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THE INFLUENCE OF COFFEE HUSK ASH AS A FILLER ADDITION IN MECHANICAL AND HYDRATION PROPERTIES OF CEMENT PASTES

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Abstract: In view of the environmental impacts caused by the construction and agro-industry industries, the aim of this work is to evaluate the potential application of coffee husk ash (CHA) as a filling element in cement pastes. For this purpose, coffee husks and their ashes were characterized. Cement pastes, with a water-to-cement ratio of 0.4, were then produced with different amounts of CHA (5, 10, 15, 20 and 25% BWOC), burned at 600°C for 3 h, and characterized. The results showed that CHA had a high content of alkalis. A reduction in the amount and kinetics of calcium hydroxide formation was observed in the pastes. In the semiadiabatic calorimetry test, it seems that the increase in CHA content leads to hydration kinetic acceleration and an increase in the cumulative heat for up to 40 hours of hydration, indicating an effective filler effect caused by CHA.
Keywords: Agro-industrial ash, filling element, coffee residues, cement hydration

INTRODUCTION

The cement manufacturing process, the main element of civil construction, is one of the main sources of carbon dioxide emissions on the planet, contributing around 8.0% of total man-made emissions [1]. In Brazil, this number is smaller but still significant; the cement production is responsible for around 2.3% of carbon dioxide emissions generated in the country [2].

In addition, cement is the most expensive material component of concrete, mainly because of its energy consumption during production [3, 4, 5]. Thus, the development of low carbon building materials, with equivalent physical and mechanical properties to the traditional concrete, is under constant constant research [6, 7].

To reduce energy consumption and the amount of cement used in concrete mixes, researchers have investigated the use of

various solid waste materials derived from biomass burning for energy generation. These materials include ashes from coconut palm leaves [8], corn straw [9], cocoa biomass [10], banana leaves [11, 12], sugarcane bagasse [13, 14], wheat straw beds [15], palm oil fuel ash [16, 17], and coffee husks [18, 19].

Among other products, Brazil produced approximately 3.3million tonnes of processed coffee grains in 2023. Given that each processed grain yields about 45% husks, it is estimated that in 2024, more than 1.4 million tonnes of this residue will be generated [20, 21]. However, a portion of this residue is often improperly discarded, leading to significant pollution of waterways and adversely affecting the areas surrounding coffee processing industries [22]. Considering the substantial volume of this residue and the environmental impact of its current disposal methods, identifying eco-friendly solutions that significantly reduce this impact presents a considerable challenge.

It has been shown that the coffee husk can be used as fertilizer for coffee crops, as nutritional additive for animals, or as fuel in furnaces, from where residual husk ash is generated [20, 21]. Regarding energy generation, studies have shown that coffee husk possesses a high specific energy (18,172J/g), making it suitable for use in high-heat applications like cement kiln furnaces. The residual Coffee Husk Ashes (CHA) from this process can later be utilized by material engineers. The construction material industry already employs CHA in various products, including glass-ceramics [23], ceramic tiles [24], and briquettes and fiber-reinforced plastics [25]. Some studies investigated its use as filler in cement matrices [18, 26, 27, 28].

Although, coffee husk ash is rich in alkalis, chemical compounds that contribute to the formation of expansive products during the initial cement hydration process [29, 30] or that can start for long periods afterwards [31]. Thus, the use of this possible composite in structural applications is not recommended, but in applications that have a turnover of less than 20 years, such as pavers [31].

Due to its alkali-rich composition, there are limited studies on the use of Coffee Husk Ash (CHA) in cement-based materials. Most of these studies have focused primarily on enhancing the final composite's strength and resistance, often overlooking the reaction kinetics and product formation. Despite the well-known detrimental effects of alkalis in cement-based materials in academic circles, there is still misinformation among the general public. This is partly due to the widespread recognition of the beneficial effects of pozzolanic ashes, leading to a misconception that all ashes yield similar benefits. Moreover, further studies on the use of CHA in cement-based materials are essential to illuminate paths that scientists should or should not follow [32, 17].

Thus, this work presents an extensive experimental program, focusing on morphological and thermal analyses, formed products, and kinetics parameters of the coffee husks and their ashes when added to a cement paste as filler. The results have shown how alkali rich ashes can impact in hydration reactions of a cement-based material and ultimately its mechanical properties.

MATERIALS AND METHODS

COFFEE HUSK

The Arabica coffee husk species used in this study was obtained from crops harvested between April and September in 2018 and 2019, in Lavras, Minas Gerais, Brazil. After collection, the husks were sieved to remove impurities from the disposal environment and then naturally dried for four days to achieve an equilibrium humidity level of 12%. The coffee husks consist of various elements including

the Epicarp, Mesocarp and Endocarp [33]. These elements will also be investigated in this study.

Scanning electron microscopy (SEM) and Dispersive energy spectropy (EDS) analises

The morphology of the coffee husks in natura was investigated using a Zeiss SEM EVO LS25 (Oberkochen, Baden- Württemberg, Germany). The microscope operated under an acceleration voltage of 15kV and a probe current of 2 nA. No precoating was performed. Specimens were fixed in a metal stub covered by carbon-coated tape. Secondary electrons (Everhart–Thornley) and backscattering (solid-state) detectors were used. A working distance of 8.5 mm was used. No tilt was applied.

Thermogravimetric Analysis (TGA)

The thermal analyses of coffee husks were performed on a Netzch STA 449 Jupiter TGA-DSC instrument (Czechoslovakia, Czech Republic). An open alumina crucible was used, and the samples were heated from 25 to 1000°C in a nitrogen flow stream at 20mL/min with a heating rate of 10°C/min. An average mass of 10 mg of sample was used in each TGA test. The degradation temperature was determined from the inflection of the baseline in the differential thermogravimetric (DTG) curve.

COFFEE HUSK ASH

The ashes were produced according to the literature, not exceeding 800°C [19]. The production of coffee husk ash (CHA) was performed at different temperatures: 500, 600, and 800°C for 3 and 6 hours in a muffle furnace at a heating rate of 10°C/min in an oxidizing environment. The cooling process was conducted naturally over a period of 24 hours by turning off the muffle furnace and keeping its door closed. This approach was employed to prevent environmental contamination and minimize high thermal gradients. According to the residence temperature and time, these coffee husk ashes were named CHA5003, CHA5006, CHA6003, CHA6006, CHA8003, and CHA8006.

All coffee husk ashes produced were characterized by x-ray diffraction (XRD). Ashes with a residence time of 3 hours were also characterized by x-ray fluorescence (XRF).

Furthermore, chemical characterizations results of CHA indicated that CHA6003 may have some chemical affinity with the cement matrix. Therefore, this particular ash underwent further characterization through the modified Chapelle test, granulometry analysis, and TGA analysis to better understand the extent of this chemical affinity with a cement paste.

Powder X-ray diffraction (XRD) analysis

Powder X-ray diffraction (XRD) patterns of the coffee husks ashes were measured with an X-ray diffractometer (Bruker D2 Phaser 2nd Generation, Billerica, Massachusetts, United States) with a Cu-Kα source (λ = 1.54184Å) in a 2θ range of 5–70° at a scan rate of 0.6°/min. A powder specimen sample holder composed of steel with a 25 mm diameter was used (Code C79298A3244D82). The samples were manually ground into a powder before the test.

X-ray Fluorescence (XRF) analysis

To estimate the chemical composition of the coffee husk ashes, a semiquantitative analysis was performed by using X-ray fluorescence spectrometry (XRF) with a Titan-Bruker 800N8578 instrument (Billerica, Massachusetts, United States) at the Fluorescence and X-ray Laboratory in the Department of Soil Science at the Federal

University of Lavras, Lavras, Minas Gerais, Brazil. The samples were dried and placed into a desiccator with silica and directly analyzed by a nondestructive method.

Modified Chapelle test

As no studies of chemical affinity of CHA with cement is available, Chapelle test was caried out to shed lights on the level of reactivity of this material. The modified Chapelle test is used to study the ability of the material to fix lime mortar when it is held in an aqueous solution with calcium oxide (CaO) [34].

To carry out the test, the CHA6003 was placed in an oven to remove residual moisture, and 1 g of the dry material was agitated with CaO and water, then stored for 16 hours in a climatized room at 22°C with 90% relative humidity. Subsequently, the content of fixed calcium hydroxide in the sample was determined by titrating it with an HCl solution and using phenolphthalein as an indicator.

Granulometry analysis

The particle size distributions of the ashes and Portland cement were determined with a HORIBA LA-950V2 (RETSCH)-type laser particle size analyzer. During the measurement, ultrasonic treatment was used for 150 seconds to disperse fine particles. Ethanol was used as the fluid medium. Three tests were carried out with refraction indices of 1, 1.35 and 1.7.

Thermogravimetric Analysis (TGA)

The TGA procedure for the coffee husk ash was carried out as described in subsection 2.1.2.

CEMENT PASTE WITH COFFEE HUSK ASH

Mix proportion

The CHA6003 influence in cement pastes with a water-to-cement ratio (w/c) of 0.4 was evaluated. Six pastes were mixed in a contact vortex mixer for 2 minutes at 3000 rpm, one with plain cement and water (reference) and others with cement substitution levels of 5, 10, 15, 20, and 25% BWOC of CHA, while keeping the same w/c. The cement used in this stage was CP V Portland cement, which met the Brazilian specifications of NBR 16697 [35] (equivalent to the European CEM I 52.5N [36]).

Curing

The curing ages studied were 1, 3, 6, and 9 days at 60°C for the thermogravimetric and mechanical tests and 16 hours for the calorimetric test. This temperature was adopetd to acelerate hydration kinetics and in another study it have show that after 8 days in this condition a cement paste reached over 95% of its hydration level [37]. The hydration of samples for the tests was stopped by adding acetone according to Röser [38]. The samples were immersed in acetone PA ACS, removed 30 minutes before the tests and manually ground into a powder. After curing, the samples were taken to semi-adiabatic calorimetry, thermogravimetry and uniaxial compression tests.

Semiadiabatic Calorimetry

The semiadiabatic calorimetry test was carried out on the pastes in a thermal box that was kept in an acclimatized room (22°C, 90% UR) for 24 hours.

The temperature curves were obtained by the Data Logger TC-08 and analyzed with the corresponding PicoLog software (Pico Technology, Cambridgeshire, United Kingdom) to investigate the hydration

kinetics through accumulated heat, heat flow, and the hydration temperature of the pastes, according to the methodology of EN 196-9 [39]. For each test, a K thermocouple (32 AWG) was placed at the geometric center of the sample.

Thermogravimetric Analysis (TGA)

The TGA procedure for the cement pastes was carried out as described in subsection 2.1.2. Since the content of cement and CHA varies, it is necessary to normalize the TGA results for a more accurate comparison. To achieve this, the results were converted to an Effective Mass Loss basis, as described in references [40, 41].

Uniaxial compressive test

Compressive strength tests were conducted following Brazilian Standard Methods [42, 43] on specimens measuring 1.0 x 1.0 x 2.5cm (base x width x height) using a universal testing machine from the Department of Forest Sciences (DCF) at UFLA. The machine was equipped with a type 'S' load cell with a maximum capacity of 500N. The tests were performed at a speed of 0.5mm/min. At least three specimens were tested for each curing time and CHA replacement level.

As the option with 25% of cement replacement by CHA6003 proved to be more viable, reference samples and samples with this replacement content were taken to the compression test.

RESULTS OF COFFEE HUSK IN NATURA CHARACTERIZATION

MORPHOLOGICAL CHARACTERIZATION

The results of scanning electron microscopy (SEM) performed on elements of the coffee husks in natura are shown in Figure 1.

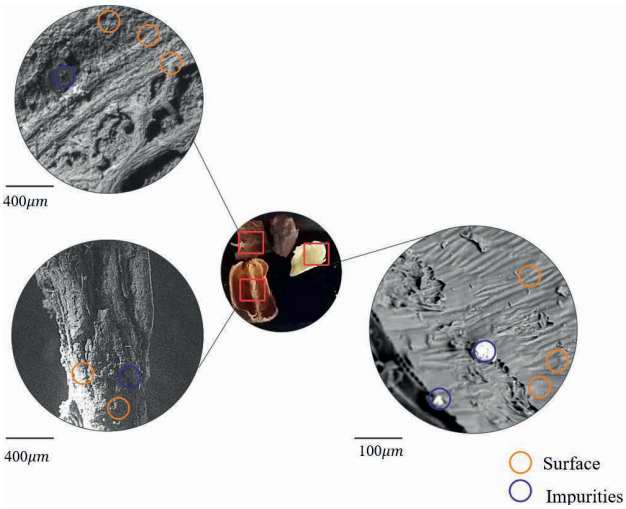


Figure 1: SEM of elements *in natura* coffee husk (center): Epicarp + Mesocarp + Endocarp (top lef), Epicarp + Mesocarp (bottom left), and Endocarp (right).

The SEM images revealed that the coffee husks are very heterogeneous. When examining the surface of different elements in more detail, as shown in Figure 1, some impurities can also be spotted on the surface of each element.

It can be seen that the structures of Epicarp + Mesocarp + Endocarp and Epicarp + Mesocarp are composed of flattened and folded helices, a common characteristic of lignocellulosic materials. The Endocarp is composed of fibers and is structurally porous.

ELEMENTAL CHARACTERIZATION BY EDS

The elemental composition of elements of the coffee husk in natura obtained by the EDS technique is shown in Table 1. The respective acquired points (orange and purple circles) are shown in Figure 1.

Overall, the results indicated a significant presence of alkali elements, such as magnesium and potassium, on the surface of all husk samples. Calcium was also identified as a secondary major element on the surface of all three analyzed husk components.

Regarding the impurities spotted on the surface of all three husk components, it was observed that they are primarily composed of potassium, calcium, and magnesium. These impurities are soil minerals and are present in very small amounts on the husk surfaces.

According to Table 1, coffee husks also have amounts of Si and Ca (3–10% and 5–76%, respectively), elements that increase the affinity of this material with the cement matrix. Similar results were found in other studies [28, 44].

THERMOGRAVIMETRIC CHARACTERIZATION

The coffee husk in natura TGA and DTG analysis curves can be seen in Figure 2.

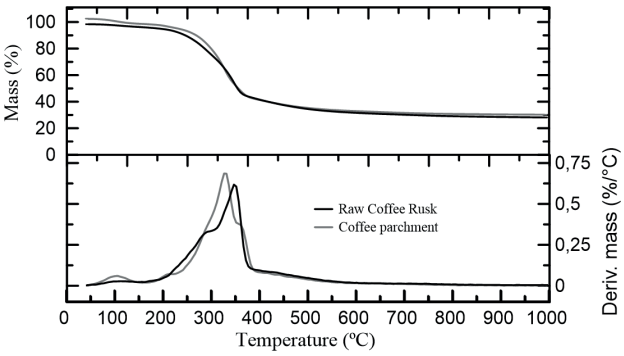


Figure 2: TGA/DTG curves of in natura coffee husks.

In the TGA graph, all the curves present a difference that can be caused by the elemental composition, given that, the husk (Epicarp + Mesocarp + Endocarp) is heterogeneous, more than the Endocarp alone. A loss of adsorbed water of 2.38 % in the Endocarp and 1.38 % in the Epicarp + Mesocarp + Endocarp can be observed below 120°C [24].

Between 200 and 400°C, there is a region of decomposition of hemicellulose and cellulose of 53.20% in the Endocarp and 56.00% in the Epicarp + Mesocarp + Endocarp. In the DTG curve, at 300°C, there is the formation of a loss peak for these materials. After 1000 °C still remain 30.21% endocarp and 28.09% husk mass, beeing a considerable content of ash.

Yiga et al. [25] found, through the chemical characterization of all the components of the coffee husk together, holocellulose valus of 66.60%, compatible with the values found in this research. According to Iwakiri and Trianoski [45], normally, the use of lignocellulosic materials is limiting, since such materials have high levels of holocellulose that can affect the physical-mechanical properties of the composites that contain them, since they have many groups of free hydroxyl groups that can adhere to water and impact the physical properties of cementitious matrices

Lignin, hydrophobic material that can interfere with cement hydration kinetics, decomposes between 400 and 500°C, and after this temperature, the mass loss is negligible [45].

RESULTS OF COFFEE HUSK ASH CHARACTERIZATION

PHASE CHARACTERIZATION BY XRD

Figure 3 shows the corresponding XRD results of different elements of CHA at different residence times and different burning temperatures to better evaluate the most efficient burning method by taking into account the energy consumption and amorphization of the material.

Chemical Components	Endocarp Surface	Endocarp Impurities*	Epicarp + Mesocarp Surface	Epicarp + Mesocarp Impurities	Husk** Surface	Husk Impurities
	(%)	(%)	(%)	(%)	(%)	(%)
Mg	26.80	11.09	10.79	-	18.74	5.05
Al	-	-	-	1.53	-	0.75
P	-	-	6.25	1.23	3.12	0.60
Si	10.65	6.16	4.32	-	7.47	3.09
S	-	-	-	22.75	-	11.33
Cl	9.62	5.26	3.36	-	6.47	2.63
K	23.71	1.17	57.88	69.23	40.67	35.03
Ca	29.21	76.32	17.40	5.27	23.53	41.51

*Particles and crystals on coffee ash surface

**Epicarp + Mesocarp + Endocarp

Table 1: EDS of the coffee husks *in natura*

Chemical Components	CHA5003 (%)	CHA6003 (%)	CHA8003 (%)
MgO	3.59	4.33	14.63
Al_2O_3	7.32	7.85	4.46
P_2O_5	3.73	4.09	13.31
SO_3	2.47	3.28	13.33
Cl	4.84	3.26	0.02
K_2O	57.35	58.17	20.24
CaO	1.78	2.27	18.42
TiO_2	-	0.19	0.01
MnO	-	-	0.02
Fe_2O_3	-	0.05	3.05
Minors	0.02	0.01	0.01
LOI*	18.91	16.49	12.53

*Loss on ignition.

Table 2: XRF of CHA with different thermal treatments and a residence time of 3 hours

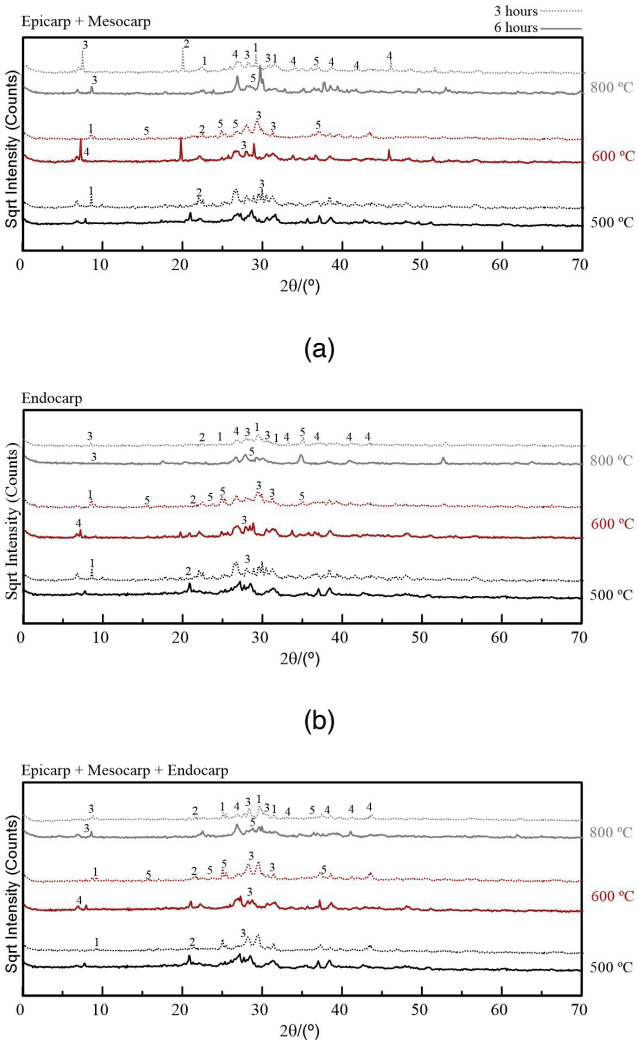


Figure 3: XRD results after each burning temperature and different residence times (3 and 6 hours) of different combinations of coffee husk elements (1 - potassium carbonate hydrate ($K_2CO_3.1.5H_2O$); 2 - arcanite (K_2SO_4); 3 - potassium carbonate (K_2CO_3); 4 - gorgeyite ($K_2Ca_5(SO_4)_6.H_2O$); 5 - fairchildite ($K_2Ca(CO_3)_2$); - ICDD PDF-2).

At 500ºC burning temperature, the elements found was potassium carbonate hydrate ($K_2CO_3.1.5H_2O$), arcanite (K_2SO_4) and potassium carbonate (K_2CO_3); with 600ºC and 800ºC appear gorgeyite ($K_2Ca_5(SO_4)_6.H_2O$) and fairchildite ($K_2Ca(CO_3)_2$) in the ashes; although the chemichal predominance could be seen in XRF results.

Nevertheless similar compounds were found in the three combinations of coffee husk elements, and these results were compatible with those achieved in other research [23, 28]. The residence time did not cause significant changes in the XRD pattern, which makes the 3-hour treatment option viable. Regarding temperature, an increase in peak intensity could be seen as the burning temperature rose. Similar results were found by Cordeiro et al. [46], who attributed this behavior to the phase recrystallization of the material.

Therefore, a treatment of 600°C for 3 hours (CHA6003) presented an XRD pattern with a good amorphization halo and lower energy consumption compared to the other options. A degree of amorphism is desirable as the resulting composite material can become more reactive; therefore CHA6003 it was selected for use when creating cement substitution materials for cement pastes [46].

ELEMENTAL CHARACTERIZATION BY XRF

The elemental quantification of coffee husk ashes CHA5003, CHA6003 and CHA8003, burned at the most viable residence time according to XRD, obtained by XRF is presented in Table 2. The results were compatible with CHA burned at 950°C carried out by other researchers [47].

The CHA5003 present 57.35% of K_2O followed by Al_2O_3 with 7.32% and the others chemical components in minor quantities, also loss on ingnition with 18.91%. CHA6003 have similar results, but the CHA8003 seems to have higher change on chemical components, K_2O Al_2O_3 reduce to 20.24% and 4.46% respectively, although, MgO, P_2O_5, SO_3, and CaO present 14.63%, 13.31%, 13.33%, and 18.42% respectively.

Most of the heat treatments performed did not meet the miimum values of SiO_2 + Al_2O_3 + Fe_2O (70.00%) and the maximum values of

SO_3 (5.00%), and Na_2O (1.50%) to be considered pozzolan [48]; the modified Chapelle test was also performed to confirm this statement to consider the CHA as filler.

A small amount of calcium was observed in all the samples. Even after 800°C burning conditions, the LOI value was still high, indicating the presence of some volatile materials and organic masses, such as coke.

In addition, the number of alkalis was high under all heat treatment conditions. This chemical compounds can contribute to the formation of expansive products during the initial cement hydration process [29, 30] or can start for long periods afterwards [31], which means that the recommendation of this composite applications have a turnover of less than 20 years, such as pavers [31] and structural applications is not recommended.

Farias et al. [23] also obtained for the same element, burned at 1500°C for 1 h, a chemical composition of 1.12% of SiO_2, 2.69% of Na_2O, 1.31% of Al_2O_3 and 92.63% of K_2O, indicating the impossibility of temperatures higher than 800 °C, as previously noted, due to the significant increase in alkalis.

MODIFIED CHAPELLE TEST

CHA6003 had the most promissing XRD/XRF test results, so modified Chapelle test analysis were applied only on this material. According to the pozzolanic activity index–modified Chapelle method, it was shown that the amount of fixated CaO was 155.08 g/mg or 15.51%, which did not reach the minimum value required by NBR12653 [49] of 75.00% to be considered as a pozzolanic material, confirming the XRF test.

The low reactivity of this material can be justified by the inadequate chemical composition since the samples have low concentrations of silica and calcium and high levels of potassium. The CHA's could therefore contribute in other ways to the cement matrix, such as filler material, for example.

GRANULOMETRIC ANALYSIS

The results of CHA6003 and cement granulometry are shown in Figure 4.

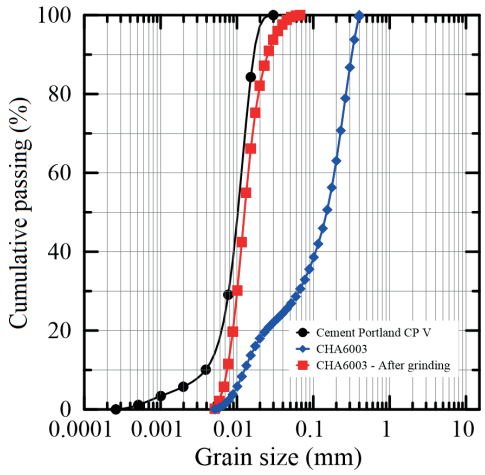


Figure 4: Granulometric analysis of cement and CHA after grinding.

CHA6003 presented a uniform granulometry distribution after manual grinding, with average D_{10}, D_{50}, and D_{90} values of 7.42, 12.55, and 25.23 µm, respectively.

CHA6003 before grinding had higher granulometry, with D_{10}, D_{50}, and D_{90} values of 12.55, 149.72, and 320 µm, respectively; cement had D_{10}, D_{50}, and D_{90} values of 3.87, 10.24, and 16.67 µm, respectively.

In order to compare, in another study using a mix of milled cocoa (20%) and wood chips (80%) ashes from industrial furnace presented a mean D_{10}, D_{50}, and D_{90} values of 5.01, 26.30, and 104.71 µm, respectively, particles smaller than that of coffee husks [10]. The reduced size of the particles is more desirable in cement matrices, as they optimize water consumption, chemical reactivity and cement strength; however, even with larger particles than the comparative literature, the CHA's, ground manually before the tests, showed good particle sizes and distributions [50, 51]

THERMOGRAVIMETRIC CHARACTERIZATION

The TGA and DTG curves of the coffee husk after heat treatment at 600°C for 3 hours are shown in Figure 5.

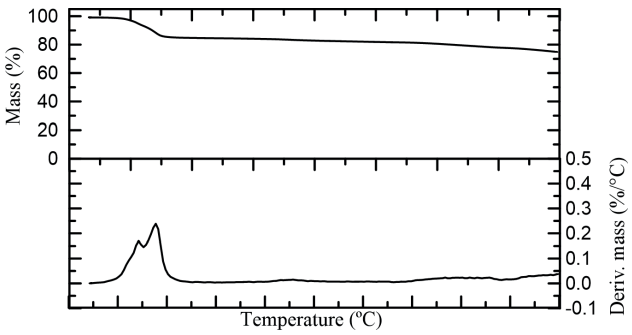


Figure 5: Results of the TGA and DTG analyses of CHA 6003.

For in natura components, the loss of water below 120°C could also be seen in the CHA6003's TGA curve at a value of 1.60 % [28]. Immediately after the water loss peak, another peak was observed that was centered at ~170°C. This peak, which may be associated with organic particles that have no proven impact on cement matrices, had a shoulder at ~140°C and a dehydration value of 1.43% [52].

Between 200 and 400°C, a place demonstrated in the in natura husk as decomposition of holocellulose; it is noted that this product was decomposed in the muffle, reducing the possible impact of this component on the physical properties of cement matrices [45].

At temperatures greater than 200°C, there was a gradual mass loss until the sample stabilized at ~600°C (~80%). Carbon particles and carbonates decompose in the range of 600 to 800°C, components present by the high LOI value presented by such ash (Table 2) [52]. The residue at 1000°C (74.82%) could be attributed to char and oxide elements.

HYDRATION OF CEMENT PASTES CONTAINING CHA6003

SEMIADIABATIC CALORIMETRY TEST

Figure 6 shows the cumulative heat curves as a function of time for the six pastes tested over 40 hours. In addition, calorimetric parameters, such as maximum values of cumulative heat and rate of cumulative heat, are presented in Table 3. The cumulative heat rate was calculated by means of a linear correlation.

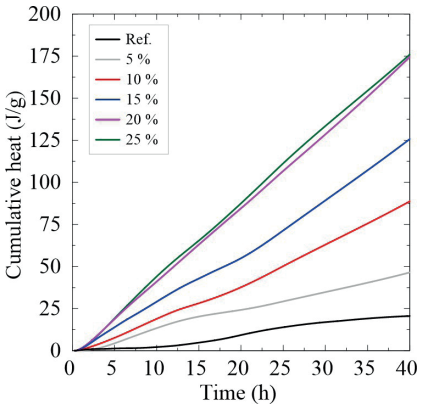


Figure 6: Cumulative heat curves resulting from the heat of hydration integral.

Scrivener et al. [53] found that the partial replacement of Portland cement caused an increase in accumulated heat due to the filler effect, which contributes to the hydration heat by providing additional nucleation sites for hydrate phases; the materials also increase the w/c content, increase the hydration degree and provide more space for hydrates to precipitate. The same authors identified that this effect is related to the material's surface area rather than its chemical composition.

This phenomenon demonstrates that the use of CHA in place of cement causes an acceleration in the hydration process, which in turn can lead to greater compressive strength at early curing ages, increasing the high initial strength characteristic of the CP V cement used. However, excessive shrinkage reactions

can be formed [54].

As seen in Table 3, an increase in the maximum cumulative heat with increasing CHA content also occurred. These observed increases can be attributed to the high amount of K and Mg that forms KOH and $Mg(OH)_2$ in the presence of water in a highly exothermic reaction. However, another reaction could potentially be the cause of the increased maximum cumulative heat.

THERMOGRAVIMETRIC CHARACTERIZATION OF PASTES

Figure 7 shows the variation in the calcium hydroxide (CH) and combined water formed in cement pastes as a function of the CHA level in 9-day-old specimens. Overall, the results showed that as the CHA content in the samples increased, there was a reduction in the calcium hydroxide content and an increase in the combined water content in the studied pastes. In the case of the reference paste, the CH content was 15.88%, while for the sample with the higher ash substitution, it reached 11.60%, indicating a reduction of 27.00% in the CH content. Additionally, there was an increase in the total combined water content in the pastes, rising from 18.12% in the reference paste to 24.03% in the sample with the highest substitution level, meaning it increased by 33.00%.

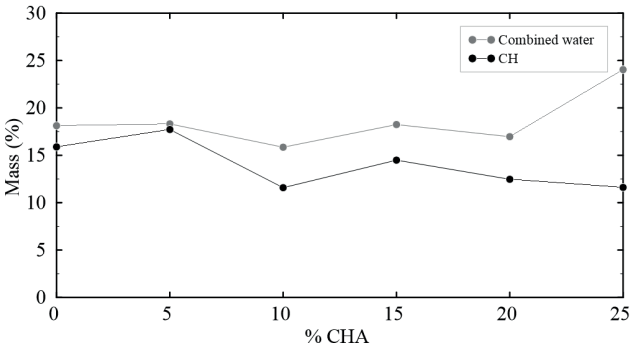
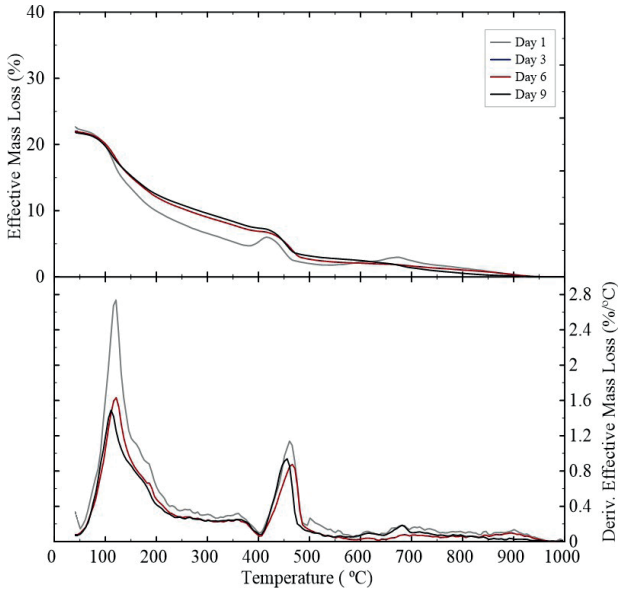


Figure 7: Combined water and calcium hydroxide content as a function of coffee husk ash content after 9 days of curing.

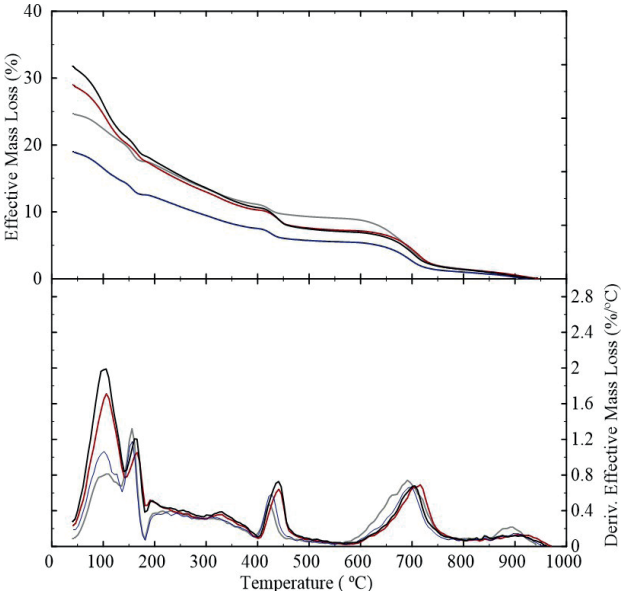
The effective mass loss and its derivative curves of the reference paste are shown in Figure 8(a) and Figure 8(b) shows these results for the paste with 25% CHA (b) at 1, 3, 6, and 9 days of curing. Table 4 shows the quantification summary of the main products formed at each respective time. Note that the results for 3 days of curing the reference paste are not presented due to problems that occurred during the test.

At first glance, the results indicate that the hydration of the pastes was significantly affected by the CHA addition. It is evident that in the CHA case, there was a rise in the peak between 120 and 180°C, which is usually attributed to the presence of ettringite and monosulfate. The appearance of calcium carbonate peaks between 580 and 780°C was also noticeable for the paste with CHA.

From Figures 8(a) and 8(b) and Table 4, it is possible to see that the amounts of Calcium silicate hydrate (C-S-H), ettringite, and monosulfate varied with the paste hydration time. For the reference paste, the amount of these products reached a maximum after 24 hours and remained stable for up to 9 days of curing. On the other hand, for the 25% CHA paste, the amount of these products rose progressively for up to 9 days of curing. Therefore, these products were formed during the initial curing period for the reference paste and the 25% CHA case, and a delay in the formation of these products could be seen, where an acceleration in the hydration process occurred between 6 and 9 days of curing. Compared to the reference case, the variation amounts of C-S-H, ettringite, and monosulfate contents were -44, -11, and +31% at 1, 6, and 9 days, respectively.



(a)



(b)

As shown in Figures 8(a) and 8(b) and Table 4, the amount of CH varied as a function of curing time. In the case of the reference paste, there was no evident trend in CH formation as a function of time, which suggests that all the CH content was formed in the early days of curing and then stabilized. In the case of paste with 25% CHA, CH formation is delayed, reaching its maximum CH content after up to 9 days of curing. Compared to the reference paste, for 1, 6, and 9 days of curing, the reduction in the CH content from the 25% CHA sample was 65, 30, and 27%, respectively.

It is also possible to see in Figures 8(a) and 8(b) and Table 4 that the other hydrate phase increased as a function of time for both pastes. However, for the 25% CHA paste, the quantity of other hydrates was more evident. Compared to the reference paste, the increase in hydrates in this phase for the 25% CHA paste was 87, 171, and 95% at 1, 6, and 9 days, respectively.

In general, carbonates have no defined tendency to reduce or increase as a function of curing time for the pastes studied. In the reference paste, for instance, one could see a slight decrease from 1 to 9 days of curing; however, this decrease can be attributed to the higher reactivity of cement pastes at early ages that facilitate environmental carbonation of the pastes [55]. In the case of the 25% CHA paste, the noticeably increased content of carbonates compared to the reference paste is attributed to the presence of CHA. The 25% CHA paste's loss in its ignition value was 16.49 %, indicating that some carbonaceous materials were still present in the CHA after 3 hours at 600°C in the muffle. This carbonaceous material may supply free CO_2 to react with Ca^{2+} in the cement paste media, leading to the extra calcium carbonates observed in the TGA results. Compared to the reference paste, the maximum carbonate increase observed was 8.9 times (at 6 days curing), and the minimum was 3.7 times (at 9 days curing). More studies are being performed to confirm this hypothesis.

UNIAXIAL COMPRESSIVE TEST

Figure 9 shows the average compressive test curves as well as their respective standard deviation for the reference cement paste (black) and the 25% CHA cement paste (blue). These compressive curves confirm the

Concentration	(%)	0	5	10	15	20	25
Maximum cumulative heat	(J/g)	20.57	46.48	88.89	125.67	174.44	175.91
Rate of cumulative heat	(J/gh)	0.51	1.16	2.22	3.15	4.37	4.41

Table 3: Maximum values of cumulative heat and rate of cumulative heat for different CHA

Hydrated products	Samples	Days			
		1	3	6	9
CSH + Ettringite + Monosulfate (%)	Ref.*	12.65	-	12.49	10.33
	25%**	7.13	8.06	11.09	13.56
Other Hydrates (%)	Ref.	3.43	-	2.70	3.93
	25%	6.43	6.31	7.33	7.65
CH (%)	Ref.	16.23	-	14.54	15.88
	25%	5.72	7.77	10.23	11.61
Carbonates (%)	Ref.	2.69	-	1.30	1.84
	25%	10.72	8.13	11.54	6.89
Combined Water (%)	Ref.	19.39	-	18.73	18.12
	25%	14.95	16.26	20.91	24.04

* Reference paste.

**Paste with 25% CHA.

Table 4: Effective mass loss of the cement products found

tendencies observed in Figures 6 and 7.

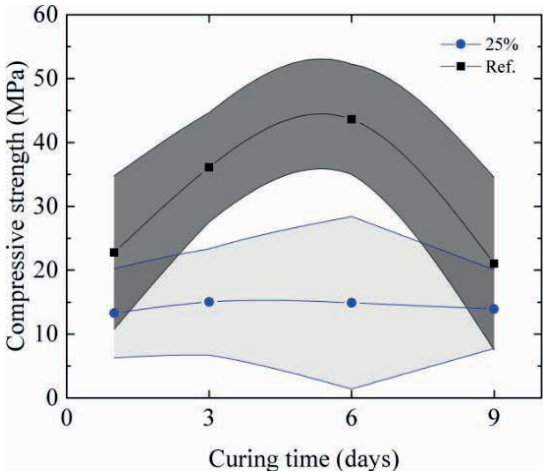


Figure 9: Uniaxial compressive test curves.

The mechanical resistance of the specimens with 25% CHA is similar to the mechanical resistance of the reference specimens in the first days of curing. However, after 3 days of curing, the resistance of the reference specimens progressively increases, while the CHA specimens present a less expressive increase. From the sixth day on, the reference sample may have cracked, even during curing. This phenomenon can be attributed to the fact that pure water and cement pastes can undergo a shrinkage phenomenon when cured under high temperatures, which leads to cracking of the samples [53, 54, 55].

These compressive strength results show that, although the presence of CHA particulars lead to a reduction in the amount of $Ca(OH)_2$ and to an acceleration of hydration in the initial ages, when its macro effects are observed, that is, in the total volume of paste, it can be seen that the effects of CHA are the same as those of filler.

It is also noted that, in accelerated curing (60°), the pastes containing CHA maintained a resistance level of approximately 15 MPa and did not suffer from cracking problems in the time period studied.

CONCLUSIONS

This work presents a study of the morphological, thermal and chemical characterization of coffee husks and their ashes, as well as a study of the effects of coffee husk ashes when used as a Portland cement replacement in cement paste. Thus far, the research has shown that the following conclusions can be drawn:

- In natura coffee husks have a heterogeneous and porous structure and are flattened and folded into helix fibers;
- There is a loss of adsorbed water of 2.38% in the Endocarp, 1.38% in the Epicarp + Mesocarp + Endocarp and 1.60% in CHA6003 below 120°C. Between 200 and 400°C, there is a region of decomposition of hemicellulose and cellulose of 53.20% in the Endocarp, 56.00% in the Epicarp + Mesocarp + Endocarp and 1,43% in CHA6003.
- Lignin decomposes between 400 and 500°C, and after this temperature, the mass loss is negligible according to the TGA test;
- The most abundant elements of coffee husk and its ashes are magnesium, potassium and calcium, which are all alkali elements, according to the EDS and XRF tests;
- In the XRD test of the CHA treated at 600°C for 3 hours, a reduction in the crystallinity of the materials is observed;
- The analyzed CHA did not meet the normative specifications to be considered a pozzolan according to the XRF and modified Chapelle tests.

In addition, we have the following conclusions about the hydration of cement pastes containing CHA:

- A reduction in the amount and kinetics of calcium hydroxide formation

is observed

- The substitution of 25% of cement with coffee husk ashes in hydrated pastes creates the lowest amount of calcium hydroxide and the highest combined water content according to the TGA test
- According to the TGA test, an increase in carbonates occurs in the paste with coffee husk ashes, which is attributed to the presence of carbonaceous materials (such as coke) in the ashes that may supply free CO_2 to react with Ca ions and form more $CaCO_2$;
- In the semiadiabatic calorimetry test, it seems that the increase in CHA content leads to hydration kinetic acceleration and an increase in the cumulative heat for up to 40 hours of hydration. Given these results, it can be concluded that CHA reacts in the cement paste media and likely releases heat due to an alkali reaction with water to form hydroxide products (such as KOH and $Mg(OH)_2$. Additionally, these hydroxide products may replace Ca, Al and Si in ordinary cement hydrated phases.

In view of the results obtained in this research, it is observed that CHA, a product that can alleviate environmental problems in civil construction and agribusiness, can be an efficient load component in the production of high turnover non-structural cementitious matrices. More durability analyzes are being carried out, and the results will be published later to analyze in more depth the trends achieved in this article. In future studies, it is recommended to carry out a possible inertization of the alkali or association of these composites with fibers to also validate the use of these components in structural applications. Furthermore, there is also a high potential for the use of CHA's in geopolymer-based matrices as chemical activators.

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