Comparison of Original and Washed Pure Sugar Cane Bagasse Ashes as Supplementary Cementing Materials

Gabriela Pitoli Lyra\textsuperscript{a}, María Victoria Borrachero\textsuperscript{b}, Lourdes Soriano\textsuperscript{b}, Jordi Payá\textsuperscript{b,*}, João Adriano Rossignolo\textsuperscript{a}

\textsuperscript{a}Department of Biosystems Engineering, University of São Paulo (USP), Pirassununga, Brazil
\textsuperscript{b}ICITECH – Institute of Science and Technology of Concrete. Universitat Politècnica de València, Valencia, Spain

*Corresponding author at ICITECH – Institute of Science and Technology of Concrete. Universitat Politècnica de València, Camino de Vera s/n 46071 Valencia (Spain), Phone: +34 96 3877564.

E-mail addresses: gabriela.lyra@usp.br (G.P. Lyra); vborrachero@cst.upv.es (M. V. Borrachero); lousomar@upvnet.upv.es (L. Soriano); jjpaya@cst.upv.es (J. Payá)*; rossignolo@usp.br (J. A. Rossignolo).

Funding: This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.
Abstract

The objective of this study was to evaluate the effects of potassium extraction on the pozzolanicity of sugar cane bagasse ash (SCBA), with the aim of producing reactive ash for use in cementitious composites. The sugar cane bagasse ashes were produced at 600°C for 60 min, with a heating rate of 4°C/min. The ashes were then ground and washed for potassium extraction. In order to assess the ash behaviour before and after potassium extraction, the following procedures were performed: energy-dispersive spectroscopy (EDS), loss on ignition (LOI), particle size distribution, x-ray powder diffraction (XRD), x-ray diffraction in calcium hydroxide paste, analysis of lime fixation by thermogravimetry, and evaluation of pozzolanic reactivity analyses. Results show that the extraction of potassium, increases the concentration of silica causing a greater pozzolanic reactivity of the ashes.

Keywords: mineral addition; sugar cane ash; pozzolanic reactivity; cement.
1. Introduction

The current worldwide production of sugar cane (*Saccharum* spp.) is approximately 1.84 billion tons per year [1], with Brazil being the largest producer in the world. In the 2018/2019 Brazilian harvest, approximately 620 million tons of sugar cane were produced, representing 34% of world production, with 29 million tons of sugar and 33 million m³ of ethanol extracted [2-4].

Bagasse is one of the by-products generated from sugar and ethanol production processes. It is estimated that each ton of sugar cane generates 300 kg of bagasse [5]. A large amount of this bagasse is burned in boilers for electric energy generation, leading to a decrease in industry energy costs, thus increasing sustainability in the sector. In 2017, 6.07% of all electricity generation in the country came from sugar cane bagasse burning, and there is an expectation of an increase in future years [3,6,7].

Each ton of bagasse burned generates approximately 25 kg of ash [8-10]. In Brazil, it is believed that 4 million tons of ash can be generated from sugar cane bagasse per year, composed of organic materials (not-burned bagasse and straw) and residual inorganic materials, which are partially used as fertilizer or discarded, and accumulate in industries, waiting for alternative uses [11-13].

The chemical composition of sugar cane bagasse ash can vary according to some factors, such as plant variety, soil composition, crop management, burning conditions, and presence of contaminants such as soil [8,14,15].

Bagasse composition contains most nutrients absorbed by the plant during growth, thus presenting significant amounts of potassium and silica [15, 16]. Potassium (K) is one of the main nutrients necessary for plant development. It plays a fundamental role in several physiological processes and is present in all crop cycles, it is a macronutrient absorbed by plants during the vegetative growth stage [17]: potassium participates in the synthesis of sugars and
proteins during the photosynthesis process to obtain energy, in the translocation of carbohydrates and proteins, and in water absorption [18].

The high levels of SiO$_2$ in SCBA are due to silicon absorbed from the soil by sugar cane roots in the form of monosilic acid (H$_4$SiO$_4$) as it accumulates on the outer wall of epidermal cells as silica gel after water leaves the plant by transpiration. In addition, there is contamination of sugar cane by sand in the harvesting process, resulting in the presence of crystalline silica [16, 19, 20].

Several studies show that sugar cane ash has a chemical element suitable for use as a pozzolanic mineral addition to Portland cement composites, mainly because of its high levels of silicon dioxide (SiO$_2$) [12, 15, 16, 20-22].

Rossignolo et al., (2018) [12] evaluated the influence of calcination in a microwave oven on the pozzolanic reactivity of sugar cane ash. Calcination in a microwave oven resulted in more reactive ash, with a higher content of amorphous silica, and a more efficient and faster burning process.

Cordeiro and Kurtis (2017) [15] evaluated the influence of particle size on the pozzolanicity of sugar cane ash and observed that the increase in specific surface area contributed to the pozzolanic activity, due to portlandite consumption and physical effects.

Cordeiro, Toledo filho and Fairbairn (2009) [16] studied the effect of calcination temperature on the pozzolanic activity of sugar cane ash. Concluding that the calcination temperature is a very important parameter for the reactivity of the ashes, and that the temperature of 600 °C, provides ashes with amorphous silica, low organic matter, high specific surface area and considerable pozzolanic activity.

The presence of amorphous silica is a necessary factor for the pozzolanic reaction to occur, although it is not the only one. Factors such as burning temperature, particle size, and amount of organic matter also play a role [23].
The application of by-products in the production of cementitious composites reduces the
problem of the disposal of these ashes and provides a reduction in the use of clinker, the main
component of Portland cement, which has high energy demand with consequent emission of
greenhouse gases such as CO$_2$ [24]. It is estimated that 800 kg of CO$_2$ are generated for each
ton of clinker. These emissions correspond to 5 to 8% of the carbon dioxide generated
worldwide [25-31]. According to Fairbairn et al. (2010, 2012) [32, 33], sugar cane ash use is
attractive because it is a by-product that possibly reduces CO$_2$ emissions into the atmosphere,
thus indicating the possibility the production of environmentally friendly pozzolans.

The high potassium content in the ash can promote the degradation process of cement
matrices, as the alkali-aggregate reaction occurs in concrete. This reaction is the chemical attack
of the reactive minerals of the aggregates by compounds resulting from the alkalis present in
the internal structure of the concrete, it has an expansive character and this expansion is one of
the main cause of the degradation of the concrete [34, 35]. An alternative is the extraction of
potassium from ash, potentially reusing it as fertilizer in soil, and the ash as a mineral addition
in cementitious materials [36, 37].

The study of the reactivity of ash from the burning of energy cane is important because
they do not have an adequate destination, being necessary the valorization of this agroindustrial
by-product as well as the availability of a pozzolan to be added to the cement, seeking to reduce
the emission of CO$_2$ by the cement industries, in addition this research proposes the use of
potassium extracted from ashes as fertilizers, in order to reduce the consumption of potassium
from a primary source, in addition to giving a destination to the potassium extracted in the
washing process.

Therefore, the goal of this work was to investigate the effects of potassium extraction on
the pozzolanicity of pure sugar cane bagasse ash – i.e., without soil contamination – seeking to
produce reactive ash to utilize in cementitious composites.
Thus, in order to assess the behavior of the ash before and after potassium extraction, physical and chemical characterizations of the ash were carried out by dispersive energy spectroscopy (EDS), loss by ignition (LOI), particle size distribution, diffraction of X-ray powder (XRD), and analysis of ash reactivity by means of X-Ray diffraction in calcium hydroxide paste, analysis of lime fixation by thermogravimetry and evaluation of pozzolanic reactivity.

### 2. Materials and Methods

#### 2.1. Materials

Sugar cane was provided by a sugar and ethanol business in the city of Pirassununga, São Paulo, Brazil. RB867515 was the chosen variety because it is the most commonly planted in the state of São Paulo (about 21%) and in Brazil (25%) [37]. Calcium hydroxide (CH) (Panreac S.A. – 95% purity) was used to prepare CH:ash paste for thermogravimetry and x-ray diffraction analyses and to produce aqueous suspensions for reactivity analyses.

#### 2.2. Methods

##### 2.2.1. Ash preparation from sugar cane bagasse

The sugar canes were washed with water to eliminate residual soil contamination and ground to extract juice, thus obtaining bagasse. This bagasse was dried at 100°C ± 5°C for 24 h and ground in a knife mill to reduce particle size.
The sugar cane bagasse was calcined in a Jung-10013 resistive oven with a power of 7000 W, at 600°C for 60 min, with a heating rate of 4°C/min. The choice of burning temperature is because up to 600 ºC there is a loss of organic matter and without the transformation of amorphous silica into crystalline silica [8,16]. The ashes were taken out immediately after calcination and cooled at room temperature (25°C ± 2°C).

After cooling, the ashes were again ground in a vibrating mill (Micro Mill Pulverisette 0, Fritsch), for 30 min with a volume of 200 cm³ and a grinding goal of 50 mm in diameter and 370 g in mass. After grinding, the ashes were subjected to a treatment of potassium extraction in batches of 5 g, they were washed with 500 ml of deionized water at 60°C and filtered. Afterwards, a second wash occurred, in which the ashes were stirred with 200 ml of deionized water at 60°C for 3 h, filtered, and dried in an oven at 60°C for 24 h. The washing was carried out with water, so that the potassium solution can be reused in fertigation, the water heating occurred to facilitate potassium solubilization. This process was carried out twice so that a greater extraction occurred. No tests were performed on washing solutions to examine their compositions. Ashes before washing are referred to as SCBA and, after washing, as SCBA-W. Both ashes were homogeneized, in order to take a representative sample for the tests. One sample of SCBA and SCBA-W was used for each test performed.

2.2.2. Material characterization

The morphological and chemical characterization of the ashes was performed in a Zeiss ULTRA 55 scanning electron microscope (SEM). Chemical analyses of oxides present in the ashes were carried out by energy-dispersive spectroscopy (EDS) in 10 different areas of 115 μm × 85 μm at 15 kV, without coating, to measure mean values and their standard deviations. Loss on ignition (LOI) was carried out at 950°C for 60 min, with a heating rate of 10°C/min.
Particle size distribution was determined using a laser particle size analyser (LDA; Malvern Mastersizer 2000). Particles were dispersed in deionized water as a non-reactive liquid. The mineralogical analyses of the ashes were carried out in an x-ray diffractometer (DRX; Bruker AXS D8 Advance) with CuKα radiation, operating at 40 kV/20 mA, using a scanning angle of 5° ≤ 20 ≤ 70° at a 0.01°/s step.

### 2.2.3. Mineralogical analysis of pastes

A DRX (Bruker AXS D8 Advance) with CuKα radiation, operating at 40 kV/20 mA, using a scanning angle of 5° ≤ 20 ≤ 70° and a 0.01°/s step, performed the mineralogical analysis of pastes. The calcium hydroxide/hydrated ash pastes were prepared using the proportions of 1:1 (by mass) of CH:ash, keeping a water/solid ratio of 0.8. X-ray diffraction analyses took place after 28 days of curing at 23°C with 100% relative humidity (RH). In order to prepare the samples for analysis, the pastes were crushed with acetone, filtered, and placed in an oven at 60°C for 30 min. Next, the samples were submitted to an 80 μm sieve.

### 2.2.4. Lime fixation analysed through thermogravimetry

A thermogravimetric analyser (Mettler-Toledo TGA850) was used to examine thermal decomposition (DTG) at a heating rate of 10°C/min, from 35 to 600°C, in a nitrogen atmosphere. For the analysis, 100 mL sealed aluminium crucibles with perforated lids were used.

The calcium hydroxide/hydrated pozzolan pastes were prepared following the methodology used in the x-ray diffraction analysis. Thermogravimetric analyses took place after 7 and 28 days of curing at 23°C with 100% relative humidity (RH).
2.2.5. Evaluation of pozzolanic reactivity

To evaluate pozzolanic reactivity of the ashes, the modified Lúxan method was used. Unsaturated aqueous suspensions of ash and calcium hydroxide (CH) were prepared with a concentration of 20 mg of CH and 50 ml of water [39, 40]. For the dilution of CH in the aqueous solution, a temperature of 80°C was used for 1 h. Then, 1 g of ash was inserted, and the temperature was reduced to 60°C. The reduction in the electrical conductivity values after the addition of ash is due to the progress of the pozzolanic reaction of ash with CH. This electrical reduction is due to the reaction of Ca$^{+2}$ and OH$^{-}$ ions dissolved in the water with amorphous silica particles present in the ashes to form stable and insoluble products [41]. An electrical conductometer monitored the progress of the pozzolanic reaction (Crison micro CM2201).

3. Results and Discussion

In Fig. 1, one can observe the presence of potentially soluble solids, such as potassium in SCBA. Because potassium is extremely important in the physiologic processes in the plant [18] one can expect that sugar cane bagasse ash, when not contaminated by soil, will present large amounts of potassium.
Fig. 1. SEM micrograph of SCBA, obtained through secondary electron detectors, and EDS composition from a spot.

Table 1 presents the mean values of ash chemical composition before and after washing. SCBA before washing showed a high content of potassium oxide (K$_2$O) (37.50%). This result was expected, because potassium (K) is the most abundant cation in plant tissues, being absorbed from the soil in large quantities. Some crops can absorb amounts of potassium superior to their needs [42]. Sodium and potassium oxides (Na$_2$O and K$_2$O), when present in high content in a cementitious matrix, can react with other materials and cause the material to disintegrate, as the alkali-aggregate reaction occurs in concrete. The maximum content of alkalis available in Na$_2$O must be 1.5% [35].

The silicon dioxide (SiO$_2$) present in SCBA before washing was 13.90%; this came from sugar cane cell walls because the residual soil particles from the harvesting process were removed. SCBA after washing (SCBA-W) presented a low K$_2$O content (3.20%), which indicates that the washing process was efficient in extracting potassium from the ashes. With
the removal of potassium, other elements were found to be concentrated in the ashes – e.g., SiO₂, which presented average values of 50.20%. Magnesium and calcium oxide (MgO and CaO, respectively) levels increased after washing, which suggests that magnesium and calcium ions are present in the form of insoluble salts, such as carbonates. Phosphorus content (P₂O₅) also increased after washing, suggesting that it may be present in ash in the form of calcium phosphate, which is also insoluble. Sulphur (SO₃) was completely removed after washing, suggesting that its presence in ash may be in the form of potassium sulphate. SCBA, calcined at 600°C for 120 min, presented an LOI of 13.4% and SCBA-W of 16.8%. This result suggests that washing did not significantly change the content of organic material in the ashes.

<table>
<thead>
<tr>
<th>Ash Types</th>
<th>Parameters</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>SO₃</th>
<th>MgO</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCBA</td>
<td>Mean value</td>
<td>13.90</td>
<td>43.30</td>
<td>10.50</td>
<td>14.30</td>
<td>9.70</td>
<td>8.30</td>
</tr>
<tr>
<td></td>
<td>Std. Dev.</td>
<td>1.80</td>
<td>3.10</td>
<td>0.60</td>
<td>0.90</td>
<td>1.00</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>17.20</td>
<td>49.20</td>
<td>11.20</td>
<td>15.80</td>
<td>11.40</td>
<td>9.20</td>
</tr>
<tr>
<td></td>
<td>Min.</td>
<td>11.40</td>
<td>40.50</td>
<td>9.90</td>
<td>12.90</td>
<td>8.00</td>
<td>7.10</td>
</tr>
<tr>
<td>SCBA-W</td>
<td>Mean value</td>
<td>50.20</td>
<td>3.20</td>
<td>14.50</td>
<td>-</td>
<td>14.90</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>Std. Dev.</td>
<td>3.10</td>
<td>0.40</td>
<td>1.50</td>
<td>-</td>
<td>1.50</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>55.90</td>
<td>3.80</td>
<td>16.80</td>
<td>-</td>
<td>16.90</td>
<td>11.30</td>
</tr>
<tr>
<td></td>
<td>Min.</td>
<td>47.60</td>
<td>2.50</td>
<td>12.30</td>
<td>-</td>
<td>12.50</td>
<td>8.50</td>
</tr>
</tbody>
</table>

Table 1 Mean values regarding chemical composition of sugar cane bagasse ash. Values were calculated from ten EDS analyses in a 115 µm × 85 µm area.

Std. Dev. = standard deviation; Max. = maximum recorded value; Min. = minimum recorded value.
SCBA and SCBA–W showed mean particle size values (Table 2) of 16.87 and 23.99 µm, respectively. The difference between particle sizes indicates that potassium comprises part of the small particles, which contributes to the reduction in all sizes of SCBA (i.e., mean size, D_{10}, D_{50}, and D_{90}).

<table>
<thead>
<tr>
<th>Ash Types</th>
<th>*D_{mea} (µm)</th>
<th>D_{10} (µm)</th>
<th>D_{50} (µm)</th>
<th>D_{90} (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCBA</td>
<td>16.87</td>
<td>1.88</td>
<td>8.65</td>
<td>36.87</td>
</tr>
<tr>
<td>SCBA–W</td>
<td>23.99</td>
<td>6.31</td>
<td>19.88</td>
<td>47.64</td>
</tr>
</tbody>
</table>

Table 2 Distribution of ash particle size.

* D_{mea} = mean particle size; D_{10}, D_{50}, and D_{90} are the maximum particle sizes that compose 10%, 50%, and 90% of sample volume, respectively. Source: own authorship.

Fig. 2 and Table 3 present the x-ray diffractograms and mineralogical components of SCBA and SCBA–W, respectively. They show the presence of arcanite (K_{2}SO_{4}), calcite (CaCO_{3}), anhydrite (CaSO_{4}), calcium potassium phosphate (KCaPO_{4}), quartz (SiO_{2}), sylvine (KCl), and hydroxyapatite (Ca_{5}(PO_{4})_{3}(OH)). SCBA presented major peaks of sylvine and arcanite, which indicates the presence of potassium and is thus consistent with the chemical composition shown in Table 1.

SCBA showed major peaks of quartz and calcite. The washing process eliminated the soluble crystalline material – all sylvine – and a large proportion of arcanite, resulting in crystalline impurities from possible soil contamination (not removed by washing) being better detected. In addition, there was a significant increase in the deviation from baseline, which indicates the presence of amorphous material.

Crystalline silicas produced in the burning process, such as tridymite and cristobalite, were not observed, indicating that the temperature of 600ºC does not promote silica crystallization. As a result, present silica, with the exception of quartz, is probably reactive.
silica in an amorphous form. There were also no crystalline magnesium compounds, which suggests that this cation is combined in the form of amorphous or poorly crystallized substances, such as MgO or Mg(OH)$_2$ or hydromagnesite.

Fig. 2. X-ray diffractograms of SCBA and SCBA-W.

<table>
<thead>
<tr>
<th>SCBA</th>
<th>SCBA – W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abbreviation</td>
<td>Mineralogical name</td>
</tr>
<tr>
<td>S</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>Quartz</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Mineralogical name</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>C</td>
<td>Calcite</td>
</tr>
<tr>
<td>Q</td>
<td>Quartz</td>
</tr>
<tr>
<td>H</td>
<td>Hydroxyapatite</td>
</tr>
<tr>
<td>A</td>
<td>Arcanite</td>
</tr>
</tbody>
</table>

Table 3 Mineralogical composition of SCBA and SCBA-W crystalline solids.

Figure 3 and Table 4 present x-ray diffractograms and mineralogical components for CH:ash paste (1:1) after 28 days of curing, respectively. The SCBA paste presented arcanite and sylvine in its composition, due to the presence of potassium in the ashes before washing. The identified hydroxyapatite was formed as a result of the reaction between calcium and magnesium phosphate in an alkaline medium. In this sample, the pozzolanic reaction between Ca(OH)₂ and amorphous silica resulted in the formation of 14Å tobermorite.

In the SCBA-W paste, the presence of arcanite or sylvine is not observed, which is in accordance with the effectiveness of ash washing. In this paste, the pozzolanic reaction produced hydrated calcium silicate (CSH, xonotlite) different from the previous case. The form generated is probably different; in the first case, there is a large amount of soluble salts (potassium chloride and sulphate) that stabilize the 14 Å tobermorite form. In the second case, a different hydrate stabilizes, and its strongest peak coincides with the most characteristic peak of calcite (~29º), resulting in a wider peak.
One can observe intense signs attributed to the presence of Portlandite in both pastes, which indicates that CH was not completely consumed for the proportion CH:ash (1:1).

Fig. 3. X-ray diffractograms of SCBA and SCBA-W pastes with lime (CH:ash 1:1, 28 days).

<table>
<thead>
<tr>
<th>SCBA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Abbreviation</strong></td>
</tr>
<tr>
<td>R</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>T</td>
</tr>
<tr>
<td>H</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SCBA – W</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Abbreviation</strong></td>
</tr>
<tr>
<td>R</td>
</tr>
</tbody>
</table>
Table 4 Mineralogical composition of crystalline solids of SCBA and SCBA-W pastes with lime (CH:ash 1:1, 28 days).

Figures 4 and 5 present the differential thermal and thermal analyses of SCBA and SCBA-W pastes cured for 7 and 28 days. All pastes showed peaks in the DTG curve between 110 and 180°C, indicating dehydration of calcium silicate hydrate (CSH or tobermorite). CSH is produced as a result of the pozzolanic reaction between the material’s amorphous silica and calcium hydroxide.

The two peaks between 350 and 520°C are attributed to magnesium compounds. It can be noted that both SCBA and SCBA-W contain significant amounts of magnesium (such as MgO: 9.7% and 14.9%, respectively). There was probably a reaction between magnesium compounds, such as MgO and the amorphous silica present in the ashes, producing hydrated magnesium silicate M-S-H [43]. These hydrates are very amorphous and cannot be detected by XRD, but their presence can be identified by the thermal decomposition that occurs from 430°C [44] and is attributed to the removal of hydroxyl groups from the gel (Mg-OH and Si-OH). In our case, the peak of maximum decomposition speed appears after 500°C. Likewise, the peak located to the left of 430°C is probably due to thermal decomposition of hydromagnesite (Mg₅(CO₃)₃(OH)₂·4H₂O) [44], which was formed as a result of the combination of magnesium salts with a carbonate anion in an alkaline medium. No presence of brucite, Mg(OH)₂, was found in the DTG analysis (440°C is the decomposition temperature for brucite in the same experimental conditions of TG analysis) of pastes and XRD diffractograms of ashes, which
means that magnesium in the ash was not in the form of reactive periclase and dimensional
stability of the paste/mortar/concrete is reached (further studies must be carried out to confirm
this statement). Probably the MgO in the ash was in amorphous phase and it reacted towards
silica to form M-S-H.

There are endothermic peaks between 520 and 580°C related to the decomposition of the
remaining Ca(OH)₂. SCBA total mass loss was 18.2% for 7 days and 18.9% for 28 days. For
SCBA-W, total mass loss was 17.3% for 7 days and 19.4% for 28 days. These data are related
to the pozzolanic reaction, which indicates that most of the reaction products were produced in
the first 7 days of hydration.

Fig. 4. Thermal analysis and differential thermal analysis of pastes curated for 7 days of a)
SCBA and b) SCBA-W, and for 28 days c) SCBA and d) SCBA-W. Temperatures
corresponding to DTG main curve peaks have been indicated.
Based on the loss of mass due to calcium hydroxide (Ca(OH)$_2$) dehydration in the pastes in a temperature range from 520 to 580°C, the fixed lime was quantified by means of the pozzolanic reaction. This value is defined by Eq. (3), where CH$_0$ and CH$_{Ash}$ are, respectively, the initial and final amounts of calcium hydroxide in the CH:ash pastes [45].

$$\text{Ca(OH)}_2 = \frac{(\text{CH})_0 - (\text{CH})_{Ash}}{(\text{CH})_0} \times 100 \quad (1)$$

Evaluation of calcium hydroxide fixation by the ashes (Fig. 6) indicates that the extraction of potassium increased the material’s capacity of fixation, forming CSH in the pastes. SCBA showed a fixation of 68% at 7 days and 75% at 28 days, whereas SCBA-W presented a fixation of 83% at 7 days and 90% at 28 days. This was probably due to the higher concentration of amorphous silica in SCBA-W. In any case, the fixation of Ca(OH)$_2$ in SCBA was relatively high, which is attributed to the presence of alkalis (specifically potassium). It has been reported [46] that the formation of C-S-H in the presence of sodium chloride solution produces a partial replacement of calcium, forming C(N)-S-H gel. Obviously, in the presence of K$^+$, released from the dissolution of arcanite and silvane, the gel produced from the pozzolanic reaction would contain this cation and the gel would be described as C(K)-S-H. The Ca$^{2+}$/K$^+$ exchange bring on the releasing of calcium and more C-S-H would be produced.

Calcium hydroxide fixation of SCBA and SCBA-W can be compared to the one for metakaolin (MK) and spent FCC catalyst [47]: in the previously reported paper, CH:MK pastes with ratios of 7:3 and 3:7 were assessed by thermogravimetric analysis: the fixed percentages were 47% and 76% for 7:3 ratio after 7 and 18 days of curing respectively, and 86% and 100% for 3:7 ratio for the same curing ages. Interpolating these values, the calcium hydroxide fixation for a 5:5 mixture would be 66% and 88% for 7 and 28 curing days respectively. Similar calculation was carried out for spent FCC catalyst: in this case the corresponding fixation values
would be 70 and 82% for 7 and 28 curing days. These results are similar to those found for SCBA; the results obtained for SCBA-W were superior, which means that the reactivity should be considered very high.

![Fixed calcium hydroxide in CH:ash (1:1) pastes cured for 7 and 28 days.](image)

**Fig. 5.** Fixed calcium hydroxide in CH:ash (1:1) pastes cured for 7 and 28 days.

In order to measure the loss of electrical conductivity (LC)(%) of ash and calcium hydroxide aqueous suspensions, Eq. (2) and (3) were employed, where $C_0$ is electrical conductivity of an unsaturated hydroxide solution of calcium before adding ash, $C_t$ is electrical conductivity measured over $t$ seconds, $C_{t,\text{ash}}$ is electrical conductivity of ash measured in deionized water over $t$ seconds, and $C_{t,C}$ is electrical conductivity corrected over $t$ seconds.

\[
\text{LC} (%) = \left(\frac{C_0 - C_{t,C}}{C_0}\right) \times 100 \tag{2}
\]

\[
C_{t,C} = C_t - C_{t,\text{ash}} \tag{3}
\]

**Fig. 7** shows the LC (%) conductivity loss curves for aqueous CH:ash suspensions. SCBA presented a loss of conductivity of 65% at 100 s, 75% at 1000 s, and 78% at 10,000 s (end of procedure). SCBA-W, on the other hand, presented a greater loss of conductivity and,
consequently, a greater pozzolanic reactivity, with 88% at 100 s, 92% at 1000 s, and 93% at 10,000 s. This greater reactivity is due to a higher concentration of amorphous silica after potassium extraction. The greatest losses of conductivity occurred in the first 100 s, which indicates that the pozzolanic reaction occurred quickly. Similar reactivity was found for spent FCC catalyst [48]: for 40°C test, 60% of electrical conductivity was reached after 100 s and for 80°C test this value was 80%. Spent FCC catalyst was considered a high reactive pozzolan [49] and SCSA-W would also be considered as highly reactive supplementary cementing admixture. In similar experimental conditions (60°C) [39], fly ash reached only 36% of electrical conductivity loss, which means that SCBA shows higher reactivity.

![Graph showing conductivity loss over time](image)

**Fig. 6.** Loss of conductivity (%) for CH:ash aqueous suspensions tested for 2.8 h.

### 4. Conclusions

This research compared the pozzolanic reactivity of pure ash from sugar cane bagasse, before and after potassium extraction. Based on the obtained results, it is possible to conclude that potassium extraction from the ashes of sugar cane bagasse benefits pozzolanic reactivity and can generates potassium as a fertilizer for agriculture. More specifically,

- the adopted ash-washing process was efficient in removing potassium, reducing the K₂O content of ash from 37.5% (before washing) to 2.65% (after washing);
- potassium extraction significantly increased the concentration of silica in the ashes;
- the calcination temperature of 600ºC was adequate to avoid crystalline silica formation in the ashes; and
- SCBA after washing (SCBA-W) presented better performance regarding pozzolanic reactivity.

Suggestions for future research:

- Evaluation of cementitious composites with partial substitutions of sugar cane ash and the comparison with commercial and non-commercial pozzolans, such as silica fume or rice husk ash;
- Use, in agriculture, of the potassium-rich solution extracted from the washing process. The washing procedure of ashes would be interesting if the released water is reused for fertilizing. In this case, the modified remaining ash would be much more interesting as component in cementing materials because the washed ash showed more pozzolanic reactivity.

Acknowledgements

Funding: This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

References


http://dx.doi.org/10.1016/j.fuel.2016.02.020.


http://dx.doi.org/10.1016/j.jclepro.2017.09.150.


