Preliminary Studies on Alkali-Activated Binder Based on Wood Waste Ash

André Augusto Silveira e Silva^{a*} (0), Bruno Cherubini Fernandes Pereira^a,

João Pedro Bittencourt Batista^a 💿, Jorge Luís Akasaki^b, João Cláudio Bassan de Moraes^a

^aInstituto Tecnológico de Aeronáutica (ITA), Laboratório de Materiais e Pavimentação, Divisão de Engenharia Civil, São José dos Campos, SP, Brasil. ^bUniversidade Estadual Paulista Júlio de Mesquita Filho (UNESP), Departamento de Engenharia Civil, Faculdade de Engenharia, Ilha Solteira, SP, Brasil.

Received: January 15, 2023; Revised: October 27, 2023; Accepted: November 8, 2023

Alkali-activated binders (AAB) are inorganic materials produced by a mixture between a solid precursor and an alkaline activator, wherein, the reaction results in a material with properties similar to Portland cement hydration. The advantages of AAB over Portland cement are the possibility of using alternative materials, demanding low energy and low CO, emission. The primary objective of this study was to produce an alkali-activated binder (AAB) using calcined wood waste ash (CWWA) as a solid precursor due to its beneficial properties. CWWA was obtained by burning wood wastes in a furnace, then calcined in a laboratory oven at 600 °C to remove unburned particles. Afterward, the ash was milled and then physiochemically characterized by chemical composition, X-ray diffraction (XRD), particle size distribution, and scanning electron microscopy (SEM). The milled CWWA was employed in AAB mortars and pastes activated with sodium hydroxide (NaOH) to assess the influence of alkaline activator concentration. In this work, the Na⁺ concentrations varied in the 6.5-12.5 mol.kg⁻¹ range. Mortars were assessed by compressive strength, whereas pastes were analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS) for samples cured after 7 days at 60 °C. Results showed that the CWWA is mainly composed of SiO₂ (67.9 wt%) and the presence of an amorphous phase and quartz as the main crystalline phase (XRD). The compressive strength of mortars showed that the CWWA activated with a Na^+ concentration of 6.5 ml.kg⁻¹ achieved the highest compressive strength (23.2 ± 1 MPa). Microstructural studies of pastes showed the formation of sodium carbonate (XRD) and reaction products (FTIR) in a dense microstructure (SEM/EDS). Hence, the key findings suggest that employing CWWA as a solid precursor offers a viable choice for producing a more sustainable AAB.

Keywords: Alkali-activated binder, wood waste ash, alternative material, compressive strength, microstructure.

1. Introduction

Materials used in Portland cement (PC) manufacture to produce cementitious concrete demand high exploration of clays and limestone. In addition, cement manufacture shows high CO₂ emissions, and high energy for the calcination of raw materials, which consists of of burning limestone (calcium oxide, CaO) and clays (Al₂O₃, Fe₂O₃, Si₂O₃) for clinker production¹. This study shows an alternative solution for the use of PC: alkali-activated binders (AAB). AAB is a material with an inorganic composition, composed of two sources: a solid precursor and an alkaline activator²⁻⁴. AAB shows cement-like properties, and when combined solid precursor with an alkaline activator in the presence of water, the reaction results in a material with hardened property showing high compressive strength. Solid precursors are materials composed mainly of aluminosilicates, which can be separated at low-calcium content and high-calcium content. An alkaline activator is a material mainly composed of an alkaline metal that promotes the increase of pH when

dissolved in water. New materials are being researched to increase the environmental advantages of AAB⁵⁻⁷. In this context, this study presents the wood waste ash.

In Brazil, wood waste is mostly used as a biomass resource for energy production by the calcination of these wastes. Only in 2020, Brazil produced energy by burning over 110 million m3 of wood residues after burning wood residues8. However, a high number of ashes is left without a proper destination: the wood waste ash. Wood waste ash is mainly obtained by the combustion of wood wastes, and it has been used as a partial replacement for Portland cement as pozzolanic material, which is such a significant resource to decrease cement bulk consumption and decrease its greenhouse gases and other pollutants of Portland cement production9. However, there are few studies of wood waste ash as a solid precursor in AAB^{10,11}, and these studies present this waste combined with other solid precursors. In this context, this study aims to assess the potential of wood waste ash with extra calcination in the laboratory to remove unburned particles from the former burnt process as the only solid precursor in AAB activated with sodium hydroxide. The main advantages of this study are technical and scientific:

^{*}e-mail: civilandre.eng@gmail.com

in the former advantage, a proper destination for the waste can be achieved; and, regarding the latter advantage, the study can be utilized as a reference to materials with similar properties.

2. Materials and Methods

2.1. Materials

The calcined wood waste ash (CWWA) used in this study as the solid precursor to produce alkali-activated binders (AAB) was provided by Arevale company (Pindamonhangaba, São Paulo, Brazil). The wood wastes were origin from pallets and sawmill wastes based in eucalyptus trees. These wastes were burnt at 800 °C in a vertical shaft kiln to produce renewable electric energy to generate the former wood waste ash. As this ash shows high unburned material, it was recalcined in the laboratory to remove the residual organic matter to generate the calcined wood waste ash, and improve the physical and mechanical properties of AAB due to the lower organic matter content. The alkaline solution was produced with sodium hydroxide (NaOH) as an alkaline activator and filtered water; sodium hydroxide was a commercial brand of caustic soda (Bradoc) with 95% purity. Filtered water was generated from the laboratory of Instituto Tecnológico de Aeronáutica. Fine aggregate was siliceous sand with a specific mass of 2.4 g/cm³ and the fineness modulus was 2.5.

2.2. Methods

The study was divided into four steps: 1. CWWA preparation and characterization; 2. Production and curing of mortars and pastes; 3. Mechanical properties of mortars; and 4. Microstructural studies of pastes.

Step 1 was carried out by taking wood waste ashes dried in a laboratory oven at 100 °C for 24 hours to remove all residual humidity of the sample. Then, the material was calcined in a laboratory furnace (18 kW, 200 L) to remove unburned particles at 600 °C. No heating rate was carried out, as the wood waste ash was added to the furnace at 600 °C. The calcination of wood waste ash was carried out with a feed of 2 kg for 3 hours to generate CWWA. After the calcination process, the calcined wood waste ash was removed from the laboratory furnace and cooled at room temperature. After the CWWA reached room temperature, a wet milling process was performed with distilled water for 4 hours. Then, the milled CWWA was analyzed by chemical composition, XRD, FTIR with particle size distribution, and SEM/EDS. XRF was carried out by an X-ray fluorescence spectrometer S8 Tiger 1 kW and software Quant Express.

The LOI test was performed based on ASTM D7348–13 (2013), in a muffle oven with a heating rate of 20 °C.min⁻¹ until 950 °C for 3 hours for three samples of 1.0 g of CWWA. For XRD analyses, an XRD PANalytical Empyrean equipment was used, following Bragg Angle 5-70°, Cu-K α radiation, step 0.02°, 30 s/step. FTIR analysis was performed by a Frontier IR/UATR with a wavenumber spectrum range of 550-4000 cm⁻¹ and spectral resolution of 1 cm⁻¹. Particle size distribution by laser diffraction analyses was carried out by a Mastersizer 3000. SEM was performed by a VEGA 3 XMU TESCAN coupled with EDS equipment of Oxford EDS 133 eV.

With respect to Step 2, mortars and pastes were produced according to the proportions described in Table 1. The water/binder and fine aggregate/binder mass ratios were maintained as constants of 0.50 and 2.0, respectively. The Na⁺ concentrations assessed were 6.5, 8.0, 9.5, 11.0, and 12.5 mol.kg⁻¹. The production of mortars started with the preparation of the alkaline solution: NaOH was mixed with filtered water until attain proper homogenization. As this mixture releases heat, then the solution was left to cool down to room temperature. The alkaline solution was poured into a bowl of mortar blender, and then CWWA was poured at parts for mixing with the solution. Then, the siliceous sand was added and mixed until homogenized the mortar. Mortars were cast in cubic triple samples of 40x40x40 mm³, wrapped with plastic to avoid contact with CO₂ of environment air and water removal, and left to cure in a thermal bath at 60 °C to accelerate the reaction of the mixtures^{12,13}. Then, the samples were demolded after 24 hours (first day) and left for more 6 days in a thermal bath, totalizing 7 days of curing. Pastes' production followed the same steps as the mortar's production, except for the addition of sand, and the 10 cm³ samples were molded in a plastic bottle (50 mL). Pastes and mortars were named according to CWWA calcination temperature and Na⁺ concentration (600-6.5: CWWA calcined at 600°C and 6.5 mol.kg⁻¹ of Na⁺ concentration).

Regarding Step 3, compressive tests were performed with a universal testing machine with 600 kN and resolution of 0.01 kN, and a load rate of 0.5 kN.s⁻¹. Compressive strength was assessed with mortars after 7 days of curing at 60 °C for mortars produced with Na⁺ concentrations of 6.5, 8.0, 9.5, 11.0, and 12.5 mol.kg⁻¹.

Finally, in Step 4, microstructural analyses of pastes were only assessed for samples of 6.5 and 12.5 mol.kg⁻¹, with XRD, FTIR, and SEM/EDS analyses after 7 days

Table 1. Materials proportions of pastes mortars.

Na ⁺ concentration (mol.kg ⁻¹)	Sand (g) (only for mortars)	CWWA (g)		H ₂ O (g)		NaOH	
		Mortar	Paste	Mortar	Paste	Mortar	Paste
6.5	720	360	10	180	5	46.9	1.3
8.0	720	360	10	180	5	57.7	1.6
9.5	720	360	10	180	5	68.5	1.9
11.0	720	360	10	180	5	79.4	2.2
12.5	720	360	10	180	5	90.2	5

of curing at 60 °C. The preparation of samples for XRD and FTIR analyses was hand milling of pastes, mixing it with acetone for stopping hydration, then it was dried in a laboratory oven at 60 °C for 30 minutes, and then the powder samples were sieved in MESH #200 (opening of 75 μ m) sieve. In the case of SEM/EDS samples, fractured samples of pastes of 1.0x1.0x0.5 cm³ were mixed with acetone for 1 hour, and then it was dried in a laboratory oven at 60 °C for 30 minutes. The tests' parameters were the same as the CWWA characterization.

3. Results and Discussions

3.1. CWWA characterization

The characterization of CWWA starts with the chemical composition of CWWA showed that this material presents a higher proportion of SiO₂ of 67.9 wt%, followed by CaO of 8.1 wt%. There are also other oxides in minor proportions of Al₂O₃ (3.0 wt%), Fe₂O₃ (5.8 wt%), K₂O (4.2 wt%), MgO (0.7 wt%), and other oxides (4.3 wt%). In addition, the Cl content was 1.2 wt%, and the LOI content was

Table 2. Chemical composition of CWWA-600.

4.7 wt% (Table 2). Other studies also showed results of the chemical composition of wood waste ashes with higher proportions of SiO₂ (67.2 wt%) and CaO (9.9 wt%)¹⁴. Particle size distribution showed that CWWA laser deviation of 1.80, 7.14, and 21.3 µm (Dv(10), Dv(50) and Dv(90)). Figure 1 presents the XRD pattern of CWWA. The presence of crystalline phases was quartz (key Q, SiO2, PDF Card 83-2467) and calcite (key C, CaCO3, PDF Card: 72-1650). In addition, a deviation in the baseline can be observed that is attributed to the presence of an amorphous phase. Figure 2 presents the FTIR spectrum of CWWA. The spectrum shows broadbands centered at 796 and 1047 cm-1 (Si-O-Si and Si-O-Al stretching vibration mode). These results are in accordance with values described in Table 2, showing a high content of SiO2. Figure 3 shows the SEM/ EDS images of anhydrous CWWA, there are two types of particle morphologies observed, one with a flat shape which is highlighted in spot A, and another with rough and irregular shape highlighted in spot B, other studies also evidenced results of rough particles on SEM images of wood waste residues ash11. The particle highlighted on spot A is correlated to a crystalline phase (e.g. quartz).





Figure 2. Fourier transform infrared spectroscopy spectra of anhydrous CWWA.



Figure 3. Scanning electron microscopy of anhydrous CWWA.

3.2. Compressive strength of mortars

The compressive strength of mortars with Na⁺ concentrations of 6.5, 8.0, 9.5, 11.0, and 12.5 mol.kg⁻¹ after 7 days of curing at 60 °C is present in Figure 4. Results show that the lower Na⁺ concentration (6.5 mol.kg⁻¹) showed a higher compressive strength of 23.2 ± 1 MPa after 7 days of curing. With respect to the sample with a Na⁺ concentration of 12.5 mol.kg⁻¹, the compressive strength was lower when compared with other concentrations (10.8 ± 1.1 MPa). This behavior shows that the Na⁺ content interferes on the mechanical properties of the mortars. Other studies analyzed the compressive strength of mortars produced with fly ash and wood ash by testing cube-shaped samples cured at elevated temperatures of 75 °C, at ages of 1-, 3- and 7-days curing, wherein results of compressive strength reached

42.3 \pm 5.0 MPa¹⁵; and the maximum strengths reached were 41.42, 42.33, 37.86 and 31.39 MPa at 90 days curing for replacement of 0, 0.5, 1 and 3 wt%, respectively¹¹. Despite other studies showing higher compressive strength, when curing at elevated temperatures mortars were produced with cement and wood ash as part replacement, and curing at lower temperatures, mortars passed for a longer curing time (until 90 days). Also, elevated curing temperatures can form secondary products, reacting in a more porous structure¹⁶.

3.3. Microstructural studies of pastes

Figure 5 presents the XRD pattern of pastes with Na⁺ concentrations of 6.5 and 12.5 mol.kg⁻¹ after 7 days of curing at 60 °C. Both pastes, Na⁺ concentrations of 6.5 and 12.5 mol.kg⁻¹, showed that the crystalline phase of quartz and calcite from the CWWA remained in the pastes after the alkali-activated reaction.

However, a sodium carbonate crystalline phase (key N, Na_2CO_3 , PDF Card: 86-289) was observed in both pastes as a newly formed phase. Carbonation can be identified in some cementitious materials¹⁷. With these conditions, the increase of sodium in the reaction increases the carbonation of sodium. Results show an increase in the intensity peaks of sodium carbonate when increasing the Na⁺ concentration. This is an indication that this material presents carbonation when being in contact with CO₂ of environment air, and the increase of NaOH in the alkaline solution results in a higher content of free Na⁺ in the AAB hydration, which further will result in a higher content of porous sodium carbonate structure, decreasing the compressive strength of mortars.



Figure 4. Compressive strength of mortars.

The spot highlighted shows a better visualization of the amorphous phase of anhydrous CWWA and pastes, whereas the peaks of sodium carbonate in 6.5 mol.kg⁻¹ sample were not presented in CWWA-600, and a visual increase of sodium carbonate peaks in 12.5 mol.kg⁻¹ sample.

Figure 6 presents the FTIR spectra of pastes with Na⁺ concentrations of 6.5 and 12.5 mol.kg⁻¹ after 7 days of curing at 60 °C. On the other hand, both pastes also present broadbands in the range of 1400-1500 cm⁻¹ (O-C-O stretching vibration mode), and the presence of broadband in 865 cm⁻¹ (C-O band vibration mode). These results show more intense bands in the range of silicates and aluminates, also in the ranges showing the presence of carbonates are correlated to the results of XRD patterns. Both pastes (6.5 and 12.5 mol.kg⁻¹) show a shift in broadbands in the range of 700-800 cm⁻¹ (Si-O stretching vibration mode) and in the range of 1000-1100 cm⁻¹ (Si-O-Si and Si-O-Al stretching vibration mode) compared to the CWWA (represented by the centered wavenumber value for each spectrum in Figure 6), which indicates the presence of hydrated products based in silicon and aluminum^{18,19}.

SEM/EDS images are presented in Figure 7 for pastes with Na⁺ concentrations of 6.5 and 12.5 mol.kg⁻¹ after 7 days of curing at 60 °C. The paste with Na⁺ concentration of 6.5 mol.kg⁻¹ (Figure 7) showed the dense morphology of reaction products of plates piled up, and a high Si/Na mass ratio of 2.8. On the other hand,



Figure 5. X-ray diffraction patterns of anhydrous CWWA, and pastes 600-6.5 and 600-12.5. The spot highlighted with crystalline phases of sodium carbonate (N) in pastes.

the paste with a Na⁺ concentration of 12.5 mol.kg⁻¹ showed a high content of porous structure mostly composed of Na, with a Si/Na mass ratio of 0.6, which indicates the presence of a crystalline phase of sodium carbonate (Figure 7b). Increasing Na⁺ concentration will lead to the increasing development of products; however, will also increase the formation of porous structures²⁰. Consequently, this porous structure might interfere negatively with the compressive strength of mortars, as the porous structure can harm the compressive strength of samples. The analyses made with SEM/EDS images are correlated to the results obtained with XRD patterns and FTIR spectra, showing that lower Na⁺ concentrations provide a higher content of hydrated products based in Si and higher Na⁺ concentration will provide a higher content of carbonates based on Na, which might interfere negatively the mechanical properties of mortars. The increase of Na⁺ concentration leads to the increase of reaction and formation of hydrated products, however, also accelerates and increases the formation of porous structures at the same range²⁰.



Figure 6. Fourier transform infrared spectroscopy of anhydrous CWWA, and pastes 600-6.5 and 600-12.5.



Figure 7. Scanning electron microscopy images of pastes of microstructural analyses (a) 6.5 mol.kg⁻¹ samples, (b) 12.5 mol.kg⁻¹ samples.

4. Conclusions

In this study, CWWA could be successfully utilized as a solid precursor in the production of AAB activated with sodium hydroxide in the Na⁺ concentrations of 6.5, 8.0, 9.5, 11.0 and 12.5 mol.kg⁻¹. Regarding the CWWA characterization, the ash was mainly composed of SiO₂ (67.9 wt%) and CaO (8.1 wt%), with a LOI content of 4.7 wt%, the main crystalline phases identified for CWWA were quartz and calcite, and the morphology of the particles is main composed of two types: one flat and another rough and irregular shapes. With respect to the mortars, the sample that achieved the highest compressive strength after 7 days at 60 °C was the one activated with Na⁺ concentrations of 6.5 mol.kg^{-1} , which achieved a strength value of $23.2 \pm 1 \text{ MPa}$. Regarding the paste studies, XRD diffractograms showed a high formation of Na₂CO₃ in the samples activated with Na⁺ concentrations of 12.5 mol.kg⁻¹, FTIR spectra showed that the CWWA reacted and formed hydrated products, and SEM/EDS images showed a formation of a dense reaction product composed of sodium and silicon, and also a formation of carbonated structures mainly for the paste with higher Na⁺ concentrations. Therefore, the promising results from the study can help to provide a proper destination for the use of wood waste ashes in civil construction in a more sustainable AAB.

5. Acknowledgments

Authors thank "Coordenação de Aperfeiçoamento de Pessoal de Nível Superior" (CAPES) for scholarship granted to A.A.S. Silva; "Conselho Nacional de Desenvolvimento Científico e Tecnológico" (CNPq) for research project grant (Process CNPq 425675/2018-1); Arevale company (Pindamonhangaba, São Paulo, Brazil, for providing wood waste ash; "Laboratório de Plasmas e Processos" from Instituto Tecnológico de Aeronáutica, Brazil, for providing analyses on XRD equipment; "Materials and Processes Department" of Mechanical Engineering Division from Instituto Tecnológico de Aeronáutica, Brazil, for the SEM/EDS equipment; "Multiuser Central Facilities" (ICAQF) from UNIFESP for providing the X-ray Fluorescence characterization techniques; "Laboratório de Processamento de Pós" of "Divisão de Materiais" from "Instituto de Aeronáutica e Espaço" for providing the vibratory mil; "Laboratório de Análises Instrumentais" of "Divisão de Propulsão" from "Instituto de Aeronáutica e Espaço" for providing WRA particle size characterization and analyses on Fourier Transformed Infrared Spectroscopy (FTIR).

6. References

- Mehta PK, Monteiro PJM. Concrete: microstructure, properties and materials. 3rd ed. Local: McGraw-Hill; 2006.
- Shi C, Day RL. Selectivity of alkaline activators for the activation of slags. Cem Concr Aggress. 1996;18(1):8-14.

- Pacheco-Torgal F, Labrincha A, Leonelli C, Palomo A, Chindaprasirt P. Handbook of alkali-activated cements, mortars and concretes. 1st ed. United Kingdom: Elsevier; 2015.
- Provis J. Activating solution chemistry for geopolymers. In: Provis J, Van Deventer, JSJ. Geopolymers: structure, processing, properties and industrial applications. Oxford, Cambridge, New Delhi: Woodhead Publishing Limited; 2009.
- Berenguer RA, Capraro APB, De Medeiros MHF, Carneiro AM, De Oliveira RA. Sugar cane bagasse ash as a partial substitute of Portland cement: effect on mechanical properties and emission of carbon dioxide. J Environ Chem Eng. 2020;8(2):103655.
- Hu L, He Z, Zhang S. Sustainable use of rice husk ash in cement-based materials: environmental evaluation and performance improvement. J Clean Prod. 2020;264:121744.
- Azevedo Basto P, Savastano H Jr, Melo AA No. Characterization and pozzolanic properties of sewage sludge ashes (SSA) by electrical conductivity. Cement Concr Compos. 2019;104:103410.
- Batt AS, Anshul G. Partial replacement of wood ash with ordinary Portland cement and foundry sand as fine aggregate. J Civ Environ Eng. 2017;7:1-5.
- SNIC: Sindicato Nacional da Indústria de Cimento. Consumo de Cimento Anual de 2021 [Internet]. Rio de Janeiro: SNIC; 2022 [cited 2023 Jan 15]. Available from: http://snic.org.br/ assets/pdf/numeros/1666965880.pdf
- Carević I, Serdar M, Štirmer N, Ukrainczyk N. Preliminary screening of wood biomass ashes for partial resources replacements in cementitious materials. J Clean Prod. 2019;229:1045-64.
- Castrillón JJ, Harveth G. Mechanical properties of mortars modified with wood waste ash. J Indian Acad Wood Sc. 2020;17(1):90-9.
- Font A, Soriano L, Moraes Pinheiro SM, Tashima MM, Monzó J, Borrachero MV, et al. Design and properties of 100% waste-based ternary alkali-activated mortars: blast furnace slag, olive-stone biomass ash and rice husk ash. J Clean Prod. 2020;243:118568.
- Moraes JCB, Font A, Soriano L, Akasaki JL, Tashima MM, Monzó J, et al. New use of sugar cane straw ash in alkali-activated materials: a silica source for the preparation of the alkaline activator. Constr Build Mater. 2018;171:171.
- Elinwa AU, Mahmood YA. Ash from timber waste as cement replacement material. Cement Concr Compos. 2002;24(2):219-22.
- Cheah CB, Part WK, Ramli M. The hybridizations of coal fly ash and wood ash for the fabrication of low alkalinity geopolymer load bearing block cured at ambient temperature. Constr Build Mater. 2015;88:41-55.
- Istuque DB, Reig L, Moraes JCB, Akasaki JL, Borrachero MV, Soriano L, et al. Behaviour of metakaolin-based geopolymers incorporating sewage sludge ash (SSA). Mater Lett. 2016;180:192-5.
- Šavija B, Luković M. Carbonation of cement paste: understanding, challenges, and opportunities. Constr Build Mater. 2016;117:285-301.
- Moraes JC, Melges JL, Akasaki JL, Tashima MM, Soriano L, Monzo J, et al. Pozzolanic reactivity studies on a biomass-derived waste from sugar cane production: sugar cane straw ash (SCSA). ACS Sustain Chem& Eng. 2016;4(8):4273-9.
- Shearer CR, Provis JL, Bernal SA, Kurtis KE. Alkali-activation potential of biomass-coal co-fired fly ash. Cement Concr Res. 2016;73:62-74.
- Tashima MM, Akasaki JL, Melges JLP, Soriano L, Monzó J, Payá J, et al. Alkali activated materials based on fluid catalytic cracking catalyst residue (FCC): Influence of SiO2/Na2O and H2O/FCC ratio on mechanical strength and microstructure. Fuel. 2013;108:833-9.