

Article

Evaluation of As-Received Green Liquor Dregs and Biomass Ash Residues from a Pulp and Paper Industry as Raw Materials for Geopolymers

Rafael Vidal Eleutério ¹, Lisandro Simão ^{2,*} , Priscila Lemes ³  and Dachamir Hotza ^{4,*} 

¹ Graduate Program in Materials Science and Engineering (PGMAT), Department of Mechanical Engineering (EQA), Federal University of Santa Catarina (UFSC), Florianópolis 88040-900, SC, Brazil; rafael.eleuterio@posgrad.ufsc.br

² Research Group on Sustainability and Waste Management, Postgraduate Program in Environmental Technology, University of Ribeirão Preto (UNAERP), Ribeirão Preto 14096-900, SP, Brazil

³ Undergraduate Program in Materials Engineering (EMT), Latin American Institute of Technology, Infrastructure and Territory (ILATIT), Federal University of Latin American Integration (UNILA), Foz do Iguaçu 85870-650, PR, Brazil; priscila.lemes@unila.edu.br

⁴ Graduate Program in Chemical Engineering (POSENQ), Department of Chemical Engineering (EQA), Federal University of Santa Catarina (UFSC), Florianópolis 88040-900, SC, Brazil

* Correspondence: lsimao@unaerp.br (L.S.); d.hotza@ufsc.br (D.H.)

Abstract: This study aimed to investigate the impact of as-received biomass fly ashes (BFA) and green liquor dregs obtained from a pulp and paper plant in Brazil as substitutes for metakaolin in geopolymeric formulations. The properties of this type of waste material vary widely between different industrial plants. This study refrains from subjecting the waste materials to any form of pretreatment, taking into account their organic matter and particle size heterogeneity, requiring extensive characterization to evaluate their influence on the compressive strength, apparent open porosity, and water absorption of the geopolymeric samples. The objective was to assess their potential for upcycling purposes as an alternative to energy-intensive materials, such as ordinary Portland cement (OPC) and advanced ceramics. This potential arises from the ability of alkali-activated materials (AAM) to undergo curing at ambient temperatures, coupled with the possibility of compositions primarily derived from waste materials. To improve the sustainability of the products, the amorphous content of the raw material, which is more reactive than crystalline phases, was quantified and used as the base for mixture ratios. This approach aimed to reduce the requirement for alkaline activators, which have significant environmental impacts, while also increasing the waste content in the formulation. The incorporation of waste materials into the geopolymer matrix generally led to a reduction in the compressive strength compared to the benchmark metakaolin sample (19.4 MPa) but did not present a trend. The dregs led to values of 4.1 MPa at 25 wt% and 7.1 MPa at 50 wt%, a behavior that is somewhat counterintuitive, and BFA at 10 wt% presented 5.7 MPa. Nevertheless, the apparent open porosity remained at high levels for all the samples, close to 50%, and the compressive strength of most of them was over the values obtained for the metakaolin-only samples with mixture ratios calculated from the total composition instead of the amorphous composition. The decrease in strength and the increase in porosity were attributed to the specific characteristics of the waste materials, such as their high crystallinity, presence of organic matter, heterogeneous particle composition, and size. Overall, this study provides insight into the variations in geopolymerization based on the bulk and amorphous content of the aluminosilicate sources and how the characteristics of the waste materials influence the geopolymer matrix. It also highlights how calculating mixture ratios based on the amorphous composition improves the possibility of waste valorization through alkali activation. Additionally, it suggests that BFA and dregs might be effectively utilized in applications other than OPC substitution, such as adsorption, filtration, and catalysis.

Keywords: alkali-activated materials; biomass fly ash; compressive strength; dregs; geopolymers



Citation: Eleutério, R.V.; Simão, L.; Lemes, P.; Hotza, D. Evaluation of As-Received Green Liquor Dregs and Biomass Ash Residues from a Pulp and Paper Industry as Raw Materials for Geopolymers. *Minerals* **2023**, *13*, 1158. <https://doi.org/10.3390/min13091158>

Academic Editor: Alexander Mikhailovich Kalinkin

Received: 2 August 2023

Revised: 29 August 2023

Accepted: 29 August 2023

Published: 31 August 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The pulp and paper industry is one of the most polluting industrial sectors, in addition to being very water and energy-intensive, as well [1]. Its wastes have been explored in sustainable applications in agriculture, wastewater treatment, construction, and energy processes [2]. They have also been studied as source materials in geopolymers [3–6], widely known as a viable option for ordinary Portland cement (OPC) replacement due to the possibility of being made almost entirely from waste materials [7,8], and more recently as alternative raw materials in products for environmental governance, being applied as adsorbents, catalysts, and filtration membranes [9,10].

Most alternatives to OPC rely on alkali activation to decrease emissions since OPC production represents 26% of the total industrial emissions of CO₂ [11]. Moreover, other environmental issues have been investigated by using wastes and by-products as raw materials [12], such as slags, fly ash, perlite, waste glass, and others [13–15], there is still a heated debate in the academic community about the environmental impact of geopolymers [7,14–17]. Recent studies have shown that besides fly ash and slags, widely employed as raw materials for AAM, waste glass is one of the most viable options to be used as eco-supplementary cementitious material in both OPC and AAM formulations due to its high chemical reactivity, which is mainly derived from the surface properties and amorphous content [13,18,19].

The scope of applications for alkali-activated materials (AAM) extends beyond civil engineering, encompassing their utilization as alternatives or additives to ordinary Portland cement (OPC). Geopolymer membranes tailored for micro-, ultra-, and nanofiltration in water and wastewater treatment and their potential in adsorption and catalysis have been investigated using various waste materials [9,10,20]. The multifaceted nature of AAM has been explored comprehensively. Luukkonen et al. [21] examined 3D printing, direct foaming, and granulation as fabrication techniques for generating geopolymer filters dedicated to water treatment [21]. Meanwhile, Su et al. [22] took advantage of the excellent adsorption properties of a slag-based geopolymer to remove Ni(II) from wastewater, and the self-growing supported nickel catalyst was used for CO₂ methanation [22].

As the result of the reaction of the amorphous content of materials containing Al₂O₃, SiO₂, and CaO with alkaline activators, geopolymers are known as alkali-activated materials (AAM). Davidovits (2017) defines a geopolymer as a mineral macromolecule of well-defined size and molecular weight [23], while, according to Provis (2018), the main difference between AAM and geopolymers is the calcium content, which is lower in geopolymers [24]. Nevertheless, both systems are inside the area of alkali activation [24].

The major source of carbon emissions in the AAM life cycle is the use of alkaline activators, which is a point of agreement among various sources regarding the potential environmental impact of these materials [16,25]. Furthermore, one of the most overlooked aspects of AAM emissions is the pretreatment of waste materials to achieve properties that allow for better product performance. For reasons of production cost and environmental impact, the valorization of waste materials in AAM has a higher potential when the wastes are subjected to the least amount of pre-treatment possible if source materials are available locally, supply chain networks are optimized, and only a small amount of alkali activators are used [25–28].

Two of the main wastes generated by this industry are biomass fly ash and green liquor dregs, which, together with grits, represent most of the 11 million tons of waste generated by pulp and paper production. They present a potential for utilization in geopolymeric mortars [4] and some successfully improved metakaolin-based geopolymer properties [3,4,29]; however, there is a great discrepancy between the materials generated in different plants, and each waste, even though from similar sources, must be evaluated regarding its suitability for valorization in geopolymer formulations. As a result, the

methodology used to upcycle a specific type of waste may not be applicable to waste from apparently similar processes but from different plants [30,31].

The Kraft process, extensively embraced by the industrial sector, entails the utilization of surplus biomass and organic-rich wastes to generate power. Consequently, the biomass fly ash produced in each industry plant exhibits considerable variation due to the distinctive attributes inherent to individual facilities. Maschowski et al. [30] examined bottom and fly ash samples from six German biomass plants and discovered significant differences in the samples' properties. Cherian and Siddiqua [31] reviewed the differences in fly ash from pulp and paper mill industries and also found substantial discrepancies in the composition, particle morphology, and trace metal concentrations. Green liquor dregs from different sources also present considerable property deviation, more specifically in composition, loss on ignition, moisture, and pH [3,32].

Novais et al. [3] investigated similar residues from different pulp and mill plants to gain a better understanding of how these wastes influenced the geopolymer matrix. One of the novel aspects of our study is the presentation of an approach that distinguishes the amorphous fraction of waste materials from their total composition and how the distinction affects the interpretation of the results. We also conducted a thorough investigation of how the waste, as received, influences the physical properties of the products compared to a benchmark metakaolin-based geopolymer. These insights diverge from the prevailing methodologies in the literature and will facilitate geopolymer applications in various areas in the future.

As each industry plant presents very diverse waste properties, this paper aims to evaluate the potential for upcycling as AAM of two types of waste from a Brazilian pulp and paper industry plant: biomass fly ash and green liquor dregs. Unlike other works, our primary goal was to assess the impact of the waste as received (without any treatment) on the properties of the products.

2. Materials and Methods

2.1. Materials

Green liquor dregs and biomass fly ash (Figure 1) were provided by a Brazilian paper pulp plant. Green liquor dregs are generated in the recovery of white liquor in paper pulp plants. In contrast, biomass ash is generated from burning surplus biomass and organic-rich wastes generated in running power generation units. The authors discussed the process of generating these wastes in previous works [2]. The waste was used as received (Figure 1) to reduce the cost of geopolymer production and improve the chances of upcycling. The role of waste materials in formulations was to replace metakaolin by evaluating the reactive fractions (amorphous content) of each waste.

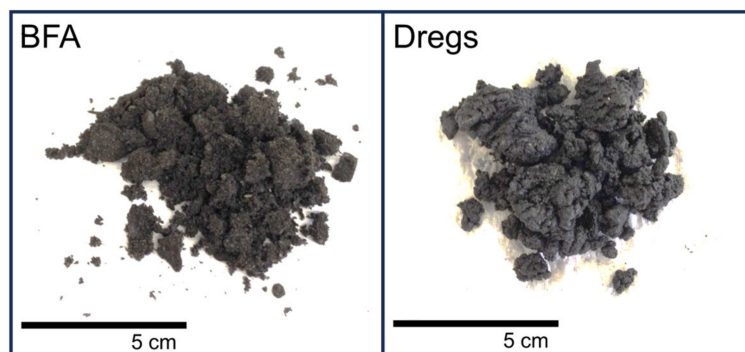


Figure 1. Waste materials as received.

Metakaolin (HP Ultra®, Jundiaí-SP, Metacaulim do Brasil) was used as the main aluminosilicate source and benchmark. Sodium silicate ($\text{H}_2\text{O} = 63 \text{ wt\%}$, $\text{SiO}_2/\text{Na}_2\text{O} = 3.38$, Lafan Química Fina, Várzea Paulista-SP, Brazil) and 8.4 M sodium hydroxide solution,

prepared from the dissolution of NaOH micro pellets (98%, Neon) in water, were employed for the alkaline activation.

2.2. Samples Processing

The geopolymer slurries were produced as shown in Figure 2 and described as follows: (i) sodium silicate was introduced to the 8.4 M sodium hydroxide solution and stirred using a magnetic stirrer for 30 min. (ii) The alkaline solution was slowly added to the solids cup while the mixture was mechanically stirred using a U-shaped helix at 400 RPM. (iii) The resulting slurry was mixed for 10 min at the same stirring speed and cast into polyvinyl chloride (PVC) cylinders with an internal diameter of 2.1 cm and a height of 5 cm. (iv) Mechanical vibration was applied to the cylinders for 30 s to eliminate any trapped air and improve particle packing. (v) The molded slurries were covered with a plastic film and cured at 50 °C for 24 h before being demolded and left in ambient conditions for an additional 27 days to complete the curing process.

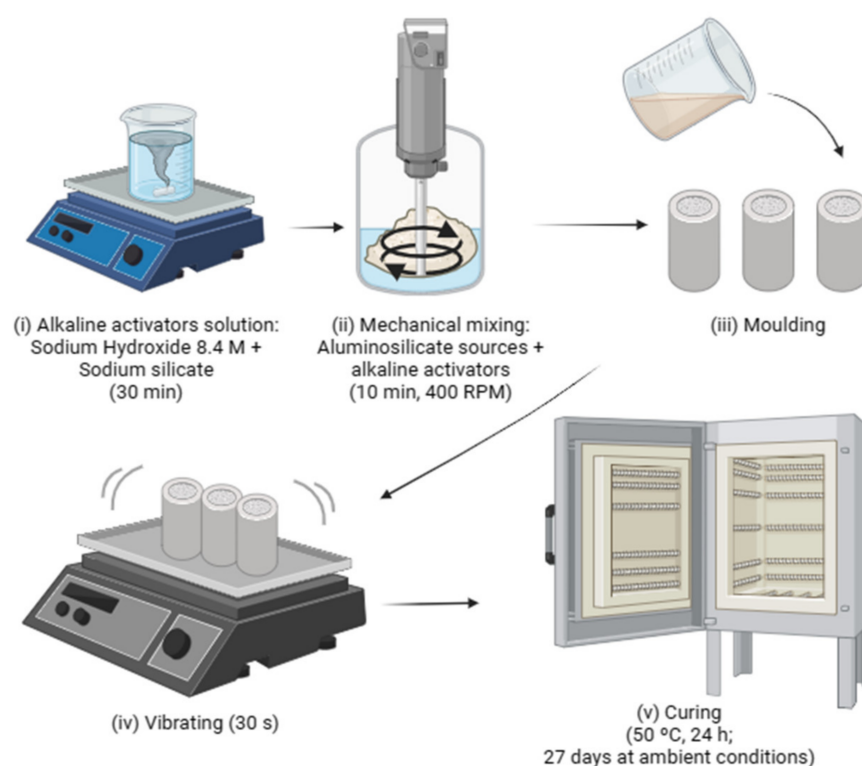


Figure 2. Samples' preparation process.

2.3. Characterization

The mineralogical composition of the raw materials was identified using X-ray powder diffraction (XRD) with a Shimadzu XRD-6000 (Shimadzu Corporation, Tokyo, Japan). Phase identification and quantification were performed using the Rietveld method, with calcium fluoride (CaF_2) mixed in as an internal reference at a concentration of 10 wt% for 7 min in a closed cylinder. The amorphous fraction of the samples was determined using the CaF_2 reference. Phase quantification was accomplished with the software GSAS-EXPGUI software package [33] and EXPGUI, and the crystallographic information was extracted from the ICSD database.

The thermal properties of the raw materials were obtained with thermal gravimetric analysis (TGA; Netzsch STA 449 F3 Jupiter, NETZSCH-Gerätebau GmbH, Selb, Germany). The materials were previously dried at 100 °C for 24 h. The analysis was performed from ambient temperature to 1000 °C. The loss on ignition was also assessed by heating the samples to 1000 °C in a generic laboratory muffle furnace. The chemical compositions of

Metakaolin (MK) Biomass Fly Ash (BFA), and the dregs were obtained by X-ray fluorescence (XRF) with a Shimadzu AXIOS Max.

The particle size distribution was determined using laser diffraction (DLS; Malvern Mastersizer 3000, Malvern Instruments Co., Ltd., Malvern, UK) in water and Darvan® (R.T. Vanderbilt Company, Inc., Norwalk, CT, USA) as a deflocculant. The microstructure of the raw materials and products was analyzed with scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) with a tabletop Hitachi TM3030 (Japan Hitachi TM3030, Chiyoda, Tokyo, Japan).

The compressive strength tests of the products were conducted on an Instron Universal Testing Machine (Series 5569, Instron, Norwood, MA, USA) with a loading rate of 0.4 MPa/s. The apparent porosity, water absorption, and bulk density values were obtained via the standard method ASTM C20, which is based on the Archimedes principle.

2.4. Experimental Plan

The evaluation of the differences between the compositions was based on parameters such as compressive strength, apparent porosity, and water absorption of the samples. The study was divided into two molar ratio calculation methods, namely, the bulk composition method (which can be also read as “total composition”) and the amorphous composition method. With the bulk composition method, the molar ratios were calculated from the XRF characterization, while in the amorphous composition method, the phase quantification values from the Rietveld refinement were used. The formulations were designed to achieve the same molar ratios: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.73$; $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.96$; and $\text{Na}_2\text{O}/\text{SiO}_2 = 0.26$. Appropriate amounts of each material were employed to reach the ratios according to the chosen method. The molar ratios were defined to meet the values determined by Davidovits [34] as the best-suited for geopolymers of properties close to OPC.

The replacement of metakaolin by BFA was tested at 10 wt%, and the dregs were tested at 10 wt%, 25 wt%, and 50 wt%. Higher fly ash incorporation values were not considered due to practical issues related to the slurries’ rheology and handling in the molding process. Additionally, a sample consisting of 75 wt% BFA and 25 wt% dregs, synthesized exclusively from the residues, was investigated. The naming convention for the samples considers the method used for molar calculations (amorphous or bulk composition), the type of waste incorporated (dregs or BFA), and the waste weight percentage in the mix. Specifically, AM represents amorphous composition, D represents dregs, B represents BFA, and the numerical value denotes the weight percentage; therefore, sample AMB10 stands for an amorphous composition with 10 wt% of BFA, while AMB75D25 stands for amorphous composition, 75 wt% of BFA and 25 wt% of dregs.

This new design considering the amount of amorphous fraction in the precursor material was used because the many works presented in the literature have only considered the XRF results to calculate the molar ratios. Using the reactive fraction of precursor materials is essential for producing new geopolymers and alkali-activated materials.

3. Results and Discussion

3.1. Chemical and Mineralogical Composition of Materials

The XRF provides a bulk composition of the raw materials as oxides, as seen in Table 1. The molar ratios between $\text{SiO}_2/\text{Al}_2\text{O}_3$ and the alkaline cations are usually based on the XRF results. If not all of the composition is reactive, these values lead to incorrect ratios [35].

For instance, the three solid raw materials contain crystalline phases, as shown in Figure 3, and are presumably much less reactive than the amorphous content, even though they might present reactivity to some minor extent, as in the kaolinite phases present in some not fully calcined metakaolin [36].

Table 1. XRF elemental composition expressed as oxides for metakaolin, BFA, and dregs. Last line: the molar ratio between SiO₂ and Al₂O₃. LOI: loss on ignition. Elements not detected are expressed as “-”.

Oxides (wt%)	Metakaolin	BFA	Dregs
SiO ₂	57.1	45.1	1.7
Al ₂ O ₃	32.6	12.1	0.7
Na ₂ O	<0.1	0.2	6.9
K ₂ O	2.1	2.3	0.4
CaO	<0.1	1.6	41.7
MgO	0.6	1.0	2.5
Fe ₂ O ₃	2.3	3.5	0.5
TiO ₂	1.5	0.8	0.1
MnO	-	0.2	0.9
P ₂ O ₅	-	1.2	0.4
SO ₃	<0.1	-	2.9
LOI	3.0	31.7	40.0
SiO ₂ /Al ₂ O ₃ (mol) (mol)	2.98	6.34	4.13

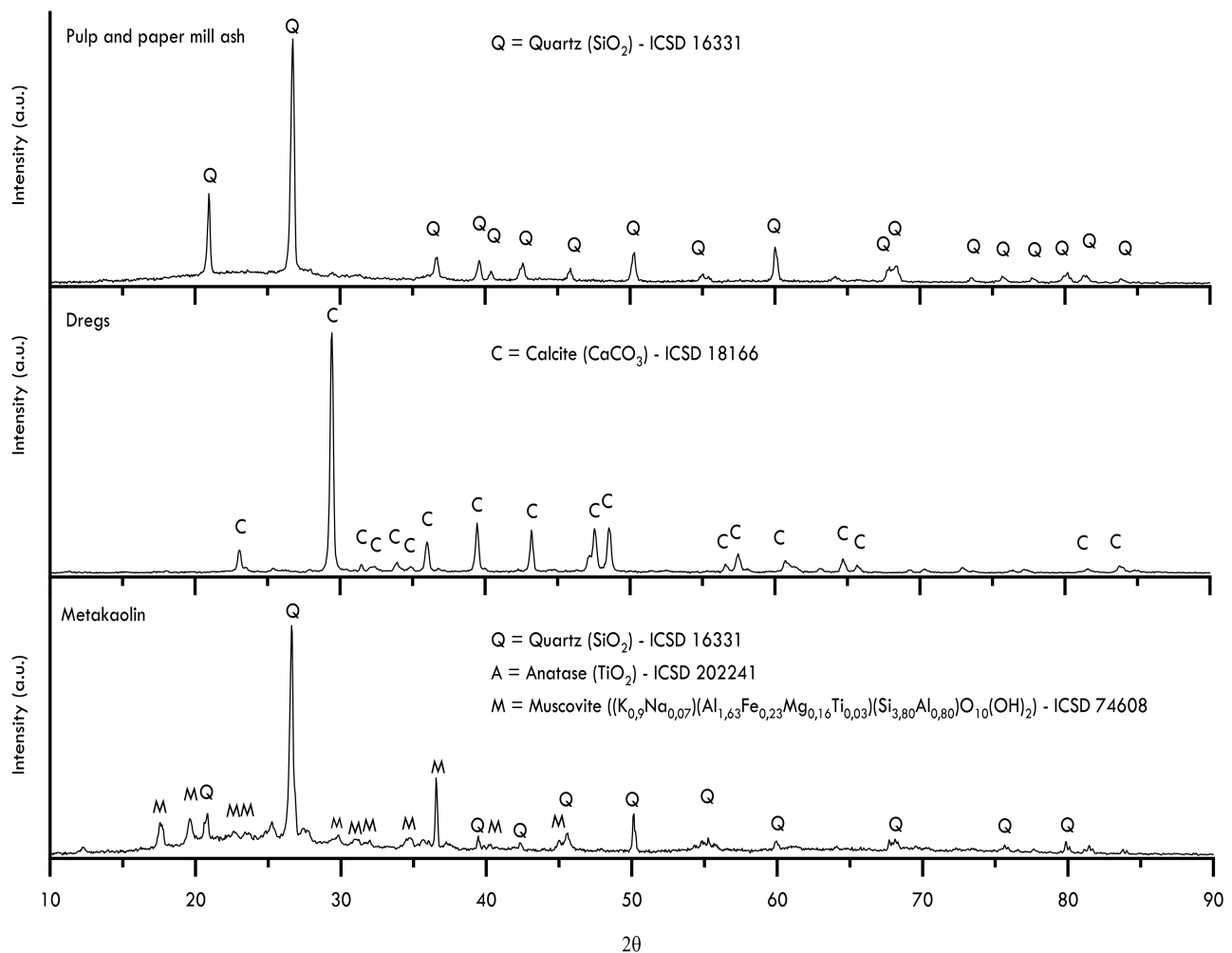


Figure 3. Crystalline profile of bottom ash, dregs, and metakaolin, and identified phases according to ICSD catalog numbers.

The presence of crystalline phases in the initial materials suggests that a portion of the produced geopolymer will retain its crystalline structure. The amount of each phase and the amorphous content were quantified using the Rietveld quantitative phase analysis, as outlined in Table 2.

Table 2. Phase quantification results from Rietveld analysis for solid raw materials.

Phase (wt%)	Metakaolin	BFA	Dregs
Muscovite	39.0	0	0
Quartz	9.0	28.0	0
Calcite	-	-	64.0
Amorphous	52.0	72.0	36.0

Combining the data from XRF and XRD, it is possible to calculate the approximate composition of the amorphous content in each material (Table 3).

Table 3. SiO₂ and Al₂O₃ amorphous wt% in metakaolin and BFA.

Amorphous wt%	Metakaolin	BFA
SiO ₂	29.0	17.0
Al ₂ O ₃	20.0	12.0
SiO ₂ /Al ₂ O ₃ (mol)	2.49	2.41

Due to their low intensity, some peaks in the XRD profiles could not be identified. Additionally, the minor percentage of elements found in the XRF results (such as Fe, K, and Ti) are not of particular interest; therefore, there is some incongruence between the sum of the amorphous content composition and the total composition that fits the proportional quantities of these elements in the XRF analysis. In spite of this, the sum of these errors and inconsistencies represents a low weight percentage in the composition of the components and falls within the margin of error for the quantification methods utilized. For instance, Williams and Van Rissen [37] reported deviations ranging from 2 to 12 weight percent in their Rietveld quantitative analysis of four different fly ashes. It is worth noting that uncertainties are also propagated through calculations as a result of the representation of elements as oxides in the XRF tables [37].

The dregs are mainly composed of crystalline calcite, and amorphous Ca (calculated as CaO) is present at a weight percentage of 6%. This amount is comparable to the supposedly amorphous content of Na₂O (6.9 wt%), indicating that the dregs are likely to interfere with the alkaline composition of the geopolymer. The phase quantification analysis further suggests that the BFA is much more reactive than the benchmark MK; however, it is important to note that fly ash reactivity is also influenced by factors such as particle morphology and size, combustion conditions, combusting material, and transport treatment [37]. The determining factors for BFA include the wood species combusted, the nature of the combustion process, and the conditions at the application site. These assumptions are investigated in the following sections.

3.2. Thermal Characterization

The loss on ignition (LOI) value for the dregs, as presented in Table 1, agrees with the value expected for a material mainly composed of calcite and is expressed as CaO in the XRF analysis. It is also in good agreement with the TGA profile for this material (Figure 4). During the analysis, a consistent mass loss was observed until exceeding 100 °C. Subsequently, a slight increase in the weight loss rate was detected after reaching 600 °C, which corresponds to the decomposition of CaCO₃ into CaO and CO₂, as predicted by Equation (1), which occurs after 700 °C.



As identified by Ribeiro dos Santos et al. [32], calcite and the dreg's thermal behavior are similar. At 600 °C, both materials begin to decompose gradually, and this leads to the release of CO₂(g), as evidenced by the 28% total weight loss depicted in Figure 3. Balancing Equation (1) to find the remaining crystallized CaO weight percentage, a value of 35.7 wt%

is calculated. Adding 6 wt% of amorphous CaO content, the total CaO content equals the value from the XRF analysis: 41.7 wt%.

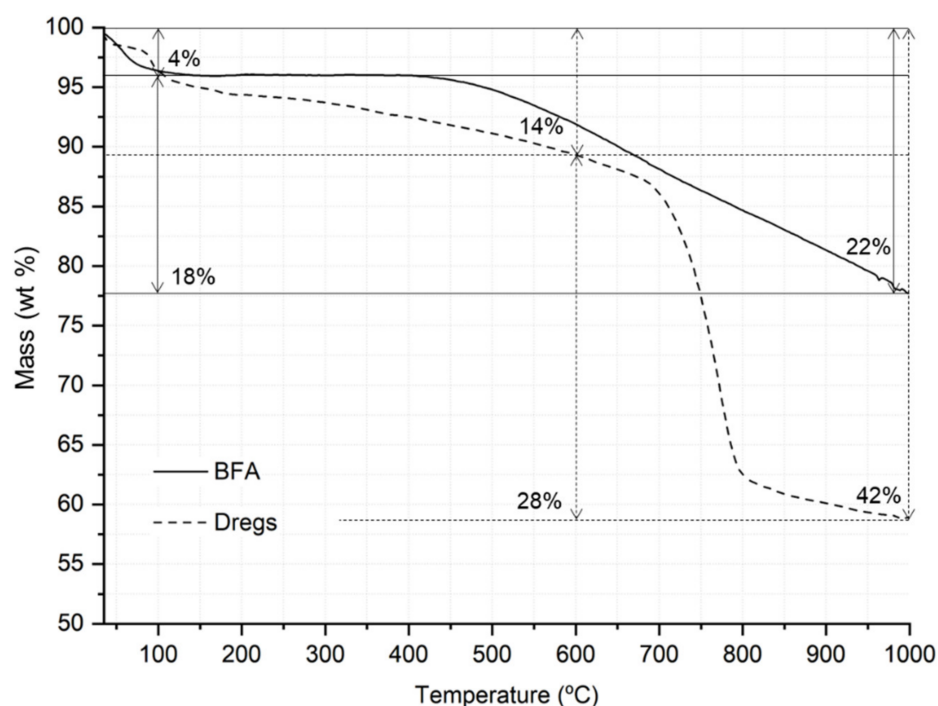


Figure 4. TGA of BFA and dregs residues after drying at 100 °C.

In contrast, the LOI value for BFA significantly exceeded those observed in most fly ashes utilized in geopolymer synthesis [38], although it is not uncommon for mill and pulp fly ash [6] and biomass ash from the paper pulp industry [3]. There is a great discrepancy between the LOI obtained via XRF analysis and TGA for BFA. This difference can be attributed to varying levels of humidity in the samples. Even though the samples were dried at 100 °C before the TGA analysis, the absence of humidity control and a delay between the drying and analysis resulted in a ~4 wt% loss observed in both the dregs and BFA curves up to 100 °C, as depicted in Figure 4. The weight loss detected for BFA at higher temperatures may be due to the presence of unburned or partially burned wood charcoal, inorganic carbonate species, and free organic carbon, as well as volatile compounds, such as sulfur, sodium, and potassium [30,31,39]. It should be noted that the investigated BFA presents low CaO wt%, which is a major source of LOI in most biomass fly ashes.

3.3. Morphological Characterization: Particle Size, SEM, and EDS

The cumulative volumetric particle size of the solid raw materials and the percentile values are presented in Figure 5. It indicates a broader particle size distribution for BFA. It also indicates median particle size of d_{50} over 100 μm and of d_{90} over 700 μm .

The SEM images in Figure 6 reveal the presence of larger particles, as well as smaller particles and porous spheres, which have been documented in prior studies on biomass fly ashes originating from pulp and paper industries [3,30]. The structure shown in Figure 6a–c has some parts that resemble fibers, suggesting that it could be the remains of unburned wood. Figure 7 displays the results of the EDS elemental mapping analysis conducted on various regions of the BFA under investigation. The presence of carbon in regions with fibrous aspects, as well as the appearance of silicon and aluminum in the smaller particles suggests that incomplete combustion of the wood may have occurred. The BFA's irregular morphology and composition are directly related to the rheological properties observed during the molding stage of the processing steps and mentioned in Section 2.4.

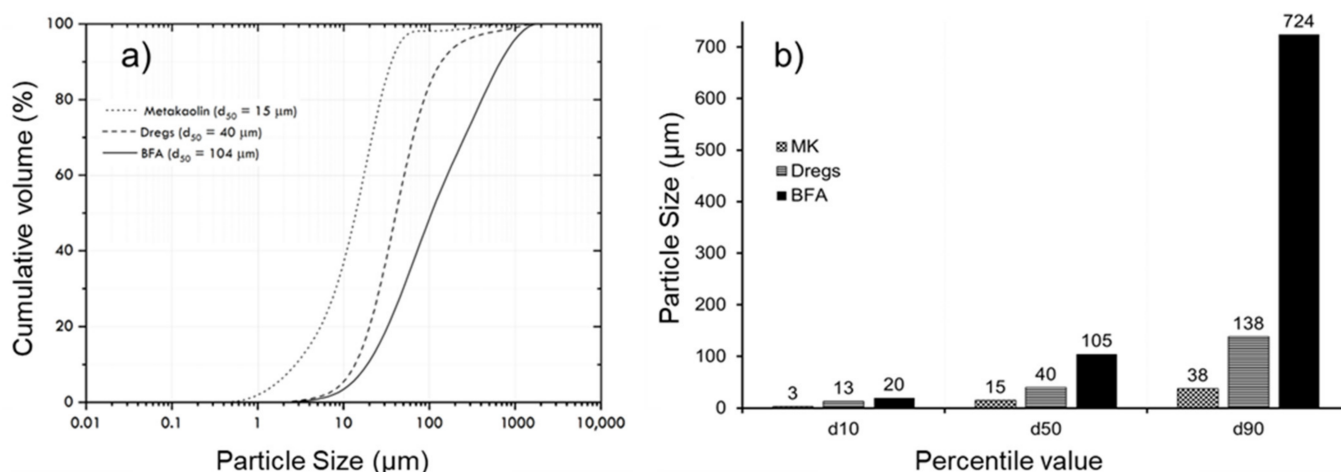


Figure 5. Particle size distribution of metakaolin, dregs, and BFA: (a) cumulative volumetric particle size distribution and median values (d₅₀) in µm; (b) particle size (d₁₀, d₅₀, and d₉₀) vs. percentile value.

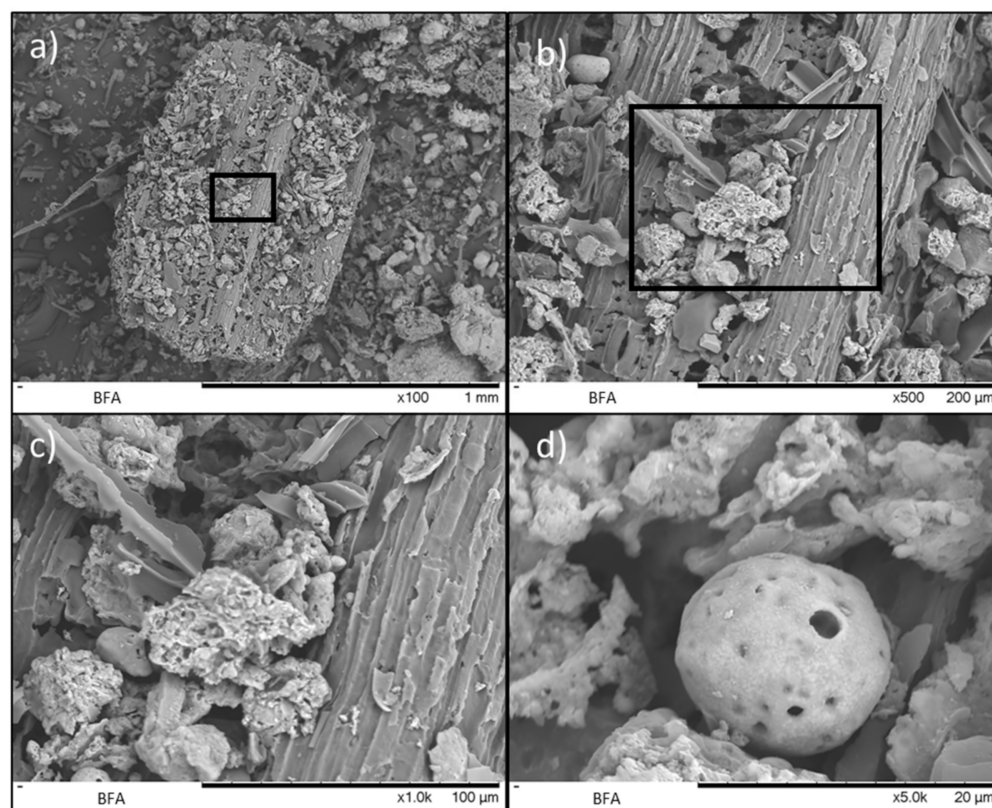


Figure 6. SEM micrographs of BFA: (a) a millimetric particle found in the fly ash; (b) magnified region in (a); (c) magnified region in (b); (d) spherical porous particle in the biomass fly ash.

The cumulative volume curve for the dregs demonstrates a sharp slope and minimal deviation between the d values, indicating a narrower particle size distribution (Figure 5). The high humidity levels in the as-received dregs material resulted in a sludgy consistency, obscuring the shape and size of the particles; therefore, evaluating the particle morphology of dregs requires drying of the material. The dried dregs are shown in Figure 7 with the EDS spectrum of the as-received material, confirming a more homogeneous particle size and presenting a regular morphology. The expected presence of alkaline metals, such as Na, K, and Ca, is observed in the spectrum.

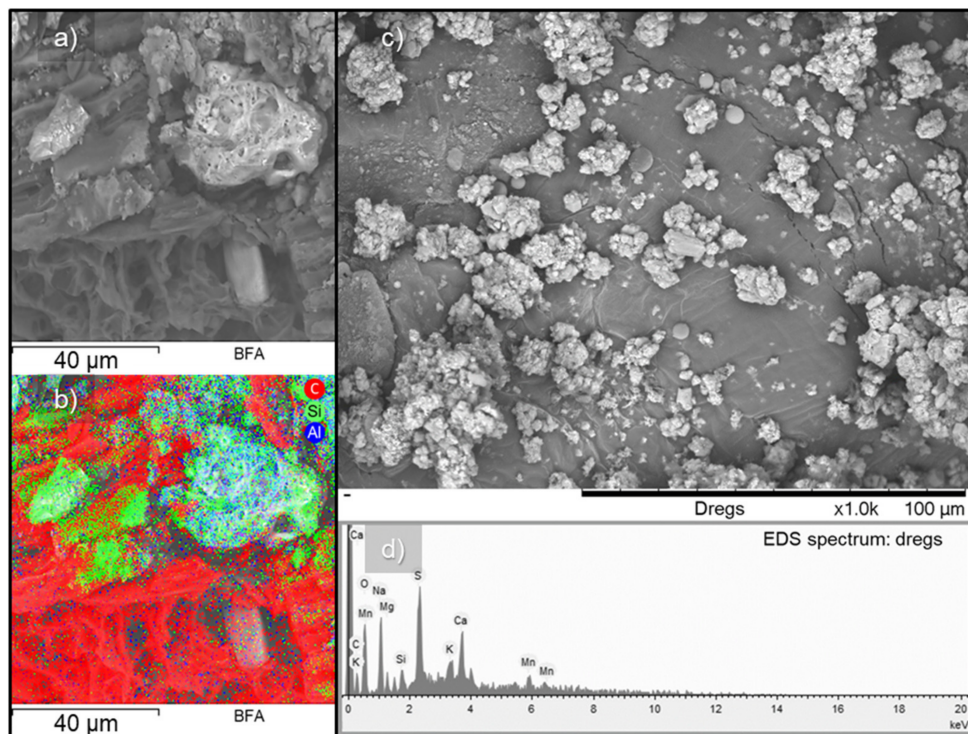


Figure 7. (a) SEM of BFA over fibrous structure and small “white” particles. (b) EDS elemental mapping of the picture above. (c) SEM micrograph of dried dregs. (d) EDS spectrum of the as-received material.

3.4. Compressive Strength: Amorphous vs. Bulk Composition

The comparison between the bulk composition and the supposedly reactive amorphous composition in the metakaolin was performed to assess the viability of only considering the amorphous content from the benchmark material and wastes.

Figure 8 shows the mechanical behavior of the two benchmark formulations with 3 and 28 days of curing. Both samples presented wide deviations from the average values of compressive strength. The amorphous composition resulted in overall higher compressive strength values when compared to the bulk composition; however, in opposition to its counterpart, it loses its average strength, and its standard deviation values increase drastically over time.

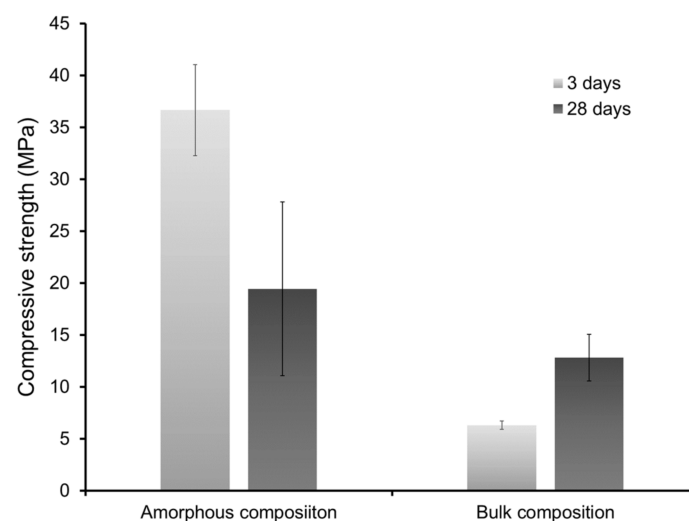


Figure 8. Bulk and amorphous composition formulations after 3 and 28 days of curing at ambient conditions.

In the SEM images of the 28-day samples, in Figure 9, micro-fissures and unreacted metakaolin particles are visible. The geopolymeric matrix of the sample made accordingly to the amorphous composition exhibits greater homogeneity.

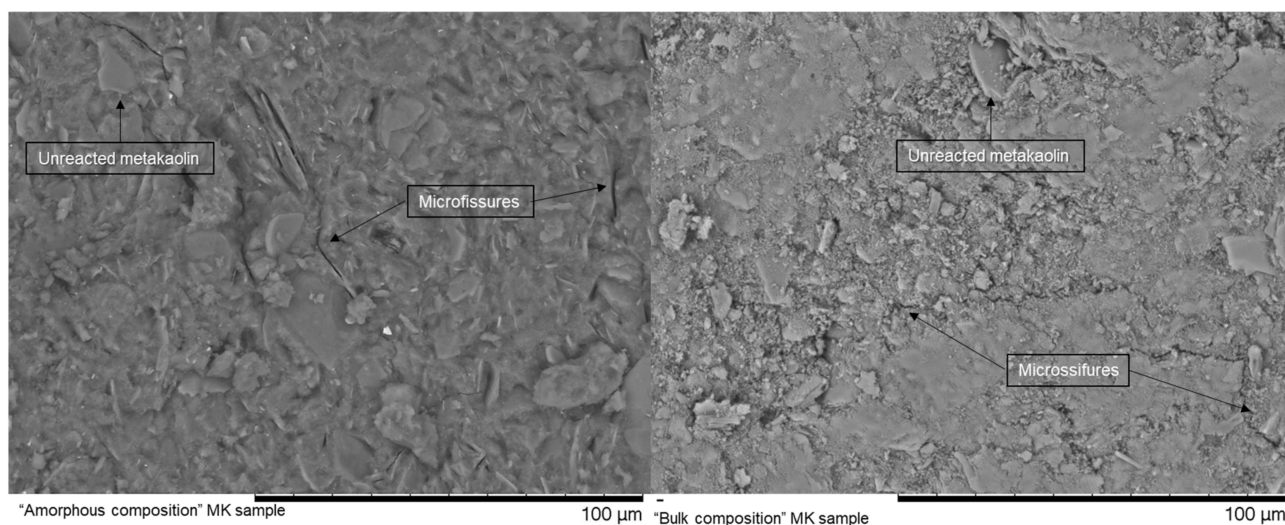


Figure 9. Geopolymeric matrix of samples based on amorphous and bulk compositions.

The visual inspection, however, contradicts the values of the apparent porosity, water absorption, and density found for both samples, as presented in Table 4.

Table 4. Apparent porosity, water absorption, and bulk density of the sample synthesized according to the amorphous and bulk composition after 28 days of curing. (Values) = standard deviation from triplicates.

Property	Amorphous Composition	Bulk
Apparent porosity (%)	66.1 (1.0)	43.8 (0.5)
Water absorption (%)	60.8 (1.3)	32.2 (0.6)
Bulk density (g/cm ³)	1.09 (0.01)	1.36 (0.04)

It is crucial to mention that both the presented samples exhibited efflorescence—an adverse chemical reaction between excess alkalis and atmospheric carbon dioxide—which is known to have a detrimental impact on the durability of the geopolymer [40]. Although the samples with amorphous content did not display the characteristic white crystals on their surfaces, areas of white stains were observed. This could also be attributed to carbonation effects [41], but differentiating between efflorescence and carbonation is beyond the scope of this paper.

The samples based on the amorphous content develop high compressive strengths at an early age, presumably due to the rapid development of a dense geopolymer matrix, which is directly linked to accentuated shrinkage and subsequent micro-cracking [42]. The access to the bulk of the samples provided by the cracks, as a function of the apparent porosity and water absorption values from Table 4, facilitates the occurrence of efflorescence or carbonation, with the movement of free alkalis in the form of carbonates to the surface further decreasing the compressive strength and increasing the dispersion of the values [40]. Similar behavior was not evidenced with the samples based on bulk composition since high alkali concentrations require more energy to initiate and promote the reaction [43].

3.5. Waste Incorporation

The dregs and BFA were incorporated into the geopolymer mix according to their amorphous compositions. The benchmark metakaolin composition was also calculated

according to its amorphous content. Samples were also made using only residues, with 75 wt% of BFA and 25 wt% of dregs.

The rheology of the slurry with BFA was too difficult to handle during the molding stage, with incorporations of over 10 wt% into the metakaolin-based mix. The struggle with workability was the irregular behavior of the slurry, which behaved like a shear-thickening suspension during the molding step. BFA has a very wide range of particle sizes and a high content of organic matter, mostly the remains of unburned wood (Section 3.3), and the problems related to the rheology of these slurries were attributed to this characteristic of the material; however, the same problems were not observed with the samples made only with wastes in the proportions cited in the previous paragraph. The reasons for such behavior were not investigated, but seem to be related to the interaction of the ash with metakaolin.

Incorporating waste into geopolymer formulations based on metakaolin results in reduced compressive strength and apparent porosity values when compared to a geopolymer composed solely of metakaolin, which serves as the benchmark composition; however, it is possible to mitigate this decline by capitalizing on the amorphous composition of the raw materials. It becomes feasible to introduce waste materials into the geopolymeric matrix while achieving comparable, or even higher, apparent porosities than the ones obtained from metakaolin-only geopolymers with mixture ratios based on the total composition (Figure 10).

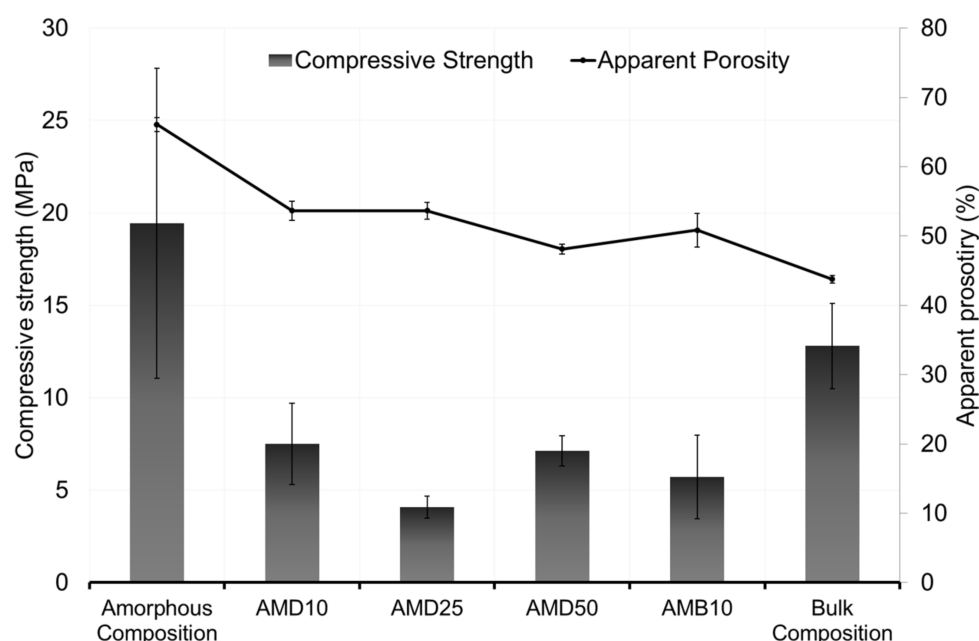


Figure 10. Compressive strength and apparent porosity at 28 days of curing.

The findings related to the inclusion of dregs in our research appear to contradict the results presented by Novais et al. [3], who found an increase in the compressive strength of geopolymeric mortars with the addition of dregs up to 25 wt% due to its effect as filler. It should be noted, however, that our samples are not mortars. Their team considered the dregs to be essentially inert, with an additive of sand for the mortars, a different approach from ours. The methodology and the raw materials were essentially diverse; therefore, the comparison is not recommended.

The incorporation of dregs at 50 wt% presented values higher than at 25 wt%. This could be related to the higher packing of the matrix, with reduced porosity compared to its counterparts. This was also noticed in the SEM micrographs (Figure 11). In AMD25, there is a clear degradation of the geopolymeric matrix, with a highly heterogeneous topology composed of efflorescence, unreacted metakaolin, and dregs particles.

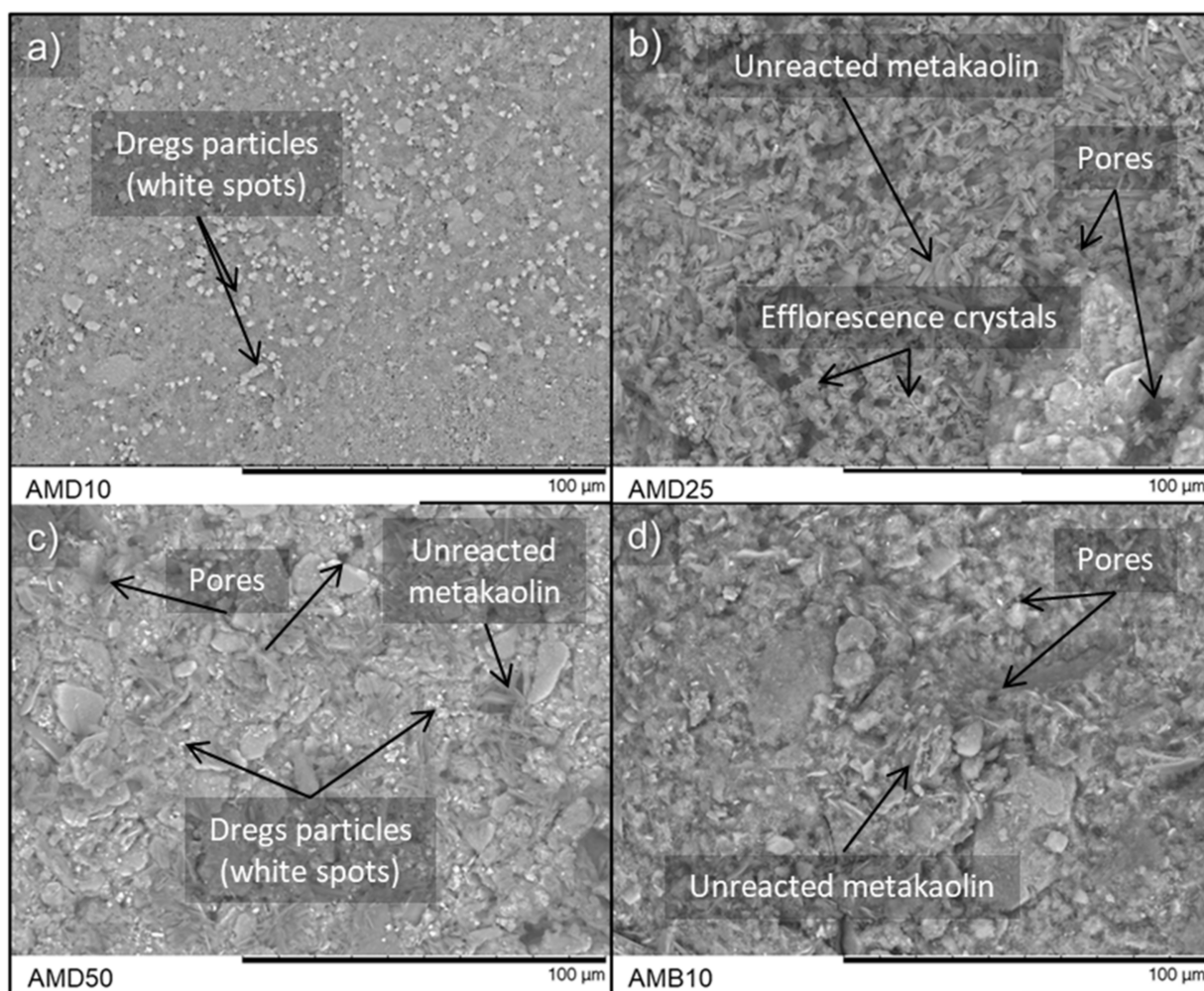


Figure 11. SEM micrographs of samples: (a) AMD10; (b) AMD25; (c) AMD50; and (d) AMB10.

In AMD50 and AMD10, the dregs are packed in the surface, making them more homogeneous, as is also evidenced by the distribution of calcium in the SEM/EDS map shown in Figure 12.

It was also noticeable upon a simple visual inspection of the samples that AMD10 and AMD50 presented little or no efflorescence crystals on their lateral surface, while the crystals were present randomly over the whole body of the AMD25 samples, suggesting a lower degree of geopolymerization in this sample, with more free alkali cations to react with the air humidity [40,41,44], thus generating more efflorescence crystals.

For AMB10, the incorporation of BFA made the matrix more heterogeneous, and the development of mechanical resistance was also delayed by it, as it was with dregs. The results were already expected due to the wide range of particle sizes, organic matter, and other impurities that are deleterious to the geopolymeric reaction and the general particle packing, but efflorescence crystals were not evident on the surface of the sample. The large unreacted particles and the high levels of organic matter in the waste material might influence the path of humidity and carbon dioxide. The development of efflorescence does not seem to be directly related to the compressive strength in these samples and more extensive investigation should be performed to reach a conclusion.

In general, the residues were responsible for smaller porosity values and compressive strength when added to the geopolymer mix, considering the amorphous contents of the raw materials. These effects are mostly related to the filling effects of the dregs and to the particle size distribution and organic impurities in BFA composition.

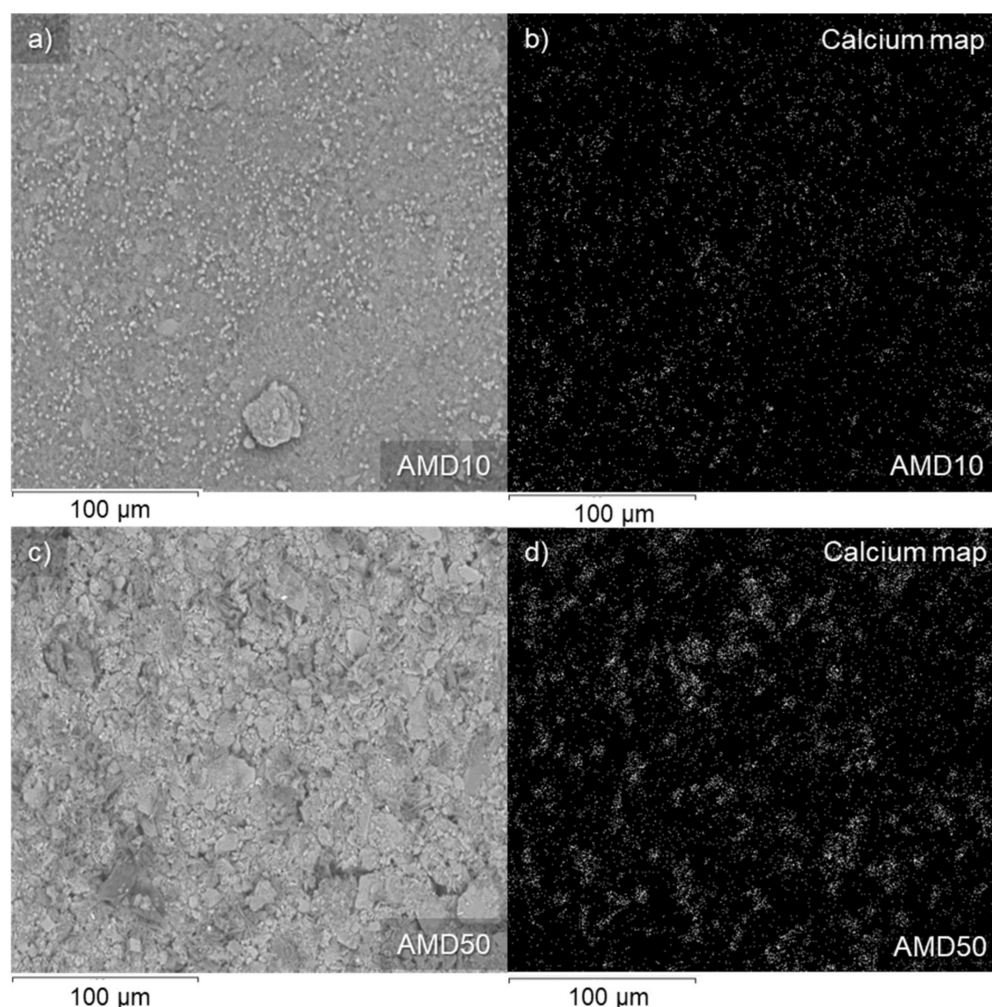


Figure 12. SEM of (a) AMD10 and (b) EDS mapping for calcium in AMD10. (c) SEM of AMD50 and (d) EDS mapping for calcium in AMD50.

In contrast to the findings by Novais et al. [3], who explored the integration of dregs into a metakaolin-based geopolymer through an approach centered on the comprehensive composition of the raw materials, the current study's samples exhibited an opposite trend in compressive strength compared to their observations. Novais et al. reported an enhancement in the compressive strength and a decrease in the porosity upon the incorporation of dregs relative to the reference sample (100 wt% metakaolin); however, when considering the amorphous constituents of the raw materials, our results indicate a general decline in the material properties. Notably, specimens based on the amorphous composition manifested a diminishing compressive strength over time, as depicted in Figure 8. This implies that the temporal evolution of curing plays a pivotal role in the efficacy of incorporating waste materials into the formulation. Additionally, it is important to acknowledge that Novais et al. [3] employed sand in their reference samples.

Despite the lower compressive strength observed in the dregs-containing samples, approximately half of that achieved by Novais et al. [3], the apparent porosity and water absorption of materials relying on amorphous composition are significantly higher. This observation suggests the potential utility of these materials in adsorption-related applications.

Based on these findings, the samples comprising solely wastes, designated as AMB75D25, presented favorable properties for applications in adsorption and catalysis [10,20,45], as presented in Table 5.

Table 5. Properties of sample AMB75D25.

Sample	Compressive Strength (28 Days, MPa)	Apparent Porosity (%)
AMB75D25	1.1 (0.4)	57.4 (0.4)
Sample	Water Absorption (%)	Bulk Density (g/cm ³)
AMB75D25	81.0 (1.6)	0.71 (0.01)

The AMB75D25 samples have extremely low density and high water absorption. They floated in the water for a while due to these properties; therefore, the results for the apparent porosity must be regarded with some skepticism since the ASTM C20 method is based on the Archimedes principle. Their compressive strength is enough so that they can be easily handled. Extensive characterization of this material should be carried out to evaluate if these AAM are indeed geopolymers and to assess their potential in applications that could enable the exploitation of the waste materials [10,20], such as in adsorption and catalysis [10].

4. Conclusions

This study aimed to evaluate the suitability of waste materials from the pulp and paper industry, namely, dregs and biomass fly ash, in substitution for metakaolin as the alkaline and aluminosilicate sources, respectively.

1. An approach based on the supposedly more reactive content of the materials was used to improve the results. Metakaolin was used as a benchmark initial material and the approach has improved its mechanical properties, even though it promoted too rapid a reaction and high shrinkage rates, with consequent high compressive strength development at an early age, but a decrease in the values after the total time of curing of 28 days due to the cracking of the matrix.
2. Dregs are essentially inert, and biomass fly ash has a wide range of particle size distribution and high levels of impurities. These characteristics lead to the degradation of the geopolymeric gel and retard the reaction rate due to the filling effect of the residues' particles, the mismatch derived from the range of their size distribution, and the presence of impurities such as organic matter possibly made of lignin and unburned wood.
3. Overall, the wastes harmed the compressive strength of the geopolymeric pastes based on metakaolin with higher or lower levels of efflorescence development that does not seem to be directly related to the mechanical behavior; however, by calculating the mixture ratios with the amorphous composition of the raw materials, it was possible to incorporate the waste materials into the geopolymeric matrix while obtaining properties equal to or superior to the ones obtained with mixture ratios calculated from the total composition.
4. The incorporation of dregs and BFA led to a reduction of the compressive strength, from 19.4 MPa in the benchmark metakaolin sample to 7.1 Mpa for 50 wt% of dregs (AMD50) and 5.1 Mpa for 10 wt% of BFA (AMB10). The apparent porosity of all the samples remained close to 50%, while the water absorption was close to 40%.

Based on the results, it is not recommended to use the studied wastes in alkaline-activated materials for applications that demand high compressive strength. The properties suggest that the potential for incorporation of these specific waste materials into metakaolin-based AAM is improved in areas regarding adsorption, filtration, and catalysis when the amorphous composition is employed in the mixture ratio calculations.

5. Recommendations for Future Work

As the results of our work highlight, there can be limited potential for valorization for biomass fly ash and green liquor dregs in alkali-activated materials as an alternative to ordinary Portland cement since the wastes generally degrade the compressive strength of the products. We therefore recommend that the substitution of OPC should not be the

aim of future works with such wastes, and there is more than enough literature to support our claim [10,20]; however, because relatively high values of apparent porosity and water absorption were verified for most of the samples, particularly AMB75D25, our findings suggest potential applications in adsorption, filtration, and catalysis. Based on our results and the literature, we recommend that future works avoid the goal of OPC substitution and focus on alternatives to add value to these residues [31,33].

The methodology used in this work considers the amorphous fractions of the materials, and it is essential for the future of geopolymerization, both for pastes and mortars, as well as in concrete. The study of concrete with other types of waste, considering the amorphous fractions of the precursors, is a good path for further studies on this topic.

Author Contributions: Conceptualization, D.H. and P.L.; methodology, L.S. and R.V.E.; formal analysis, D.H., P.L., R.V.E. and L.S.; investigation, R.V.E.; data curation, R.V.E.; writing—original draft preparation, R.V.E.; review, L.S., P.L. and D.H.; supervision, D.H.; funding acquisition, D.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Coordination for the Improvement of Higher Education Personnel (CAPES/Brazil); the National Council for Scientific and Technological Development (CNPq/Brazil); and the Agency for Foundation Stemmer for Research, Development, and Innovation (FEESC)—RHAE-MCTI/SETEC/CNPq No. 54/2013.

Data Availability Statement: Data will be made available on request from the corresponding author.

Acknowledgments: The authors are very grateful to Jeanini Jiusti and to SENAI/SC for the external services provided.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Mandeep; Gupta, G.K.; Liu, H.; Shukla, P. Pulp and Paper Industry–Based Pollutants, Their Health Hazards and Environmental Risks. *Curr. Opin. Environ. Sci. Health* **2019**, *12*, 48–56. [\[CrossRef\]](#)
2. Simão, L.; Hotza, D.; Raupp-Pereira, F.; Labrincha, J.A.; Montedo, O.R.K. Wastes from Pulp and Paper Mills—A Review of Generation and Recycling Alternatives. *Cerâmica* **2018**, *64*, 443–453. [\[CrossRef\]](#)
3. Novais, R.M.; Carvalheiras, J.; Senff, L.; Labrincha, J.A. Upcycling Unexplored Dregs and Biomass Fly Ash from the Paper and Pulp Industry in the Production of Eco-Friendly Geopolymer Mortars: A Preliminary Assessment. *Constr. Build. Mater.* **2018**, *184*, 464–472. [\[CrossRef\]](#)
4. Saeli, M.; Micale, R.; Seabra, M.P.; Labrincha, J.A.; La Scalia, G. Selection of Novel Geopolymeric Mortars for Sustainable Construction Applications Using Fuzzy Topsis Approach. *Sustainability* **2020**, *12*, 5987. [\[CrossRef\]](#)
5. Simão, L.; Hotza, D.; Raupp-Pereira, F.; Labrincha, J.A.; Montedo, O.R.K. Characterization of Pulp and Paper Mill Waste for the Production of Waste-Based Cement. *Rev. Int. De Contam. Ambient.* **2019**, *35*, 237–246. [\[CrossRef\]](#)
6. Simão, L.; De Rossi, A.; Hotza, D.; Ribeiro, M.J.; Novais, R.M.; Klegues Montedo, O.R.; Raupp-Pereira, F. Zeolites-Containing Geopolymers Obtained from Biomass Fly Ash: Influence of Temperature, Composition, and Porosity. *J. Am. Ceram. Soc.* **2021**, *104*, 803–815. [\[CrossRef\]](#)
7. Habert, G.; Ouellet-Plamondon, C. Recent Update on the Environmental Impact of Geopolymers. *RILEM Tech. Lett.* **2016**, *1*, 17–23. [\[CrossRef\]](#)
8. La Scalia, G.; Saeli, M.; Adelfio, L.; Micale, R. From Lab to Industry: Scaling up Green Geopolymeric Mortars Manufacturing towards Circular Economy. *J. Clean. Prod.* **2021**, *316*, 128164. [\[CrossRef\]](#)
9. Zhang, Y.J.; Han, Z.C.; He, P.Y.; Chen, H. Geopolymer-Based Catalysts for Cost-Effective Environmental Governance: A Review Based on Source Control and End-of-Pipe Treatment. *J. Clean. Prod.* **2020**, *263*, 121–156. [\[CrossRef\]](#)
10. Della Rocca, D.G.; Peralta, R.M.; Peralta, R.A.; Rodríguez-Castellón, E.; de Fatima Peralta Muniz Moreira, R. Adding Value to Aluminosilicate Solid Wastes to Produce Adsorbents, Catalysts and Filtration Membranes for Water and Wastewater Treatment. *J. Mater. Sci.* **2021**, *56*, 1039–1063. [\[CrossRef\]](#)
11. Guo, Y.; Luo, L.; Liu, T.; Hao, L.; Li, Y.; Liu, P.; Zhu, T. A Review of Low-Carbon Technologies and Projects for the Global Cement Industry. *J. Environ. Sci.* **2024**, *136*, 682–697. [\[CrossRef\]](#)
12. Lanjewar, B.A.; Chippagiri, R.; Dakwale, V.A.; Ralegaonkar, R.V. Application of Alkali-Activated Sustainable Materials: A Step towards Net Zero Binder. *Energies* **2023**, *16*, 969. [\[CrossRef\]](#)
13. Xiao, R.; Huang, B.; Zhou, H.; Ma, Y.; Jiang, X. A State-of-the-Art Review of Crushed Urban Waste Glass Used in OPC and AAMs (Geopolymer): Progress and Challenges. *Clean. Mater.* **2022**, *4*, 100083. [\[CrossRef\]](#)
14. Acar, M.C.; Çelik, A.İ.; Kayabaşı, R.; Şener, A.; Özdöner, N.; Özkılıç, Y.O. Production of Perlite-Based-Aerated Geopolymer Using Hydrogen Peroxide as Eco-Friendly Material for Energy-Efficient Buildings. *J. Mater. Res. Technol.* **2023**, *24*, 81–99. [\[CrossRef\]](#)

15. Meskhi, B.; Beskopylny, A.N.; Stel'makh, S.A.; Shcherban', E.M.; Mailyan, L.R.; Shilov, A.A.; El'shaeva, D.; Shilova, K.; Karalar, M.; Aksoylu, C.; et al. Analytical Review of Geopolymer Concrete: Retrospective and Current Issues. *Materials* **2023**, *16*, 3792. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Sandanayake, M.; Law, D.; Sargent, P. A New Framework for Assessing the Environmental Impacts of Circular Economy Friendly Soil Waste-Based Geopolymer Cements. *Build. Environ.* **2022**, *210*, 108702. [\[CrossRef\]](#)
17. Morsy, A.M.; Ragheb, A.M.; Shalan, A.H.; Mohamed, O.H. Mechanical Characteristics of GGBFS/FA-Based Geopolymer Concrete and Its Environmental Impact. *Pract. Period. Struct. Des. Constr.* **2022**, *27*, 04022017. [\[CrossRef\]](#)
18. Jiang, X.; Zhang, Y.; Zhang, Y.; Ma, J.; Xiao, R.; Guo, F.; Bai, Y.; Huang, B. Influence of Size Effect on the Properties of Slag and Waste Glass-Based Geopolymer Paste. *J. Clean. Prod.* **2023**, *383*, 135428. [\[CrossRef\]](#)
19. Çelik, A.İ.; Tunç, U.; Bahrami, A.; Karalar, M.; Othuman Mydin, M.A.; Alomayri, T.; Özkılıç, Y.O. Use of Waste Glass Powder toward More Sustainable Geopolymer Concrete. *J. Mater. Res. Technol.* **2023**, *24*, 8533–8546. [\[CrossRef\]](#)
20. Tochetto, G.A.; Simão, L.; de Oliveira, D.; Hotza, D.; Immich, A.P.S. Porous Geopolymers as Dye Adsorbents: Review and Perspectives. *J. Clean. Prod.* **2022**, *374*, 133982. [\[CrossRef\]](#)
21. Luukkonen, T.; Yliniemi, J.; Sreenivasan, H.; Ohenoja, K.; Finnälä, M.; Franchin, G.; Colombo, P. Ag- or Cu-Modified Geopolymer Filters for Water Treatment Manufactured by 3D Printing, Direct Foaming, or Granulation. *Sci. Rep.* **2020**, *10*, 7233. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Su, Q.; Yang, S.; He, Y.; Qin, Z.; Cui, X. Prepared Self-Growing Supported Nickel Catalyst by Recovering Ni (II) from Metal Wastewater Using Geopolymer Microspheres. *J. Hazard. Mater.* **2020**, *389*, 121919. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Davidovits, J. Geopolymers: Ceramic-like Inorganic Polymers. *J. Ceram. Sci. Technol.* **2017**, *8*, 335–350. [\[CrossRef\]](#)
24. Provis, J.L. Alkali-Activated Materials. *Cem. Concr. Res.* **2018**, *114*, 40–48. [\[CrossRef\]](#)
25. Habert, G.; De Lacaillerie, J.D.E.; Roussel, N. An Environmental Evaluation of Geopolymer Based Concrete Production: Reviewing Current Research Trends. *J. Clean. Prod.* **2011**, *19*, 1229–1238. [\[CrossRef\]](#)
26. Abdulkareem, M.; Havukainen, J.; Nuortila-Jokinen, J.; Horttanainen, M. Environmental and Economic Perspective of Waste-Derived Activators on Alkali-Activated Mortars. *J. Clean. Prod.* **2021**, *280*, 124651. [\[CrossRef\]](#)
27. Komkova, A.; Habert, G. Optimal Supply Chain Networks for Waste Materials Used in Alkali-Activated Concrete Fostering Circular Economy. *Resour. Conserv. Recycl.* **2023**, *193*, 106949. [\[CrossRef\]](#)
28. Abdulkareem, M.; Komkova, A.; Havukainen, J.; Habert, G.; Horttanainen, M. Identifying Optimal Precursors for Geopolymer Composite Mix Design for Different Regional Settings: A Multi-Objective Optimization Study. *Recycling* **2023**, *8*, 32. [\[CrossRef\]](#)
29. De Rossi, A.; Simão, L.; Ribeiro, M.J.; Hotza, D.; Moreira, R.F.P.M. Study of Cure Conditions Effect on the Properties of Wood Biomass Fly Ash Geopolymers. *J. Mater. Res. Technol.* **2020**, *9*, 7518–7528. [\[CrossRef\]](#)
30. Maschowski, C.; Kruspan, P.; Garra, P.; Talib Arif, A.; Trouvé, G.; Gieré, R. Physicochemical and Mineralogical Characterization of Biomass Ash from Different Power Plants in the Upper Rhine Region. *Fuel* **2019**, *258*, 116020. [\[CrossRef\]](#)
31. Cherian, C.; Siddiqua, S. Pulp and Paper Mill Fly Ash: A Review. *Sustainability* **2019**, *11*, 4394. [\[CrossRef\]](#)
32. dos Santos, V.R.; Dezena Cabrelon, M.; de Sousa Trichês, E.; Quinteiro, E. Green Liquor Dregs and Slaker Grits Residues Characterization of a Pulp and Paper Mill for Future Application on Ceramic Products. *J. Clean. Prod.* **2019**, *240*, 118220. [\[CrossRef\]](#)
33. Toby, B.H.; Von Dreele, R.B. GSAS-II: The genesis of a modern open-source all purpose crystallography software package. *J. App. Cryst.* **2013**, *46*, 544–549. [\[CrossRef\]](#)
34. Davidovits, J. *Geopolymer: Chemistry & Applications*, 2nd ed.; Davidovits, J., Ed.; Institut Géopolymère: Saint-Quentin, France, 2008; ISBN 9782954453118.
35. Chen-Tan, N.W.; Van Riessen, A.; Ly, C.V.; Southam, D.C. Determining the Reactivity of a Fly Ash for Production of Geopolymer. *J. Am. Ceram. Soc.* **2009**, *92*, 881–887. [\[CrossRef\]](#)
36. Zhang, Z.; Wang, H.; Provis, J.L.; Bullen, F.; Reid, A.; Zhu, Y. Quantitative Kinetic and Structural Analysis of Geopolymers. Part 1. The Activation of Metakaolin with Sodium Hydroxide. *Thermochim. Acta* **2012**, *539*, 23–33. [\[CrossRef\]](#)
37. Williams, R.P.; Van Riessen, A. Determination of the Reactive Component of Fly Ashes for Geopolymer Production Using XRF and XRD. *Fuel* **2010**, *89*, 3683–3692. [\[CrossRef\]](#)
38. Toniolo, N.; Boccaccini, A.R. Fly Ash-Based Geopolymers Containing Added Silicate Waste. A Review. *Ceram. Int.* **2017**, *43*, 14545–14551. [\[CrossRef\]](#)
39. Martínez-García, R.; Jagadesh, P.; Zaid, O.; Șerbănoiu, A.A.; Fraile-Fernández, F.J.; de Prado-Gil, J.; Qaidi, S.M.A.; Grădinaru, C.M. The Present State of the Use of Waste Wood Ash as an Eco-Efficient Construction Material: A Review. *Materials* **2022**, *15*, 5349. [\[CrossRef\]](#) [\[PubMed\]](#)
40. Simão, L.; Fernandes, E.; Hotza, D.; Ribeiro, M.J.; Montedo, O.R.K.; Raupp-Pereira, F. Controlling Efflorescence in Geopolymers: A New Approach. *Case Stud. Constr. Mater.* **2021**, *15*, e00740. [\[CrossRef\]](#)
41. Allahverdi, A.; Najafi Kani, E.; Shaverdi, B. Carbonation Versus Efflorescence in Alkali-Activated Blast-Furnace Slag in Relation with Chemical Composition of Activator. *Int. J. Civ. Eng.* **2017**, *15*, 565–573. [\[CrossRef\]](#)
42. Bernal, S.A.; Mejía De Gutiérrez, R.; Provis, J.L. Engineering and Durability Properties of Concretes Based on Alkali-Activated Granulated Blast Furnace Slag/Metakaolin Blends. *Constr. Build. Mater.* **2012**, *33*, 99–108. [\[CrossRef\]](#)
43. Nath, S.K.; Kumar, S. Role of Alkali Concentration on Reaction Kinetics of Fly Ash Geopolymerization. *J. Non. Cryst. Solids* **2019**, *505*, 241–251. [\[CrossRef\]](#)

44. Longhi, M.A.; Walkley, B.; Rodríguez, E.D.; Kirchheim, A.P.; Zhang, Z.; Wang, H. New Selective Dissolution Process to Quantify Reaction Extent and Product Stability in Metakaolin-Based Geopolymers. *Compos. Part B Eng.* **2019**, *176*, 107172. [[CrossRef](#)]
45. Bai, C.; Colombo, P. Processing, Properties and Applications of Highly Porous Geopolymers: A Review. *Ceram. Int.* **2018**, *44*, 16103–16118. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.