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Additional Information

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

3
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26 **Abstract**

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

37 **Keywords:** mineral addition; sugar cane ash; pozzolanic reactivity; cement.

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51 **1. Introduction**

52 The current worldwide production of sugar cane (*Saccharum* spp.) is approximately 1.84
53 billion tons per year [1], with Brazil being the largest producer in the world. In the 2018/2019
54 Brazilian harvest, approximately 620 million tons of sugar cane were produced, representing
55 34% of world production, with 29 million tons of sugar and 33 million m³ of ethanol extracted
56 [2-4].

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

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

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

71 Bagasse composition contains most nutrients absorbed by the plant during growth, thus
72 presenting significant amounts of potassium and silica [15, 16]. Potassium (K) is one of the
73 main nutrients necessary for plant development. It plays a fundamental role in several
74 physiological processes and is present in all crop cycles, it is a macronutrient absorbed by plants
75 during the vegetative growth stage [17]: potassium participates in the synthesis of sugars and

76 proteins during the photosynthesis process to obtain energy, in the translocation of
77 carbohydrates and proteins, and in water absorption [18].

78 The high levels of SiO_2 in SCBA are due to silicon absorbed from the soil by sugar cane
79 roots in the form of monosilic acid (H_4SiO_4) as it accumulates on the outer wall of epidermal
80 cells as silica gel after water leaves the plant by transpiration. In addition, there is contamination
81 of sugar cane by sand in the harvesting process, resulting in the presence of crystalline silica
82 [16, 19, 20].

83 Several studies show that sugar cane ash has a chemical element suitable for use as a
84 pozzolanic mineral addition to Portland cement composites, mainly because of its high levels
85 of silicon dioxide (SiO_2) [12, 15, 16, 20-22].

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

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

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

98 The presence of amorphous silica is a necessary factor for the pozzolanic reaction to
99 occur, although it is not the only one. Factors such as burning temperature, particle size, and
100 amount of organic matter also play a role [23].

101 The application of by-products in the production of cementitious composites reduces the
102 problem of the disposal of these ashes and provides a reduction in the use of clinker, the main
103 component of Portland cement, which has high energy demand with consequent emission of
104 greenhouse gases such as CO₂ [24]. It is estimated that 800 kg of CO₂ are generated for each
105 ton of clinker. These emissions correspond to 5 to 8% of the carbon dioxide generated
106 worldwide [25-31]. According to Fairbairn et al. (2010, 2012) [32, 33], sugar cane ash use is
107 attractive because it is a by-product that possibly reduces CO₂ emissions into the atmosphere,
108 thus indicating the possibility the production of environmentally friendly pozzolans.

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

116 The study of the reactivity of ash from the burning of energy cane is important because
117 they do not have an adequate destination, being necessary the valorization of this agroindustrial
118 by-product as well as the availability of a pozzolan to be added to the cement, seeking to reduce
119 the emission of CO₂ by the cement industries, in addition this research proposes the use of
120 potassium extracted from ashes as fertilizers, in order to reduce the consumption of potassium
121 from a primary source, in addition to giving a destination to the potassium extracted in the
122 washing process.

123 Therefore, the goal of this work was to investigate the effects of potassium extraction on
124 the pozzolanicity of pure sugar cane bagasse ash – i.e., without soil contamination – seeking to
125 produce reactive ash to utilize in cementitious composites.

126 Thus, in order to assess the behavior of the ash before and after potassium extraction,
127 physical and chemical characterizations of the ash were carried out by dispersive energy
128 spectroscopy (EDS), loss by ignition (LOI), particle size distribution, diffraction of X-ray
129 powder (XRD), and analysis of ash reactivity by means of X-Ray diffraction in calcium
130 hydroxide paste, analysis of lime fixation by thermogravimetry and evaluation of pozzolanic
131 reactivity.

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135 **2. Materials and Methods**

136

137 **2.1. Materials**

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

143

144 **2.2. Methods**

145

146 **2.2.1. Ash preparation from sugar cane bagasse**

147 The sugar canes were washed with water to eliminate residual soil contamination and
148 ground to extract juice, thus obtaining bagasse. This bagasse was dried at $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 24
149 h and ground in a knife mill to reduce particle size.

150 The sugar cane bagasse was calcined in a Jung-10013 resistive oven with a power of 7000
151 W, at 600°C for 60 min, with a heating rate of 4°C/min. The choice of burning temperature is
152 because up to 600 °C there is a loss of organic matter and without the transformation of
153 amorphous silica into crystalline silica [8,16]. The ashes were taken out immediately after
154 calcination and cooled at room temperature (25°C ± 2°C).

155 After cooling, the ashes were again ground in a vibrating mill (Micro Mill Pulverisette 0,
156 Fritsch), for 30 min with a volume of 200 cm³ and a grinding goal of 50 mm in diameter and
157 370 g in mass. After grinding, the ashes were subjected to a treatment of potassium extraction
158 in batches of 5 g, they were washed with 500 ml of deionized water at 60°C and filtered.
159 Afterwards, a second wash occurred, in which the ashes were stirred with 200 ml of deionized
160 water at 60°C for 3 h, filtered, and dried in an oven at 60°C for 24 h. The washing was carried
161 out with water, so that the potassium solution can be reused in fertigation, the water heating
162 occurred to facilitate potassium solubilization. This process was carried out twice so that a
163 greater extraction occurred. No tests were performed on washing solutions to examine their
164 compositions. Ashes before washing are referred to as SCBA and, after washing, as SCBA-W.
165 Both ashes were homogeneized, in order to take a representative sample for the tests. One
166 sample of SCBA and SCBA-W was used for each test performed.

167

168 **2.2.2. Material characterization**

169 The morphological and chemical characterization of the ashes was performed in a Zeiss
170 ULTRA 55 scanning electron microscope (SEM). Chemical analyses of oxides present in the
171 ashes were carried out by energy-dispersive spectroscopy (EDS) in 10 different areas of 115
172 µm × 85 µm at 15 kV, without coating, to measure mean values and their standard deviations.
173 Loss on ignition (LOI) was carried out at 950°C for 60 min, with a heating rate of 10°C/min.

174 Particle size distribution was determined using a laser particle size analyser (LDA;
175 Malvern Mastersizer 2000). Particles were dispersed in deionized water as a non-reactive liquid.

176 The mineralogical analyses of the ashes were carried out in an x-ray diffractometer (DRX;
177 Bruker AXS D8 Advance) with $\text{CuK}\alpha$ radiation, operating at 40 kV/20 mA, using a scanning
178 angle of $5^\circ \leq 2\theta \leq 70^\circ$ at a $0.01^\circ/\text{s}$ step.

179

180 **2.2.3. Mineralogical analysis of pastes**

181 A DRX (Bruker AXS D8 Advance) with $\text{CuK}\alpha$ radiation, operating at 40 kV/20 mA,
182 using a scanning angle of $5^\circ \leq 2\theta \leq 70^\circ$ and a $0.01^\circ/\text{s}$ step, performed the mineralogical analysis
183 of pastes.

184 The calcium hydroxide/hydrated ash pastes were prepared using the proportions of 1:1
185 (by mass) of CH:ash, keeping a water/solid ratio of 0.8. X-ray diffraction analyses took place
186 after 28 days of curing at 23°C with 100% relative humidity (RH). In order to prepare the
187 samples for analysis, the pastes were crushed with acetone, filtered, and placed in an oven at
188 60°C for 30 min. Next, the samples were submitted to an $80\ \mu\text{m}$ sieve.

189

190 **2.2.4. Lime fixation analysed through thermogravimetry**

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

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

198

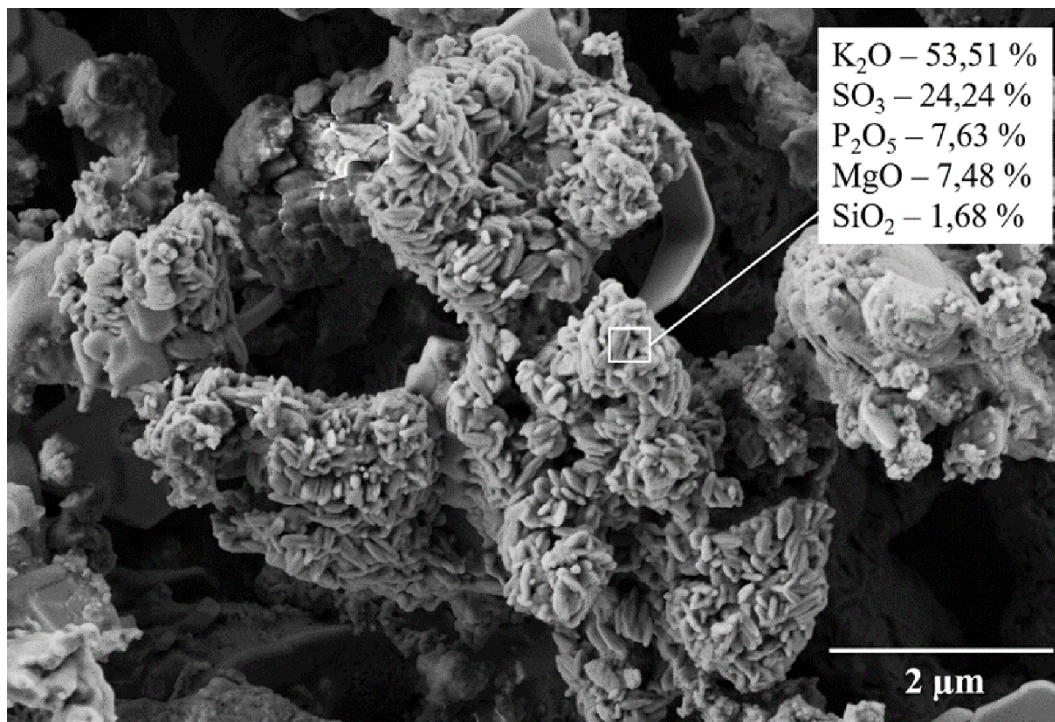
199 **2.2.5. Evaluation of pozzolanic reactivity**

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

209

210 **3. Results and Discussion**

211 In Fig. 1, one can observe the presence of potentially soluble solids, such as potassium
212 in SCBA. Because potassium is extremely important in the physiologic processes in the plant
213 [18] one can expect that sugar cane bagasse ash, when not contaminated by soil, will present
214 large amounts of potassium.



215

216 **Fig. 1.** SEM micrograph of SCBA, obtained through secondary electron detectors, and EDS
 217 composition from a spot.

218

219 Table 1 presents the mean values of ash chemical composition before and after washing.
 220 SCBA before washing showed a high content of potassium oxide (K_2O) (37.50%). This result
 221 was expected, because potassium (K) is the most abundant cation in plant tissues, being
 222 absorbed from the soil in large quantities. Some crops can absorb amounts of potassium
 223 superior to their needs [42]. Sodium and potassium oxides (Na_2O and K_2O), when present in
 224 high content in a cementitious matrix, can react with other materials and cause the material to
 225 disintegrate, as the alkali-aggregate reaction occurs in concrete. The maximum content of
 226 alkalis available in Na_2O must be 1.5% [35].

227 The silicon dioxide (SiO_2) present in SCBA before washing was 13.90%; this came from
 228 sugar cane cell walls because the residual soil particles from the harvesting process were
 229 removed. SCBA after washing (SCBA-W) presented a low K_2O content (3.20%), which
 230 indicates that the washing process was efficient in extracting potassium from the ashes. With

231 the removal of potassium, other elements were found to be concentrated in the ashes – e.g.,
 232 SiO₂, which presented average values of 50.20%. Magnesium and calcium oxide (MgO and
 233 CaO, respectively) levels increased after washing, which suggests that magnesium and calcium
 234 ions are present in the form of insoluble salts, such as carbonates. Phosphorus content (P₂O₅)
 235 also increased after washing, suggesting that it may be present in ash in the form of calcium
 236 phosphate, which is also insoluble. Sulphur (SO₃) was completely removed after washing,
 237 suggesting that its presence in ash may be in the form of potassium sulphate. SCBA, calcined
 238 at 600°C for 120 min, presented an LOI of 13.4% and SCBA-W of 16.8%. This result suggests
 239 that washing did not significantly change the content of organic material in the ashes.

240

Ash Types	Parameters	SiO ₂	K ₂ O	CaO	SO ₃	MgO	P ₂ O ₅
SCBA	Mean value	13.90	43.30	10.50	14.30	9.70	8.30
	Std. Dev.	1.80	3.10	0.60	0.90	1.00	0.80
	Max.	17.20	49.20	11.20	15.80	11.40	9.20
	Min.	11.40	40.50	9.90	12.90	8.00	7.10
SCBA-W	Mean value	50.20	3.20	14.50	-	14.90	10.6
	Std. Dev.	3.10	0.40	1.50	-	1.50	1.10
	Max.	55.90	3.80	16.80	-	16.90	11.30
	Min.	47.60	2.50	12.30	-	12.50	8.50

241 **Table 1** Mean values regarding chemical composition of sugar cane bagasse ash. Values were
 242 calculated from ten EDS analyses in a 115 µm × 85 µm area.
 243 Std. Dev. = standard deviation; Max. = maximum recorded value; Min. = minimum recorded
 244 value.

245

246 SCBA and SCBA–W showed mean particle size values (Table 2) of 16.87 and 23.99 μm ,
 247 respectively. The difference between particle sizes indicates that potassium comprises part of
 248 the small particles, which contributes to the reduction in all sizes of SCBA (i.e., mean size, D_{10} ,
 249 D_{50} , and D_{90}).
 250

Ash Types	* D_{mea} (μm)	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)
SCBA	16.87	1.88	8.65	36.87
SCBA-W	23.99	6.31	19.88	47.64

251 **Table 2** Distribution of ash particle size.

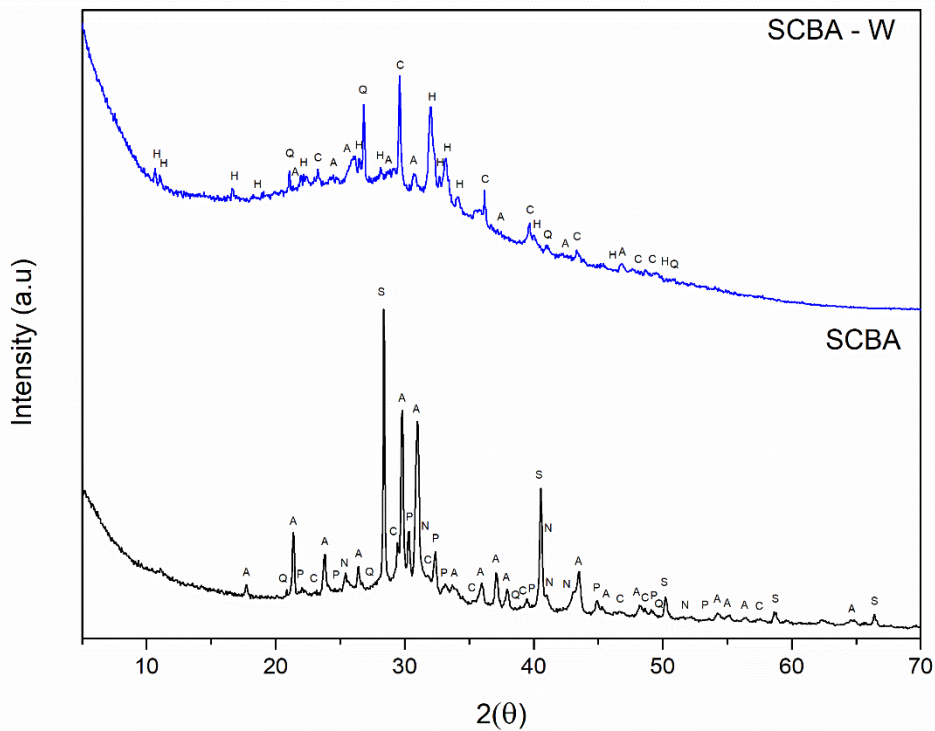
252 * D_{mea} = mean particle size; D_{10} , D_{50} , and D_{90} are the maximum particle sizes that compose
 253 10%, 50%, and 90% of sample volume, respectively. Source: own authorship.

254
 255 Fig. 2 and Table 3 present the x-ray diffractograms and mineralogical components of
 256 SCBA and SCBA-W, respectively. They show the presence of arcanite (K_2SO_4), calcite
 257 (CaCO_3), anhydrite (CaSO_4), calcium potassium phosphate (KCaPO_4), quartz (SiO_2), sylvine
 258 (KCl), and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$). SCBA presented major peaks of sylvine and
 259 arcanite, which indicates the presence of potassium and is thus consistent with the chemical
 260 composition shown in Table 1.

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

266 Crystalline silicas produced in the burning process, such as tridymite and cristobalite,
 267 were not observed, indicating that the temperature of 600°C does not promote silica
 268 crystallization. As a result, present silica, with the exception of quartz, is probably reactive

269 silica in an amorphous form. There were also no crystalline magnesium compounds, which
 270 suggests that this cation is combined in the form of amorphous or poorly crystallized
 271 substances, such as MgO or Mg(OH)₂ or hydromagnesite.



272
 273 **Fig. 2.** X-ray diffractograms of SCBA and SCBA-W.

274

SCBA			
Abbreviation	Mineralogical name	Chemical formula	Comments
S	Sylvine	KCl	Major
A	Arcanite	K ₂ SO ₄	Major
N	Anhydrite	CaSO ₄	Minor
P	Calcium Potassium Phosphate	KCaPO ₄	Minor
C	Calcite	CaCO ₃	Traces
Q	Quartz	SiO ₂	Traces
SCBA – W			

Abbreviation	Mineralogical name	Chemical formula	Comments
C	Calcite	CaCO ₃	Major
Q	Quartz	SiO ₂	Major
H	Hydroxyapatite	Ca ₅ (PO ₄) ₃ (OH)	Major
A	Arcanite	K ₂ SO ₄	Traces

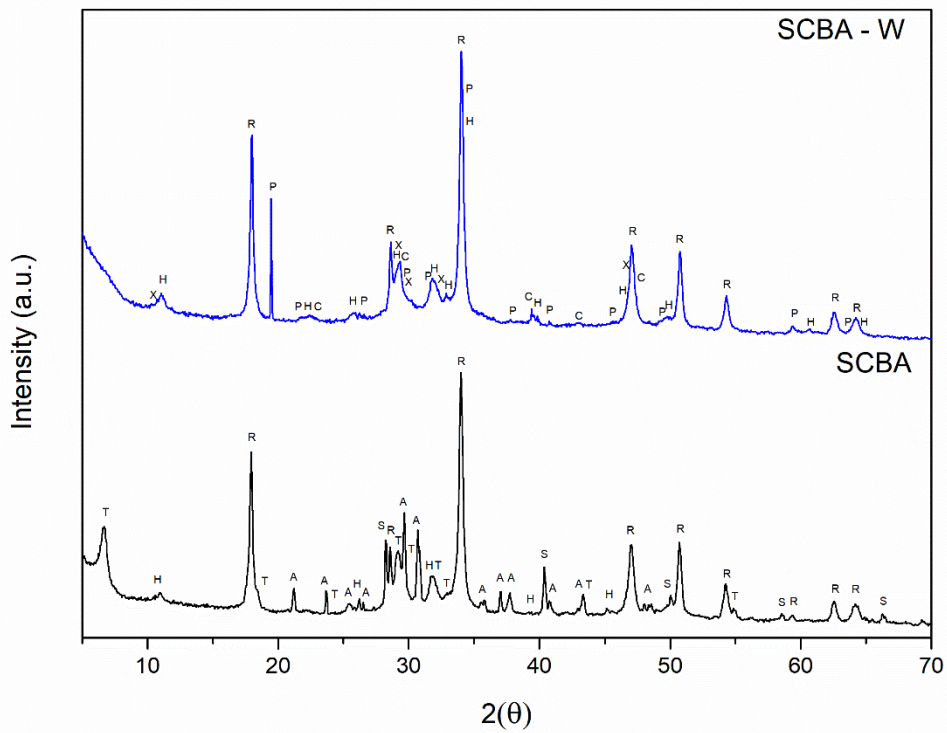
275 **Table 3** Mineralogical composition of SCBA and SCBA-W crystalline solids.

276

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

283 In the SCBA-W paste, the presence of arcanite or sylvine is not observed, which is in
 284 accordance with the effectiveness of ash washing. In this paste, the pozzolanic reaction
 285 produced hydrated calcium silicate (CSH, xonotlite) different from the previous case. The form
 286 generated is probably different; in the first case, there is a large amount of soluble salts
 287 (potassium chloride and sulphate) that stabilize the 14 Å tobermorite form. In the second case,
 288 a different hydrate stabilizes, and its strongest peak coincides with the most characteristic peak
 289 of calcite (~29°), resulting in a wider peak.

290 One can observe intense signs attributed to the presence of Portlandite in both pastes,
 291 which indicates that CH was not completely consumed for the proportion CH:ash (1:1).



292
 293 **Fig. 3.** X-ray diffractograms of SCBA and SCBA-W pastes with lime (CH:ash 1:1, 28 days).
 294

SCBA			
Abbreviation	Mineralogical name	Chemical formula	Comments
R	Portlandite	$\text{Ca}(\text{OH})_2$	Major
S	Sylvine	KCl	Minor
A	Arcanite	K_2SO_4	Minor
T	Tobermorite 14Å	$\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$	Traces
H	Hydroxyapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	Traces

SCBA – W			
Abbreviation	Mineralogical name	Chemical formula	Comments
R	Portlandite	$\text{Ca}(\text{OH})_2$	Major

C	Calcite	CaCO_3	Minor
H	Hydroxyapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	Minor
X	Xonotlite	$\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$	Minor
P	Magnesium hydrogen phosphate hydrate	$\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$	Traces

295 **Table 4** Mineralogical composition of crystalline solids of SCBA and SCBA-W pastes with
 296 lime (CH:ash 1:1, 28 days).

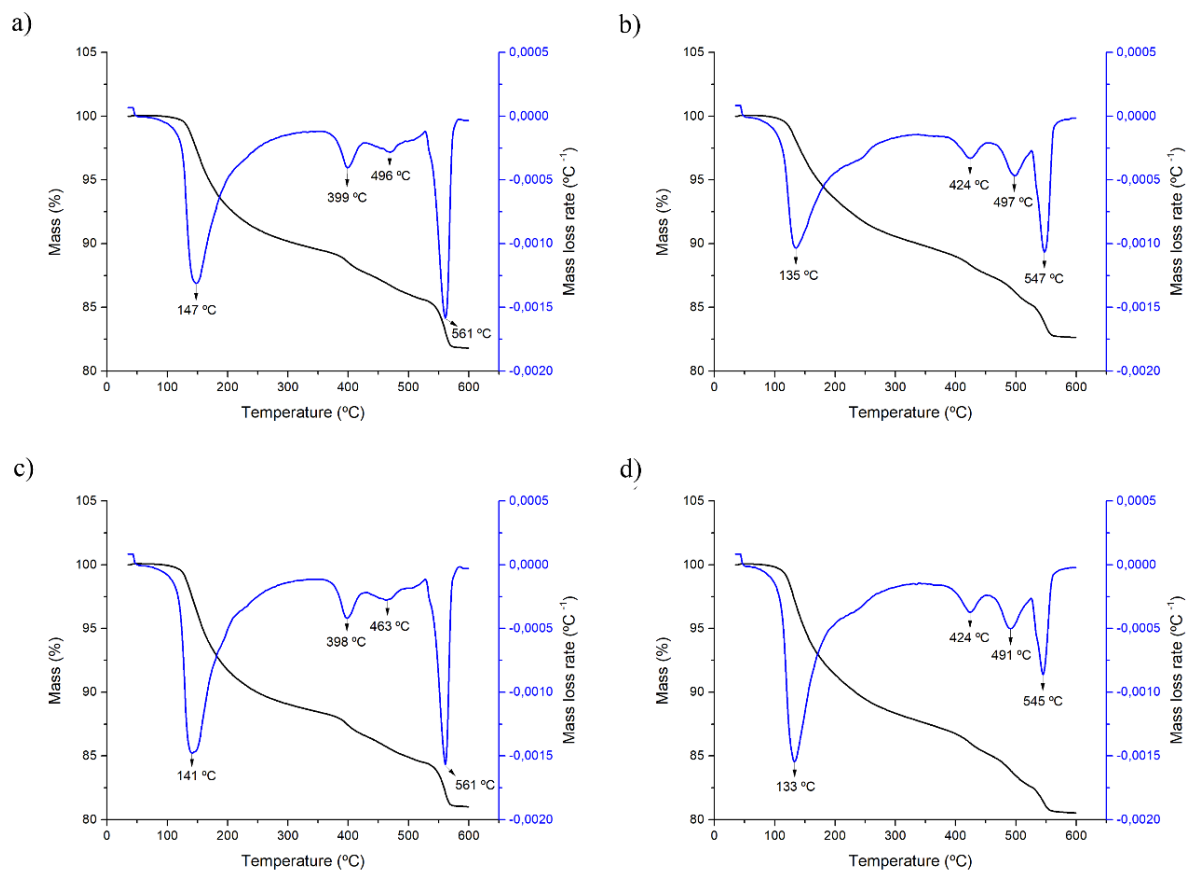
297

298 Figures 4 and 5 present the differential thermal and thermal analyses of SCBA and
 299 SCBA-W pastes cured for 7 and 28 days. All pastes showed peaks in the DTG curve between
 300 110 and 180°C, indicating dehydration of calcium silicate hydrate (CSH or tobermorite). CSH
 301 is produced as a result of the pozzolanic reaction between the material's amorphous silica and
 302 calcium hydroxide.

303 The two peaks between 350 and 520°C are attributed to magnesium compounds. It can be
 304 noted that both SCBA and SCBA-W contain significant amounts of magnesium (such as MgO:
 305 9.7% and 14.9%, respectively). There was probably a reaction between magnesium compounds,
 306 such as MgO and the amorphous silica present in the ashes, producing hydrated magnesium
 307 silicate M-S-H [43]. These hydrates are very amorphous and cannot be detected by XRD, but
 308 their presence can be identified by the thermal decomposition that occurs from 430°C [44] and
 309 is attributed to the removal of hydroxyl groups from the gel (Mg-OH and Si-OH). In our case,
 310 the peak of maximum decomposition speed appears after 500°C. Likewise, the peak located to
 311 the left of 430°C is probably due to thermal decomposition of hydromagnesite
 312 ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) [44], which was formed as a result of the combination of magnesium
 313 salts with a carbonate anion in an alkaline medium. No presence of brucite, $\text{Mg}(\text{OH})_2$, was
 314 found in the DTG analysis (440°C is the decomposition temperature for brucite in the same
 315 experimental conditions of TG analysis) of pastes and XRD diffractograms of ashes, which

316 means that magnesium in the ash was not in the form of reactive periclase and dimensional
317 stability of the paste/mortar/concrete is reached (further studies must be carried out to confirm
318 this statement). Probably the MgO in the ash was in amorphous phase and it reacted towards
319 silica to form M-S-H.

320 There are endothermic peaks between 520 and 580°C related to the decomposition of the
321 remaining $\text{Ca}(\text{OH})_2$. SCBA total mass loss was 18.2% for 7 days and 18.9% for 28 days. For
322 SCBA-W, total mass loss was 17.3% for 7 days and 19.4% for 28 days. These data are related
323 to the pozzolanic reaction, which indicates that most of the reaction products were produced in
324 the first 7 days of hydration.



325
326 **Fig. 4.** Thermal analysis and differential thermal analysis of pastes cured for 7 days of a)
327 SCBA and b) SCBA-W, and for 28 days c) SCBA and d) SCBA-W. Temperatures
328 corresponding to DTG main curve peaks have been indicated.

329

330 Based on the loss of mass due to calcium hydroxide (Ca(OH)₂) dehydration in the pastes
331 in a temperature range from 520 to 580°C, the fixed lime was quantified by means of the
332 pozzolanic reaction. This value is defined by Eq. (3), where CH₀ and CH_{Ash} are, respectively,
333 the initial and final amounts of calcium hydroxide in the CH:ash pastes [45].

334

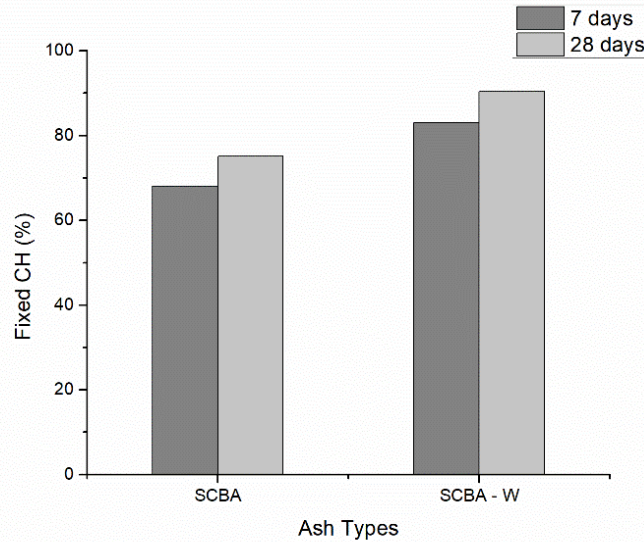
$$335 \text{Ca(OH)}_2 = \frac{(\text{CH})_0 - (\text{CH})_{\text{Ash}}}{(\text{CH})_0} \times 100 \quad (1)$$

336

337 Evaluation of calcium hydroxide fixation by the ashes (Fig. 6) indicates that the extraction
338 of potassium increased the material's capacity of fixation, forming CSH in the pastes. SCBA
339 showed a fixation of 68 % at 7 days and 75% at 28 days, whereas SCBA-W presented a fixation
340 of 83% at 7 days and 90% at 28 days. This was probably due to the higher concentration of
341 amorphous silica in SCBA-W. In any case, the fixation of Ca(OH)₂ in SCBA was relatively
342 high, which is attributed to the presence of alkalis (specifically potassium). It has been reported
343 [46] that the formation of C-S-H in the presence of sodium chloride solution produces a partial
344 replacement of calcium, forming C(N)-S-H gel. Obviously, in the presence of K⁺, released from
345 the dissolution of arcanite and silvine, the gel produced from the pozzolanic reaction would
346 contain this cation and the gel would be described as C(K)-S-H. The Ca⁺²/K⁺ exchange bring
347 on the releasing of calcium and more C-S-H would be produced.

348 Calcium hydroxide fixation of SCBA and SCBA-W can be compared to the one for
349 metakaolin (MK) and spent FCC catalyst [47]: in the previously reported paper, CH:MK pastes
350 with ratios of 7:3 and 3:7 were assessed by thermogravimetric analysis: the fixed percentages
351 were 47% and 76% for 7:3 ratio after 7 and 18 days of curing respectively, and 86% and 100%
352 for 3:7 ratio for the same curing ages. Interpolating these values, the calcium hydroxide fixation
353 for a 5:5 mixture would be 66% and 88% for 7 and 28 curing days respectively. Similar
354 calculation was carried out for spent FCC catalyst: in this case the corresponding fixation values

355 would be 70 and 82% for 7 and 28 curing days. These results are similar to those found for
 356 SCBA; the results obtained for SCBA-W were superior, which means that the reactivity should
 357 be considered very high.



358
 359 **Fig. 5.** Fixed calcium hydroxide in CH:ash (1:1) pastes cured for 7 and 28 days.

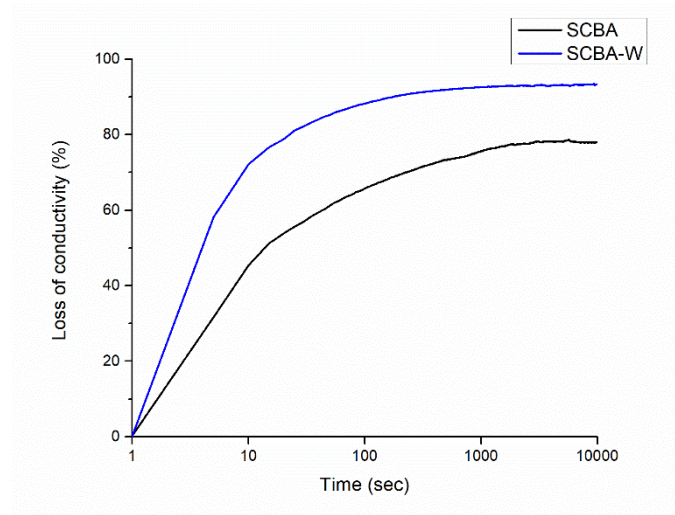
360
 361 In order to measure the loss of electrical conductivity (LC)(%) of ash and calcium
 362 hydroxide aqueous suspensions, Eq. (2) and (3) were employed, where C₀ is electrical
 363 conductivity of an unsaturated hydroxide solution of calcium before adding ash, C_t is electrical
 364 conductivity measured over t seconds, C_{t,ash} is electrical conductivity of ash measured in
 365 deionized water over t seconds, and C_{t,C} is electrical conductivity corrected over t seconds.

366
 367
$$LC (\%) = \frac{C_0 - C_{t,C}}{C_0} \times 100 \quad (2)$$

368
$$C_{t,C} = C_t - C_{t,ash} \quad (3)$$

369
 370 Fig. 7 shows the LC (%) conductivity loss curves for aqueous CH:ash suspensions. SCBA
 371 presented a loss of conductivity of 65% at 100 s, 75% at 1000 s, and 78% at 10,000 s (end of
 372 procedure). SCBA-W, on the other hand, presented a greater loss of conductivity and,

373 consequently, a greater pozzolanic reactivity, with 88% at 100 s, 92% at 1000 s, and 93% at
374 10,000 s. This greater reactivity is due to a higher concentration of amorphous silica after
375 potassium extraction. The greatest losses of conductivity occurred in the first 100 s, which
376 indicates that the pozzolanic reaction occurred quickly. Similar reactivity was found for spent
377 FCC catalyst [48]: for 40°C test, 60% of electrical conductivity was reached after 100 s and for
378 80°C test this value was 80%. Spent FCC catalyst was considered a high reactive pozzolan [49]
379 and SCBA-W would also be considered as highly reactive supplementary cementing admixture.
380 In similar experimental conditions (60°C) [39], fly ash reached only 36% of electrical
381 conductivity loss, which means that SCBA shows higher reactivity.



382

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

384

385 4. Conclusions

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

- 390 - the adopted ash-washing process was efficient in removing potassium, reducing the
391 K_2O content of ash from 37.5% (before washing) to 2.65% (after washing);

- 392 - potassium extraction significantly increased the concentration of silica in the ashes;
393 - the calcination temperature of 600°C was adequate to avoid crystalline silica
394 formation in the ashes; and
395 - SCBA after washing (SCBA-W) presented better performance regarding pozzolanic
396 reactivity.

397 Suggestions for future research:

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

406

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410

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