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Sustainable approach to simultaneously improve the pozzolanic activity of sugarcane bagasse ash and the vinasse fertilization potential

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A R T I C L E I N F O

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A B S T R A C T

The purpose of this study was to evaluate the viability of sugarcane bagasse ash as a sustainable supplementary cementitious material and its association with improving the fertilizing properties of vinasse, used as a leaching agent. Thus, a bagasse ash with low quartz contamination was divided into three parts: one kept *in natura*, one submitted to citric acid leaching and the third to vinasse leaching. After production, which was concluded with re-calcination and ultrafine grinding, the three ashes were characterized according to their chemical and mineralogical composition, particle size, porosity, density, and pozzolanic activity. Paste hydration with 20 wt% cement replacement by each ash was assessed in isothermal calorimetry and chemical shrinkage tests. The elemental and oxide composition of vinasse before and after leaching was also obtained. The results showed that vinasse leaching promoted an increase in specific surface area and pozzolanic activity of ash, comparable to that observed for citric-acid leaching procedure. Tests with pastes containing vinasse-leached ash confirmed the improvement in cement hydration. In addition, after leaching, vinasse exhibited a decline in heavy metal concentration, increased pH (neutralization) and macronutrient concentration. Thus, vinasse leaching improved the pozzolanic characteristics of ash, making vinasse a more environmentally friendly fertilizer.

1. Introduction

Sugarcane is cultivated in more than 120 countries, with production of 1.8 billion metric tons in 2017 (Silalertruksa and Gheewala, 2020). It is estimated that by 2025 sugarcane production will be around 2.1 billion metric tons, primarily aimed at sugar and ethanol (FAO, 2016). Brazil is the largest sugarcane producer with an estimated production of 640 million tons for the 2021/22 growing season, 35% of which destined for sugar and 65% for ethanol (Companhia Nacional de Abastecimento, 2021). Currently, sugarcane is one of the most promising sources for the generation of bioenergy in Brazil, with generation of 20.2×10^3 GWh in 2021 (União da Indústria de Cana-de-açúcar e Bioenergia, 2022).

Numerous wastes are generated during sugarcane processing, including filter cake, bagasse and vinasse. Filter cake is produced by clarifying sugarcane juice and is used as fertilizer to produce citric acid and biogas (Gupta et al., 2011). Around 27 kg of this waste is generated from 1 metric ton of processed sugarcane. Approximately 300 kg of bagasse is generated for each metric ton of processed sugarcane and its burning as biomass can supply the entire energy demand of sugar mills (Hofsetz and Silva, 2012). Bagasse ash is generated after burning (around 2.5 kg for each metric ton of bagasse), with worldwide production in 2020 estimated at more than 10 million metric tons. Vinasse, in turn, consists of dark brown slurry, a complex acidic compost (pH of 3.5–5.0) with high organic content (Lara and Cordeiro, 2019). For each liter of ethanol, between 10 and 15 L of vinasse are produced, depending on the distillery equipment (Cortez et al., 1992).

Bagasse ash has been widely studied as a sustainable supplementary cementitious material due to its pozzolanic properties (Morales et al., 2009) and the more severe environmental laws for its disposal (Bahurudeen et al., 2014). Partial replacement of Portland cement by bagasse ash promotes a cleaner production and really affects concrete by improving its rheology (Moretti et al., 2018), long-term compressive behavior (Cordeiro et al., 2018), durability (Rukzon and Chindaprasirt, 2012), and heat released during hydration (Bahurudeen et al., 2015). In turn, vinasse has been used as fertilizer (fertigation) in sugarcane plantations or as a bioenergy source (Meghana and Shastri, 2020). The continuous use of vinasse in fertigation promotes soil salinization, heavy

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metal deposition and hinders sugarcane yield (Meghana and Shastri, 2020). As such, Gebreeyessus et al. (2019) concluded there is an enormous gap to fill with research to develop integrated vinasse treatment using an interdisciplinary approach that improves the environmental performance of distilleries.

By removing metal oxides, acid leaching improves the chemical and physical properties of rice husk ash (Krishnarao et al., 2001), elephant grass ash (Cordeiro and Sales, 2015), and other types of biomass ashes (Cordeiro et al., 2020). This procedure may contribute to mitigating the significant chemical composition variability of biomass ash (Mali and Nanthagopalan, 2021), one of the main obstacles to applying this residue as a clean and renewable supplementary cementitious material. In this respect, the present study aimed at characterizing highly reactive bagasse ash production using vinasse leaching pretreatment. In addition, vinasse tends to be neutralized in the leaching process, which makes its use as biofertilizer more efficient and environmentally friendly.

2. Materials

Bagasse ash and vinasse were collected in a sugarcane mill in northern Rio de Janeiro state, Brazil. The ash was collected dry, during boiler cleaning, where bagasse is burned at around 800 °C. The vinasse was collected in the discharge duct of the distiller. The vinasse temperature at collection was around 90 °C.

Pastes and mortars were produced using Brazilian class G cement (ABNT. Brazilian Association of Technical Standards, 2020), which consists of clinker and gypsum for oil well cementing, as well as polycarboxylate-based superplasticizer and deionized water. Standard quartz sand was also used in mortar production (ABNT. Brazilian Association of Technical Standards, 2015a).

3. Methods

3.1. Pozzolanic ash production

After collection, the ash was homogenized, followed by densimetric fractionation (Cordeiro et al., 2022) to remove the quartz, the main ash contaminant. Densimetric fractionation was performed by placing 9 kg of ash in a tank containing 70 L of deionized water. Next, the solution was agitated manually for 1 min (approximately 80 rpm) and left to rest for an additional 1 min. The supernatant (denominated SCBA-S) was collected with a 1.0 mm sieve. The sieve opening size was established by the particle size distribution of the material deposited on the bottom (D_{90} of 0.28 mm) after a preliminary test. Next, the SCBA-S was oven dried at 110 °C for 24 h. SCBA-S yield was 60% of the total ash collected.

The SCBA-S was divided into three equal parts. Two parts underwent a hot leaching process, one with vinasse and the other with citric acid. The temperature during both leachings was maintained between 70 and 90 °C in order to simulate vinasse discharge temperature in the mill. To that end, a 13 L leaching prototype heated by electric resistance (3600 W) was produced using a low-rotation (10 rpm) rod-helix coupled system for suspension homogenization. The solute-solvent ratio was 350 g of SCBA-S for 10 L of acid solution. The solution was prepared with 700 g of anhydrous citric acid (99.5%) diluted in 10 L of deionized water. Citric acid and vinasse leaching duration was 1 and 2 days, respectively. These times were optimized in preliminary tests according to the chemical composition of ashes.

The three ash samples underwent conjugated burning to reduce residual carbonaceous compound content and, consequently, increase silica concentration. Re-calcination is a typical procedure for ashes with high loss on ignition (Mali and Nanthagopalan, 2021). Ashes underwent autogenous burning in a pilot oven (De Siqueira and Cordeiro, 2022) adapted from Sugita (1994). The ratio of sample to internal pilot oven chamber volumes was maintained at 0.25 for all burnings. Temperature was monitored for 12 h to prevent temperatures above 800 °C, which could cause crystalline phase formation in the ash (Cordeiro et al., 2009a). Fig. 1a shows a typical burning with a maximum temperature of 684 °C and heating rate of approximately 6.5 °C min^{-1}.

After autogenous burning, the ashes were submitted to controlled burning in a muffle furnace at 600 °C for 15 min at a heating rate of 10 °C min^{-1} (Fig. 1a) to compensate for the 5% loss on ignition (ABNT. Brazilian Association of Technical Standards, 2015b). The ratio of sample to furnace chamber volumes was maintained at 0.05 and the sample was cooled down inside the furnace.

After re-calcination, the three ashes were ground in a 1-S Batch Attritor VFD mill (Union Process) with 50% filling. Dry grinding was carried out at 500 rpm for 60 min with 100 g of ash and 3 kg of 2-mm Zirconox (ceria-stabilized zirconia) grinding balls. Grinding conditions were optimized in prior trials based on the Flores et al. (2017) study. The *in natura* ground ash was denominated SCBA-1 and those ground after vinasse and citric acid leaching, SCBA-2 and SCBA-3, respectively.

3.2. Material characterization

Ash and cement oxide composition was determined by X-ray spectrometry (Shimadzu EDX-720 analyzer) and loss on ignition according to ASTM International, 2018. Particle size distribution was obtained by light scattering analysis using a Mastersizer 3000E analyzer (Malvern Instruments) in liquid medium (ethanol 99.9% p.a. for cement and deionized water for ash), with 15 min of agitation (2000 rpm) and ultrasound in the final minute. Density was in line with ABNT. Brazilian

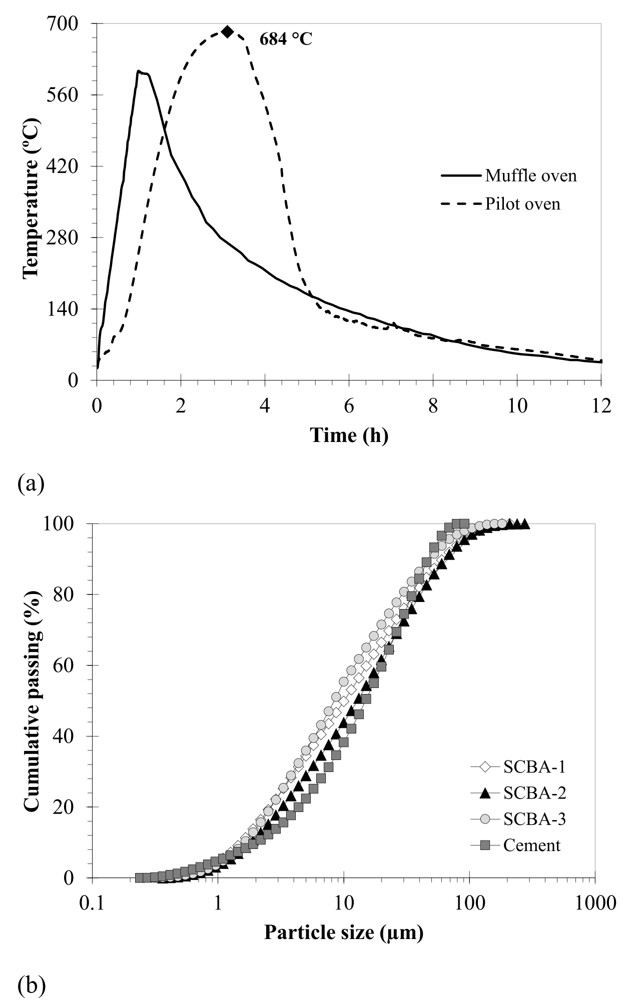


Fig. 1. Temperature evolution over time for two burning processes (a). Particle size distributions of SCBA-1, SCBA-2, SCBA-3, and cement (b).

Association of Technical Standards, 2017.

The specific surface area and pore structure of the ashes were assessed applying a nitrogen adsorption-desorption test at their boiling temperature using a Micromeritics Tristar II Kr 3020 analyzer. The samples were preheated to 120 °C in a vacuum for 12 h. The specific surface area was determined using the BET method (Brunauer et al., 1938). Pore structure was assessed by the DFT (Density Functional Theory) method, adapted for mesopores and micropores (Landers et al., 2013). SCBA-1, SCBA-2 and SCBA-3 showed a TSE (Tensile Strength Effect), characteristic of pores with a narrow neck size and much larger inner diameters. Thus, N_2 evaporation is delayed until critical pressure $(P/P_0)_{TSE}$ is reached, where the hemispherical menisci collapse and pores are immediately emptied (Thielemann et al., 2011). In this case, mesopore emptying occurs through smaller pores, wall micropores or narrower sections along the mesopores (De Souza et al., 2019). Finally, the pore structure of each ash was classified according to its isotherm, in line with IUPAC (International Union of Pure and Applied Chemistry) recommendations (Thommes et al., 2015).

Mineralogical analysis was obtained by X-ray diffraction using a Rigaku Miniflex 600 diffractometer with Cu-Kα radiation, operating at 40 kV and 15 mA. The scans occurred between 8 and 70°, with step of 0.02° at 5° min^{-1}. The PDXL V-2 program was used to identify the crystalline phases. Amorphous content was quantified using the Rietveld refinement with ultrafine anatase (TiO_2) p.a. (99.5% purity) as internal standard (20 wt%). The quantification was repeated in triplicate and results were expressed as mean ± standard deviation.

The pozzolanic activity of the ashes was obtained using a modification to the method proposed by Luxán et al. (1989), as suggested by De Lima and Cordeiro (2021). The test assesses reactivity by the variation in electrical conductivity of 70 mL of saturated solution of calcium hydroxide (2 g of $Ca(OH)_2$ p.a. in 1 L of distilled water) with 1.75 g of sample, maintained under constant agitation at a temperature of 40 ± 1 °C. This test was continuously monitored for 20 min using a portable conductivity meter (Alfakit AT 230). Conductivity tests were also conducted, exchanging the $Ca(OH)_2$ solution for deionized water. In this case, ash conductivity was calculated as the difference between $Ca(OH)_2$ and water conductivity values. The Luxán method was modified due to the presence of K_2O in the samples.

Ash pozzolanic activity was also assessed using the mechanical performance index (ABNT. Brazilian Association of Technical Standards, 2014), which consists of the relationship between the compressive strength at 28 days of a mortar, replacing 25% of Portland cement mass by ash, and the strength of a reference mortar containing only cement as binder. Mortar dosage was established for water-binder and sand-binder ratios of 0.48 and 3.0, respectively. Superplasticizer content (carboxylic-ether-modified with 28.9% oven-dried residue and 1.12 g cm^{-3}) was 0.018% to produce SCBA mortars with the same consistency of the reference mix. Three 50-mm cubic test specimens were molded for each mix and kept in the molds for 24 h in a moist environment. After this period, the specimens were demolded and kept immersed in a saturated solution with limewater for 28 days. The axial compression test was conducted in a Shimadzu UHI-500kNI universal testing machine, with loading velocity of 0.5 mm min^{-1}.

3.3. Production and characterization of cement-based pastes

The influence of different SCBA samples on cement paste early hydration was assessed in isothermal calorimetry (sealed samples) and chemical shrinkage (open samples) tests. Four pastes were used, one as reference (P-REF) and the others with 20 wt% of SCBA-1, SCBA-2 and SCBA-3 as a replacement for cement (P-SCBA-*X*, where *X* refers to the type of SCBA). A 20% ash content was used based on Bahurudeen and Santhanam (2015), Cordeiro and Kurtis (2017), and Barbosa and Cordeiro (2021) studies. The pastes were produced with a water-binder ratio of 0.4 and fixed superplasticizer content of 0.03% in relation to binder mass. They were manually mixed with a spatula for 30 s. After that, pastes were mixed using an electric hand mixer (600 rpm) for more 2 min.

Isothermal calorimetry tests in 50-g duplicate samples were performed at 25 ± 0.02 °C using a two-channel calorimeter (Calmetrix I-CAL 2000). Prior to the test, the materials (solids and water) were stored at 25 °C for 12 h, and immediately after mixing, the pastes were placed in the calorimeter to monitor heat rate evolution for 3 days. Chemical shrinkage was performed according to ASTM International, 2017 in a thermostatic bath at 25 °C for 7 days. The test was conducted in triplicate and each sample consisted of a 7-g layer of paste in a 25-mL glass flask filled with water. Each flask was sealed with a silicone rubber stopper and coupled to a graduated pipette (1 mL) through a central hole. Shrinkage monitoring and reading were carried out every 30 min using an autonomous image acquisition system. The water meniscus in the pipettes was covered with drops of red paraffin oil to prevent evaporation and facilitate visualizing pipette water level.

3.4. Vinasse characterization

The chemical composition of vinasse was obtained before and after bagasse ash leaching. Two samples representative of 2 L of vinasse were evaporation-dried in a water bath for 8 h, then oven dried at 25 °C for 24 h and ground in a mortar and pestle. Oxide composition was obtained as previously described. In addition, elemental composition was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian 720-ES). In this case, vinasse inorganic nutrients were extracted from 0.750 g of sample. The samples were placed in Teflon tubes (X-press), added with 8 mL of nitric acid p.a. (65%) and 2 mL of hydrofluoric acid p.a. (48%). The extracts were left to rest for 12 h at ambient temperature and then heated to 175 °C for 40 min (15 min heating and 25 min in isotherm) using a laboratory microwave oven (Mars Xpress CEM) – Filgueiras et al. (2000). After a 30-min cooling period, 12 mL of H_3BO_3 were added to neutralize the HF and the tubes were once again placed in the microwave oven at 170 °C for 25 min (15 min heating and 10 min in isotherm). After a further 30 min of cooling, the final extract was filtered in Whatman 40 filter paper, obtaining a final volume of 30 mL with HNO_3 0.5 N in a volumetric balloon.

The isotopic ratios ($\delta^{13}C$ and $\delta^{15}N$) were determined in an isotope ratio mass spectrometer (IRMS, Thermo Delta V Advantage) in combination with a Flash-2000 elemental analyzer. Inorganic compounds, oxidized in the presence of ultrapure oxygen and catalysts, were transformed into CO_2, N_2 and H_2O. These gases are separated on-line by chromatography, before elemental and isotopic analysis, also using an on-line approach. The detection limits for C and N were 0.05 and 0.02%, respectively.

4. Results

4.1. Characterization of the ashes

Similar particle size distributions are obtained for the three ashes produced by controlled grinding. Indeed, Fig. 1b shows that the ashes exhibit comparable particle size with D_{50} of around 10 μm (Table 1), and similar to that of class G cement. Cordeiro and Kurtis (2017) and Bahurudeen and Santhanam (2015) used the same methodology with

Table 1
Properties of SCBA-1, SCBA-2, and SCBA-3.

Property	SCBA-1	SCBA-2	SCBA-3
D_{50} (μm)	10.1	12.8	8.4
Density (g cm^{-3})	2.60	2.45	2.50
Pore volume (cm^3 g^{-1})	0.051	0.061	0.055
BET specific surface area (m^2 g^{-1})	14 ± 2	20 ± 2	21 ± 2
2-min ΔC (mS cm^{-1})	1.2	2.0	2.8
Performance index (%)	111	128	123

satisfactory results. The D_{50} of around 10 μm is chosen based on studies that showed adequate pozzolanic activity of the bagasse ash with different chemical compositions (Barbosa and Cordeiro, 2021). Moreover, it is worth noting that the particle size distributions of the different ashes needed to be similar for the purposes of the present study since pozzolanic activity is strongly dependent on particle size for the same material (Cordeiro et al., 2009b).

Table 2 shows the chemical composition of the three ashes. Loss on ignition is less than 3%, confirming the efficiency of conjugated burning (thermal processing) used in this study for the three ashes, as previously observed in research with different biomass ashes (Cordeiro et al., 2020). There are no significant differences between loss on ignition for the three ashes, although SCBA-3 obtains a slightly lower value than the others. It is important to note that ABNT. Brazilian Association of Technical Standards, 2015b establishes a maximum value of 6% for pozzolanic materials, while ASTM International, 2017 defines 10% as the maximum value for class N pozzolan.

The original ash (SCBA-1) exhibits 61.2% of SiO_2 and 12.2% of Al_2O_3. In addition, the sum of SiO_2, Al_2O_3 and Fe_2O_3 (77.6%) is higher than the 70% minimum established by ASTM International, 2017. This characteristic is positive for the use of pozzolan. However, SCBA-1 shows 6.8% of K_2O, which provides an alkali content of ash (sodium oxide equivalent) of 4.8%. Thus, the maximum substitution of cement with SCBA-1 should be carefully observed to prevent harmful reactions in cementitious systems. The presence of K_2O is typical in bagasse ashes and is an important parameter for selecting an ash suitable for use as pozzolan (Rodier et al., 2019).

Table 2 also demonstrates that the ashes submitted to two leaching processes exhibit declines in Na_2O and K_2O contents, reducing sodium oxide equivalent. Citric acid leaching eliminates Na_2O and maintains the K_2O content at only 1.2%, which makes it possible to obtain an ash with sodium oxide equivalent of 0.8%. Reductions in alkaline oxides through citric acid leaching were previously observed in agro-industrial ashes (Cordeiro et al., 2020; de Lima and Cordeiro, 2021).

For SCBA-2, which is produced with vinasse leaching, Na_2O and K_2O contents decline to 0.1 and 2.8%, respectively. As such, these decreases, albeit lower than those obtained for SCBA-3, guarantee an ash with sodium oxide equivalent of 1.9%, which is a value corresponding to around 40% of the sodium oxide equivalent of SCBA-1. The advantage of vinasse leaching when compared to citric acid leaching is that the former does not form new residue since vinasse as an extractor can be used in fertigation, for example. The decline in Na_2O and K_2O slightly raises the concentration of the sum of SiO_2, Al_2O_3 and Fe_2O_3 in SCBA-2 (sum of 80.5%) and SCBA-3 (85.5%), which is promising for pozzolan applications. The variation in chemical composition causes a small decrease in density in the ashes produced after leaching, as shown in Table 1.

Fig. 2 shows the gas adsorption-desorption isotherms of the ashes. The curves demonstrate that the three ashes display similar behavior,

Table 2
Oxide composition and loss on ignition values (% of mass) of cement, SCBA-1, SCBA-2, and SCBA-3.

Oxide	Cement	SCBA-1	SCBA-2	SCBA-3
SiO_2	21.8	61.2	63.8	73.1
Al_2O_3	3.6	12.2	12.9	7.4
CaO	64.2	6.3	6.6	4.4
Fe_2O_3	4.6	4.2	4.8	5.0
K_2O	0.3	6.8	2.8	1.2
SO_3	2.7	3.4	2.6	4
Na_2O	0.1	0.3	0.1	–
P_2O_5	–	1.8	2.2	1.2
TiO_2	–	0.8	1.2	1.3
MnO	–	0.2	0.3	0.4
MgO	1.5	–	–	–
Na_2O	0.2	–	–	–
Loss on ignition	1.1	2.8	2.8	2.0

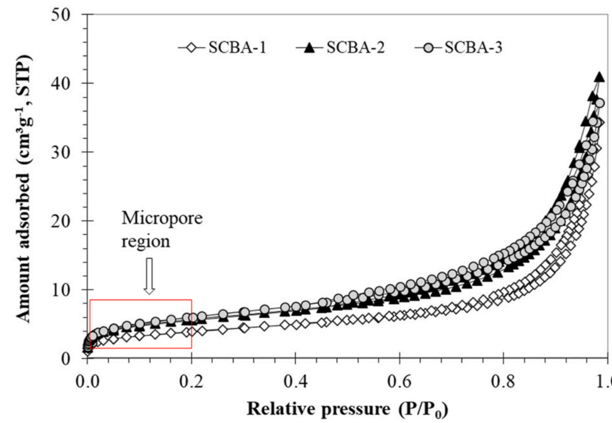


Fig. 2. Adsorption-desorption isotherms of SCBA-1, SCBA-2, and SCBA-3.

typical of meso and macroporous materials according to IUPAC classification (Thommes et al., 2015). In addition, the type of hysteresis is also the same for the three ashes and may be characterized as H3, with characteristics near those presented by Vieira et al. (2020) and Cordeiro et al. (2020) for pozzolanic biomass ashes. This type of hysteresis is characteristic of materials with interconnected pores with poorly defined mesoporous regions (Thommes et al., 2015).

Pore volume and BET specific surface area are presented in Table 1. Given that they are governed by the number of mesopores and macropores, ash pore volume is similar for the three ashes. The adsorption-desorption results also indicate an increase in the BET specific surface area as a function of K_2O removal from the ash, with no significant change in pore volume. Zhan et al. (2019) reported that potassium embeds itself in the micropores of carbon samples and blocks them. This significantly reduces the specific surface area without changing pore volume. In addition, isotherms (Fig. 2) in the micropore region show higher nitrogen adsorption for SCBA-2 and SCBA-3. Thus, hot leaching promotes potassium removal, even with a weak acid such as vinasse as extractor medium. Consequently, the specific surface area of bagasse ash increases due to the decrease in K_2O, as previously observed in rice husk (Vayghan et al., 2013), elephant grass (Cordeiro and Sales, 2015), sugarcane bagasse (Barbosa and Cordeiro, 2021), sugarcane straw (Cordeiro et al., 2017), and corn straw (De Lima and Cordeiro, 2021) ashes.

X-ray diffraction patterns shown in Fig. 3 reveal the predominant presence of quartz in all the samples. Quartz, a common phase in bagasse ash, originates in soil adhered to sugarcane (Cordeiro et al., 2009b) and in sand used for boiler cleaning. The presence of amorphous halo is observed for the three ashes between 2θ angles of 20 and 30°. As can be observed by Rietveld refinement quantification, the two leaching processes increase the amorphous content from 51.0% in SCBA-1 to 54.0% and 60.5% for SCBA-2 and SCBA3, respectively, as shown in Table 3. Amorphous silica concentration, in this case, is obtained by removing solubilized metal oxides from vinasse and citric acid, especially K_2O. The highest K_2O content in SCBA-1 favors cristobalite formation during burning, which is not perceptible in the leached ashes (SCBA-2 and SCBA-3). K_2O can act as a catalyzing agent for amorphous silica crystallization in cristobalite at temperatures around 700 °C (Nakata et al., 1989). Although the maximum temperature at the center of the sample was 684 °C (Fig. 1), slightly higher temperatures can be reached at different points during combustion. A previous study showed an increase in the amorphous content in corn straw ash leached with citric acid (De Lima and Cordeiro, 2021). The anhydrite identified in the samples likely originated from the use of calcium sulfate to correct the sugarcane soil (EMBRAPA, 2019).

Fig. 4a shows the variation in electrical conductivity of the three ashes in 20 min. All the ashes exhibit pozzolanicity according to the classification proposed by Luxán et al. (1989), which suggests a minimum variation of 1.2 mS cm^{-1} for solution conductivity at 2 min testing

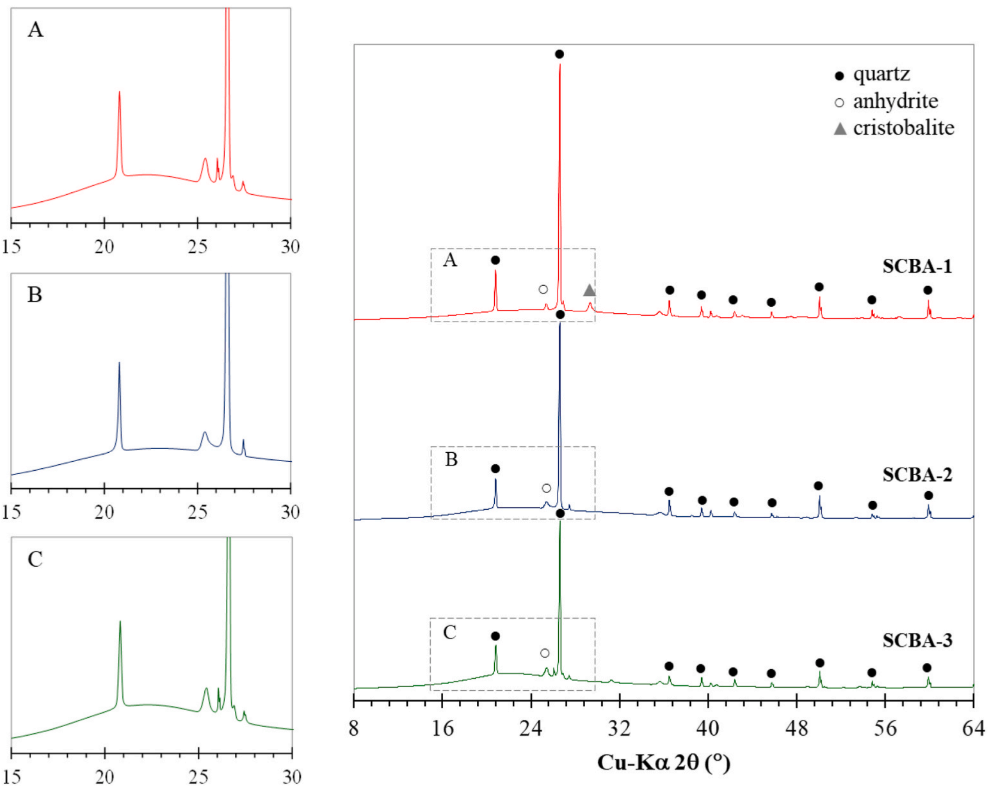


Fig. 3. X-ray diffractions patterns of SCBA-1, SCBA-2 and SCBA-3.

Table 3
Composition of SCBA samples (mass %) from X-ray diffraction-Rietveld refinement. Standard deviation values are indicated in parentheses.

Phase	SCBA-1	SCBA-2	SCBA-3
Quartz	43.3 (±1.2)	42.2 (±1.3)	38.5 (±2.1)
Cristobalite	2.3 (±0.7)	–	–
Anhydrite	3.5 (±1.4)	3.9 (±0.6)	1.1 (±0.9)
Amorphous	51.0 (±0.5)	54.0 (±0.8)	60.5 (±1.1)

(2-min ΔC). SCBA-1 displays a minimum conductivity variation, which is associated with the presence of 51% amorphous compounds, especially SiO_2 and Al_2O_3 (Table 1). Indeed, Fig. 4b shows a direct relationship between amorphous content and conductivity variation, a relationship that is valid only for ashes with low loss on ignition. A similar relationship between amorphous content and 2-min ΔC was observed by Barbosa and Cordeiro (2021) for bagasse ashes with different chemical compositions. It is worth noting that although Fig. 4b shows a clear relationships between 2-min ΔC and amorphous content and BET specific surface area, more data points are needed to establish good statistical validity.

The conductivity variation for solutions with two leached ashes is significantly higher than that observed for SCBA-1. SCBA-2 and SCBA-3 obtain 2-min ΔC values of 2.0 and 2.8 mS cm^{-1}, respectively. Increases in conductivity variation after metal oxide leaching were previously observed for rice husk ash (Feng et al., 2004), sugarcane straw ash (Cordeiro et al., 2017), and corn straw ash (De Lima and Cordeiro, 2021). The differences between samples after 2 min and at the end of the experiment (20 min) do not vary significantly. In this case, the sharp initial drop in conductivity may be associated with Ca^{2+} and OH^- ion adsorption to the ash particles of bagasse due to electrostatic forces. This effect is more pronounced the larger the specific surface area of the ash, which makes the conductivity results merely indications of pozzolanic activity (Vayghan et al., 2013), and complementary tests should be conducted. In addition, the ashes with a higher BET specific surface area

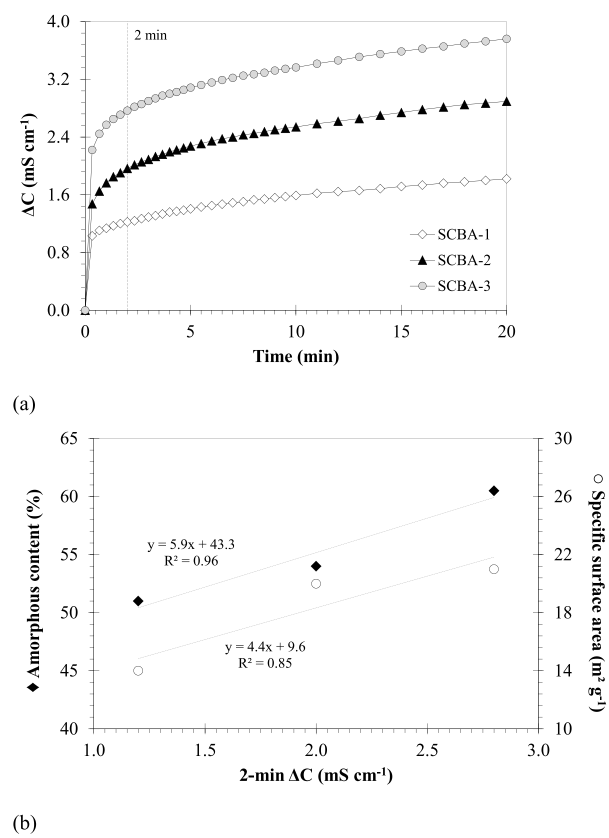


Fig. 4. Electrical conductivity variation (ΔC) in 20 min (a) and the relationships between 2-min ΔC and amorphous content and BET specific surface area (b) for all SCBA samples.

exhibit greater conductivity variations (Fig. 4b), as previously reported in other biomass ash studies (Cordeiro et al., 2020; Vieira et al., 2020).

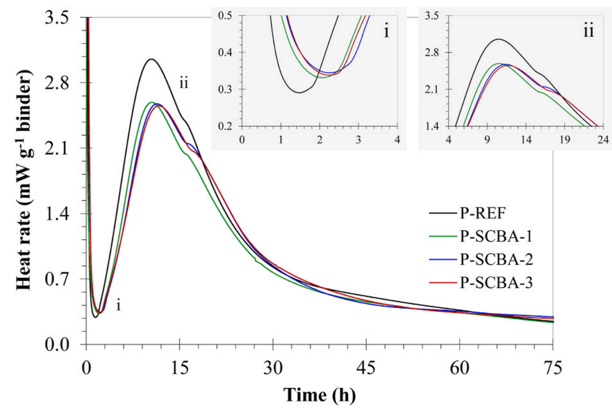
Mechanical performance index tests are carried out to better assess the influence of the two bagasse leaching procedures on the bagasse ash behavior. ABNT. Brazilian Association of Technical Standards, 2015b is restrictive and establishes a minimum index of 90% for the material to be classified as pozzolan. The three bagasse ashes significantly exceed the minimum index. SCBA-1 reaches an index of 111%, which corroborates the electrical conductivity result for this material. The high sum of SiO_2, Al_2O_3 and Fe_2O_3 (77.6%), the predominant presence of amorphous phases (51.0%), and the high specific surface area (14 m^2 g^{-1}) explain the good ash performance, even though the material has 6.8% K_2O and sodium oxide equivalent to 4.8%. Indeed, earlier studies showed that the presence of alkaline oxides did not compromise the pozzolanic activity of bagasse ash (Rossignolo et al., 2018), except for the lower active phase concentration.

Although SCBA-1 exceeds the minimum mechanical index, the ash produced by citric acid leaching shows a considerable increase in performance directly linked to the decline in ash contamination. In fact, the index obtained for SCBA-3 is 123%, a value 37% higher than the minimum established by the standard. The high mechanical indices in ashes produced after leaching were previously reported (Cordeiro et al., 2020). When compared to SCBA-1, the increase in the index is even greater for the ash leached with vinasse. The index obtained of 128% may also be attributed to the reduction in contaminants, but in this case, there is a significant increase in Al_2O_3 content, in contrast to what is observed for SCBA-3. The presence of Al_2O_3 is common in bagasse ash and may contribute to the formation of calcium aluminosilicate hydrate (CASH) that contribute positively to mechanical performance (Maldonado-García et al., 2018). This behavior shows the advantage of vinasse leaching when compared to citric acid as an extractor agent of contaminants.

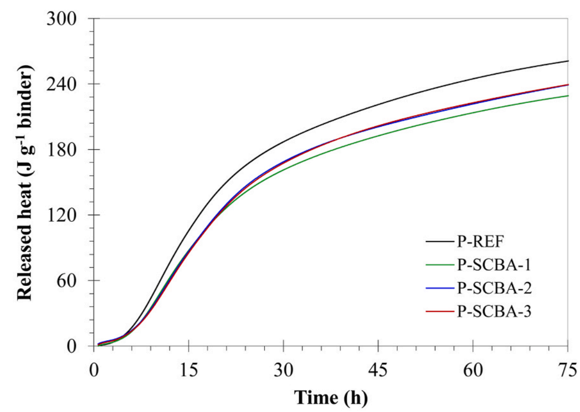
4.2. Hydration in cement-based pastes

Fig. 5a shows the specific heat rate results per gram of binder obtained by isothermal calorimetry for the pastes studied, which exhibit the typical behavior of cement pastes. The first exothermic peak is related to the initial wetting and dissolution of raw materials, but it cannot be measured accurately because the mix was made outside the calorimeter. The SCBA pastes show a significant delay in hydration, with displacement of heat rate curves to the right, as demonstrated in the inset **i** of Fig. 5a. In this case, the loss on ignition and SO_3 concentration in the ashes are higher than those of cement (Table 1) and slightly lengthened the dormancy period (Odler and Schüppstuhl, 1981). This effect was previously observed in bagasse ash pastes (Barbosa and Cordeiro, 2021). In addition, Deschner et al. (2012) reported that pastes containing pozzolan with Al_2O_3 exhibit extra reactions of these aluminates with Ca^{2+}, delaying C–S–H nucleation. It is important to note that the heat flow of pastes with ashes increases slightly during the dormancy period due to the rise in Al_2O_3 content in pastes associated with the effect of heterogeneous nucleation (Novotný et al., 2016), both effects promoted by SCBA samples. The effect of heterogeneous nucleation is more pronounced in pastes with the two leached ashes, which display similar behavior and greater specific surface area when compared to SCBA-1. Inset **ii** in Fig. 5a shows a similar heat rate in the second peak (between 9 and 14 h) for the pastes containing ash, as presented in Table 4. In addition, the peak is amplified between 14 and 19 h, also as a function of an increase in aluminates (Lothenbach et al., 2011; Avet and Scrivener, 2018) in the pastes with SCBA.

The released heat per gram of binder curves (Fig. 5b) show that heat decreases when cement is replaced by different ashes, as expected. However, a comparison of the heat released by the pastes containing ash indicates greater reactivity for pastes with leached ash, confirming the results of electrical conductivity and performance index tests. Although the replacement rate was 20%, the heat generated after 75 h of testing in



(a)



(b)

Fig. 5. Specific heat rate (a) and cumulative released heat (b) curves calculated by the solid (binder) mass for all pastes.

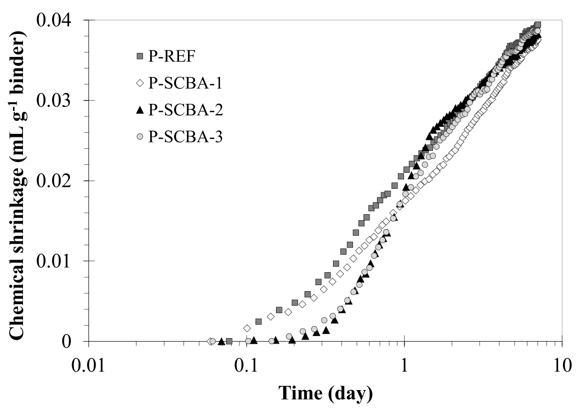
P-SCBA-1 is only 12% lower than that observed for P-REF, as shown in Table 4. For SCBA-2 and SCBA-3 pastes, the decline in accumulated heat is only 8% after 75 h of hydration. Decoupling of released heat curves is observed from 24 h onwards, which confirms the higher contribution of leached ash to paste hydration.

The chemical shrinkage results shown in Fig. 6a enable better visualization of the hydration differences for pastes containing ash when compared to the reference mix. During the first hours of the experiment, P-SCBA-1 exhibits a chemical shrinkage similar to that observed for P-REF and higher than that of P-SCBA-2 and P-SCBA-3. This behavior may be associated with the smaller SO_3/K_2O ratio of the P-SCBA-2 mix provided by SCBA-2. The highest pozzolanic activity of the leached ashes occurs after 1 day of hydration, corroborating the released heat results shown in Fig. 5b. After 7 days of testing, no significant differences are observed between the chemical shrinkage of the four pastes (Table 4). The magnitude of the shrinkage values of SCBA pastes is in line with the results previously reported for pastes with 20 wt% cement replaced by different bagasse ashes (Barbosa and Cordeiro, 2021).

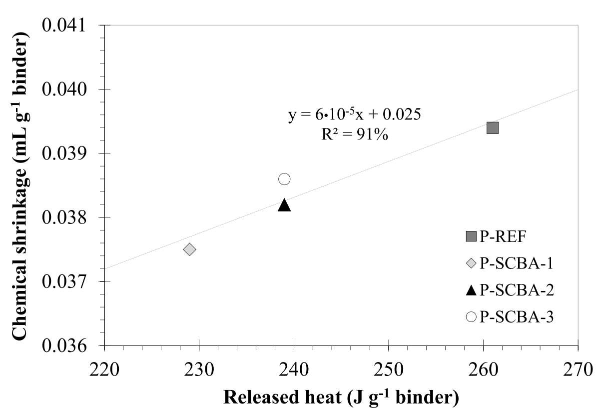
Fig. 6b shows the good correlation between isothermal calorimetry and chemical shrinkage for the pastes studied. In addition, the correlation between the two experiments reveals the different behavior of pastes with leached ash in relation to P-SCBA-1. This behavior is very positive, given that leaching improves the chemical composition of bagasse ash without compromising paste hydration. In the case of vinasse leaching, the advantage is even greater, since no new waste is generated, such as the extractor solution created in citric acid leaching that would require appropriate disposal.

Table 4
Main indicators of paste hydration measured by isothermal calorimetry and chemical shrinkage experiments.

Paste	Main heat rate peak (mW g^{-1})	75-h cumulative released heat (J g^{-1})	7-day chemical shrinkage (mL g^{-1})
P-REF	3.05	261	0.0394
P-SCBA-1	2.59	229	0.0375
P-SCBA-2	2.57	239	0.0382
P-SCBA-3	2.55	239	0.0386



(a)



(b)

Fig. 6. Chemical shrinkage calculated for binder mass over time (in log scale) for all pastes (a). Correlation between released heat and chemical shrinkage for all pastes (b).

4.3. Characterization of sugarcane vinasse before and after SCBA leaching

Fresh vinasse obtained after collection presents a pH of 3.5, typical for this type of ethanol waste, whose organic matter in the form of organic acids is its main component (Hoarau et al., 2018). This acidic trait may be extremely harmful to the aquatic, subterranean or surface medium, if fresh vinasse is applied to crops as fertilizer in an uncontrolled manner (Botelho et al., 2012). The elemental composition of fresh vinasse shown in Table 5 is also typical for this type of waste (Robertiello, 1982).

After vinasse is used as a leaching agent of SCBA-S to produce SCBA-2, its pH increases to 7. Vinasse neutralized by leaching in aqueous medium is better for fertigation and less toxic to fish and crustaceans (Botelho et al., 2012). In addition, vinasse is diluted during SCBA filtering, thereby reducing its heavy metal (Zn and Cu) concentrations and significantly increasing macronutrient (P, K, Ca, Mg and S) and micronutrient (Fe) concentrations, as shown in Table 5. These nutrients are essential for sugarcane cultivation and other crops (De Oliveira et al., 2010). Thus, applying neutralized vinasse to sugarcane crops improves yield without the typical negative environmental impacts caused by this type of fertigation (Christofoletti et al., 2013; Dos Santos et al., 2013).

Table 5
Elemental composition, C–N content, and oxide composition of sugarcane vinasse before and after leaching and the variation between both results.

Elemental composition (mg g^{-1})			
Element	**Before leaching**	**After leaching**	**Variation (%)**
K	39.875	155.890	+290.9
S	29.927	43.635	+45.8
Ca	27.619	47.858	+73.3
P	3.505	6.160	+75.8
Mg	1.853	39.450	+2029.4
Al	1.102	0.958	−13.1
Fe	0.785	1.724	+119.6
Mn	0.242	0.229	−5.3
Zn	0.118	0.080	−32.2
Cu	0.012	0.004	−62.9
Carbon and nitrogen content (%)			
C	33.5	21.30	
N	1.67	0.52	
Oxide composition (%)			
Oxide		**Before leaching**	**After leaching**
K_2O		13.8	15.0
CaO		7.1	9.0
Cl		3.6	4.0
SO_3		2.7	4.4
SiO_2		1.0	1.3
P_2O_5		0.2	–
Fe_2O_3		0.2	0.3
Loss on ignition		71.5	66.1

SCBA-S leaching decreases carbon concentration and loss on ignition of vinasse, as shown in Table 5. Fresh vinasse presents a C–N ratio of 20, while leached vinasse exhibits a decline in carbon and nitrogen concentrations, which significantly changes the C–N ratio. This increase in the C–N ratio (41 for vinasse after leaching) prevents excessive mineralization of the immobilized forms of nitrogen in the soil (De Souza et al., 2015). Thus, soil salinization resulting from the use of vinasse for years could be reduced. It is important to note that a more in-depth study is needed to determine the characteristics of this solution in laboratory and real scale applications, but the results obtained to date are very promising.

5. Conclusions

A systematic combination of different experimental procedures in this study shows that pozzolanic bagasse ash using vinasse as a leaching agent benefitted both important agro-industrial wastes. The following conclusions can be drawn from the results of this study: (i) The production procedure proposed results in an SCBA with low quartz content, loss on ignition, and K_2O and SO_3 concentrations; (ii) Leaching with vinasse increases the specific surface area, pore volume, and amorphous content of ash, which, in turn, raises pozzolanic activity and improves hydration in cement pastes; (iii) After being used as extractor medium, the vinasse is neutralized (increase of pH). In addition, ash leaching reduces heavy metal (Zn and Cu) concentration and significantly increases the macronutrient (P, K, Ca, Mg, and S) and micronutrient (Fe) concentrations of vinasse.

In summary, the proposed methodology may become an important tool for producing added-value materials from two agro-industrial wastes (bagasse ash and vinasse) generated in large amounts worldwide. Moreover, the present work indicates that a large-scale production can be facilitated as both materials are generated in the same industrial unity, thus reducing transportation costs. Further research must be placed in line to investigate the fertilization potential of different crops with vinasse improved by leaching bagasse ash. It is worth noting that the use of green cementitious materials and pre-treated bio-fertilizers will have critical importance in the near future. Finally, innovative products derived from agro-industrial wastes must greatly contribute to improving our planet, strengthening the bioeconomy and environmental sustainability.

CRediT authorship contribution statement

Rodolfo Pimentel Azevedo Almeida: Conceptualization, Investigation, Writing - original draft. Guilherme Chagas Cordeiro: Conceptualization, Supervision, Visualization, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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