

# Development of geopolymeric structures to prioritize the use of waste from paper industries

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## Abstract

Geopolymers were synthesized using metakaolin obtained from the waste of white paper pulping process. The waste is mainly composed by cellulose, calcium carbonate and kaolin. Chemical and physical procedures were conducted aiming to separate its components and obtain metakaolin. The cellulose was eliminated by burning the waste at 450 °C. The CaCO<sub>3</sub> was removed by reacting the material with a 1.8 M HCl solution. The purified kaolin went through heat treatment 850 °C for 2 h, in order to be transformed into metakaolin by dehydroxylation. Geopolymers were produced to assess the performance of the resulting metakaolin. The aluminosilicate alkaline activation was executed using four solutions - composed of 8 M and 12 M of KOH and NaOH, each combined with Na<sub>2</sub>SiO<sub>3</sub> in a 2:1 fixed ratio. The results pointed out that the metakaolin obtained from the waste treatment was a quality one, enabling it to be applied in the development of geopolymers.

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*Keywords:* waste; purified kaolin; metakaolin; alkaline activation; geopolymer.

## 1. Introduction

The problems of environmental pollution and the consequences caused by inadequate waste deposition have been the subject of several studies. In order to lessen the environmental pollution and meet the needs of new materials, green technologies have been prioritized.

Among the different products that had increased demand are the construction materials, since most of the industrial sector needs buildings to be effective. Cement is one of the main construction materials used all around the world and its technology has been the subject of several researches. In 2015, 64.4 million-tons of cement were sold in Brazil alone. The world production reached levels over 4000 Mton in 2013 [1]. Currently, the most used, known and well-studied cement is the Portland type. This type of cement has been of great importance to mankind in recent decades. It is an easy-handling and well-accepted material by the specialized engineering, therefore it is

beyond doubt the economic benefits created by its discovery. However, a few problems related to its elevated energy consumption, high CO<sub>2</sub> emission, especially during clinker burn [2,3], the constant need for restauration, caused by its elevated level of wear, and the extraction of natural resources influenced some researchers to study the production of new material with lower energy expenditure and lower environmental impact [4,5]. Especially under the topic of CO<sub>2</sub> emission, and taking into account the shift of priorities in the recent decades to green-oriented production, OPC alone is responsible for 5-8% of all the man-made CO<sub>2</sub> emissions [6]. Hence, the search for newer and lower carbon-footprint processes is essential.

The use of industrial waste can be environment-friendly in several aspects, for instance: the reduction of the quantities of waste and of treatment and management costs, and, in addition, has the benefit of supporting the sustainable development by minimizing the extraction of raw resources from nature.

The waste from white paper pulping, the aim of this paper for the production of geopolymers, is produced in large quantities, namely, in 2012, 166,641 million-

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ton of cellulose and 399,985 million-ton of paper were produced all around the world. Brazil alone has produced 13,977 million-ton of cellulose and 10,260 million-ton of paper. However, the high demand for paper also increases the generation of industrial waste, especially since the world per capita medium has been of 57 kg of paper [7]. According to Rashad (2013) the kaolin present in waste paper sludge can be an environmentally viable alternative for the production of new materials [8].

An alternative material that can be produced from industrial waste is geopolymeric cements [9], which by not needing clinker in its composition and accepting as feedstock various types of aluminosilicate rich industrial wastes, for example: red mud, fly ash., bottom ash, waste kaolin [5,9]. The use of industrial waste that has already undergone thermal treatment can reduce substantially both energetic demand and greenhouse gases emission.

Geopolymers are formed from the dissolution of an aluminosilicate source and an alkaline base, the latter participating as the reaction activator. The reaction starts by mixing the aluminosilicate source with the base, reacting very quickly [10]. According to Provis [11], alkali-activated binders, which include geopolymers, can be defined as products from the reaction of an aluminosilicate source with an alkaline activator, usually in concentrated aqueous solution.

Geopolymers, because they are alkaline activated materials and not only hydrated as OPC type cements, can also contribute to the emission of some pollutants if industrial reagents are used, so it is important to also evaluate the source of the reagents used in the process. Whereas the use of some type of reagents can increase the economic and environmental costs of the material, depending on the raw material and the production process involved. Thus, the use of residual reagents or obtained from industrial by-products, such as sodium silicate may be a viable alternative. Carrasco et al. (2015) used alkaline activator waste glass and obtained rheological results similar to commercial activated materials waterglass [12]. According to Kamseu et al. (2017) geopolymers activated with sodium silicate solutions produced from the rice husk ash (RHA-NaOH) presented good results and were considered environmentally favorable to reduce global warming [13]. Ashes from rice hulls were also used for producing sodium waterglass and for application to the activation of geopolymers by the researchers Tchakouté et al. (2016), according to data from the studies the process was effective [14]. Thus, it is concluded that it is possible to obtain alternative

activators for the production of geopolymers and contribute to the minimization of generated wastes and problems caused by the high emission of greenhouse gases.

The steps of the polymerization reaction are described in detail by Provis and Van Deventer [15], Duxson et al. [16], but, in short, the aluminosilicate source, firstly, is dissolved in the alkaline medium, releasing Si and Al and transforming them into silicate and aluminate; next, the species now present in the medium are incorporated in the aqueous phase and, finally, the condensation of the species forms the aluminosilicate network proper of the geopolymers.

Thus, this work was carried out prioritizing the use of industrial waste - namely, kaolin obtained via waste from white paper pulping processes. This research, also, focused in the assessment of three different alkaline activators, varying twice their concentration.

## 2. Materials and methods

### 2.1. Materials

As aluminosilicate source for the geopolymer synthesis, metakaolin derived from kaolin present in the white paper pulping waste - obtained from industries located in the southern region of Brazil - was used. As reagents, two solutions were prepared: one consisting of sodium hydroxide (NaOH) (Synth) combined with sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) (Manchester) and the other consisting of potassium hydroxide (KOH) (Synth) combined, too, with  $\text{Na}_2\text{SiO}_3$ . Each solution was prepared in two concentrations: 8 M and 12 M. The ratio of the mixtures between NaOH/ $\text{Na}_2\text{SiO}_3$  and KOH/ $\text{Na}_2\text{SiO}_3$  was fixed in 2:1.

### 2.2. Purification of the waste

Moisture constituted only 1% of the weight of the waste from white paper pulping process. Its composition consists mainly of cellulose, kaolin and calcium carbonate ( $\text{CaCO}_3$ ).

The waste was, firstly, characterized and, afterwards, was possible to estimate the HCl concentration needed to the material's purification process. Using stoichiometric operations, it was possible to determine that a thorough  $\text{CaCO}_3$  cleanse would need 1 L of a 1.8 M solution of HCl for each 150 g of waste [9,17].

In order to assess the fractions of the components, the waste was weighed and went through thermal treatment - 450 °C for 2 hours - aiming to eliminate the cellulose. In this process, the loss of ignition was 29.97%. Since the chief component to the geopolymeric synthesis is metakaolin, the post-

thermal-treatment-waste went through acid purification, designed to remove the  $\text{CaCO}_3$ .

The acid wash consisted of adding the waste in the HCl solution for 2 hours. Next, the material was washed with distilled and deionized water and filtered in order to separate the aqueous calcium chloride ( $\text{CaCl}_2$ ) - formed from the reaction between HCl and  $\text{CaCO}_3$  - from the feedstock. Then, the waste was dried in an oven under  $100\text{ }^\circ\text{C}$  for 24 hours. Lastly, the material, now composed solely by kaolin, went through its final thermal treatment - which consisted of  $850\text{ }^\circ\text{C}$  for 2 hours - in order to be converted from kaolin to metakaolin.

### 2.3. Obtaining the geopolymeric cement

The geopolymeric samples were obtained by mixing the purified metakaolin with the alkaline activators - namely,  $\text{NaOH}/\text{Na}_2\text{SiO}_3$  and  $\text{KOH}/\text{Na}_2\text{SiO}_3$  - under 10 min of constant agitation. The samples were cured for 28 days in room temperature and, afterwards, characterized.

### 2.4. Characterization techniques

The chemical composition of the waste pre and post acid wash was obtained via X-Ray Fluorescence (XRF) analyses, using a Philips spectrometer, model PW 2400, through wavelength dispersive method (WDXRF). To evaluate the crystalline phases and the presence of amorphous materials, X-Ray Diffraction (XRD) analyses were made in a Philips diffractometer, model X'pert, with radiation  $\text{K}\alpha$  ( $\lambda = 1.5418\text{ \AA}$ ) and 40 kV and 30 mA output. The Fourier Transform Infrared Spectroscopy (FTIR) technique was utilized to assess the material's functional groups. The equipment used was an Agilent Technologies – Cary 600 Series FTIR Spectrometer. In addition, Scanning Electron Microscopy (SEM) analyses were conducted in a SEM-EDS system Phillips XL30 – UFSC/LCME and a JEOL JSM-6390LV Scanning Electron in order to evaluate the morphology of the samples.

## 3. Results and discussion

Table 1 brings the XRF analyses containing the chief elements present in the waste *in natura*, in the post-cellulose-removal waste and, also, in the waste after HCl purification and final calcination. The results show that, after the cellulose burn, the acid rinse and the dehydroxylation thermal treatment, the resulting metakaolin is composed by 52.2% of  $\text{SiO}_2$  and 41.2% of  $\text{Al}_2\text{O}_3$ .

Table 1. XRF: (a) waste (W) *in natura*; (b) calcined (C) ( $450\text{ }^\circ\text{C}$ ) to burn the cellulose and (c) metakaolin (M) after purification in HCl and heat treatment at  $850\text{ }^\circ\text{C}$ .

Oxide	W (a)	C (b)	M (c)
CaO	32.4	42.9	0.7
$\text{SiO}_2$	7.7	26.3	52.2
$\text{Al}_2\text{O}_3$	6.1	20.9	41.2
$\text{Fe}_2\text{O}_3$	0.2	0.7	1.6
MgO	0.6	1.2	1.5
$\text{TiO}_2$	0.1	0.57	1.5
$\text{Na}_2\text{O}$	0.1	0.1	1.1
$\text{Na}_2\text{O}$	52.6	1.3	0.57

The proportion of CaO, originating from the  $\text{CaCO}_3$  present in the waste *in natura*, was reduced from 32.4% [17] to 0.7%.

It is possible to observe, making use of the diffractograms in Figure 1, the phases: in the waste *in natura* (a), after acid washing (b) and, lastly, after thermal treatment (c) – which transforms kaolin into metakaolin. It is observable the reduction of the peaks linked to calcite and, also, the formation, in the metakaolin sample (c), of a halo which can be interpreted as amorphous material, essential to the alkaline activation and geopolymeric formation [18].

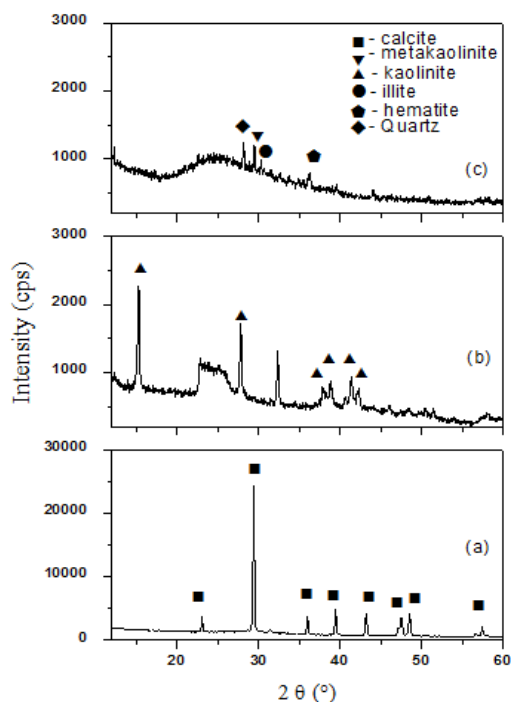


Fig. 1. XRD: (a) waste *in natura*; (b) waste after HCl washing and (c) resulting metakaolin.

The calcined kaolinite, or metakaolin, is one of the main feedstock utilized by Davidovits as aluminosilicate source in the production of geopolymers and also has been used by several independent researchers in several applications, including activated cements. In the geopolymerization, the metakaolin may define the material's structure [19].

Figure 2a-d presents the results from the analyses conducted in the geopolymers samples. The geopolymeric matrices studied in this paper were synthesized using two different concentrations and three different activating compounds. As can be observed in the diffractograms of the samples synthesized using 8 and 12 M of KOH mixed with  $\text{Na}_2\text{SiO}_3$  and using 12 M of NaOH mixed with  $\text{Na}_2\text{SiO}_3$ , the changes in the structures of these materials were the most significant when comparing to metakaolin (Figure 1c).

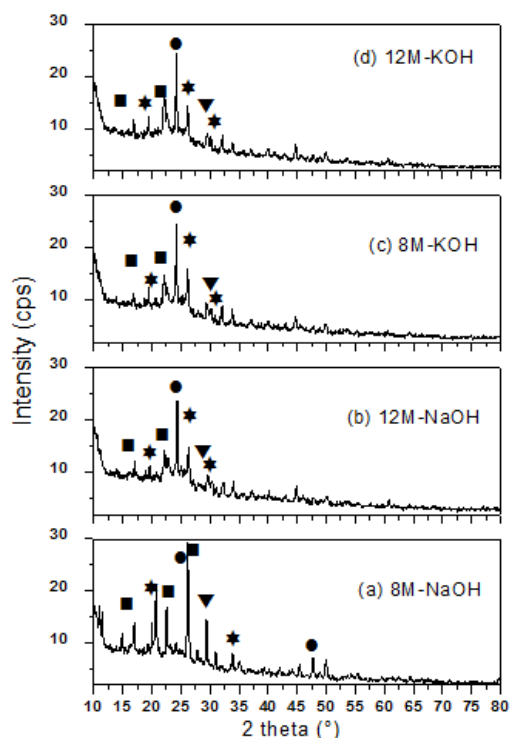


Fig. 2. Diffractogram of the geopolymer materials obtained from the metakaolin recovered from the white paper pulping process waste. (a) 8M, (b) 12 M of NaOH and (c) 8 M, (d) 12 M of KOH.

In the sample related to the alkaline activation using 8 M of NaOH mixed with  $\text{Na}_2\text{SiO}_3$  alterations in the peaks were present. However, the extension of the gel phase was reduced. The use of industrial wastes may, in many cases, increase the complexity of the system

[20]. However, the formation of the geopolymeric structure is, normally, identified within the  $2\theta=20^\circ$  to  $40^\circ$  region. Higher proportions of amorphous reactive materials and the formation of the amorphous gel are located in this interval, shifting their halo and peaks when compared to the source material [21]. The crystalline peaks present in the XRD diffractograms are related to the crystalline materials that did not react, although, as mentioned in the researches of Xu and Deventer [22], their intensity was reduced. The appearance of new crystalline phases (reference code: ICSD) after alkaline activation is observed in the diffractograms.

The crystalline phases of the materials were identified using the reference code: ICSD, obtained by X'pert software (Table 2).

Table 2. Code ICSD - crystalline phases of the materials.

Elements	CODE (ICSD)
Calcite	01-081-2027
Kaolinite	00-001-0527
Quartz	01-085-0797
Sodium	01-001-0850
Silicion oxide	01-089-1961
Sodium aluminum silicate	00-048-0504
Calcium silicate aluminum hydrate	01-089-1580

The metakaolin and the samples from the synthesized geopolymer were analyzed using the Fourier Transform Infrared Spectroscopy (FTIR) method. The objective of the FTIR analyses in this paper is to define important functional groups in the geopolymerization process. Figure 3a shows the FTIR analysis of metakaolin before the activation, in which is possible to observe, in the vibrations spectrum that occurred in the region between ( $3400\text{-}3600\text{ cm}^{-1}$  and  $2400\text{-}1700\text{ cm}^{-1}$ ), an axial deformity in the hydroxyl ( $\text{OH}^-$ ) groups. The stretching of the proportions of O-Si-O and O-Al-O may be seen in the regions between ( $1100\text{-}900\text{ cm}^{-1}$ ) [23]. In  $788\text{ cm}^{-1}$ , a vibration related to the presence of quartz is present.

In the regions where the asymmetric and symmetric vibrations of O-Si-O and O-Al-O were found within  $1100\text{-}900\text{ cm}^{-1}$  - Figure 3b,c,d,e related to the samples synthesized using 8 M and 12 M of NaOH and KOH, respectively -, it is possible to observe a shift of the waves to smaller regions, decreasing their intensities, and the waves were elongated when compared to Figure 3a, related to metakaolin. In the region close to  $1000\text{ cm}^{-1}$  the  $\text{SiO}_4^{4-}$  is replaced by  $\text{AlO}_4^{3-}$  to form the polymeric chain.

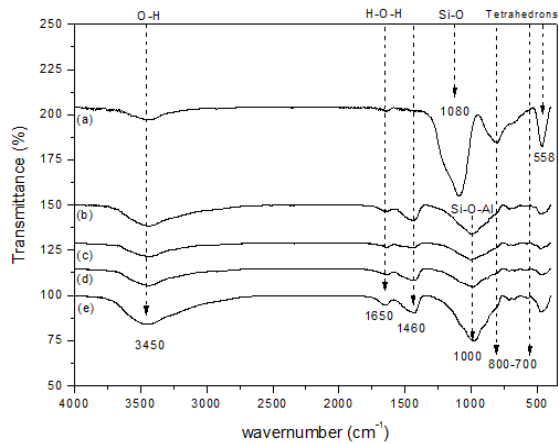


Fig. 3. FTIR spectra: (a) metakaolin from white paper pulping waste; (b-e) geopolymers synthesized using 12 M, 8 M of NaOH and 12 M, 8 M of KOH, respectively.

The ions  $\text{Na}^+$ ,  $\text{K}^+$ , or others, depending the activator used, balance the charge difference [24].

Other visible characteristic in the spectra may be observed in the  $850\text{--}693\text{ cm}^{-1}$  region, namely, the disappearance of the band and the formation of minor vibrations in lower regions, near  $700\text{ cm}^{-1}$ , which may be due to the tetrahedrons of inorganic polymers, indicating formation of new structures, a characteristic of geopolymeric cement matrix with geometric rearrangements of the  $\text{SiO}_4$  and  $\text{AlO}_4$  [25–27].

As can be seen in the SEM micrographs (Figs. 4 and 5), a dense and homogeneous matrix formed in almost all samples synthesized with 8 and 12 KOH (Fig. 4). The samples synthesized using 8 and 12 M NaOH showed dense surface (Fig. 5a and 5b, respectively). However, in the fractured sample (Fig. 5c) it is possible to see particles that have not reacted, and Fig. 5d shows carbonation points. A possible explanation for the results presented in Fig. 5c is the activator concentration, since the inability of the activator to dissolve the aluminosilicate particles could cause low availability of Si and Al in the medium, difficulting the formation of the geopolymeric matrices. The activator scarcity may not provide sufficient  $\text{Na}^+$  or  $\text{K}^+$  to balance the charges formed by the presence of Al and Si in the geopolymeric network. Since Al and Si yield, respectively,  $5^-$  and  $4^-$  charge deficiency, cations are needed from the base in order to balance the charge deficit. According to Rattanaask et al. [28], in order to the geopolymerization to occur in a homogeneous way, it is fundamental to have high concentration of the activator. However, the excess of the activator may form sodium carbonate when in contact with air [19].

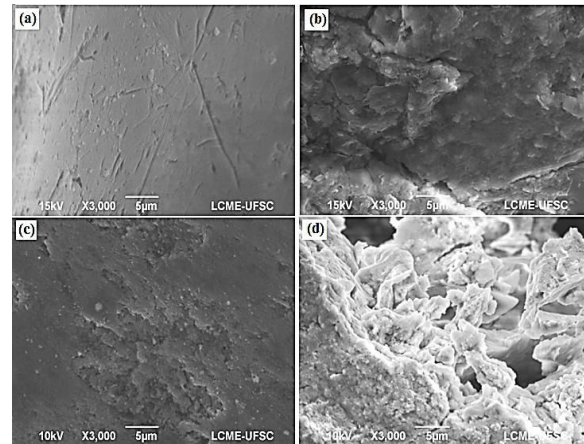


Fig. 4. SEM images of surface (a,c) and fracture (b,d) of geopolymer samples synthesized using 8 (a,b) and 12 (c,d) M KOH/ $\text{Na}_2\text{SiO}_3$ .

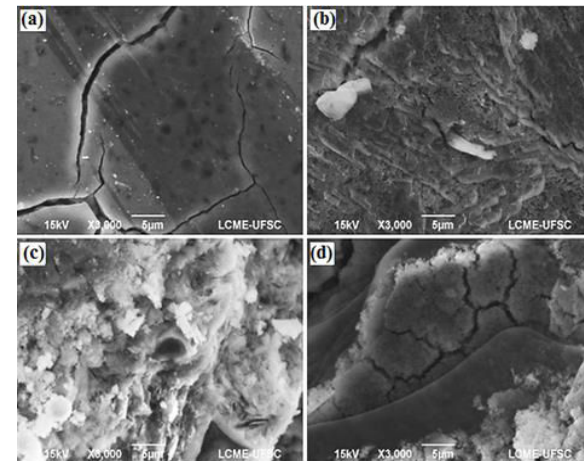


Fig. 5. SEM images of surface (a,b) and fracture (c,d) of geopolymer samples synthesized using 8 (a,c) and 12 M (b,d) NaOH/ $\text{Na}_2\text{SiO}_3$ .

It is also possible to observe some cracks in the samples of geopolymer matrices. According to Forsgreen et al. [29], drying too fast or at elevated temperatures may cause them because water is released very quickly, disrupting the cementation process. Cracks can also be caused by improper handling of the samples during analyses.

The differences between the two types of alkaline activators used may highlight the presence of smoother and more compact surfaces in the samples that were activated using the KOH /  $\text{Na}_2\text{SiO}_3$  mixture. There is a propensity for KOH to dissolve more efficiently materials rich in  $\text{Na}_2\text{O}$ , while  $\text{K}_2\text{O}$  rich materials experience negative influence when leached using the same base. The same happens when NaOH leaches  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  rich materials: the former does not respond well while the latter dissolves efficiently. In that way, cations can affect the geopolymeric structure in two different ways: by being present in

the alkaline solution and, also, by being inserted in the aluminosilicate structure [30]. The same researcher also reports that synthesized samples using KOH, when comparing to the ones using NaOH, presented higher endothermal peaks, higher disorder in its structure, hence, larger amorphous phase.

#### 4. Conclusions

Aiming the conservation of natural resources by using waste as feedstock, this paper was constructed using a methodology in which kaolin was purified from white-paper-pulping-waste in order to produce geopolymers.

After the purification, the resulting product was characterized indicating elevated metakaolin yield and, according to the results of the microstructural analyses, favorable properties to be used in industrial processes.

In the next step, the samples were synthesized using three types of activators, varying twice their concentrations, in order to assess the best parameters to produce the best material. The activators and the concentrations used were the following: 8 M and 12 M of KOH; 8 M and 12 M of NaOH. To all four, 33% of  $\text{Na}_2\text{SiO}_3$  was added and the samples were cured in room temperature and characterized after a period of 28 days.

The XRD, FTIR and SEM results indicated that the metakaolin from industrial wastes can be utilized in the synthesis of geopolymers. However, different concentrations and types of activators produced materials with different structures. The samples synthesized using 12 M, 8 M of KOH and 12 M of NaOH presented well-formed structures and large gel phase extension.

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