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Article

Chemical Treatments for Coffee Husks: Application in Mortar for Coating and Laying Blocks

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Abstract: (1) The use of agro-industrial wastes, such as coffee husks, in cementitious materials is a viable way to achieve the sustainable development of new construction materials. Traditionally, these wastes are applied after calcination, spending energy and financial resources. Furthermore, the calcination of these wastes contributes to a more sustainable environment. This is interesting because calcination treatments are usually more expensive than those using chemical treatments. Thus, the objective of this research is to evaluate the possibility of using coffee husks with the use of chemical treatments with sodium and potassium hydroxide in mortars for coating and laying blocks. (2) The methodology of this article consists of producing test specimens of mortar for coating and laying blocks in the composition 1:1:6:1.55 (cement: hydrated lime: sand: water), using coffee husks that will be incorporated in quantities of 2.5% in relation to the mass of the cement in its natural state and after treatment with sodium and potassium hydroxide. Compositions containing calcined coffee husks are evaluated for comparison purposes. The evaluated parameters were the mass density in the hardened state, water absorption by immersion and compressive strength. To complement these analyses, XRD, SEM and calorimetry tests were executed to compare the proposed treatments. (3) The results indicate that the use of treatments with NaOH and KOH allows for the use of coffee husks in mortars, since the parameters obtained were compatible with this type of application. The use of natural coffee husks is not possible due to their low compressive strength and high water absorption, caused by porosity. The use of alkaline treatments, especially with KOH, does not affect the hydration of the cement, allowing for the obtention of values statistically equivalent to the reference composition. The results with calcined coffee husks are even more promising due to the high content of amorphous potassium, which promotes the conversion of ettringite into hydrous calcium aluminate monosulfate. (4) It is concluded that, for the application of coffee husks in mortars for coating and laying blocks, the chemical treatment with KOH meets the necessary parameters—for example, a compressive strength greater than 2 MPa, making sustainable building materials and promoting the use of agro-industrial waste in building materials.

Keywords: agro-industrial wastes; fibers; construction; sodium hydroxide; potassium hydroxide

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1. Introduction

Agrobusiness is one of the sectors that most contributes to the Brazilian economy, with an estimated participation of 26.6% of the Brazilian Gross Domestic Product (GDP) in 2020 [1] and 25.5% of the Brazilian GDP in the year 2022 [2]. This sector is important not only for contributing to the country's economy but also for feeding the population, generating primary consumption products. However, agriculture has its negative aspects, such as: soil degradation, high water consumption, deforestation and inadequate disposal of agro-industrial wastes. It is worth highlighting that the agro-industrial sector is not only relevant in Brazil but also in several other world economies, presenting the same problems and negative aspects. Lu et al. [3] highlight the problems generated by the agricultural sector in European Union countries, with emphasis on the incorrect disposal of agro-industrial waste. The same happens with countries located in the Mediterranean and North Africa [4]. The authors highlight the generation of agricultural waste, such as olive pomace, orange peel and grape pomace, which are native of the region.

Agro-industrial wastes are generated from the processing of different raw materials, such as fibers, seed cultivation, dairy production, cattle raising, the planting and extraction of wood and the sugar and alcohol industry. According to recent sources, approximately 30% of agricultural goods produced in the world become waste [5]. Waste can represent a loss of nutrients and biomass, in addition to increasing the pollution of soil and water resources if disposed of improperly, because of hazardous and toxic waste [5]. Thus, the use of these wastes, such as the production of by-products, becomes an opportunity to add lost value and their sustainable use. Pharmaceutical ingredients, materials for packaging, the production of fuel or biochar or natural aggregates are some possible recyclable materials that can be used in concrete and asphalt [6,7].

The use of agro-industrial waste in civil construction has been more explored in recent years, with the purpose of reducing environmental impacts and reducing the exploitation of non-renewable natural resources, in addition to reusing these wastes that may be discarded. Cintura et al. [8] highlight the possibility of using agro-industrial wastes in the form of natural fibers as aggregate materials or as pozzolanic materials to substitute Portland cement. The versatility of this class of waste is clear, which, if properly treated, can be recycled into building materials. The research by Monteiro et al. [9] explored the potential of utilizing açaí seeds as a lightweight aggregate in concrete and mortar. The researchers achieved promising outcomes, demonstrating the feasibility of this approach.

An alternative would be the replacement of synthetic fibers by natural fibers. This was studied in the research by Aquino et al. [10], where the authors evaluated the use of corn straw fibers in mortar. The authors found that, when treating the fibers with sodium hydroxide, there was a reduction in water absorption in the mortar, in addition to reducing the stiffness of the studied mortar [10]. The results were satisfactory because one of the properties desired in the mortar is low stiffness. The use of pozzolanic materials, which have binding properties in the presence of water and hydrated lime, has been studied by several researchers as a partial replacement for Portland cement. In the context of this application, Jagadesh et al. [11] conducted a study to assess the pozzolanic properties of sugarcane bagasse ash. Their research demonstrated the feasibility of substituting Portland cement with this agro-industrial waste, highlighting its potential as a viable alternative. Aliu et al. [12] evaluated the pozzolanic properties of maize straw ash as a binder supplement in concrete. This research concluded that the pozzolanic reactivity is greatly affected by calcination and grinding.

It is possible to observe that this article presents an important contribution to the sustainability of civil construction. Jiang et al. [13] highlight the importance of developing low-carbon cementitious materials. This need is justified by the high CO_2 content emitted by the Portland cement industry. Some data show that cement production produces 5% of anthropogenic carbon emissions and 2–3% of energy consumption. Furthermore, it is projected that cement production will increase by 50% by 2050 [14,15]. These numbers justify the purpose of the present research, since there is urgency in the development of alternative materials and eco-friendly construction components. Based on the previous paragraphs, it is possible to understand the importance of the agro-industrial sector not only in Brazil but worldwide. Thus, the main purpose of this article is to investigate the feasibility of using recyclable agro-industrial waste in mortars. Dealing specifically with agricultural products in Brazil, it is observed that the main products are: soy, corn in grain, sugar cane and coffee [16]. Regarding the last, by way of comparison, in 2021, Brazil produced about 3 million tons of coffee, generating a production value of 34,896,546 thousand reais, with approximately 50% of this value referring to the production of Minas Gerais [17]. It is worth mentioning that Brazil is the largest coffee producer in the world, leading the ranking in the last 100 years [18]. Coffee production is a multi-step process. In the processing stage, the beans are separated from the husk and other impurities, and the coffee, after being processed, generates approximately 50% of husk and 50% of actual coffee beans [19]. This crystallizes the need for different methodologies that reuse coffee husks, especially when considering recent data that show that global coffee consumption is increasing and should reach 12.24 million tons by 2030 [20].

Some reported applications for the use of coffee husks are: use for the production of gaseous bioenergy or biodiesel and biogas for fuels [21,22]; and use as a fertilizer for coffee or other agricultural crops. One possibility to be explored is the use of coffee husks in mortars to obtain an ecological building material. In this type of application, the waste can be tested for its pozzolanic properties, after going through a calcination process, or through alkaline chemical treatments. The basis for this treatment is the research by Shen et al. [22], where the authors studied the efficiency of pretreatments on spent coffee grounds and concluded that there was an increase in the energy efficiency of coffee husks after treatments with hydroxides [23].

Therefore, the main objective of this work is to evaluate the effects of different chemical treatments for coffee husks in order to apply the material in mortars. As the main novelty, the use of different alkaline treatments stands out, not just the calcination treatments typically performed for these materials. If alkaline treatments prove to be efficient, this represents an economic advantage for this type of material. The basis of this work is to respond to the following question: Is the use of chemical treatments for coffee husks viable for mortars?

2. Materials and Methods

To carry out this study, the following materials were used: Portland cement CP-II-E-32 (NBR 16697) [24], equivalent to CEM-I (EN 197-1) [25], hydrated lime CH III, washed river quartz sand, sodium hydroxide and potassium hydroxide solution with a 5% concentration. The chemical composition of Portland cement, hydrated lime and sand is presented in Table 1, while Figure 1 presents the granulometry of the materials. The chemical analysis of Portland cement, hydrated lime and sand was performed using energy-dispersive X-ray fluorescence (XRF) analysis. The granulometry of the materials was carried out by laser diffraction. The sand was passed through a 2.36 mm sieve.

Table 1. Chemical composition of the materials, expressed in terms of oxides.

%	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	Others
Portland Cement	49.01	29.54	10.86	2.04	0.99	0.93	0.55	0.43	5.65
Hydrated Lime	91.55	1.87	-	0.62	-	0.88	-	1.28	3.80
Sand	0.74	86.44	7.50	0.58	-	-	-	1.33	3.41

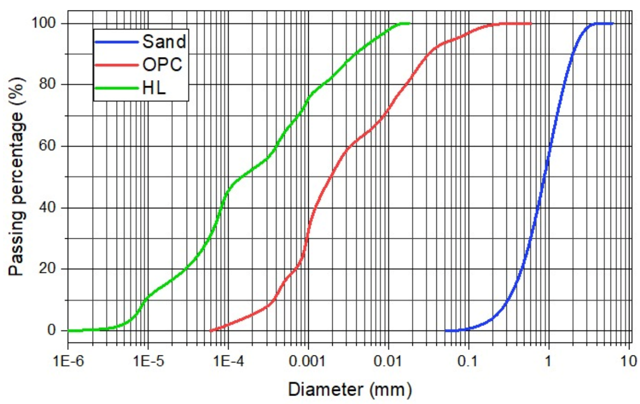


Figure 1. *Cont.*

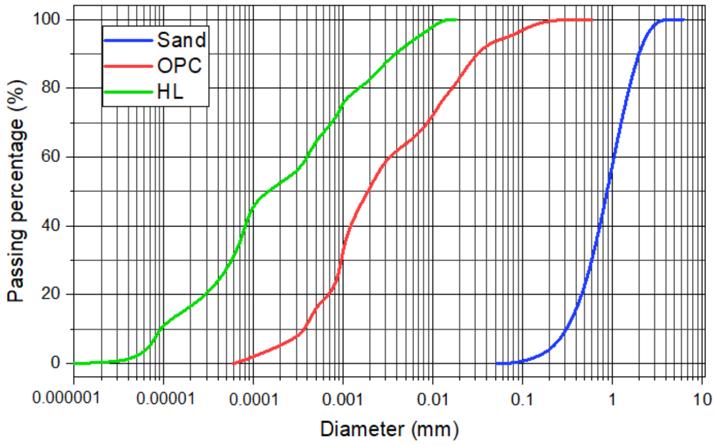


Figure 1. Granulometry of the materials.

The coffee husk used was extracted from a coffee farm located in the region of Triângulo Mineiro and Alto Paranaíba in the municipality of Serra do Salitre, Minas Gerais. The coffee, of the Arabica type, was air-dried and after processing the beans. The material used in the research was the husk of the material, which contains impurities such as sticks and leaves, removed manually from the husk. Figure 2 illustrates coffee husks in their natural state, treated with sodium hydroxide, treated with potassium hydroxide and calcined.

(**a**) (**b**) (**c**) (**d**)

Figure 2. (**a**) Natural coffee husk; (**b**) coffee husk treated with NaOH; (**c**) coffee husk treated with KOH; (**d**) coffee husk calcined.

To improve some characteristics of the husk, some chemical treatments were carried out. The first treatment was with the use of sodium hydroxide (NaOH) to reduce the impurities that are present in the composition, in addition to increasing the surface roughness. The treatment was executed using a solution of 2 L of water, in which 5% of sodium hydroxide was dissolved, with the subsequent addition of coffee husks. After 10 min, the solution was removed under running water, and the material was placed in an oven at a temperature of approximately 100 °C for a period of 24 h to dry completely. The second treatment was carried out in the same way, but with the chemical agent potassium hydroxide (KOH). This treatment was evaluated for being more alkaline and aggressive than the NaOH treatment and for the chemical composition of the coffee husk, which is usually rich in potassium. The treatment with 5% is based on previous research [26,27]. It is known that 5% of sodium hydroxide or potassium hydroxide does not in fact remain on the coffee husks; however, this amount is sufficient to remove the impurities from this material.

According to some authors [28,29], the use of coffee husk ash is the most advantageous form of use in terms of results, because it eliminates the organic part and improves the fineness and reactivity parameters of the material. Therefore, the waste was burned in a gas coffee roaster, with temperature control through the gas register achieving a maximum temperature of 500 °C, using the same equipment available in the coffee industry. The roasting was carried out in the machine, with constant rotation of the material, until all the husks changed from beige and brown to black. This process took approximately one hour for one kilogram of coffee husks. After this procedure, part of the material was ground in an electric grinder until it became a fine powder, and the other part remained in its original state.

Based on studies by Nayak et al. [30] and De Aquino et al. [10], mortars with a ratio of 1:1:6:1.55 (cement: lime: sand: water) were prepared. All the mortar mixes, except for the reference, were added with 2.5% of waste in relation to the Portland cement mass, according to Table 2. Portland cement is used to improve strength parameters and promote adhesion, while hydrated lime is essential for water retention and workability.

Table 2. Studied mortar compositions.

Composition	Portland Cement (g)	Hydrated Lime (g)	Sand (g)	Coffee Husk (g)	Water (g)
Reference	300.0	300.0	1800.0	0.0	465.0
Natural	300.0	300.0	1800.0	7.5	465.0
NaOH	300.0	300.0	1800.0	7.5	465.0
KOH	300.0	300.0	1800.0	7.5	465.0
Calcined	300.0	300.0	1800.0	7.5	465.0

The mortar was mixed following the procedures of NBR 7215 [31], which starts with the addition of water and binders and mixing them at a low speed (140 rpm) for 30 s. After that time, the sand and coffee husk were added and mixed for another 30 s at the same speed. After the first minute, the mixer speed was changed to 285 rpm, and it was mixed for 30 s. Subsequently, the mixture was rested for 90 s and, to finish, mixed at a high speed for 60 s.

With the mortar ready, six specimens were molded (50 mm in diameter and 10 mm in height), according to NBR 7215 [31], for each composition studied. After 24 h, the specimens were removed from the molds, identified and immersed in a tank with a saturated solution of hydrated lime at 25 °C, where the samples were kept until rupture. To evaluate the compressive strength, tests were made after 7 and 28 days of curing in an INSTRON universal testing machine, using a loading speed of 0.25 $MPa \cdot s^{-1}$. Another evaluated parameter was water absorption and density, which is performed according to NBR 9778 [32]. Both are accomplished by determining the mass of the samples in their saturated form and after drying in a kiln for 24 h, at a temperature of approximately 100 °C. The procedure established by the Brazilian standard is equivalent to other international standards, such as BS 1881 [33]. Although it is necessary to dry the material at 100 °C, this does not promote the degradation of hydration products, which only degrade at temperatures of 400–600 °C [34].

Subsequently, a complementary characterization was carried out through X-ray diffraction (XRD) using photomanufacturing equipment with a 2θ sweep of 5–60°, with 2 mA current generation, 30 kV voltage generation and a 5 mm divergence slit. This test is important, as it verifies which minerals are formed through the Portland cement hydration process and how this was affected by the presence of coffee husks and their treatments. The morphological characterization was performed using a scanning electron microscope (SEM) of the Jeol brand, model JSM 6460 LV.

The chemical analysis of the coffee husk was performed using energy-dispersive X-ray fluorescence (XRF) analysis in Axios Max equipment manufactured by Malvern Panalytical. In this test, the compositions of natural coffee husks and those after the calcination process were analyzed.

Finally, calorimetry analysis was carried out on pastes produced with Portland cement in the proportion of 1:0.28 (Portland cement: water). It was decided to evaluate two pastes: one of reference, containing only Portland cement, and another modified with a 2.5% addition of calcined coffee husks. In the test, an isothermal calorimeter I-CAL 2000 HP from Calorimetry was used, using a calorimeter composed of a constant speed stirrer, insulating wooden box, Dewar flask, Beckham differential thermometer and funnel.

3. Results and Discussion

3.1. Evaluation of the Properties of Mortars with Coffee Husks

Figure 3 presents the compressive strength results at 7 and 28 days of curing the mortars studied in this research. Through the analysis of Figure 3, it is observed that, at 7 days, all compositions, except for the reference one, presented a compressive strength lower than 2 MPa. According to NBR 13281 [35], the mortar for coating and laying blocks must have a minimum strength of 2 MPa. As this value is not reached in any composition in 7 days, there is a need for prolonging the curing beyond 7 days to make the application of coffee husks feasible.

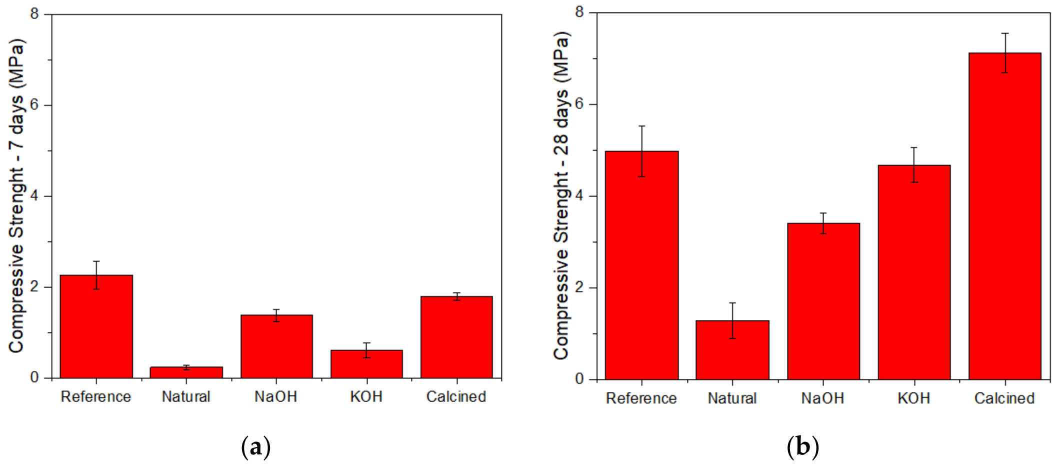


Figure 3. Compressive strength (**a**) after 7 days and (**b**) 28 days of curing the mortar with coffee husks.

The results of 28 days showed discrepant values: the composition with natural husk obtained a compressive strength of approximately 1 MPa, and the composition with calcined husk obtained a compressive strength of approximately 7 MPa. The results obtained with the addition of calcined husk are even better than those of the reference mortar, of approximately 5 MPa. This indicates that the calcination process of the material promotes some strength gain [36], which will be discussed later in the text. Still on the compressive strength at 28 days, it is observed that the natural husk is the only one with strength lower than 2 MPa, the recommended value for the application proposed in the research, in mortar for coating and laying blocks. It is known that, in this type of application, the strength cannot be too high, although there is no maximum value, as this indirectly impairs the rigidity of the material [37]. Therefore, compositions containing NaOH and KOH make it possible to apply coffee husks in mortars of this type, without the need for heat treatment, which is usually more economically expensive.

Other relevant information needs to be highlighted: comparing the results at 7 and 28 days, it is observed that the composition with NaOH presents superior strength to the KOH composition at 7 days, but the opposite pattern happens at 28 days. This indicates that the husk is impregnated with alkaline materials, which clean impurities from the material and promote greater adhesion between the husk and mortar. If there was no impregnation, the results for NaOH and KOH should follow the same statistical pattern at 7 and 28 days, that is, the most resistant composition at 7 days should be the most resistant at 28 days. The explanation for the alternation of behavior is that KOH is more alkaline than NaOH [38]. Therefore, in the long term, it favors the strength of the mortar. However, the dissolution of KOH is more difficult than that of NaOH in a strongly alkaline medium, such as in the Portland cement hydration process [39]. If dissolution took place in a neutral medium, KOH would undergo faster dissolution. But in the hydration process, this behavior is reversed, which is why the strength values at 7 days for the NaOH composition are higher than those of the KOH composition. Although there is an improvement in the resistance of the mortar after 28 days with the alkaline treatments, the values obtained are lower than those of the reference mortar. This may indicate a retardation mechanism in the mortar with coffee husks, even those with an alkaline treatment.

In general terms, for the proposed application, in mortar for coating and laying blocks, where the minimum strength required is 2 MPa, it is more advantageous to carry out alkaline treatments on the coffee husk. However, the results of the calcination composition demonstrate that the material has the potential for strength gain. In studies of other applications, such as cementitious materials with structural functions, the composition with calcined husk is more indicated.

Another important analysis for assessing the feasibility of using coffee husks in mortar for coating and laying blocks is water absorption, illustrated in Figure 4. Coffee husks are a porous organic material that decomposes more easily than industrialized materials, which may cause problems for the durability of the material [28]. In Figure 4, it is noted that the composition containing natural coffee husks showed water absorption of approximately 21.5%, indicating the hygroscopic nature of the material. This can be the result of the irregular and bulky size of the husk particles and the absence of treatments that eliminate its impurity. Mortars containing organic materials, even if treated, tend to show higher water absorption results than the reference mortars [40]. However, mortars containing coffee husks treated with NaOH and KOH present water absorption close to the reference value. This demonstrates the efficiency of alkaline treatments. Another important issue is related to the workability of the material.

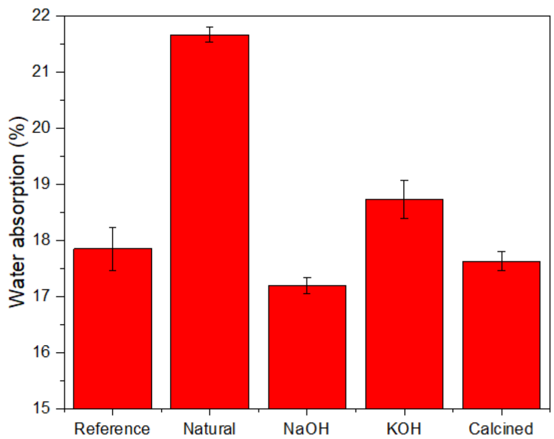


Figure 4. Water absorption of mortars with coffee husks.

According to Prado and Spinacé [41], mortars containing treated organic materials have better workability than those containing organic materials in their natural state. This is directly related to the water absorption of the material. Therefore, the results obtained are promising. Mortars with calcined coffee husks present statistical equivalence, considering the experimental error bars, when compared to the reference composition, whose absorption is approximately 17.5%. It is known that water absorption is directly related to the open porosity of cementitious materials [42]. Therefore, the fact that the composition with calcined coffee husks presents greater strength than the reference composition, but the water absorptions of the two compositions are statistically equivalent, indicates that some chemical mechanism was promoted using calcined coffee husks. This will be discussed later in the text.

Figure 5 presents the mass density results in the hardened state of mortars containing coffee husks, with 28 days of cure. The density results obtained ranged from 1.68 g·cm^{-3} to 1.70 g·cm^{-3}, showing statistical equivalence according to the deviation bar. This may be due to the husk content used, which was 2.5% in relation to the cement mass. This value was maintained for all treatments. When comparing with other studies that incorporated 2.5% of natural fibers in mortars, such as that by Aquino et al. [10] and Azevedo et al. [40], similar results were obtained, with densities of 1.7 g·cm^{-3} for natural corn fiber and 1.8 g·cm^{-3} for natural pineapple fiber. Furthermore, in the study by Azevedo et al. [40], by incorporating higher percentages of natural and treated fiber into the mortar, there was a reduction in the density property. With this, it proves that there is a potential for coffee husks to reduce the density of the mortar, if it is used in quantities greater than 2.5%.

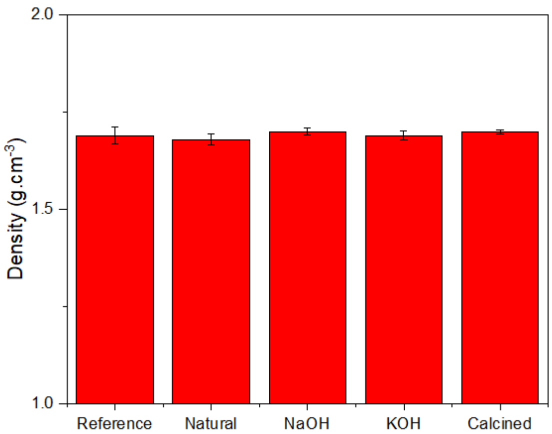
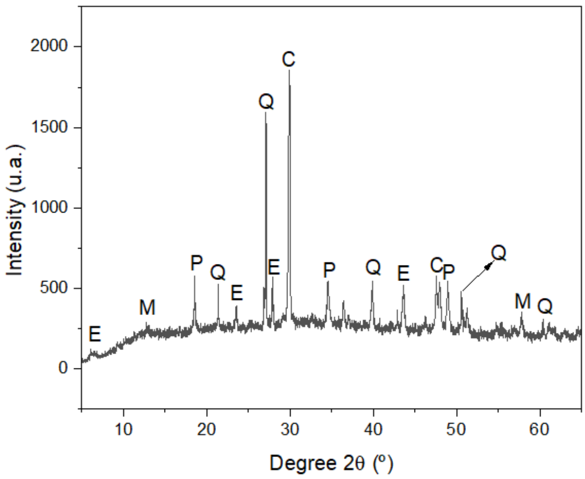


Figure 5. Density of mortars with coffee husks.

Through the results of compressive strength, water absorption and mass density, a pattern can be observed: the use of chemical treatments with NaOH and KOH provides an improvement in the results, in relation to the composition with coffee husks. Chemical treatments make it possible to use coffee husks without the need for the calcination of the material. On the other hand, the calcination process increases the mechanical strength of mortars. In other applications, such as structural function, the use of calcination is encouraged. However, it is necessary to find an explanation for the increase in strength of calcined coffee husks.

3.2. Comparison between Reference and Coffee Husk Mortars Treated with NaOH and KOH

Figure 6 presents the XRD results for the reference mortars and those with coffee husks treated with NaOH and KOH with 28 days of cure, while Figure 7 presents the SEM microscopy results of the same compositions. An important concern about using coffee husks in mortars is whether the material impairs mechanical performance. If this happens, it is likely that there is a change in the hydration of the Portland cement present in the material or a change in the porous structure of the mortars. Observing the results of Figure 6, the composition with NaOH (Figure 6b) presents more intense ettringite peaks than those of the reference composition (Figure 6a). This becomes clear by analyzing the peaks that occur at 27° and 33°. In addition, the peaks related to hydrated calcium silicate, which is mainly responsible for cement strength [43], are less intense for the NaOH composition, as observed in the peak at 30°. The identification of CSH is possible through Rietveld refinement, since CSH is a compound with low crystallinity, according to the methodology defined in other studies [44]. It is known that ettringite is a needle-shaped and bulky phase, which hinders the contact of the cement particle with water and reduces the intensity of hydration [45,46]. Therefore, the presence of ettringite in greater quantity in the NaOH composition indicates that the coffee husk treated with NaOH induces the formation of this phase. This is related to the alkalinity of the medium. The hydration of Portland cement takes place in a strongly alkaline medium. The presence of sodium hydroxide in low amounts can accelerate the hydration process. However, if this material is in a high concentration, it may impair the opposite effect, which was what happened with the use of coffee husks treated with NaOH.



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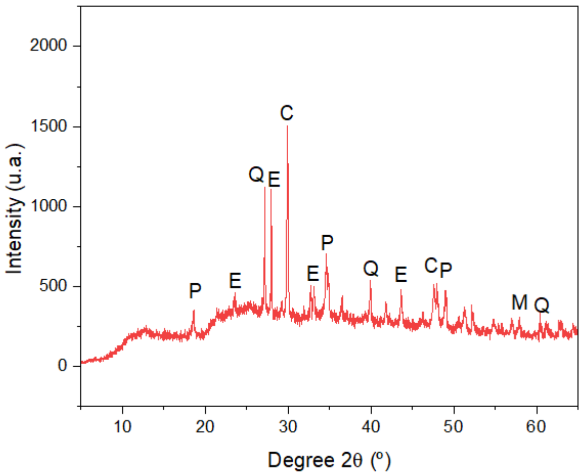

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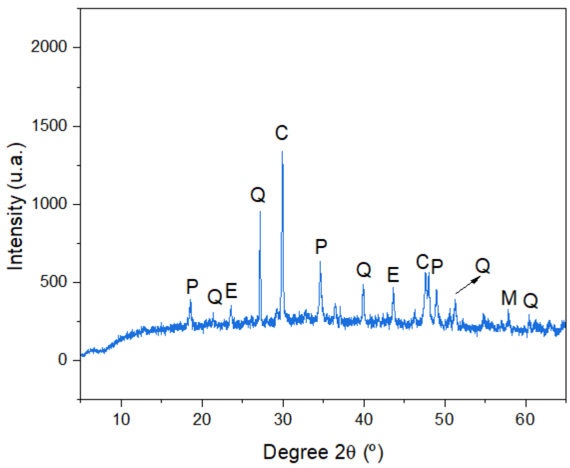
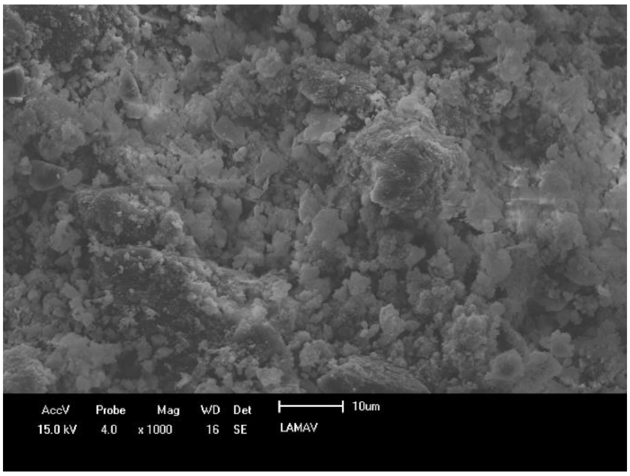


(**c**)

Figure 6. XRD results of the compositions: (**a**) reference; (**b**) NaOH; and (**c**) KOH. Caption: C = hydrated calcium silicate (C-S-H); P = portlandite; Q = quartz; E = ettringite (AFt); M = hydrated calcium aluminate monosulfate (AFm).



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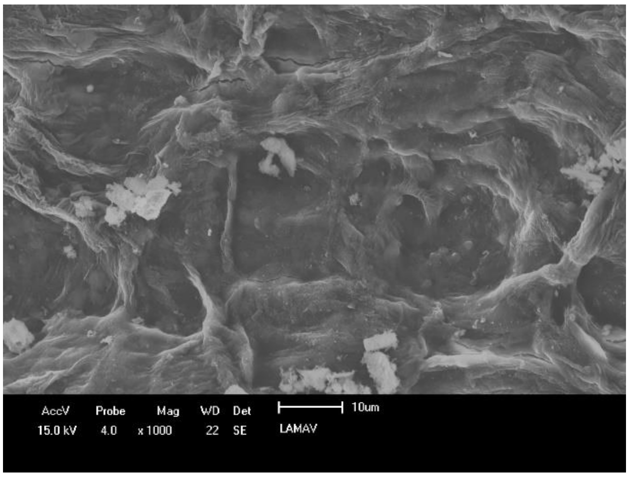

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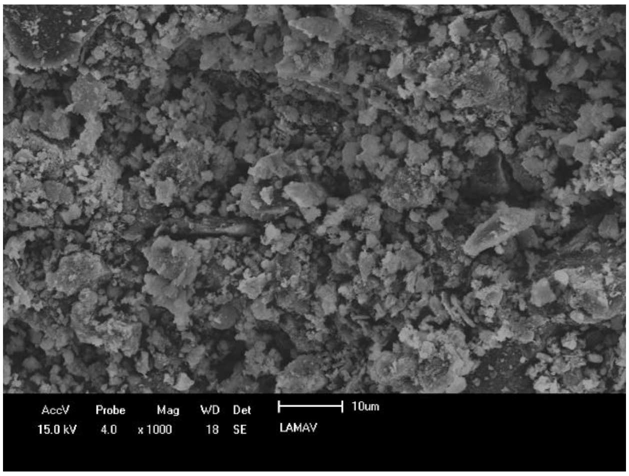


(**c**)

Figure 7. SEM results of the compositions: (**a**) reference; (**b**) NaOH; and (**c**) KOH.

In the case of the composition with KOH (Figure 6c), the observed phases are essentially the same. It is observed that the intensity of the peak at 30° relative to the hydrated calcium silicate is similar to that of the reference composition and superior to that of the composition with coffee husks treated with KOH. A point that deserves to be highlighted is that the peaks related to ettringite are less intense in the composition with KOH, as observed at 27° and 33°. As reflected by the results in Figure 3, potassium hydroxide is very alkaline. Initially, this material has difficulty dissolving in the cement hydration solution, resulting in very low strength results at 7 days when compared to the reference composition. With the hydration process, the dissolution of potassium hydroxide is intensified until 28 days, when the strengths of the reference composition and KOH composition are statistically equivalent [47]. The lower intensity of ettringite in the KOH composition, when compared to the reference composition, suggests that coffee husks treated with this material have a long-term hydration potential. The analysis of the compressive strength results at ages greater than 28 days is recommended to validate this hypothesis.

SEM results support this analysis. Figure 7a,c shows, relative to the Reference and KOH compositions, the presence of whitish crests with hexagonal and irregular shapes. The morphology of these phases suggests that they are hydrated calcium silicate and portlandite, consistent with the XRD results in Figure 6. In the case of Figure 7b, concerning the NaOH composition, the formation of these phases is less clear, which indicates a decrease in the formation of hydrated calcium silicate and portlandite. These results explain the compressive strength values obtained at 28 days, where it was observed that the reference composition and the KOH composition present equivalent strengths, while the NaOH mortar composition presents statistically lower compressive strength. This happened due to the non-formation of phases such as C-S-H and portlandite, responsible for the strength of the cement [43], and due to the NaOH content having acted as a retardant in the hardening process of the material.

Although treatments with hydroxides are a viable alternative for use in mortars, it is important to highlight that the use of high levels of alkali in cementitious materials can promote the alkali-aggregate reaction. Therefore, it is important to choose the right material that will be used as sand in these mortars. Another important concern is the potential leaching of the alkaline products present in the treatment. Azevedo et al. [48] carried out an appropriate analysis on the leaching of alkaline products used to treat natural fibers in mortars. The authors concluded that the cement matrix itself confines the material, reducing problems related to leaching.

3.3. Comparison between the Reference Mortars and Those with Natural and Calcined Coffee Husks

Before discussing the results obtained in mortars with natural and calcined coffee husks, it is important to understand the chemical differences obtained between the two types of husks. Table 3 shows the chemical composition of natural and calcined coffee husks. It is possible to notice that the coffee husk is mainly composed of potassium oxide (K_2O), whose values are 46.32% for the natural husk and 66.10% for the calcined husk. This information is equivalent to the values of other authors, such as Lima [49], who obtained 53.51% and 68.87% for natural and calcined husk, respectively. An important point highlighted by these authors is that, after the calcination process, the K_2O present in the coffee husk is an amorphous and reactive material. Therefore, if the results obtained using coffee husks treated with KOH were promising, even though potassium is superficially impregnated, the use of calcined coffee husks is even more interesting due to the amorphism of the material.

Table 3. Chemical composition of coffee husks.

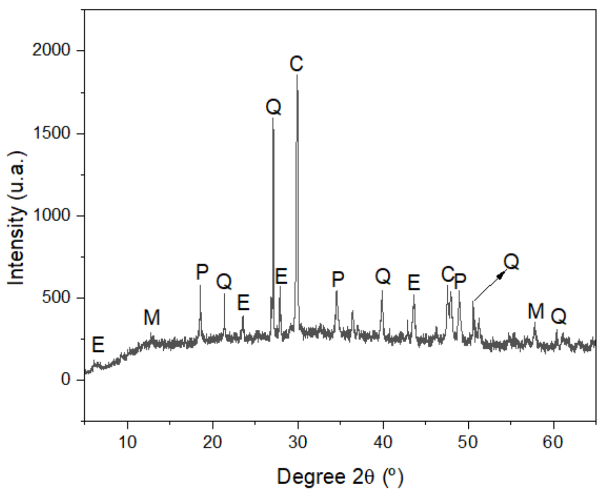
Composition (%)	K_2O	CaO	SiO_2	SO_3	Fe_2O_3	TiO_2	P_2O_5	Others
Natural	46.32	28.76	9.58	6.27	5.64	1.92	0.00	1.51
Calcined	66.10	21.99	3.19	3.02	2.25	0.80	1.36	4.31

Calcium oxide (CaO) is the second-most present component in the husk, totalling 28.76% in the natural one and 21.99% in the calcined one. Silicon dioxide (SiO_2), sulfur trioxide (SO_3)), iron oxide (Fe_2O_3), titanium dioxide (TiO_2) and diphosphorus pentoxide (P_2O_5) are present in smaller amounts. The chemical composition of calcined coffee husks depends on several factors, such as the temperature and burning time, organic material content, amount of silica and impurities and loss on ignition. According to research, the composition can vary greatly depending on the calcination method adopted [50]. However, it is possible to identify a pattern: there was an increase in the K_2O content from 46.32 to 66.10%. Furthermore, the potassium found in roasted coffee husks is probably amorphous and more reactive.

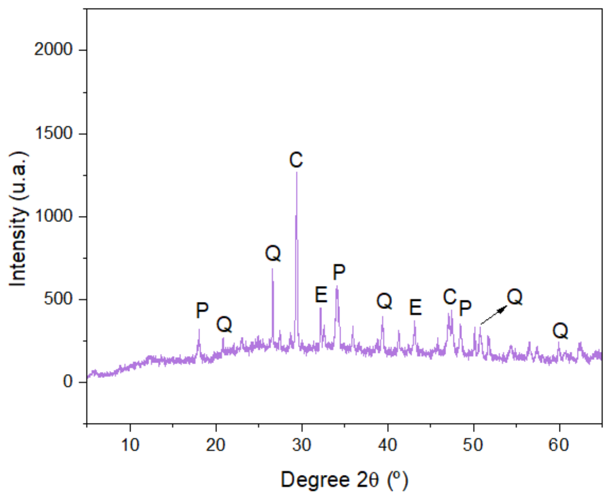
According to NBR 12653 [51], for a material to be considered pozzolanic, the sum of SiO_2, Fe_2O_3 and Al_2O_3 values must be greater than or equal to 50%. Therefore, calcined coffee husks cannot be considered as a pozzolanic material. Also, according to NBR 12653 [51], there is a maximum SO_3 value of 5%. In this case, only after the calcination process does the material comply with that recommendation. This information helps to understand why natural coffee husks were proved to reduce mortar strength when compared to the reference mortar. The presence of SO_3 delays the hydration process of Portland cement, due to the formation of ettringite, which will be analyzed below [52]. On the other hand, the presence of K_2O in the calcined coffee husk helps the hydration process due to its amorphism.

Another important piece of information should be highlighted regarding the results in Table 3. The information in the table is obtained after ignoring the loss of ignition (LOI) of the coffee husks. The LOI values obtained in the research were 21.26% for natural coffee husks and 3.43% for calcined coffee husks. A considerable reduction in this property is observed, which is related to the loss of organic material in the material, which is essential for enabling its application in cementitious materials. The results obtained are consistent with those of other similar studies. Lima et al. [29] obtained results of 19.08% of LOI for natural coffee husks, compatible with the results obtained in this research. Figure 8 presents the XRD results for the reference mortars and those with natural and calcined husks. Figure 9 presents SEM results for the same compositions. Regarding the reference composition (Figure 8a), it is observed that the composition with calcined coffee husks presents intense hydrated calcium silicate peaks (30° and 47°). Another interesting piece of information is observed by analyzing the peaks of hydrated calcium monosulfate (AFm), at approximately 12° and 58°. The composition with calcined coffee husks presents more intense AFm peaks. It is known that the formation of AFm is possible after the decomposition of ettringite [53,54]. Therefore, it is observed that the calcined coffee husk promotes the hydration process, which is attributed to the presence of amorphous and more reactive potassium in the material. AFm is a hydration product that is little studied in research, but some authors have already proven its role in the strength of hardened cement [53,54]. Therefore, the formation of AFm promoted by calcined coffee husks is a very promising result. This information is also related to a smaller amount of SO_3 observed in the chemical composition of this mortar, as observed in Table 3. In the case of the natural composition (Figure 8b), a reduction in hydrated calcium silicate peaks is observed. In general, the hydration products formed are less intense, which is directly related to the compressive strength results observed in Figure 3.

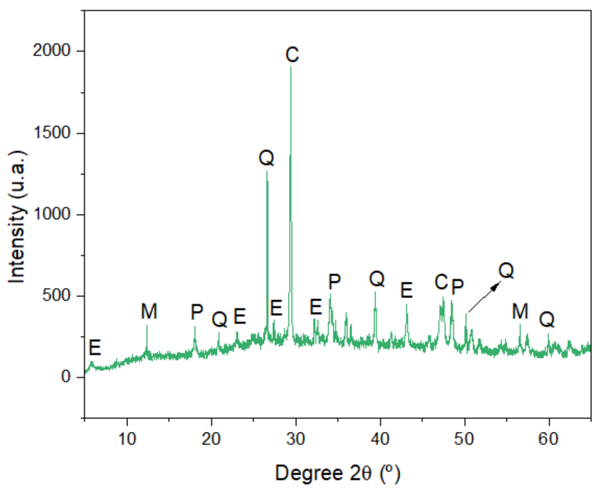
Figure 9 shows the presence of porosity in the mortar with a natural husk (Figure 9b), especially when compared to the reference composition. This information is concomitant with the water absorption results (Figure 4). Figure 9c presents a much more compact structure than the other images, related to the composition with calcined coffee husks. The presence of whitish crystals of irregular and hexagonal shapes is clear, which represent the presence of hydrated calcium silicate and portlandite. In Figure 9b, in addition to porosity, it is possible to observe the presence of needle-shaped phases, attributed to the formation of ettringite. The information is consistent with the information obtained from the XRD results (Figure 8).



(**a**)

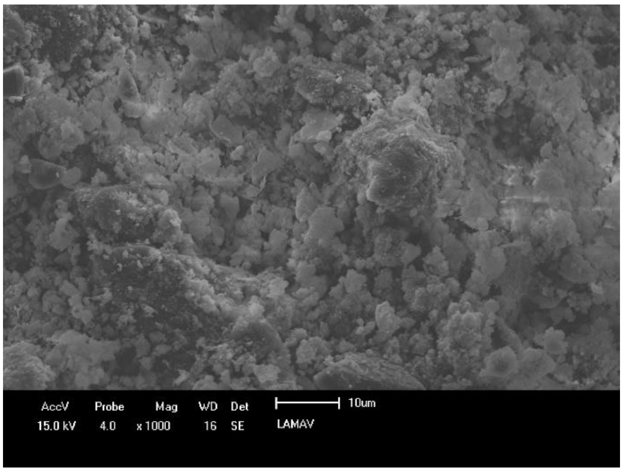


(**b**)

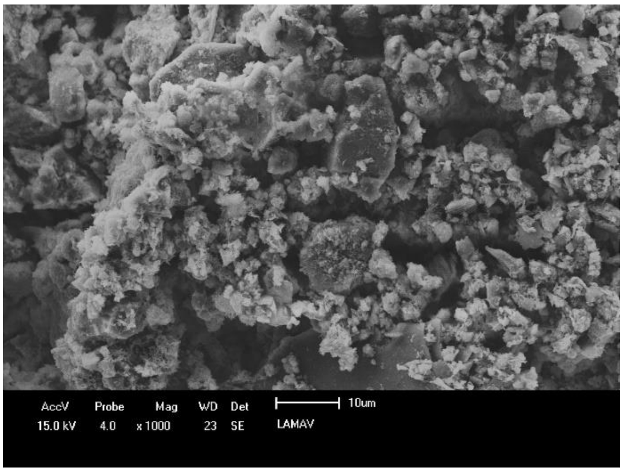


(**c**)

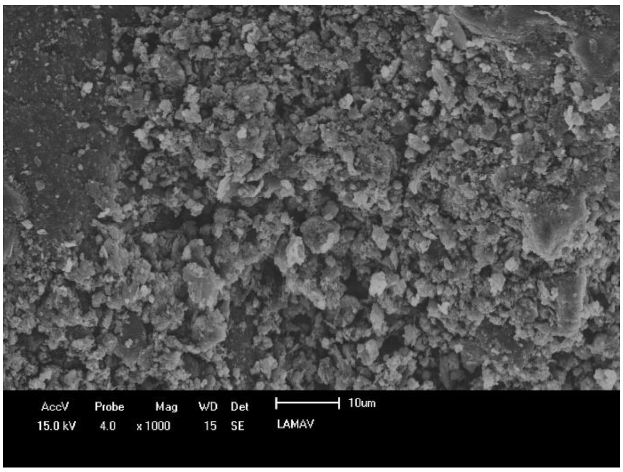
Figure 8. XRD results of the compositions: (**a**) reference; (**b**) natural coffee husk; and (**c**) calcined coffee husk. Caption: C = hydrated calcium silicate (C-S-H); P = portlandite; Q = quartz; E = ettringite (AFt); M = hydrated calcium aluminate monosulfate (AFm).



(**a**)



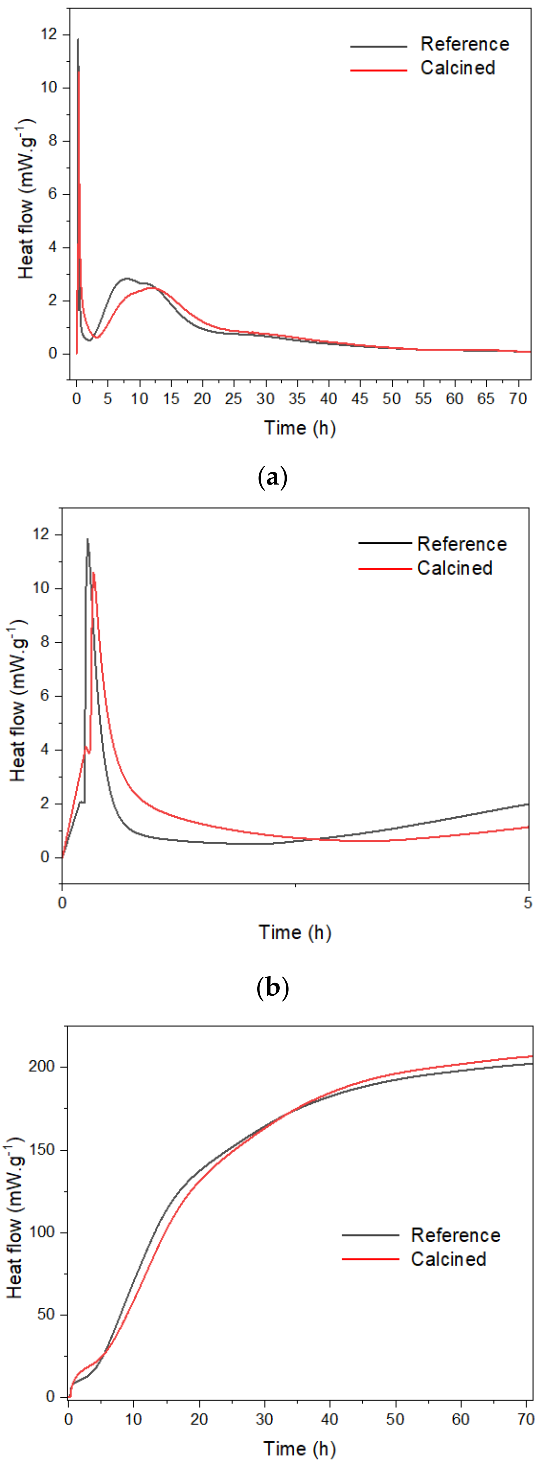
(**b**)



(**c**)

Figure 9. SEM results of the compositions: (**a**) reference; (**b**) natural; and (**c**) calcined.

A crucial point of the research is to understand how the calcined coffee husk affects the cement hydration process. With this objective in mind, the calorimetry test was conducted, as shown in Figure 10. It is known that the hydration reaction is divided into 5 periods: (1) initial reaction, which takes place in the first peak of heat around 30 min; (2) dormancy period; (3) acceleration period; (4) period of deceleration; and (5) slow reaction period [47,55]. The initial reaction occurs due to the reaction of C_3A with gypsum, promoting the formation of ettringite [56]. The reference sample has a first heat peak, relative to the initial dissolution, of approximately 12 mW·g^{-1}, while the sample with calcined coffee husks has a value of around 10 mW·g^{-1}. The values are remarkably close, even though the sample with calcined coffee husks has a lower initial dissolution rate. This indicates less initial ettringite formation since cement hydration is accelerated by the presence of, most likely, potassium oxide.



(**a**)

(**b**)

(**c**)

Figure 10. Results of isothermal calorimetry: (**a**) in 70 h; (**b**) in 5 h; (**c**) heat flow.

Another important piece of information occurs in the time interval between 5 and 10 h, related to the hydration of C_3S together with the hydration of C_3A and C_4AF and the formation of AFm [55]. It is observed that, in the reference composition, the hydration of these materials happens first, but the reaction slows down around 10 h [47,57]. In the composition with calcined coffee husks, the reaction takes place after the reference one, but there is no deceleration observed in the reference composition since the AFm is formed continuously. In the reference composition, this pattern is not observed, and the hydration reaction is hindered by the formation of ettringite, which, in the composition with calcined coffee husks, due to the high content of amorphous potassium, allows for the formation of AFm. In summary, the presence of amorphous potassium in the composition with calcined coffee husks promotes the faster dissolution of ettringite and the faster formation of AFm, which contributes to the strength of the hydrated cement. This indicates a potential for using higher levels of calcined coffee husks, provided that the studied material is used for structural applications.

The integrated results are presented in Figure 10c. It is known that heat flow is directly linked to the cement hydration process. It is observed that, initially, the reference composition presents a higher heat flow, but after 30 h of hydration, the behavior is reversed. This indicates that the composition with calcined coffee husks has the potential to present better mechanical performance, as evidenced by the compressive strength results at 28 days. Thus, it is observed that the results obtained are consistent.

4. Conclusions

The main objective of this work was to evaluate alternative methodologies for the treatment of coffee husks, aiming at their application in coating and wall laying mortars. Specifically, the objective was to evaluate the effect of chemical treatments with sodium and potassium hydroxide as an alternative to the calcination of coffee husks. It is concluded that:

- Executing alkaline treatments with NaOH and KOH has the desired effect of improving the mechanical performance of the coffee husk, since, at 28 days, the mortar compositions with NaOH and KOH present a compressive strength greater than 2 MPa, whereas these values are not achieved with the natural coffee husk.
- Comparing the compositions of mortar with coffee husks treated in NaOH and KOH, it is observed that potassium hydroxide, because it is more alkaline, presents less dissolution in the cement hydration process. This implies that the compressive strength results at 7 days are lower for the KOH composition. However, at 28 days, this pattern is reversed due to the dissolution of KOH. The composition with KOH presents the formation of hydrated calcium silicate in levels compatible with the reference composition, as observed by the XRD and SEM results. The composition with NaOH, on the other hand, presents a greater intensity of ettringite formation than the reference composition. These same peaks of ettringite are observed in the natural husk mortar composition.
- The water absorption results show that the composition with natural coffee husks has greater porosity. Furthermore, the compressive strength results for the natural coffee husk composition do not meet the minimum of 2 MPa. This highlights the importance of chemical treatments or calcination in making the application of coffee husks feasible. The density results do not present statistical differences, preventing any interesting conclusion.
- The calcination of the coffee husk promotes an increase in the amorphous potassium content in the material and reduces the SO_3 content in relation to the natural husk. This allows for a strength gain mechanism, especially at 28 days, although calcined coffee husks cannot be considered a pozzolanic material. However, the higher amorphous potassium content promotes the formation of AFm due to the degradation of ettringite, representing an efficient gain in mechanical strength since ettringite, as a very voluminous phase, hinders the hydration process of the cement. It is recommended to use calcined coffee husks in structural applications.

- It is concluded that, in order to achieve the objective of the work, that is, the application of coffee husks in mortars for coating and laying blocks, the use of chemical treatments, especially with KOH, allows for the proper use of coffee husks. On the other hand, the increase in strength provided by the calcined coffee husk is not recommended for this type of application.

Suggestions for future research:

- Evaluation of properties such as adhesion, workability and drying shrinkage in mortar containing coffee husks.
- Evaluation of other alkaline treatments, such as calcium hydroxide.
- Evaluation of the rheological properties of the mortars with coffee husks.

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