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Effect of sawdust as porosity agent on final properties of geopolymers

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Abstract

The geopolymers synthesis are based on geopolymerization, a sequence of reactions processed in an alkaline medium through oligomers providing a three-dimensional molecular structure. In this work, the polycondensation of metakaolin was performed with alkaline activators (NaOH and sodium silicate), wood sawdust and other additives. Two different compositions were evaluated after and before sintering at a high temperature (850 °C). The effect of sawdust addition and the thermal treatment of geopolymers were evaluated by scanning electronic microscopy, X-ray diffraction, mechanical properties, apparent density and porosity by different characterization techniques to guide of development of high porous and low-density materials for thermal and noise control application on building/home construction engineering applications.

Keywords: geopolymer, activated metakaolin, refractory material, sawdust.

INTRODUCTION

Geopolymers are defined as inorganic polymers formed by SiO_4^- and AlO_4^- tetrahedrons linked by oxygen bridges and are classified into three different groups according to the atomic ratio between silicon (Si) and aluminum (Al): i) poly(sialate) (M-PS), ii) poly(sialate siloxo) (M-PSS), and iii) poly(sialate disiloxo) (M-PSDS), where M stand for a cation as calcium, potassium or sodium [1]. The repeating units of geopolymers are normally based in (-Si-O-Si-O-), (-Si-O-Al-), (Fe-O-Si-O-Al-O-) or (-Al-O-P-O-) compounds, which are obtained through polycondensation reactions, from an amorphous compound to a semi-crystalline structure [2]. The term geopolymer was used for the first time by Davidovits and initial studies on such materials started around the 1950s, generating a great interest in Kiev, a scientist from the civil engineering institute in Ukraine, especially because of the excellent performance of those materials when compared to the ordinary Portland cement - OPC [3]. The final compound materials, mainly composed by clay and an alkaline reactant (KOH or NaOH), present good mechanical, thermal and chemical properties generating structures with promising properties for applications like insulators, refractories, and coatings. However, several applications have been explored for those materials as advanced ceramics, toxic waste management, cementitious binders, composites, refractories, fire barrier, cements and concretes [1].

A crucial factor for the production of geopolymers is related to the final molar ratio of components. Several molar ratios have been studied for different authors, as described in Table I, and basically, four relationships should be noticed, leading to materials with good mechanical properties. Time and temperature of curing of geopolymers also present a direct impact on the final mechanical properties of the material. Those parameters have been explored in many studies ranging from 20 to 85 °C and from 1 to 28 days [12, 13] depending on the prepared formulation. In addition, relative humidity has also been controlled in some studies [13]. All parameters as density, porosity and mechanical properties of the geopolymer play an important role for the final application. Hence, a control and evaluation of parameters are required according to the desired application, and then an improvement in acoustic and thermal comfort, for example, in civil construction might also be explored.

Table I - Molar ratios of geopolymer formulations from literature: Na_2O/SiO_2; SiO_2/Na_2O; Na_2O/Al_2O_3; and SiO_2/Al_2O_3.

Na_2O/SiO_2	SiO_2/Na_2O	Na_2O/Al_2O_3	SiO_2/Al_2O_3	Ref.
-	-	-	3.40-3.80	[4]
-	1.60	-	2.65	[5]
-	-	-	3.10-3.30	[6]
-	-	1.00	2.33	[7]
-	-	1.00	5.50	[8]
-	0.50-1.00	-	1.15-1.90 1.15-2.15	[9, 10]
0.20-0.48	3.20	0.80-1.20	3.30-4.50	[11]
0.30	1.58 2.20	-	3.80 4.70 3.78	[12]

This work showed the development of geopolymers, the evaluation of temperature of sintering and the effect of the addition of sawdust on final properties, always aiming

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high mechanical properties. The final features of materials were mainly regulated by parameters of synthesis as chemical composition and sawdust percentage. Mechanical and morphological properties of all prepared samples were evaluated by compression strength, elastic modulus and SEM images. X-ray diffractions were performed for evaluation of main phases of geopolymers before and after the heat treatment, searching as a goal the development of high porous and low-density material with potential application in thermal and noise control for building and home construction.

MATERIALS AND METHODS

Geopolymer materials were synthesized based on Na_2O-Al_2O_3-SiO_2 system, in order to attempt specific composition relationship ratios of ternary phase diagram and reach final good mechanical properties after sintering at 850 °C and with porosity and density control. Table II shows each component that was used with its respective function. Sawdust was composed of several types of wood dried and sieved at 40 °C and 48 mesh, respectively, presenting particle sizes between 55-350 μm; the chemical composition of metakaolin was SiO_2 57%, Al_2O_3 34%, CaO+MgO <0.1%, SO_3 <0.1%, Na_2O <0.1%, alkaline equilibrium Na_2O <1.5%, Fe_2O_3 2%, TiO_2 1.5% (source: Metacaulim do Brasil).

Two different compositions were defined using linear programming to optimize the chemical composition (Solver routine program of software MS Excel). The compositions and molar ratios of prepared samples are described in Table III and IV, respectively. The formulations C1 and C2 are shown on Na_2O-SiO_2-Al_2O_3 ternary phase diagram (Fig. 1). The porosity agent, sawdust, was a low value-added biomass residue from a local sawmill of São Paulo State (Brazil). Samples were prepared with 0 to 20 wt% of porosity agent in cylindrical form (25 mm in diameter and 80 mm in height). Curing time ranged from 7 to 10 days at room temperature (~25 °C) and then the samples were dried in an oven at 110 °C. Differential thermal analysis was performed in a TG/DTA equipment (Netzsch, STA 900) under synthetic air atmosphere from 25 to 1400 °C at 10 °C/min using the non-heat-treated samples. After drying, the two compositions were also heated treated at 3.5 °C/min in a muffle oven (Jung, LF04213), from room temperature to 850 °C and the set point was maintained for 2 h.

Table III - Chemical compositions (wt%) of prepared samples.

Composition	Na_2O	SiO_2	Al_2O_3
C1	22.50	33.70	43.80
C2	21.20	51.00	28.00

Table IV - Molar ratios of C1 and C2 formulations.

Composition	Na_2O/SiO_2	SiO_2/Na_2O	Na_2O/Al_2O_3	SiO_2/Al_2O_3
C1	0.64	1.56	0.85	1.31
C2	0.40	2.51	1.27	3.20

The compression tests for raw dried and thermal treated samples were performed with a Kratos universal hydraulic testing machine according to ASTM NBR7215 standard [14], using a 5000 kgf load cell with a constant load rate of 5.0 mm/min, where stress and strain were continuously and simultaneously recorded. Cold compressive strength (CCS) was calculated as a function of the transversal area of each sample. Cylindrical specimens were used for determination of Young's modulus, performed with Sonelastic equipment (mod. SA-BC) using the software Sonelastic v. 3.0. This technique, a non-destructive method, is based on the impulse excitation of the sample for the determination of elastic modulus through the natural vibration frequencies of the material. The apparent density (AD) was measured by Archimedes method, using water as a liquid in a Shimadzu semi-analytical balance - AY220 [15], and the apparent porosity (AP) was calculated from such density. The tests were performed with at least four samples. Surface morphology and porosity of geopolymers, previously metalized with gold, were investigated by scanning electron microscopy (SEM, FEI, Inspec F50). The chemical elements on the surface of geopolymers were analyzed by energy dispersive X-ray spectroscopy (EDS) using EDAX and TEAM software. The phase compositions before and after thermal treatment were evaluated by X-ray diffraction (XRD) in a Bruker diffractometer with CuKα radiation, λ=1.54178 Å, and a scan rate of 0.02 °/s.

Table II - Raw materials and chemicals used.

Material	Supplier	Type	Function
Metakaolin	Metacaulim do Brasil	Binder	Provide structure and formation of geopolymer/alumina sodium silicate
Sawdust	Local supplier	Porosity agent	Adjust porosity
Sodium hydroxide (p.a.)	Neon	Activator	Activator, source of Na^+
Sodium silicate (p.a.)	Diatom Co.	Activator	Activator, source of Na^+
Microsilica (960)	Elkem	Component	Source of SiO_2
Calcined alumina (A1000 SG)	Almatis	Component	Source of Al_2O_3

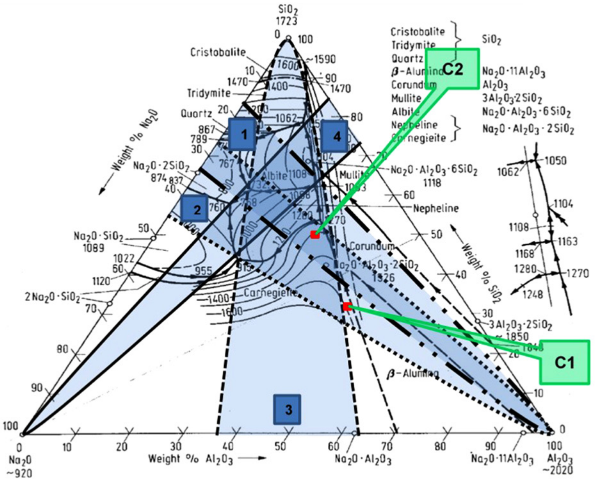

Figure 1: SiO_2-Al_2O_3-Na_2O phase diagram with geopolymers molar ratios (regions 1-4); adapted from [16]

RESULTS AND DISCUSSION

The thermal behavior of two studied compositions in presence of air was evaluated from DTA analysis (synthetic air, 10 °C/min of heating rate, Fig. 2). Thermal analysis of C1 and C2 compositions showed important phase transformations at temperatures up to 800 °C. The main contributions from 250-600 °C were related to evaporation of free water and condensation of aluminol and silanol groups [7]. The main crystalline phases of C1 and C2 before and after treatment are presented on Fig. 3. The XRD patterns showed the presence of hydrosodalite and low quartz for both compositions before calcination. However, after the thermal treatment, C1HT was basically composed of nepheline and cristobalite while the main phases found for C2HT were nepheline, cristobalite, and low quartz.

Fig. 4 shows the effect of both the sawdust percentages and the thermal treatment on apparent density of all samples. A reduction of apparent density was observed for samples without heat treatment, probably due to the lower specific gravity of sawdust compared to metakaolin, in agreement with geopolymers prepared with a different biomass source (rice husk) [17]. The apparent density always increased after sintering at 850 °C and tended to increase with the sawdust addition. Apparent porosity was higher for C2 compositions compared to C1, regarding the samples without heating, showing that compositions presented different behavior (Fig. 5a). However, after thermal treatment, porosity increased in a higher proportion for C1, values ranging from 34% to 47%, in contrast to 25% to 34% of C2. Besides, the C2HT-20% sawdust showed no increase in porosity, remaining at 34%. Those differences on porosity were also due to the volume shrinkage, clearly seen in Fig. 6. The composition 2 presented higher shrinkage values leading to more compact materials, especially the C2HT-20% sawdust,

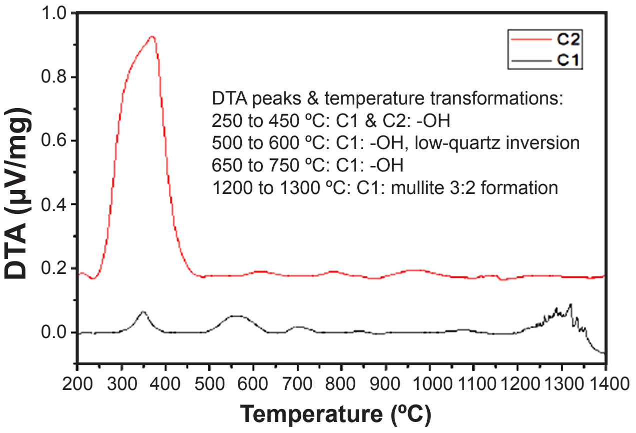

Figure 2: Differential thermal analysis behavior of compositions C1 and C2.

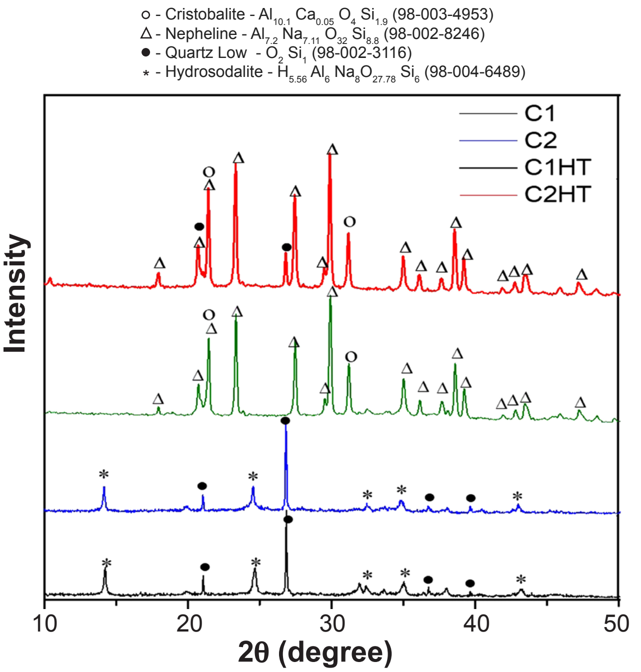

Figure 3: XRD patterns of geopolymers before (C1, C2) and after (C1HT, C2HT) calcination.

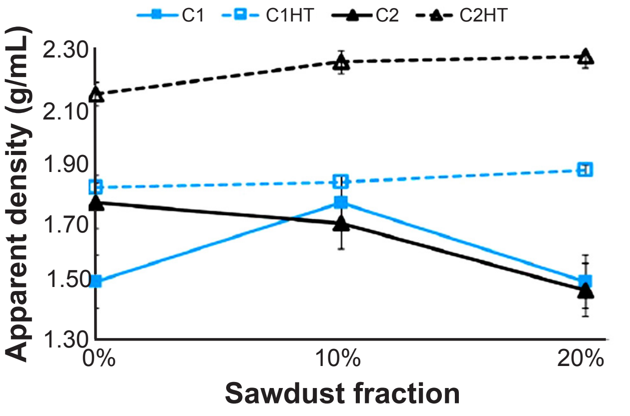

Figure 4: Apparent density for the samples with different percentages of sawdust before and after thermal treatment (HT), full and empty symbols, respectively.

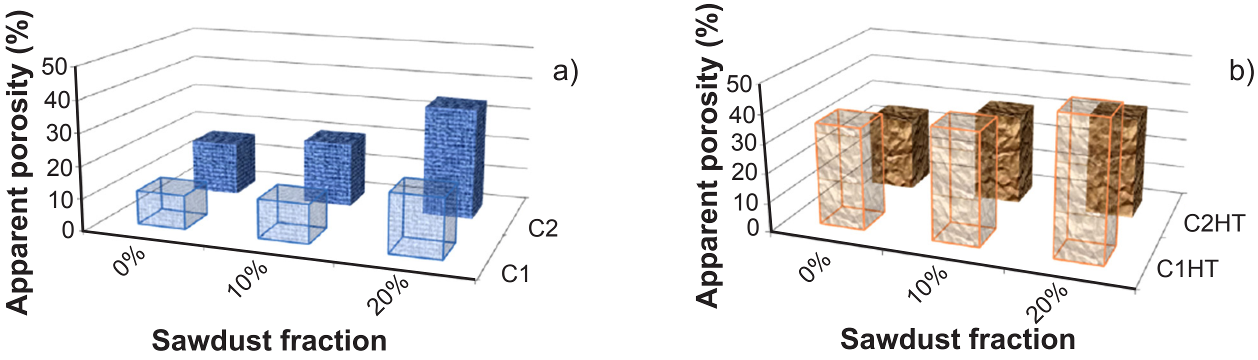

Figure 5: Apparent porosity (AP) for samples before (a) and after (b) heat treatment with different percentages of sawdust.

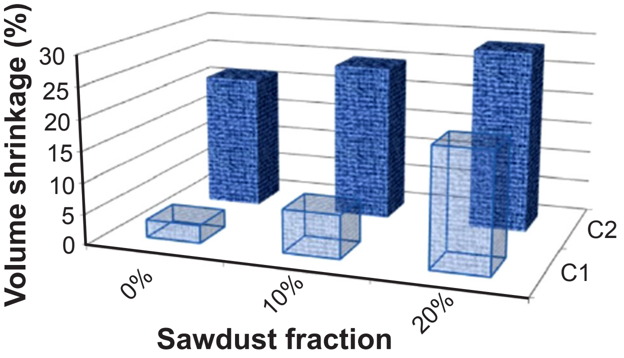

Figure 6: Volume shrinkage for samples after treatment at 850 °C.

corroborating the absence of increment of porosity for such composition after the calcination.

Morphology and porosity were evaluated by SEM at different magnifications. Micrographs clearly showed the increase in porosity with the addition of sawdust (Fig. 7b) compared to the morphology of the geopolymeric matrix (Fig. 7a). A large distribution of pores, with different sizes, was found on the matrix probably due to the air entrapment during the mixing, assisted by the presence of sawdust particles on the composition (Fig. 7c); such pores were mostly isolated (closed porosity). Furthermore, porosity also increased with the thermal treatment at 850 °C resulting in a rough surface and a highly porous matrix (Figs. 7d and 7e). Such final structure might represent an important characteristic for applications as thermal insulators or sound absorbing materials [18]. The sawdust fiber found on the geopolymer structure, as shown in Fig. 7c, was confirmed by EDS analysis, which showed a remarkable peak of carbon normally found for biomass materials (pore forming agent) in a raw form.

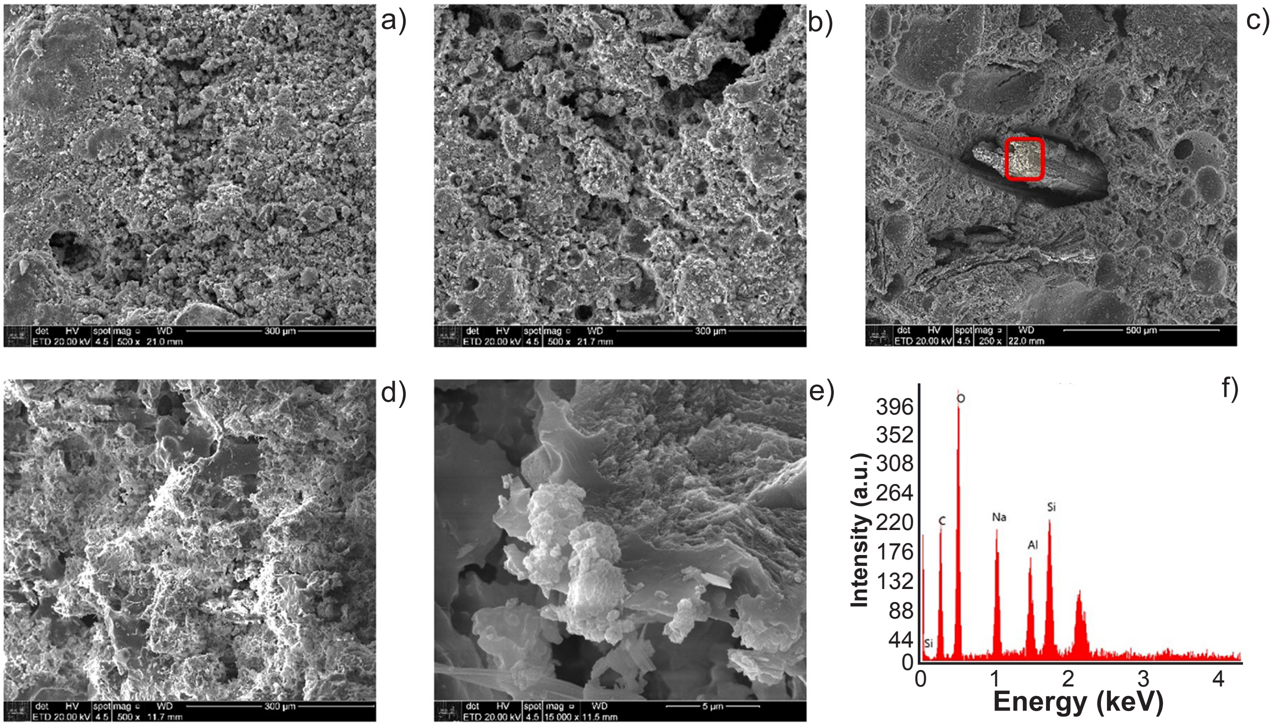

Figure 7: SEM micrographs of the samples (fraction of sawdust): a) C1 (0%); b) C1 (10%); c) C2 (20%); d,e) C1HT (0%) at different magnifications; and EDS spectrum (f) of the region indicated with a red square in (c).

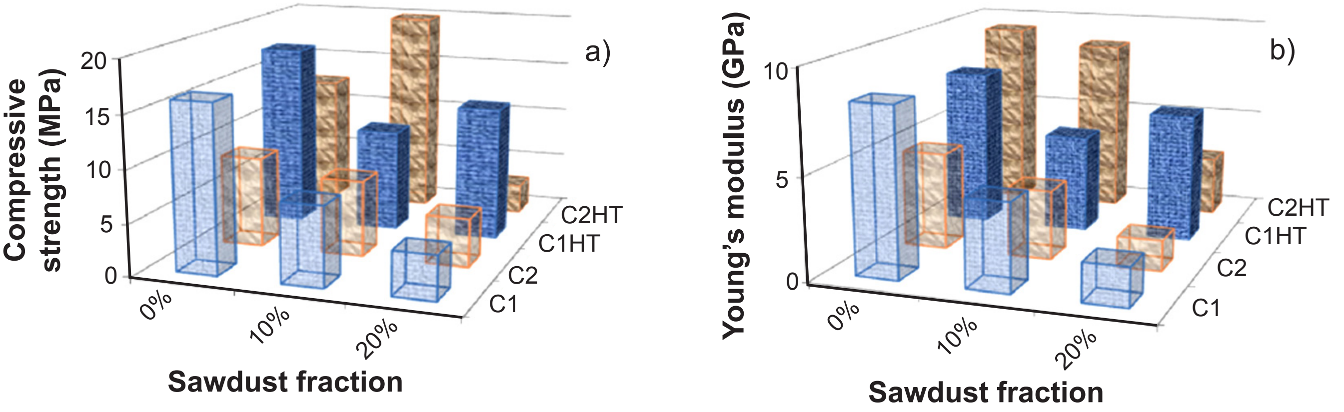

Figure 8: Cold compressive strength, CCS (a), and Young's modulus, E (b), for all samples before and after thermal treatment with different percentages of sawdust.

The mechanical properties of metakaolin-based geopolymers were evaluated before and after the sintering process. Before the heat treatment, the values ranged from 4.21 to 16.04 MPa (Fig. 8a) in agreement to a large variety of values found in the literature (0-132 MPa) [6, 13, 17, 19, 20]. However, it is important to point out that the final properties of geopolymers as compressive strength have a direct relationship with the synthesis conditions, calcination temperature of metakaolin, properties, proportions, and kinds of raw material, among others [20]. The increase in temperature of the geopolymers usually causes loss of compressive strength attributed to evaporation of free, chemically and physically bonded water in the geopolymeric structure. This 'vapor effect' is defined by the water pressure in the geopolymer reaching the maximum limit, causing shrinkage and cracks in the geopolymer matrix [13, 19]. However, in this study only C2HT composition (20% sawdust) showed loss of compressive strength (40%). All other formulations showed significant increases: 10% to 67% for C1 formulations, while composition 2 showed an increase of 45% and 172% for C2HT (0%) and C2HT-10% sawdust, respectively. Probably, the expected reduction of mechanical properties associated to the vapor generation effect and to the wood (sawdust) thermal decomposition was by far compensated by both the sintering process and the high shrinkage of materials. Another factor that worked to decrease the mechanical compressive strength of C2HT compared with C1HT came from the volumetric transformation of low quartz inversion around 573 °C. These results are relevant when compared with values of geopolymers from metakaolin or fly ash sintered between 300 and 1000 °C, because in these cases there was always a significant loss of mechanical properties [13, 19]. The Young's modulus of geopolymers followed the general trend of compressive strength (Fig. 8b). Further modifications were observed in C2HT because for this formulation the heat treatment caused a significant increase in such parameter, especially for 0% and 10% of sawdust. In general, the values found in this work were slightly higher (1.5 to 9.4 GPa) than those found in the literature (0.9-7.0 GPa) [9, 10], also confirming the high rigidity of the synthesized materials.

CONCLUSIONS

In the system Na_2O-Al_2O_3-SiO_2, different compositions were obtained, in order to attempt the Davidovits molar ratios and special ternary phase compositions, aiming to produce geopolymers with low sintering temperature. The sawdust addition, the chemical composition, and the thermal treatment produced a direct impact on final properties of geopolymers. As expected, the increase of apparent porosity decreased the cold compressive strength values. However, the prepared compositions of Na_2O-Al_2O_3-SiO_2 presented high mechanical properties even after calcination with higher proportions of the porous agent, showing that several applications might be explored with these samples, such as the production of special geopolymer panels to control heat transferring and noise in building construction walls and slabs.

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