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POTENTIAL USE OF BINARY AND TERNARY BLENDED CEMENT IN FIBER CEMENT COMPOSITES

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ABSTRACT

The industrial production of vegetable fiber cement composites is limited by the lack of durability of the fiber in the cement matrix. The aim of this study is, primarily, evaluate the potential use of new blended cements from agro-industrial wastes to improve durability of vegetable fibers in fiber cement composites. Secondly, the influence of rice husk ashes (RHA) on the mechanical properties of cementitious composites reinforced by coconut fibers and cellulose pulp was studied. In the first part, ashes were prepared from sugar cane bagasse (SCBA) calcined at 700°C and bamboo leaf (BLA) calcined at 600°C. Pozzolanic activity was evaluated using conductometric test and thermogravimetric analysis. Effect of ashes on cement hydration was determined using isothermal calorimetry. In the second part, thermogravimetric analysis and four-point bending tests were used to evaluate the mechanical properties of fiber cement composites where cement was partially replaced by RHA calcined at 1000°C.

In calcium hydroxide solution, the results showed that ternary mixture of SCBA, BLA and lime presents a higher pozzolanic activity than binary mixture of SCBA and lime. Cementitious pastes prepared from binary and ternary binder of SCBA and BLA present lower amount of calcium hydroxide than the ordinary Portland cement (OPC), as a control. The ternary binder composed of 80 wt.% of cement, 10 wt.% of bamboo leaves ashes and 10 wt.% of sugar cane bagasse ashes showed a decrease of 46% of total heat of hydration in comparison to OPC at 48 h. Moreover, the use of RHA in fiber cement composites allows to decrease of matrix alkalinity and consequently reducing vegetable fibers degradation in fiber cement composites. Binary or ternary binder made with only agro-industrial residues can be a solution to improve durability of fibers in cement composites.

KEYWORDS

Ashes; pozzolanic materials; cement; isothermal calorimetry; thermogravimetric analysis.

INTRODUCTION

Durability of vegetable fibers in cement matrix is the main problem of these fibers in cement composites. The chemical deterioration of fibers in alkaline environment is mainly due to the migration of calcium hydroxide to the fiber lumen, middle lamella and cell walls (Aziz et al., 1981).

There are various approaches to increase durability of vegetable fibers in cement matrix. One of them is the use of pozzolanic compounds, mainly constituted of amorphous silica, which reacts with calcium hydroxide to form calcium silicate hydrates (CSH). The decrease in calcium hydroxide content in the cement matrix leads to an increase of the fiber durability (Tolêdo Filho et al., 2003; Almeida Melo Filho et al., 2013; Marmol et al., 2015).

Tolêdo Filho et al. (2003) studied the effect of partial substitution of cement by non-densified silica fume on the durability of sisal fiber-cement composites. They showed that the durability of the composites improved by reducing the alkalinity in the pore solution through the addition of the non-densified silica fume.

Almeida Melo Filho et al. (2013) showed that mineralization of the fibers is not observed when the cement matrix is partially substituted by 50 wt.% of amorphous metakaolin in sisal fiber cement composites (Almeida Melo Filho et al., 2013).

Marmol et al. (2015) showed that the low alkalinity of the cement matrix can be associated with a better mechanical performance of the fiber cement composite. According to the authors, the use of the pozzolanic additions as partial replacement of cement can improve the durability of fibers in the alkaline environment of cementitious matrix.

The main advantage for the fiber cement industry of using pozzolanic compounds is the decrease of the final cost of the product. Indeed, the replacement of cement by residues lead to energy saving. The energy necessary to produce this blended cement is potentially lower than the plain cement. Moreover, the environmental impact of this blended cement is reduced; less cement consumption contributes to less greenhouse gas produced.

Agriculture by-products and natural resources such as sugar cane wastes, bamboo leaves, when calcined at controlled temperature and finely ground, show a pozzolanic activity that is to say a capacity to react with calcium hydroxide (Morales et al., 2009; Frias et al., 2012). These materials can also be used in fiber cement composites to reduce the available amount of free calcium hydroxide.

There are few studies on the use of only agro-industrial wastes in ternary blended cement. Cordeiro et al. (2012) studied the use of rice husk (RHA) and sugar cane bagasse ashes (SCBA) in binary and ternary conventional and high strength concrete. The ternary concretes presented lower electric charges and the replacement of cement by 40% SCBA and RHA decreased significantly the maximum adiabatic temperature rise of conventional concrete.

Ettu et al. (2013) studied the potential of use rice husk and saw dust ash in binary and ternary blended cement. From 10 wt.% of cement replacement, the authors showed that ternary concretes prepared with rice husk and saw dust ashes presented higher compressive strengths than binary concrete prepared with saw dust ashes.

The aim of this study is to evaluate the potentiality of the use of binary and ternary cement blended pastes containing only agro-industrial wastes in fiber cement composites. The first part of the paper was a study of the pozzolanic activity of bamboo leaf and bagasse ashes and their influence on the hydration of cement. The second part was an application of using rice husk ashes in fiber cement composites reinforced by coconut fibers and cement bag recycled pulp. Mechanical tests were carried out to evaluate the influence of partial substitution of cement on performance of composites, before and after their exposure to the accelerated aging process.

MATERIAL AND METHODS

Study of the pozzolanic activity of bamboo leaf and bagasse ashes

The bamboo (*Bambusa tuldoides*) leaves were collected in the Pirassununga Campus, University of São Paulo, Brazil. Sugar cane bagasse was collected in the Abengoa sugar cane commercial milling plant in Pirassununga, SP, Brazil. Sugar cane bagasse (SCB) and bamboo leaves were primarily calcined in a muffle furnace at 400°C for 60 min to remove the excess of organic matter. Then, calcined at 700°C for 60 min in the case of sugar cane bagasse and 600°C for 60 min in the case of bamboo leaves with a heating rate of 10°C/min (Cordeiro et al., 2008; Villar-Cociña et al., 2011). Ashes produced were passed through a sieve opening of 45 μm.

The pozzolanic reaction of ashes was evaluated by conductivity method. 250 mL of saturated $Ca(OH)_2$ solution mixed with 5.25 g of ashes (which is the proportion commonly found in the literature for similar experiments) and magnetically stirred at 40°C. The conductivity measurements began immediately after the introduction of ashes in the saturated $Ca(OH)_2$ solution. The mixture formulations are shown Table 1.

Table 1 – Mixture dosages of ashes-calcium hydroxide solution.

Samples	SCBA (g)	BLA (g)	Saturated calcium hydroxide solution (mL)
50SCBA-50BLA	2.625	2.625	250
60SCBA-40BLA	3.150	2.100	250
70SCBA-30BLA	3.675	1.575	250
100SCBA	5.250	0	250
100BLA	0	5.250	250

Obs.: SCBA = Sugar cane bagasse ash; BLA = bamboo leaf ash.

Thermogravimetric analysis was performed in a simultaneous thermal analyzer NETZSCH STA 409 PC/PG. The mix proportions and water amount for cementitious pastes are summarized in Table 2. All samples were cured in water at 30°C. Cement pastes were analyzed under nitrogen atmosphere (flow rate 20 mL/min) with a heating rate of 10°C/min from 30 to 1000°C. Hydration of cement pastes was stopped using acetone, then the samples were put in an oven at 60°C and in a desiccator under vacuum atmosphere before testing.

The weight loss of samples was used to determine the fixed lime according to the equation (1):

$$\text{Fixed lime (\%)} = [(CH_{OPC} * \%_{cement}) - CH_{pozz}] / [(CH_{OPC} * \%_{cement}) \qquad (1)$$

Where CH_{OPC} is the amount of calcium hydroxide in OPC, CH_{Pozz} is the amount of calcium hydroxide in the paste containing SCBA, BLA and $\%_{cement}$ is the proportion of cement in the cementitious paste.

The isothermal calorimetry study in the pastes was conducted in an isothermal calorimeter TAM Air (TA Instruments). The dried cement powder was added to the flask and the water added with a syringe, keeping a water/binder ratio equal to 0.4. The monitoring of the heat released during the hydration of the binder was carried out for 48 h. The temperature of the calorimeter was maintained at 25°C during the experiment.

Table 2 – Mix proportion of cementitious pastes containing agro wastes.

Samples	Cement (%)	SCBA (%)	BLA (%)	Water/binder
OPC	100	0	0	0.5
20%SCBA	80	20	0	0.5
20%BLA	80	0	20	0.5
10%SCBA-10%BLA	80	10	10	0.5

Obs.: OPC = ordinary Portland cement (high initial strength); SCBA = Sugar cane bagasse ash; BLA = bamboo leaf ash.

Study of use of rice husk ashes in fiber cement composites

Rice husk ashes (RHA) were provided by Maicerías Españolas DACSA S.A. They were obtained in a high temperature furnace (T > 1000°C). Before being used, the ashes were milled for 20 min in a Gabrielli-2 jar mill with 18 mm diameter-alumina balls, to increase their reactivity.

The coconut fibers were provided by the company Coco Verde, Rio de Janeiro, Brazil. The fibers were mechanically extracted from the husks with an initial length of 14.8 cm and passed through the cutting process in a knife mill, brand JFS®, JF5 model, with a 4 mm screening separation.

The cellulose pulp was obtained from the disintegration of cement bags produced with unbleached Kraft paper according to the process described by Pereira at al. (2013).

A simultaneous thermal analyzer Mettler Toledo brand, model 850 TGA, was utilized to determine the reactivity of the RHA and the amount of calcium hydroxide fixed by pozzolanic reaction in the cementitious pastes. Cement pastes were prepared with cement partially replaced by 50% by weight of RHA (CEM50RHA), and the water/binder ratio was constant and equal to 0.5. A control specimen without RHA was also prepared with the same conditions (OPC). A part of samples was cured for a period 28 days in water at laboratory temperature and the other part remained in thermal bath at 65°C (accelerated aging process) for another 28 days. After curing, the samples were ground in acetone. The powder generated was separated through a sieve nº 120 (125 µm) and the residual moisture of the sample was removed using acetone followed by filtration and drying at 65°C. The TG analyses were performed under an atmosphere of dry air with gas flow equal to 75 mL/min, heating rate of 10°C/min and temperature range between 35°C and 600°C. Eq. 1 was used to calculate the fixed lime at all ages.

For the production of the composites, two formulations were tested (Table 3). Flat pads were molded with dimensions of 200 mm × 200 mm and 5 mm thick. They were prepared in laboratory scale using a slurry vacuum dewatering followed by pressing technique described in detail by Savastano Jr. et al. (2000). Composites were prepared with ordinary Portland cement CEM I 52.5 R partially replaced by 50% by weight of RHA, cellulose pulp and coconut fibers (CEM50RHA5P5F). Composites without RHA were also prepared with the same conditions (Reference).

The test pads were submitted to wet curing for two days in sealed plastic bags and then kept in a climatic chamber at 20°C and 90% relative humidity until the completion of the 28-day period. The pads were then cut into test specimens (200 mm × 40 mm) for mechanical tests using a diamond disk cooled by water.

Table 3 – Mix proportion of fiber cement composites.

Samples	Cement (%)	RHA (%)	Cellulose pulp (%)	Coconut fibers (%)	Water/binder
Reference	100	-	5	5	0.42
CEM50RHA5P5F	50	50	5	5	0.63

Half of the specimens were subjected to the mechanical tests after the initial curing period (28 days) and the other half remained in thermal bath at 65°C (aging process) for another 28 days before the tests, totaling 56 days of curing + degradation.

The four-point bending tests (equidistant distances between the supports) were carried out in the universal testing Instron model 3382 using a 5 kN cell machine Instron model 2714- 010®, with the cross-head speed of 1.5 mm/min, for the calculation of the following mechanical properties: modulus of rupture (MOR) and specific energy (SE). The completion of the tests was achieved after observing a decrease of 70% of the maximum load (Savastano and Pimentel, 2000).

RESULTS AND DISCUSSION

The pozzolanic activity of bamboo leaf and bagasse ashes

Figure 1 shows the conductivity versus time of saturated calcium hydroxide solution containing sugar cane ashes (SCBA) and bamboo leaves ashes (BLA). As expected, a decrease of the electrical conductivity of the ashes/calcium hydroxide system is observed for all samples. This behavior is attributed to the pozzolanic reaction between amorphous silica and lime, which produces CSH (Villar-Cociña et al., 2011). It can be noted that BLA presents a higher pozzolanic activity than SCBA. The electrical conductivity is related to the concentration of Ca^{2+} ions in the solution (Villar-Cociña et al., 2003). The Ca^{2+} ions react with the amorphous silica present in the ashes to produce CSH gel with a decrease of the electrical conductivity. These results show that ashes from agricultural and industrial wastes show pozzolanic activity.

The loss of conductivity of samples at 48 h was calculated according the equation (2):

$$\xi = (C_0 - C_{48}) * 100 / C_0 \qquad (2)$$

With ξ the loss of conductivity (%), C_0 the initial conductivity at t = 0 (mS/cm) and C_{48} the initial conductivity at t = 48 h (mS/cm).

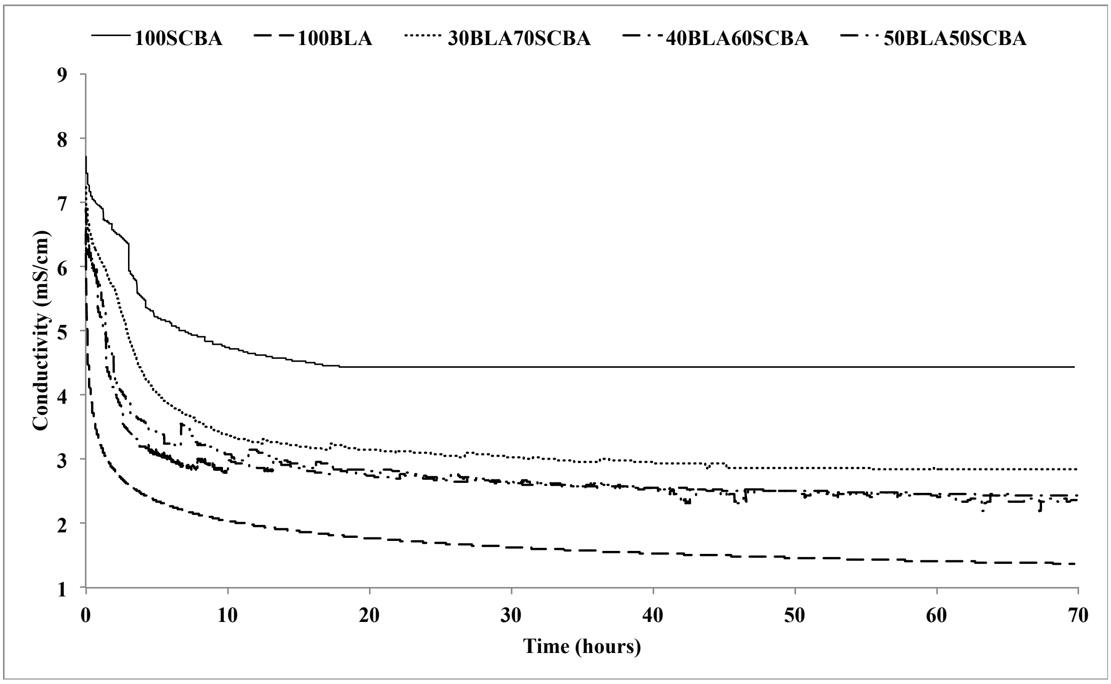

Figure 1 – Electrical conductivity versus time of SCBA and BLA in binary and ternary mixture with saturated calcium hydroxide solution.

Table 4 shows the loss of conductivity (ξ) calculated for all combinations of ashes. The loss of conductivity of 100SCBA (42.49%) is lower than 100BLA (79.18%). This behavior is due to the amount of reactive silica present in the ashes equal to 36.2 and 70.5 wt.% for SCBA and BLA respectively.

For ternary mixtures, the higher reactivity is achieved by 60SCBA-40BLA followed by 50SCBA-50BLA and 70SCBA-30BLA. This result demonstrates the importance of use of ternary mixtures using a material mixed with another in a lower proportion but with a higher reactivity. Compared to 100SCBA, all ternary mixtures present a higher loss of conductivity, that is to say a higher pozzolanic activity.

Table 4 - Loss of conductivity of ashes/lime solution

Samples	ξ (%)
100SCBA	42.49
100BLA	79.18
50SCBA-50BLA	63.58
60SCBA-40BLA	65.65
70SCBA-30BLA	60.63

Table 5 shows the calcium hydroxide fixed by SCBA and BLA in binary and ternary cementitious pastes at 28 days.

The use of SCBA and BLA in binary or ternary blended cement allows fixing between 23 and 33% of calcium hydroxide, this result confirms the pozzolanic activity of ashes. This type of matrix can be a solution to fabrication of cement composite reinforced with vegetable fibers, which requires low content of free calcium hydroxide to improve durability of the fibers. It can be noted that the binary cementitious pastes containing SCBA fixes more calcium hydroxide than the one containing BLA. This result is different than the one obtained in conductivity tests in saturated calcium hydroxide solution (Table 4). This behavior can be explained by the difference between the temperature of curing of cementitious pastes (30°C) and the temperature of the conductivity tests (40°C).

Table 5 – Fixed lime by SCBA and BLA in cementitious pastes containing at 28 days.

Cementitious pastes	Fixed lime (%)
20%SCBA	33.30
20%BLA	25.15
10%SCBA-10%BLA	23.42

Figure 2 shows the total heat of hydration released up to 48 h in cementitious pastes containing SCBA and BLA. The curve of OPC shows a higher heat accumulation than other pastes. Thus, the replacement of cement by 20 wt.% of SCBA and/or BLA in binary and ternary mixtures, promotes a smaller heat release.

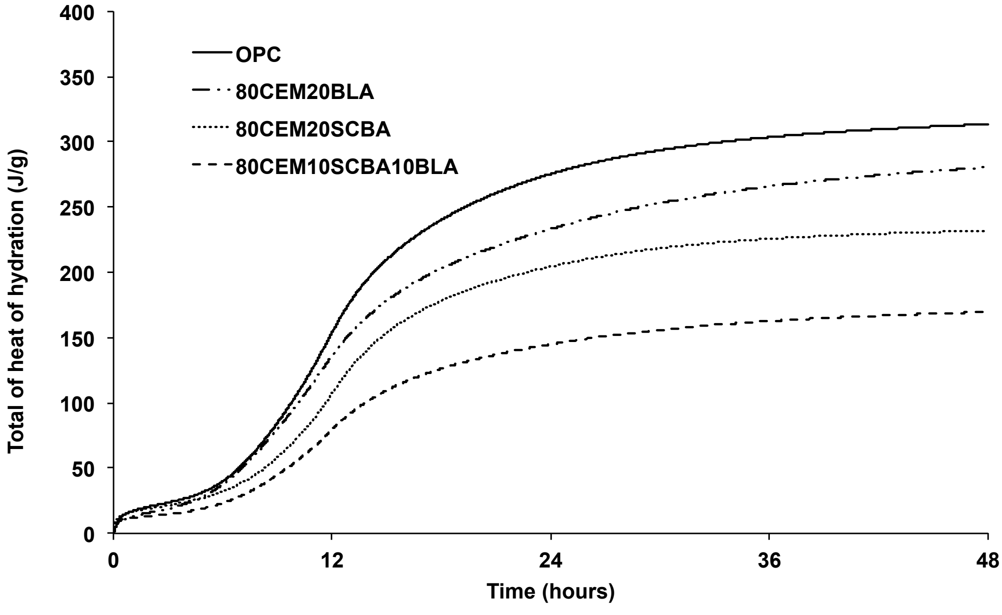

Figure 2 - Total heat of hydration of cementitious pastes.

Figure 3 shows the heat of hydration of all cementitious pastes for 48 h in cementitious pastes containing agro-wastes. The heat of hydration obtained from replacing 20% of the commercial cement by ashes confirms the effectiveness of binary and ternary blend matrix in reducing the heat of hydration of cementitious material. This significant decrease in the heat of hydration, 46% in the case of ternary binder, could lead to a loss of strength of the fiber-cement composite at early age prepared with this ternary binder.

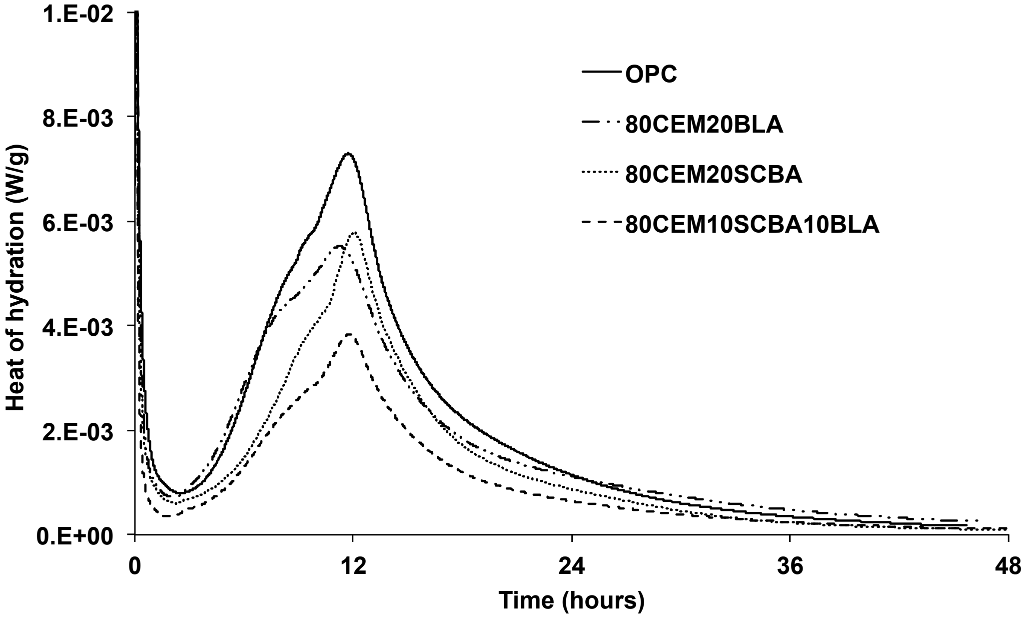

Figure 3 - Comparison of heat hydration of different cementitious pastes.

The use of rice husk ashes in fiber cement composites

Table 6 shows the calcium hydroxide fixed by RHA in cementitious pastes at 28 days and after accelerated aging process. The result shows that the partial replacement of cement by 50% by weight of RHA allows fixing a higher amount of calcium hydroxide after accelerated aging process. This result confirms the pozzolanic behavior of the ashes.

Table 6 – Fixed lime by RHA in cementitious pastes at 28 days and after aging process.

Sample	Fixed lime 28 days (%)	Fixed lime After aging (%)
CEM50RHA	93.4	100.0

Table 7 shows the mechanical properties in bending test of the fiber cement composites with and without RHA. For CEM50RHA5P5F compared to reference, an increase of 40.17 and 71.70% of MOR was observed at 28 days and after aging process respectively. The behavior is due to the pozzolanic reaction between the amorphous silica present in RHA and the calcium hydroxide produced during the hydration of the ordinary Portland cement (OPC).

The results also showed that the aging period of 28 days in a water bath at 65°C was important to complement the curing process. The pozzolanic reaction between the reactive silica from RHA and the portlandite (calcium hydroxide) from the hydration of OPC produced an appropriate environment for the chemical stabilization of coconut fibers.

Table 7 – Mechanical properties of fiber cement composites at 28 days and after aging process.

Samples	MOR (MPa) 28 days	MOR (MPa) After aging	SE (kJ/m^2) 28 days	SE (kJ/m^2) After aging
Reference	11.2 ± 0.6	10.6 ± 1.5	2.7 ± 0.2	0.6 ± 0.1
CEM50RHA5P5F	15.7 ± 1.1	18.2 ± 0.5	3.7 ± 0.9	1.6 ± 0.3

After the aging process, the composite containing 50% by weight of RHA showed an average specific energy significantly higher than the Reference, which supports that the use of high amount of RHA allows to preserve the coconut fibers and the recycled cellulose pulp in the cementitious matrix.

CONCLUSIONS

Based on the experimental results obtained in this study, the following conclusions can be drawn:

1. Electrical conductivity tests of ashes/calcium hydroxide solution showed that SCBA and BLA demonstrate pozzolanic activity.
2. The use of sugar cane bagasse ash (SCBA) and bamboo leaf ash (BLA) lead to binary and ternary cementitious pastes with lower calcium hydroxide content than OPC.
3. Ternary binder composed of 80 wt.% of cement, 10 wt.% of bamboo leaves ashes and 10 wt.% of sugar cane bagasse ashes showed a decrease of 46% of total heat of hydration in comparison of OPC at 48 h.
4. The use of RHA in fiber cement composites decreases matrix alkalinity and consequently reduces vegetable fibers degradation in fiber cement composites.

For fiber cement industry, the use of binary or ternary blended cement can be a very promising approach to improve the durability and performance of fiber cement composites in those regions where agro-industry ashes are available. This study has to be supplemented by additional experiments on the degradation of fibers in the composite such as wet/dry cycling and natural aging.

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