443 cm⁻¹ (Si-O
38
39 vibration). For the raw materials, the vibration band at 3641 cm⁻¹ is related to calcium hydroxide
40
41 (CH), and the peak at 1030 cm⁻¹ is from the amorphous phase of the pozzolan (SCSA). For the
42
43 pastes, the four selected vibration bands have important roles in the pozzolanic reaction. With
44
45 increasing curing age, the vibration band at 956 and 443 cm⁻¹ increases, whereas the other two
46
47 peaks, at 3641 and 1030 cm⁻¹, decrease. This results from the consumption of calcium hydroxide
48
49 (vibration band at 3641 cm⁻¹) by the amorphous phase of SCSA (vibration band at 1030 cm⁻¹)
50
51 with curing. Consequently, a new vibration band resulting from the pozzolanic reaction appears
52
53
54
55
56
57
58
59
60 at 956 cm⁻¹. In both pastes, from the first day of curing the vibration band at 1030 cm⁻¹ is

1
2
3 reduced in intensity, showing dissolution of the amorphous network of the SCSA (dissolution of
4
5 SiO₄ units), occurred mainly during the early part of the reaction. For the 5:5 CH:SCSA paste,
6
7 the vibration band at 3641 cm⁻¹ reduced from the first to the third day of curing, and remained
8
9 practically constant afterwards. This means that the SCSA could not consume all of the calcium
10
11 hydroxide after 28 days of curing, and the pozzolanic reaction occurred mainly in the first seven
12
13 days. The vibration band at 956 cm⁻¹ was practically unchanged from days 1 to 28. For the 3:7
14
15 CH:SCSA paste, the peak at 3641 cm⁻¹ almost disappeared after one day of curing. This suggests
16
17 that the SCSA consumed almost all of the calcium hydroxide after this time. The peak at 875 cm⁻¹
18
19 is related to C-O bond vibration from the carbonate anion. This peak appeared on the pure
20
21 SCSA spectrum due the presence of calcite (see Figure 4). In the CH:SCSA pastes, this peak is
22
23 related to carbonate from the ash and from calcium hydroxide, and its intensity was maintained
24
25 practically constant for all curing times, showing that the sample did not carbonated. The FTIR
26
27 studies show that SCSA presents good reactivity, since the pozzolanic reaction at both CH:SCSA
28
29 proportions took place at early curing ages.
30
31
32
33
34
35
36
37
38
39
40

41 **Thermogravimetric analysis.** The DTG curves of the 5:5 and 3:7 CH:SCSA pastes from 1 to
42
43 28 days of curing at 40°C are shown in Figure 5. The main peaks of these analyses are in the
44
45 range 125–175°C, which represents the dehydration of products from pozzolanic reaction, and at
46
47 500–575°C, resulting from the dehydroxylation of calcium hydroxide. In the 5:5 paste the 500–
48
49 575°C peak reduced from days 1 to 3 of curing and remained practically constant until 28 days,
50
51 meaning that the pozzolanic reaction occurred in the first three days. The peak near to 150°C
52
53 increased from days 1 to 3 of curing, and did not show any changes after this time. This behavior
54
55 is due the pozzolanic reaction, which consumes the calcium hydroxide and forms cementing gels
56
57
58
59
60

1
2
3 (mainly C-S-H). For the 3:7 paste, on the first day of curing there was no peak at 550°C, as a
4
5 result of complete calcium hydroxide consumption by the SCSA. Since the pozzolanic reaction
6
7 took place within the first day, the peak related to the gel from this reaction (near to 150°C)
8
9 remained practically constant from 1 to 28 days of curing time. These results of
10
11 thermogravimetric analysis are in accordance with those from the FTIR studies.
12
13
14
15
16
17
18
19

20 Table 2 shows the mass loss of pozzolanic reaction products (P_P) and calcium hydroxide (P_{CH}),
21
22 as well the lime fixation of all pastes in the curing time studied. For the paste with a CH:SCSA
23
24 proportion of 5:5, the lime fixation²⁹ had a high value after one day of curing (81.46%),
25
26 suggesting the good pozzolanic reactivity from the SCSA. After three and seven days, the lime
27
28 fixation had similar values (92.76% and 92.29%, respectively) and after 28 days of curing, the
29
30 lime fixation did not significantly change. Therefore for the 5:5 CH:SCSA paste, the major
31
32 pozzolanic reaction took place in the first day of curing. In the 3:7 CH:SCSA paste the lime
33
34 fixation was 100% within the first day of curing. At this proportion, the SCSA was able to
35
36 consume all of the calcium hydroxide in only one day of curing. These DTG curves and lime
37
38 fixation values show that the reactivity of the SCSA is of interest for potential applications.
39
40 Concerning the mass loss from dehydration of the pozzolanic reaction products (P_P), in both
41
42 pastes studied, the values did not vary significantly with the curing time. Since the SCSA
43
44 presents good reactivity, the major part of pozzolanic reaction occurred in the first day of curing,
45
46 resulting in only minor changes in the mass loss related to the dehydration of pozzolanic reaction
47
48 products. These minor changes can be related to changes in water bonds of the C-S-H gels
49
50 during the curing time. In previous studies³⁰, more important changes in the mass loss related to
51
52
53
54
55
56
57
58
59
60

formed hydrates at 20°C were observed after the calcium hydroxide was completely combined, differently to that found at 40°C.

Table 2. Mass loss related to the dehydration of pozzolanic reaction products (P_P) and calcium hydroxide (P_{CH}), and lime fixation of CH:SCSA pastes

CH:SCSA	Curing time (days)	P_P (%)	P_{CH} (%)	Lime fixation (%)
5:5	1	12.58	2.14	81.46
	3	14.03	0.90	92.76
	7	13.47	0.89	92.29
	28	13.94	0.17	98.50
3:7	1	13.50	0	100
	3	14.44	0	100
	7	15.05	0	100
	28	15.39	0	100

Comparison of results from different techniques. The results of the three techniques for samples cured at 40°C were compared. The three studies showed a high consumption of calcium hydroxide by the 3:7 CH:SCSA paste in the first days of testing. In electrical conductivity

1
2
3 studies, the Lc started to increase after 120 hours, whereas FTIR and TG studies showed no
4
5 presence of calcium hydroxide after three days of curing. For studies with higher amounts of
6
7 calcium hydroxide (4.5:5.5 for electrical conductivity studies and 5:5 for FTIR/TG studies), the
8
9 SCSA did not consume all of the calcium hydroxide in the first seven days of curing. For the
10
11 4.5:5.5 system, the Lc did not increase during the test, which means that the solution remained
12
13 saturated. The DTG curve of the filtered material presented small amounts calcium hydroxide.
14
15 FTIR/TG studies showed that the calcium hydroxide was not totally consumed after seven days
16
17 of curing. In general, the results from the electrical conductivity studies are similar to those
18
19 found by the FTIR and TG techniques. The new method proposed by Tashima et al.²⁰ has the
20
21 advantage of being simpler and cheaper, and also gave interesting results on pozzolanic
22
23 reactivity behavior.
24
25
26
27
28
29
30
31
32

33
34 **Scanning electron microscopy.** SEM images of 3:7 pastes after 28 days of curing at 40°C are
35
36 shown in Figure 6. These images show a substantial presence of gel formed by the pozzolanic
37
38 reaction. In addition, calcium hydroxide particles were not identified, indicating that all of it had
39
40 been consumed by the SCSA (Figure 6a and Figure 6b). In Figure 6c, cementing gel is the main
41
42 product. This gel is rich in calcium and silicon (spot A, mass percentage: SiO₂ = 35.7%; CaO =
43
44 35.2%) and showed a Ca/Si atomic ratio of 1.06. In addition a quartz particle can be seen
45
46 surrounded by cementing gel (spot B). In Figure 6d, fibrillary C-S-H is highlighted. This phase is
47
48 rich in calcium and silicon, and also contained aluminum and iron (spot C, SiO₂ = 38.3%; CaO =
49
50 38.2%), with a Ca/Si atomic ratio of 1.07. This fibrous phase also appeared in Figure 6b.
51
52
53
54
55
56
57
58
59
60

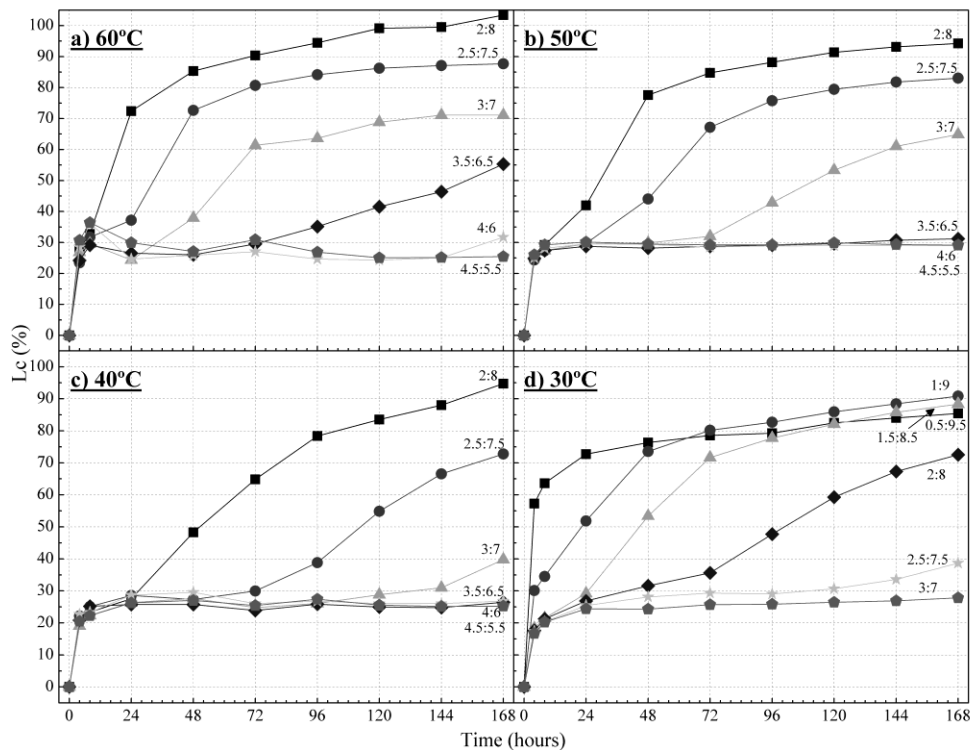


Figure 1. Loss of Electrical Conductivity (Lc) of suspensions studied at a) 60°C; b) 50°C; c) 40°C and d) 30°C.

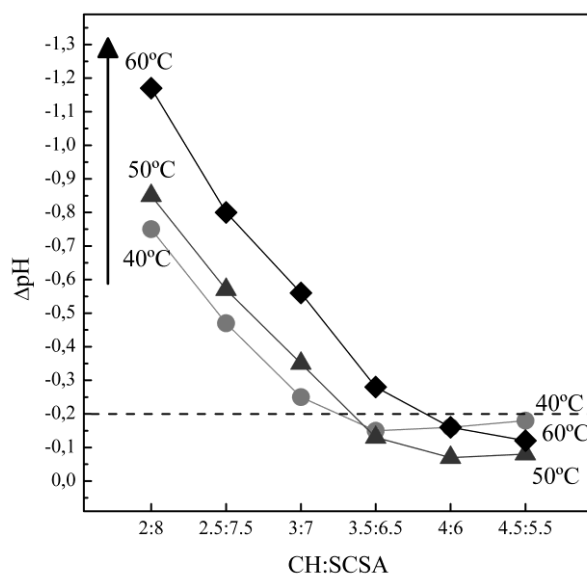


Figure 2. pH variation (ΔpH) of the CH:SCSA suspensions at each temperature studied.

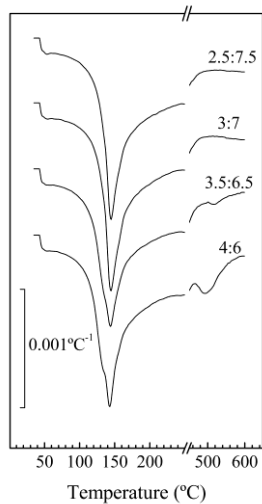


Figure 3. DTG curves of the solid part of the suspensions after electrical conductivity measurements at 40°C.

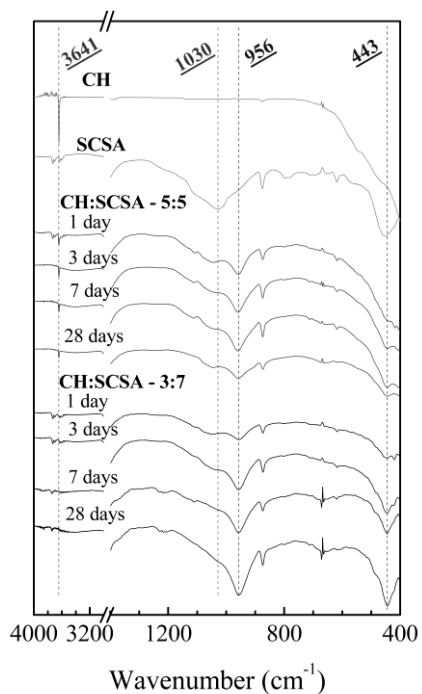


Figure 4. FTIR spectra of 3:7 and 5:5 CH:SCSA pastes after 1, 3, 7 and 28 days of curing at 40°C.

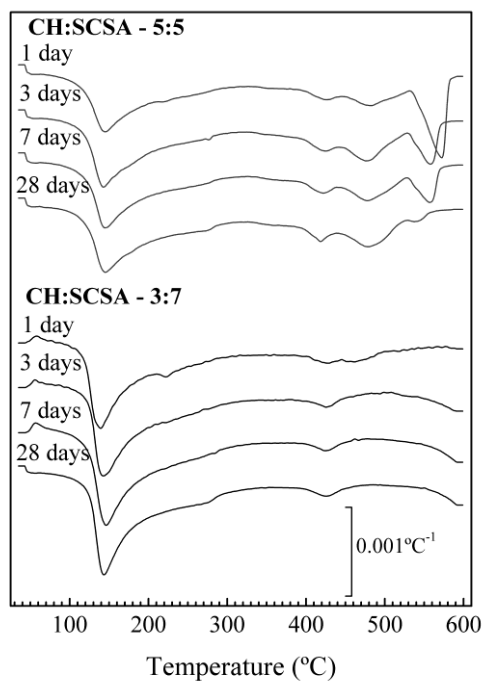


Figure 5. DTG curves of 5:5 and 3:7 CH:SCSA pastes from 1 to 28 days of curing at 40°C.

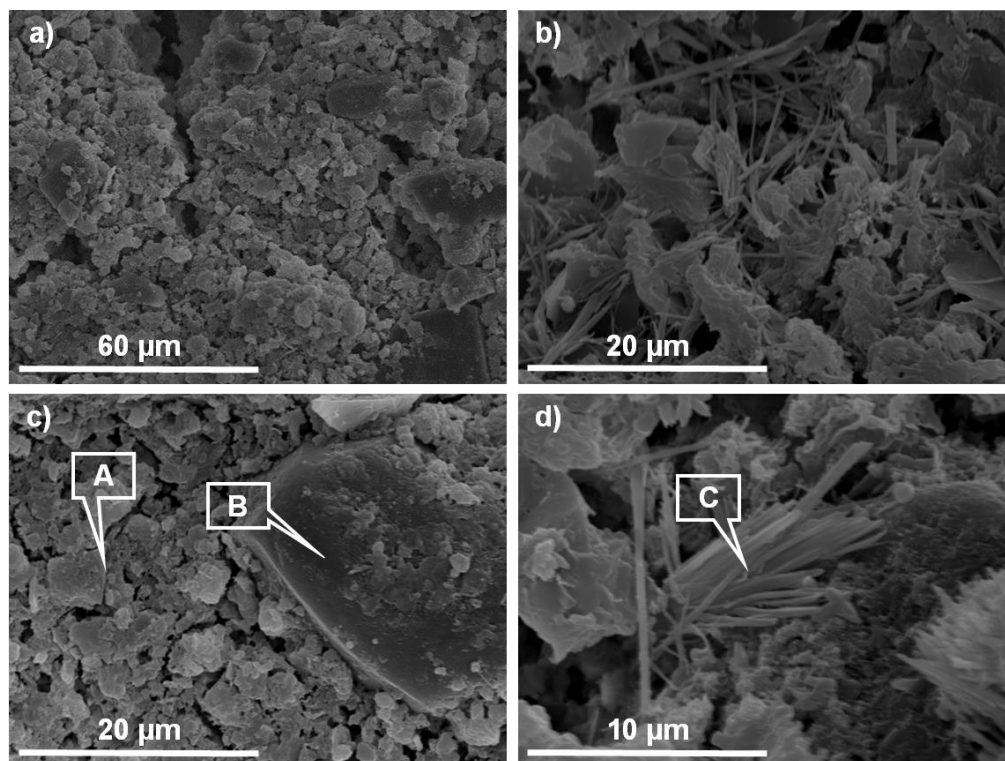


Figure 6. SEM images of 3:7 CH:SCSA paste after 28 days of curing cured at 40°C.

CONCLUSIONS

There is good potential for the valorization of sugar cane straw ash as a pozzolanic material. An increase in the use of biomass is inevitable because of the need for sustainable energy sources. The wastes generated from biomass burning show interesting properties as construction materials, and SCSA seems likely to be used in the same way due to the promising results concerning its reactivity. In addition, the valorization of the ash in building construction has a sustainable profile, since non-renewable materials, such as Portland cement, can be replaced. The three techniques used in this study presented similar results for SCSA reactivity. The electrical conductivity technique has the advantage of being simpler and cheaper than TGA and FTIR

1
2
3 studies. The evaluation by thermogravimetric analysis shows high pozzolanic reactivity of SCSA
4
5 in CH:SCSA mixes, finding values of lime fixation, for 5:5 proportion, higher than 80% after 1
6
7 day of curing at 40°C and higher than 98% after 28 days. FTIR studies on CH:SCSA pastes
8
9 yielded important qualitative data: diminution of vibration bands related to raw materials
10
11 (3641cm⁻¹ for CH and 1030 cm⁻¹ for SCSA) and increase of vibration band related to pozzolanic
12
13 reaction products (956 cm⁻¹). Electrical conductivity measurements let to classify the ash as
14
15 medium reactivity type, accordingly to Tashima's method, similar to densified silica fume.
16
17 Measurements of pH on these suspensions showed that a decrease in 0.2 units or higher confirms
18
19 reaching unsaturated state of the aqueous suspension. This study showed the potential for
20
21 valorization of a biomass waste and assessed its pozzolanic reactivity using an interesting
22
23 recently proposed technique.
24
25
26
27
28
29
30
31
32

33 **ACKNOWLEDGMENT**

34
35 The authors would like to thank CNPq (processo nº 401724/2013-1) and the “Ministerio de
36
37 Educación, Cultura y Deporte” of Spain (“Cooperación Interuniversitaria” program with Brazil
38
39 PHB-2011-0016-PC). Thanks are also due to the Electron Microscopy Service of the Universitat
40
41 Politècnica de València
42
43
44
45
46
47
48

49 **REFERENCES**

50
51
52
53
54 (1) Gallezot, P. Catalytic conversion of biomass: challenges and issues. *ChemSusChem* **2008**, 1,
55
56 734–737; DOI 10.1002/cssc.200800091
57
58
59
60

1
2
3 (2) Vassilev, S. V.; Baxter, D.; Anderson, L. K.; Vassileva, C. G. An overview of the
4 composition and application of biomass ash. Part 1. Phase–mineral and chemical composition
5 and classification. *Fuel* **2013**, 105, 40–76; DOI 10.1016/j.fuel.2012.09.041.
6
7

8
9
10
11 (3) Vassilev, S. V.; Baxter, D.; Anderson, L. K.; Vassileva, C. G. An overview of the
12 composition and application of biomass ash. Part 2. Potential utilisation, technological and
13 ecological advantages and challenges. *Fuel* **2013**, 105, 19–39; DOI 10.1016/j.fuel.2012.10.001.
14
15
16

17
18
19 (4) James, A. K.; Thring, R. W.; Helle, S.; Ghuman, H. S. Ash management review—
20 applications of biomass bottom ash. *Energies* **2012**, 5 (10), 3856–3873; DOI
21 10.3390/en5103856.
22
23
24

25
26
27 (5) Alyoseft, H. A.; Schneider, D.; Wassersleben, S.; Roggendorf, H.; Weiß, M.; Eilert, A.;
28 Denecke, R.; Hartmann, I.; Enke, D. Meso/macroporous silica from miscanthus, cereal remnant
29 pellets, and wheat straw. *ACS Sustain. Chem. Eng.* **2015**, 3 (9), 2012–2021; DOI:
30 10.1021/acssuschemeng.5b00275.
31
32
33

34
35
36 (6) Chen, H.; Wang, W.; Martin, J. C.; Oliphant, A. J.; Doerr, P. A.; Xu, J. F.; DeBorn, K. M.;
37 Chen, C.; Sun, L. Extraction of lignocellulose and synthesis of porous silica nanoparticles from
38 rice husks: a comprehensive utilization of rice husk biomass. *ACS Sustain. Chem. Eng.* **2013**, 1
39 (2), 254–259. DOI 10.1021/sc300115r.
40
41
42
43
44
45

46
47
48 (7) Sugar cane production. *FAOSTAT – Food and Agriculture Organization of the United*
49 *Nations, Statistics Division*; <http://faostat3.fao.org/home/E>
50

51
52
53 (8) Sugar cane production. UNICA – União da Indústria de Cana-de-Açúcar Website;
54 <http://www.unicadata.com.br/index.php?idioma=2>
55
56
57
58
59
60

- 1
2
3 (9) Leal, M. R. L. V.; Galdos, M. V.; Scarpore, F. V.; Seabra, J. E. A.; Walter, A.; Oliveira, C. O.
4
5 F. Sugar cane straw availability, quality, recovery and energy use: A literature review. *Biomass*
6
7 *Bioenerg.* **2013**, 53, 11–19; DOI 10.1016/j.biombioe.2013.03.007.
8
9
10
11 (10) Sugar cane-based bioethanol: energy for sustainable development. BNDES (Banco Nacional
12
13 de Desenvolvimento Econômico e Social) and CGEE (Centro de Gestão e Estudos Estratégicos):
14
15 1st ed. Rio de Janeiro, Brazil, **2008**.
16
17
18
19 (11) Moraes, M. S. A.; Georges, F.; Almeida, S. R.; Damasceno, F. C.; Maciel, G. P. S.; Zini, C.
20
21 A.; Jacques, R. A.; Caramão, E. B. Analysis of products from pyrolysis of Brazilian sugar cane
22
23 straw. *Fuel Process. Technol.* **2012**, 101, 35–43; DOI 10.1016/j.fuproc.2012.03.004.
24
25
26
27 (12) Lemos, S. V.; Denadai, M. S.; Guerra, S. P. S.; Esperancini, M. S. T.; Bueno, O. C.;
28
29 Takitane, I. C. Economic efficiency of two baling systems for sugar cane straw. *Ind. Crop Prod.*
30
31 **2014**, 55, 97–101; DOI 10.1016/j.indcrop.2014.02.010.
32
33
34
35 (13) Mesa-Pérez, J. M.; Rocha, J. D.; Barbosa-Cortez, L. A.; Penedo-Medina, M.; Luengo, C. A.;
36
37 Cascarosa, E. Fast oxidative pyrolysis of sugar cane straw in a fluidized bed reactor. *Appl.*
38
39 *Therm. Eng.* **2013**, 56, 167–175; DOI 10.1016/j.applthermaleng.2013.03.017.
40
41
42
43 (14) Chao-Lung, H.; Anh-Tuan, B. L.; Chun-Sun, Chen. Effect of rice husk ash on the strength
44
45 and durability characteristics of concrete. *Cons. Build. Mat.* **2011**, 25, 3768–3772; DOI
46
47 10.1016/j.conbuildmat.2011.04.009.
48
49
50
51 (15) Cordeiro, G. C.; Toledo Filho, R. D.; Almeida, R. S. Influence of ultrafine wet grinding on
52
53 pozzolanic activity of submicrometre sugar cane bagasse ash. *Adv. Appl. Ceram.* **2011**, 110,
54
55 453–456; DOI 10.1179/1743676111Y.0000000050.
56
57
58
59
60

- 1
2
3 (16) Hewlett, P. C. *Lea's chemistry of cement and concrete*; Elsevier, 4th ed., 2008.
4
5
6
7 (17) Malhotra, V. M.; Mehta, P. K. *Pozzolanic and Cementitious Materials*; Gordon and Breach
8
9 Publishers, 1st vol., **1996**.
10
11
12 (18) Guzmán, A.; Gutiérrez, C.; Amigó, V.; Gutiérrez, R. M.; Delvasto, S. Pozzolanic evaluation
13
14 of the sugar cane leaf. *Mater. Constr.* **2011**, 61, 213–225; DOI 10.3989/mc.2011.54809.
15
16
17
18 (19) Frías, M. Villar-Cociña, E.; Valencia-Morales. Characterisation of sugar cane straw waste
19
20 as pozzolanic material for construction: calcining temperature and kinetic parameters. *Waste*
21
22 *Manage.* **2007**, 27, 533–538; DOI doi:10.1016/j.wasman.2006.02.017.
23
24
25
26 (20) Tashima, M. M.; Soriano, L.; Monzó, J.; Borrachero, M. V.; Akasaki, J. L.; Payá, J. New
27
28 method to assess the pozzolanic reactivity of mineral admixtures by means of pH and electrical
29
30 conductivity measurements in lime:pozzolan suspensions. *Mater. Constr.* **2014**, 64 (316), 1–12;
31
32 DOI 10.3989/mc.2014.00914.
33
34
35
36 (21) Luxán, M. P.; Madruga, F.; Saavedra, J. Rapid evaluation of pozzolanic activity of natural
37
38 products by conductivity measurement. *Cem. Concr. Res.* **1989**, 19 (3), 63-68; DOI
39
40 10.1016/0008-8846(89)90066-5.
41
42
43
44 (22) McCarter, W. J.; Tran, D. Monitoring pozzolanic activity by direct activation with calcium
45
46 hydroxide. *Constr. Build. Mater.* **1996**, 10, 179-184; DOI 10.1016/0950-0618(95)00089-5.
47
48
49
50 (23) Walker, R.; Pavía, S. Physical properties and reactivity of pozzolans, and their influence on
51
52 the properties of lime–pozzolan pastes. *Mater Struct* **2011**, 44, 1139-1150; DOI 10.1617/s11527-
53
54 010-9689-2.
55
56
57
58
59
60

1
2
3 (24) Payá, J.; Borrachero, M.V.; Monzó, J.; Peris-Mora, E.; Amahjour, F. Enhanced conductivity
4 measurement techniques for evaluation of fly ash pozzolanic activity. *Cem. Concr. Res.* **2001**, 31
5
6
7
8 (1), 41-49; DOI 10.1016/S0008-8846(00)00434-8.
9

10
11 (25) ASTM C618-15. Standard Specification for Coal Fly Ash and Raw or Calcined Natural
12
13
14 Pozzolan for Use in Concrete. *ASTM International* **2015**; West Conshohocken, PA.
15

16
17 (26) Demis, S.; Tapali, J.G.; Papadakis, V. G. An investigation of the effectiveness of the
18
19
20 utilization of biomass ashes as pozzolanic materials. *Constr. Build. Mat.* **2014**, 68, 291–300; DOI
21
22 10.1016/j.conbuildmat.2014.06.071.
23

24
25 (27) Hong, S.Y.; Glasser, F. P. Alkali bindings in cement pastes: Part I. The C-S-H phase. *Cem.*
26
27
28 *Concr. Res.* **1999**, 29, 1893-1903; DOI: 10.1016/S0008-8846(99)00187-8.
29

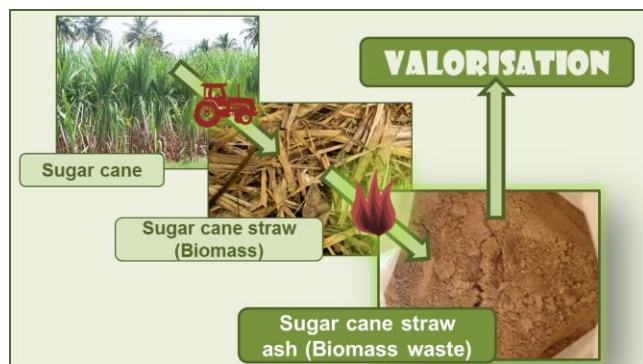
30
31 (28) Thomas, M. The effect of supplementary cementing materials on alkali-silica reaction: A
32
33
34 review. *Cem. Concr. Res.* **2011**, 41, 1224-1231; DOI: 10.1016/j.cemconres.2010.11.003.
35

36
37 (29) Payá, J.; Monzó, J.; Borrachero, M.V.; Velázquez, S.; Bonilla, M. Determination of the
38
39
40 pozzolanic activity of fluid catalytic cracking residue. Thermogravimetric analysis studies on
41
42
43 FC3R–lime pastes. *Cem. Concr. Res.* **2003**, 33, 1085-1091; DOI 10.1016/S0008-8846(03)00014-
44
45 0.
46

47 (30) Moraes, J. C. B.; Aksaki, J. L.; Melges, J. L. P.; Monzó, J.; Borrachero, M. V.; Soriano, L.;
48
49
50 Payá, J.; Tashima, M. M. Assessment of sugar cane straw ash (SCSA) as pozzolanic material in
51
52
53 blended Portland cement: Microstructural characterization of pastes and mechanical strength of
54
55
56 mortars. *Constr. Build. Mater.* **2015**, 94, 670-677; DOI 10.1016/j.conbuildmat.2015.07.108.
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

For Table of Contents Use Only:



Pozzolanic reactivity studies on a biomass-derived waste from sugar cane production: sugar cane straw ash (SCSA)

João C. B. Moraes[†], José L. P. Melges[†], Jorge L. Akasaki[†], Mauro M. Tashima[†], Lourdes Soriano[‡], José Monzó[‡], María V. Borrachero[‡], Jordi Payá^{‡}.*

The possibility of valorisation of an agroindustry residue, the sugar cane straw ash, as pozzolanic material was successfully assessed by different characterization techniques.