

Physico-mechanical properties of geopolymers prepared with the partial incorporation of ceramic wastes

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Abstract

The utilization of waste or by-products in geopolymers is an effective strategy that contributes to the development of more sustainable ceramics. The present study aimed to evaluate the physico-mechanical properties of compositions prepared by partially replacing aluminosilicate precursors (metakaolin or calcined diatomite) with solid wastes (granite, roof tile chamotte, or glass powder) at contents of 10, 20, and 40 wt%. Geopolymers were synthesized by blending the solid raw materials (precursor+wastes) with an alkaline activating solution comprising NaOH and colloidal silica suspension. The samples were cured at 40 °C for 24 h, and the following analyses were conducted: elastic modulus, compressive strength, porosity, density, X-ray diffraction, and Fourier-transform infrared spectroscopy measurements. The results demonstrated that the formulation containing 10 wt% of chamotte exhibited the best performance, showing a remarkable mechanical strength of 31.7 MPa after one day of curing. Therefore, by incorporating waste materials into geopolymers, not only can the environmental impact be minimized, but it also presents an opportunity to utilize resources that would otherwise go to waste.

Keywords: geopolymers, metakaolin, diatomite, solid wastes, properties.

INTRODUCTION

The generation, treatment, and proper disposal of waste remain ongoing challenges across various industrial sectors. However, ceramics offer a promising solution by harnessing their potential to incorporate solid waste as alternative raw materials in their formulations. One effective strategy is the utilization of industrial, agricultural, or municipal waste in the composition of geopolymers. By replacing thermally activated precursors with these materials, researchers and industries can contribute to reducing reliance on traditional raw materials and minimize the environmental impact of ceramic production. This approach aligns with the sustainable development goals advocated by the United Nations [1-3]. However, the type and quantity of materials selected have a significant influence on the processing, phase transformations, and properties of the resulting products. Consequently, the performance of geopolymers is contingent upon the synthesis procedures and reaction products, which, in turn, rely on the nature of the chosen precursor components [4, 5].

By appropriately combining selected raw materials, it is possible to obtain more sustainable ceramics and construction products. For instance, Azevedo et al. [6] highlighted the potential use of brick waste as a geopolymeric precursor for tile manufacturing. Mendes et al. [7] demonstrated the effective utilization of chamotte and glass waste to produce geopolymers with suitable mechanical strength.

Furthermore, Kamseu et al. [8] confirmed the feasibility of employing marble waste and rice husk ash in the synthesis of geopolymer cement. In this context, this study evaluated the physico-mechanical behavior of geopolymeric compositions by partially replacing aluminosilicate precursors (metakaolin or calcined diatomite) with waste powders, such as granite residue, roof tile chamotte, or flat glass waste, at concentrations of 10, 20, and 40 wt%.

EXPERIMENTAL

The selected precursors for the preparation of geopolymeric matrices were: 1) commercial metakaolin (MK, $\text{SiO}_2/\text{Al}_2\text{O}_3 \sim 1.66$ mol/mol, Metacaulim HP, Metacaulim do Brasil, Brazil) and 2) diatomite calcined at 800 °C/2 h (referred to as D-800, MMK-325, $\text{SiO}_2/\text{Al}_2\text{O}_3 \sim 2.25$ mol/mol, Minasolo, Brazil). To partially replace the thermally activated precursors with ceramic waste, granite powder, roof tile chamotte, and flat glass powder were selected for recycling purposes. This recycling methodology was only applied to the reference composition with higher mechanical performance. Geopolymeric compositions were prepared by partially replacing the aluminosilicate precursor with the selected waste materials at contents of 10, 20, and 40 wt%. Table I shows the chemical composition of the raw materials used in this study.

The geopolymers (with and without ceramic waste) were synthesized using an activating solution with a silica modulus of approximately 1.40, obtained by combining a 12 M NaOH aqueous solution with a colloidal silica suspension (CS, Levasil CS40-120, Nouryon, Brazil), following the methodology proposed in [9]. Precursors, P,

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Table I - Chemical composition of the selected raw materials.

Raw material	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	Fe ₂ O ₃	TiO ₂
Metakaolin	46.89	48.12	-	0.95	0.64	0.08	3.32	-
Diatomite	54.06	40.86	0.02	3.43	0.53	0.31	0.79	-
Granite	72.58	16.57	1.27	7.37	0.24	1.00	0.97	-
Roof tile chamotte	62.74	24.23	0.23	4.23	2.01	0.43	5.45	0.68
Glass powder	77.02	20.48	1.70	0.45	-	0.30	0.05	-

and activating solutions, AS (with a P/AS mass ratio of 0.8), were processed in a high-energy mixer (Solotest, Brazil), and the resulting pastes were molded under vibration for 1 min. Subsequently, these samples were wrapped in plastic films and kept at 40 °C for 24 h.

The prepared geopolymers underwent the following characterization tests: 1) crushing strength in cylindrical samples (40x40 mm, ASTM C133-97) using a universal testing machine (DL10000, Emic, Brazil); 2) apparent porosity (PA) based on the Archimedes principle using water as the immersion liquid (ASTM C830-00); 3) density determined via helium pycnometry (AccuPyc 1330, Micromeritics); 4) total porosity calculated as indicated in [10]; and/or 5) elastic modulus measurements at room temperature using prismatic specimens (150x25x25 mm) and the impulse excitation technique (ATCP, Sonelastic, Brazil; ASTM E1876-15). Powdered samples of precursors and geopolymers were also analyzed using: 1) Fourier-transform infrared spectroscopy (ATR-FTIR, Spectrum 3, PerkinElmer; 4000-400 cm⁻¹, 20 scans, and 4 cm⁻¹ resolution); and 2) X-ray diffraction [XRD, D8 Focus, Bruker; CuK α radiation (λ =1.5418 Å), with a nickel filter, 40 mA, 40 mV, and a step size of 0.02°].

RESULTS AND DISCUSSION

The X-ray diffractograms presented in Fig. 1a indicate that the utilized metakaolin (MK) was predominantly amorphous but displayed characteristic peaks associated with quartz and kaolinite crystals. The presence of kaolinite in the MK is a result of incomplete dehydroxylation during the formation of the metastable metakaolin phase. On the other hand, the diatomite calcined at 800 °C/2 h (D800) contained crystalline phases of quartz and illite. Upon geopolymerization, the investigated compositions exhibited a semi-crystalline nature (Fig. 1a), with the MK-based composition (G-MK) exhibiting a typical profile of a geopolymer comprising an amorphous matrix with residual crystalline phases from the precursor [9, 11, 12]. On the other hand, the formulation containing diatomite, G-D800, presented a lower degree of geopolymerization, as indicated by the absence of the characteristic amorphous band observed in the XRD patterns of these materials. This can be attributed to the highly crystalline nature of D800, where the present phases did not actively contribute to the

polycondensation process. Consequently, the dominant crystalline phases of this precursor remained unchanged, resulting in a sample with a semi-crystalline character (G-D800). Diatomite (with or without calcination) is not commonly considered a geopolymeric precursor, and its chemical-structural characteristics vary depending on the mineral's origin [13, 14]. However, under the conditions evaluated in this study, rigid samples with adequate mechanical strength could still be obtained. Since an activating solution containing dissolved reactive silica was used, these results suggest that the solubility of aluminum species from the metastable phases of calcined diatomite may have been accelerated in a highly alkaline environment.

The investigated compositions displayed characteristic FTIR spectra of geopolymers (Fig. 1b). The presence of water used in the processing, which was physically trapped within the porous structure and/or adsorbed on the particle surface, is indicated by the bands observed at approximately 3365 and 1643 cm⁻¹, corresponding to the stretching and bending vibrations of O-H bonds, respectively [15]. The occurrence of the geopolymerization process was confirmed by the slight shift of bands located around 1033 cm⁻¹ (T-O-T vibrations in the precursor, where T= Si or Al) to values of ~983 cm⁻¹ [11]. The bands in the wavelength range of 1000-400 cm⁻¹ corresponded to asymmetric stretching vibrations of Si-O-Si and Si-O-Al bonds [16].

To evaluate the impact of the resulting phases on the performance of geopolymers, physico-mechanical tests were conducted on cured samples (maintained at 40 °C for 24 h). Fig. 2a illustrates that Young's modulus of the tested geopolymers remained relatively stable for a period of 15 days after the curing process. Notably, pastes prepared with MK presented higher stiffness (E ~9.17-9.31 GPa) compared to those based on D800 (E ~8.47-8.90 GPa). This can be attributed to the combined properties of the intrinsic phases (crystalline and/or amorphous) present in the resulting microstructure, as well as the physical characteristics (density and porosity) and macroscopic features (surface finish) of the samples obtained. The G-D800 composition exhibited higher density and lower apparent porosity (d =1.51 g/cm³ and PA=27.4%) in comparison to G-MK (d =1.45 g/cm³ and PA=32.2%, Fig. 2b). However, despite these differences, the geopolymer containing MK demonstrated superior mechanical

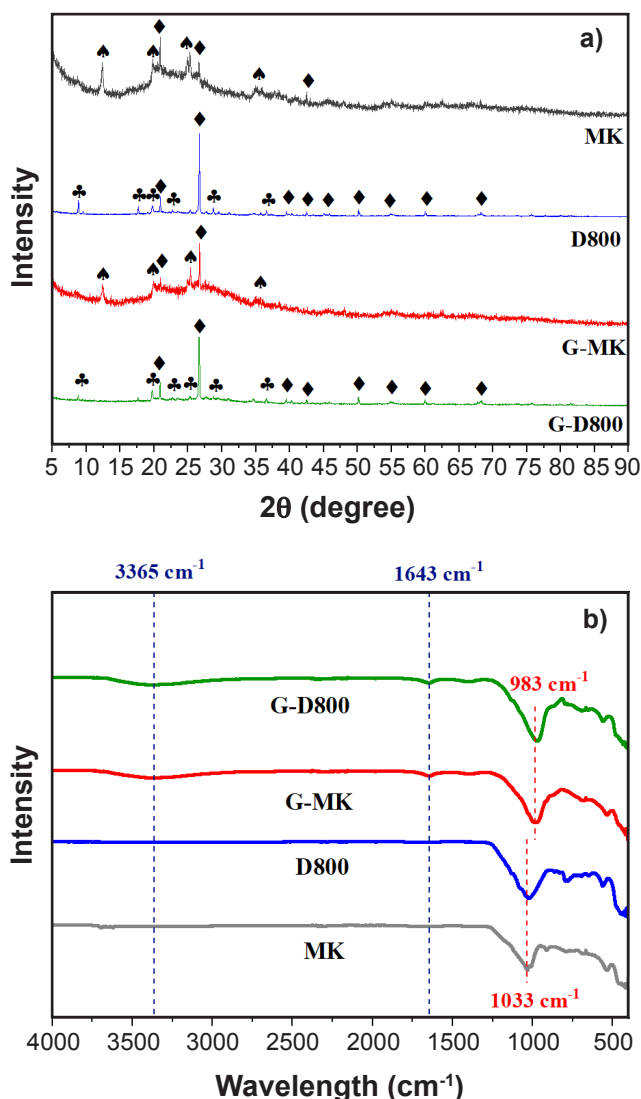


Figure 1: Structural features of the selected precursors [metakaolin (MK) and diatomite calcined at 800 °C (D800)] and their respective geopolymers: a) XRD patterns [♠ kaolinite - $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (ICSD 68698); ♦ quartz - SiO_2 (ICSD 18172); ♣ illite - $\text{K}(\text{Al}_4\text{Si}_2\text{O}_9)(\text{OH})_3$ (ICSD 90144)]; and b) ATR-FTIR spectra.

performance (Fig. 2c). This could be attributed to the lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (MK-based ~ 2.19 < D800-based ~ 3.59) and the higher density of strong Si-O-Si bonds present in this composition. As a result, the G-MK paste was selected for the implementation of the waste recycling strategy involving granite waste, tile chamotte, and flat glass powder.

Physico-mechanical tests were conducted to evaluate the performance of geopolymers based on metakaolin and incorporating varying amounts of solid waste. Fig. 3 presents the results of the evaluated physical properties. The type and amount of incorporated ceramic waste did not have a major influence on the apparent density of the obtained specimens (Fig. 3a). However, these samples showed significantly lower values of apparent porosity compared to the reference composition (waste-

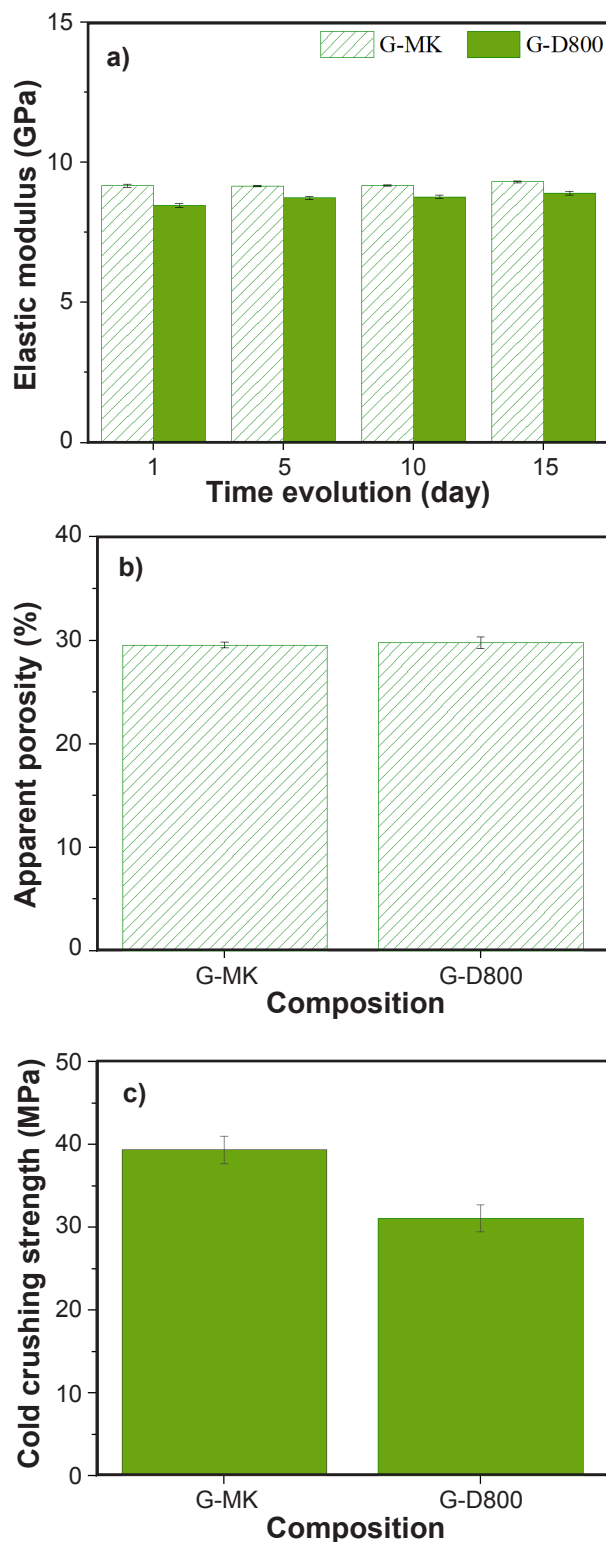


Figure 2: Physico-mechanical properties of the geopolymeric pastes (G-MK and G-D800) after curing at 40 °C for 24 h: a) elastic modulus evolution; b) apparent porosity; and c) crushing strength.

free, G-MK, Fig. 3b), indicating a tendency of the new compositions to consolidate porous structures (Fig. 3c), with a predominance of closed pores. As a result, the waste-containing geopolymers exhibited low water

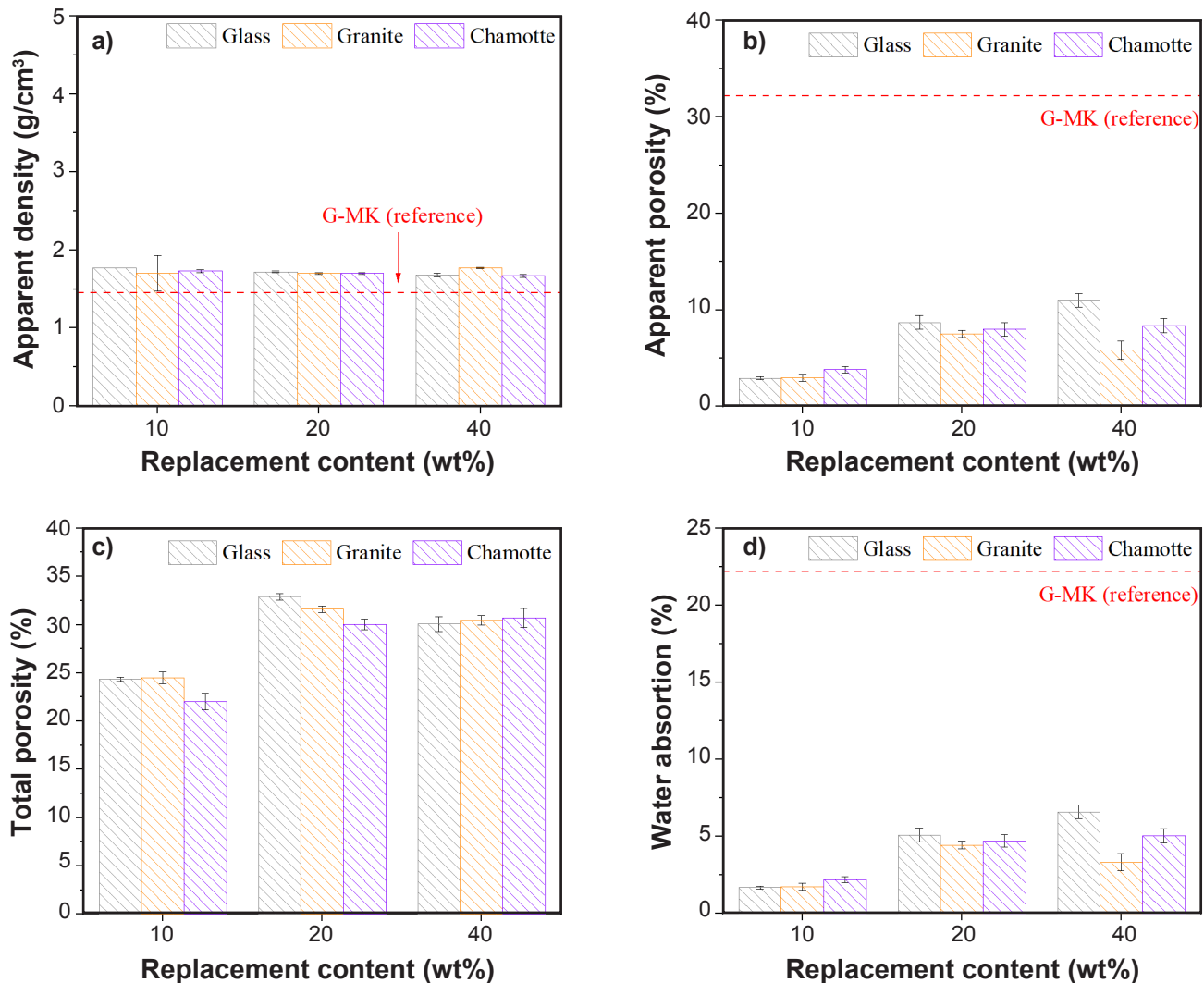


Figure 3: Effect of type and content of ceramic waste on the physical properties of geopolymeric composites obtained after 24 h of curing at 40 °C: a) apparent density; b) apparent porosity; c) total porosity; and (d) water absorption.

absorption (Fig. 3d) due to the limited presence of open and interconnected pores. It is important to highlight that the formulations with a 10% replacement of metakaolin with waste displayed lower porosity (Fig. 3c).

Despite the new formulations evaluated displaying higher density than G-MK (Fig. 3a), the mechanical strength of these materials decreased by up to 47.4% with increasing waste incorporation in the tested system (Fig. 4a). This behavior could be attributed to variations in the extent of the geopolymerization process and the formation of different reaction products with specific properties. Although the presence of waste increases the overall $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of the compositions, diffractograms of the selected wastes (results not shown here) revealed that, except for the flat glass powder, these materials are primarily crystalline and composed predominantly of inert phases that do not contribute to the geopolymerization process (such as quartz, hematite, and mica). This limitation restricts the amount of gel that

can be formed, and the number of strong Si-O-Si bonds generated in the polymeric structure. Consequently, the chamotte and granite may have primarily acted as fillers in the formulation of the geopolymer pastes [17]. The geopolymers that presented higher mechanical strength were those characterized by lower total porosity and a lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio, as indicated by the surface map shown in Fig. 4b. The formulation incorporating a 10 wt% replacement of metakaolin with chamotte exhibited a more promising mechanical performance, with the produced samples achieving values approaching 31.7 MPa after one day of curing.

CONCLUSIONS

This study investigated the physico-mechanical behavior of geopolymeric compositions by partially replacing the aluminosilicate precursor (metakaolin or calcined diatomite) with granite waste, tile chamotte, or

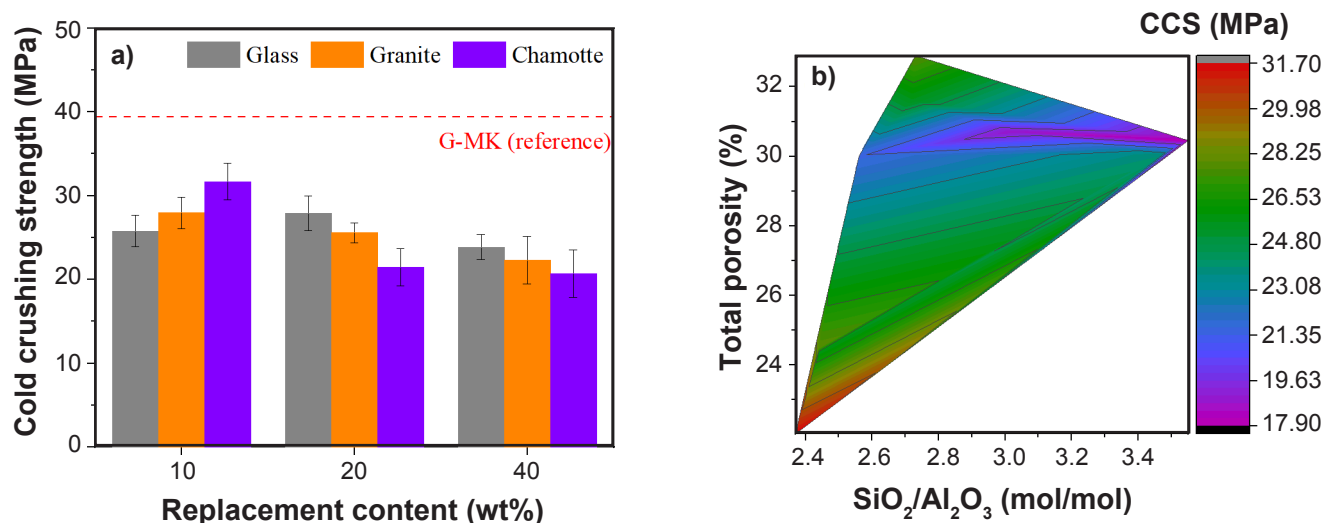


Figure 4: Mechanical performance of the geopolymeric composites obtained after 24 h of curing at 40 °C: a) effect of type and content of ceramic waste on cold crushing strength (CCS); b) dependence of CCS on total porosity and $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of the compositions.

flat glass waste powders at varying contents of 10, 20, and 40 wt%. Based on the obtained results, the following conclusions can be made: i) the chosen precursors, metakaolin and calcined diatomite, proved to be viable options for producing geopolymers with high mechanical performance in the early stages; however, metakaolin-based geopolymers exhibited slightly better mechanical strength than those based on diatomite; this difference can be primarily attributed to variations in the amorphicity/reactivity of the precursors and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in the compositions, with metakaolin having a lower ratio compared to calcined diatomite; ii) the inclusion of waste materials in the geopolymeric paste containing metakaolin resulted in a reduction of up to 47.4% in the mechanical strength of the produced specimens when compared to the reference composition; iii) among the different formulations, the composition that replaced 10% of metakaolin with chamotte demonstrated a more promising mechanical strength performance; after one day of curing, this particular composition achieved crushing strength values close to 31.7 MPa. Hence, adopting the use of waste as alternative raw materials in geopolymers represents a step towards a circular economy, where waste is transformed into valuable resources. This approach not only enhances the sustainability of ceramic manufacturing but also contributes to the broader goals of achieving a more resource-efficient and environmentally conscious society.

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