

# Recycling of roof tile waste in the manufacturing of high-temperature metakaolin-based geopolymer composites

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## Abstract

The possibility of recycling solid wastes in the production of geopolymers and advanced ceramic products has received special attention recently. This work investigated the feasibility of replacing a high amount (70-90 wt%) of metakaolin with roof tile waste (CW) in the production of Na-geopolymer composites. Additionally, the influence of this alternative material, in the phase transformations and properties evolution (elastic modulus, compressive strength, porosity, density, and linear shrinkage) of the prepared compositions after distinct thermal treatments (40-1000 °C) was evaluated. The results showed that the incorporation of CW powder into the geopolymeric compositions enhanced their thermal and mechanical properties up to 1000 °C. The best performance was reached when using 80 wt% of the selected waste, which led to ceramic specimens with high crystallinity (presenting quartz, hematite, and albite phases), compressive strength (39.6 MPa), suitable linear shrinkage (-7.4%), and improved thermal stability (without visual cracks) after firing at 1000 °C.

**Keywords:** recycling, ceramic wastes, geopolymer composites, properties, phase evolution.

## INTRODUCTION

Geopolymers are ceramic-like inorganic polymers produced through chemical reactions between a highly reactive aluminosilicate source (metakaolin, slag from the steelmaking process, fly ash, etc.) and an alkaline liquid reagent, which give rise to final products (well-polymerized nanoparticles) that may present sustainable benefits as well as outstanding mechanical, thermal and chemical properties [1-3]. When exposed to high temperatures, such materials may undergo several thermal phenomena, such as: i) dewatering; ii) crystallization and phase transformations; iii) liquid formation; and iv) sintering and densification [4, 5]. As a result, significant dimensional changes and cracks/flaws generation may be observed in geopolymer-based ceramics due to the mismatch in coefficient of thermal expansion (CTE) among the resulting phases (amorphous and/or crystalline ones) contained in their microstructure after heating treatments [6-8].

Nevertheless, geopolymer composites can have their thermal behavior engineered and optimized with the reinforcement of the resulting microstructure with organic or inorganic fibers, inorganic fillers, etc. [6, 8-13]. For example, Hemra and Aungkavattana [12] reported that 50 wt% of cordierite addition to a metakaolin-based matrix resulted in specimens with improved thermo-mechanical properties, as the prepared compositions kept their compressive strength values (19.8 MPa) even after 15 thermal shock cycles.

Wattanasiriwech et al. [13] stated that the replacement of fly-ash powder by 20-60 wt% of cordierite-mullite particles favored the development of ceramics with mechanical resistance around 15-20 MPa and suitable thermal stability up to 1000 °C. Lemougna et al. [14] investigated the addition of 67.5-79.5 wt% of spodumene tailings (ST) and glass wool (GW) to one-part metakaolin-based geopolymer composites. The authors observed that GW and ST-containing compositions presented thermal stability up to 500 and 1200 °C, respectively.

Some strategies have been proposed in the United Nations 2030 Agenda to promote sustainable consumption and production that can support the needs of the present and future generations. In this sense, the recycling of a wide range of ceramic wastes (e.g. red clay bricks, sanitary ware, roofing tiles, concrete, etc.), as low-cost alternative materials (precursors or fillers) for the design of sustainable geopolymer systems, is a good alternative to be explored [15-17]. Despite the continuous efforts to develop waste-based geopolymers [17] and incorporate recycled aggregates into geopolymer composites [18-21], few studies [14, 22, 23] have discussed the effects of temperature exposure and the benefits or drawbacks of adding high-contents (>40 wt%) of solid wastes to the formulations of such materials. In this context, this work evaluated the feasibility of replacing a high amount (70-90 wt%) of metakaolin with roof tile waste (CW) in the production of Na-geopolymer composites. Additionally, the influence of this alternative material in the synthesis, phase/bond changes, physico-mechanical properties, and dimensional stability of the designed composites were evaluated in a 40-1000 °C temperature range.

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## EXPERIMENTAL PROCEDURE

A clay-based roof tile waste (CW,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio  $\sim 4.40$ ,  $\text{SiO}_2=62.74$  wt%,  $\text{Al}_2\text{O}_3=24.26$  wt%,  $\text{Na}_2\text{O}=0.23$  wt%,  $\text{K}_2\text{O}=4.23$  wt%,  $\text{Fe}_2\text{O}_3=5.45$  wt%, and others=3.12 wt%) presenting density of  $2.73$  g/cm<sup>3</sup>, mean particle size=8.94  $\mu\text{m}$ , and quartz and hematite as main crystalline phases, was selected for the design of the geopolymer composites. Metakaolin (MK, kaolin calcinated at  $800$  °C/2 h,  $\text{SiO}_2/\text{Al}_2\text{O}_3 \sim 1.43$ ,  $d_{50}=6.87$   $\mu\text{m}$ , Minasolo, Brazil - additional data can be found elsewhere [7]) was selected as the precursor of the designed formulations. As pointed out in Table I, a reference geopolymer comprising only MK (CW-free) as the initial solid component, and three additional compositions considering the replacement of MK by 70, 80, or 90 wt% of CW, were evaluated. The geopolymers were synthesized using a reactive water glass ( $\text{Na}_2\text{O}-1.4\text{SiO}_2-15\text{H}_2\text{O}$ ) [7], based on a mix of NaOH pellets (NR-00660, Nox Lab Solutions, Brazil), colloidal silica suspension (Levasil CS40-125, Nouryon, Brazil; 40 wt%  $\text{SiO}_2$ , pH=10.3) and distilled water. Homogeneous and viscous pastes were prepared with the combination of solid particles (MK or MK/CW blends) and alkaline liquid reagent (water glass, Table I) in a high-energy planetary mixer [7]. The fresh mixtures were cast into cylindrical ( $\phi 40 \times 40$  mm) or prismatic ( $150 \times 25 \times 25$  mm) molds under vibration ( $\sim 100$  Hz) for 2 min. The prepared samples were wrapped with plastic film and kept at  $40$  °C for 12 h. After that, they were demolded and left resting at room temperature ( $\sim 25$  °C) for another 12 h. On the following day, the cured geopolymers were also thermally treated at  $800$  or  $1000$  °C for 2 h and using a heating rate of  $2$  °C/min.

The physico-mechanical properties of the evaluated geopolymer compositions were investigated, considering: i) Young's modulus (E) measurements to assess the stiffness evolution of prismatic cured samples ( $40$  °C/12 h) up to 16 days and using the impulse excitation technique (Sonelastic, ATCP, Brazil, ASTM E1876-15); ii) cold crushing strength (CCS) tests in cylindrical samples, using a universal mechanical testing machine (DL10000, Emic, Brazil) and according to ASTM C133-97; iii) apparent porosity (AP) and density (D) experiments based on Archimedes principle and using water as immersion liquid (ASTM C830-00); and/or iv) permanent linear change (PLC, ASTM C113-14) measurements of cured bar samples subjected to firing treatment at  $800$  or  $1000$  °C/2 h. A total

of five specimens were evaluated for each selected testing condition and the presented results are average values with their respective standard deviation. Furthermore, phase and bond transformations of the synthesized geopolymers were investigated by X-ray diffraction (XRD, D8 Focus, Bruker) with  $\text{CuK}\alpha$  radiation ( $\lambda=1.5418$  Å) using a nickel filter, 40 mA, 40 mV and step= $0.02^\circ$ , and Fourier-transform infrared spectroscopy (FTIR, Spectrum 3, PerkinElmer) with a universal attenuated total reflectance (ATR) sampling accessory, using  $4000-400$  cm<sup>-1</sup> wavenumber range, 20 scans and  $4$  cm<sup>-1</sup> resolution.

## RESULTS AND DISCUSSION

### *Structural characteristics and physico-mechanical properties after curing step*

XRD and ATR-FTIR analyses were carried out to evaluate the influence of the selected ceramic waste on the structure of the designed geopolymers. Fig. 1a confirms the crystalline features of plain ceramic roof tile waste (CW) and the resulting composite containing 80 wt% of this material (80CW), where quartz, hematite ( $\text{Fe}_2\text{O}_3$ ), and microcline ( $\text{KAlSi}_3\text{O}_8$ ) were the main identified phases. On the other hand, metakaolin (MK) and the reference geopolymer matrix (CW-free, 100MK) were comprised of an amorphous structure containing a limited amount (small peaks) of crystalline compounds, such as quartz, muscovite, and  $\text{NaAl}_3\text{Si}_3\text{O}_{11}$ . The latter is derived from the polycondensation reaction in 100MK composition during the geopolymerization (Fig. 1a). ATR-FTIR profiles (Fig. 1b) highlighted the partial contribution of the roof tile waste in the geopolymerization process, which induced the shift of the bands located at  $1054$  cm<sup>-1</sup> (CW) to  $975$  cm<sup>-1</sup> (80CW), as they represent Si-O-T bonds (T= Si or Al) [7, 24, 25]. However, the high crystallinity degree and inert mineralogical composition of CW inhibited the preparation of a composition based on 100 wt% of this material (totally replacing MK) due to the low extent of the geopolymerization reactions, resulting in samples that did not set along 24 h at  $40$  °C. Consequently, 90CW samples also presented low elastic modulus (E  $\sim 5.5$  GPa, Fig. 2a) and crushing strength values (CCS  $\sim 8.1$  MPa, Fig. 2b) after curing. Besides that, such material partially dissolved when placed in contact with water during the apparent porosity measurements, which confirmed the incomplete geopolymerization of this

Table I - Formulation (wt%) of the evaluated geopolymer composites.

Composition	Metakaolin - MK	Ceramic roof tile waste - CW	Water glass	$\text{SiO}_2/\text{Al}_2\text{O}_3^*$	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3^*$
100MK	100	-	90.0	2.09	0.42
70CW	30	70	46.8	2.51	0.73
80CW	20	80	44.9	2.94	1.06
90CW	10	90	44.0	4.29	2.07

\*: overall molar ratio of the geopolymers (MK+waterglass).

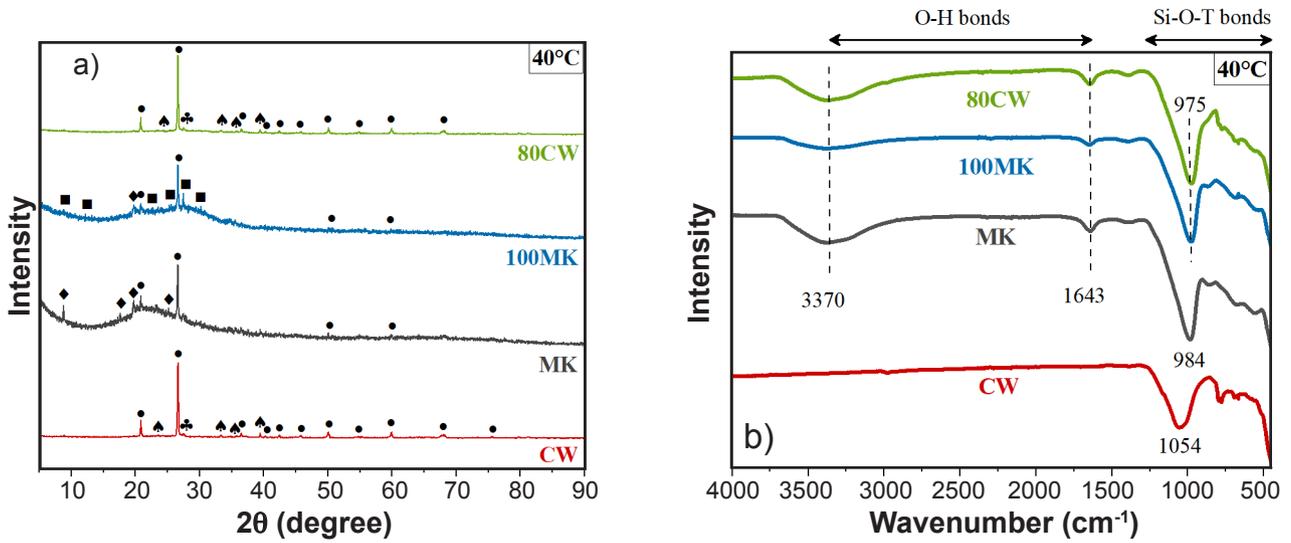


Figure 1: XRD profiles (a) and ATR-FTIR spectra (b) of the geopolymers (100MK and 80CW) obtained after curing (40 °C/12 h). T= Si or Al; ● quartz (SiO<sub>2</sub>, ICSD 01-078-1252); ◆ muscovite [KAl<sub>3</sub>Si<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub>, ICDD 01-075-0948]; ■ NaAl<sub>3</sub>Si<sub>3</sub>O<sub>11</sub> (ICDD 00-046-0740); ◆ microcline (KAlSi<sub>3</sub>O<sub>8</sub>, ICDD 00-001-0705); ◆ hematite (Fe<sub>2</sub>O<sub>3</sub>, ICDD 01-079-1741).

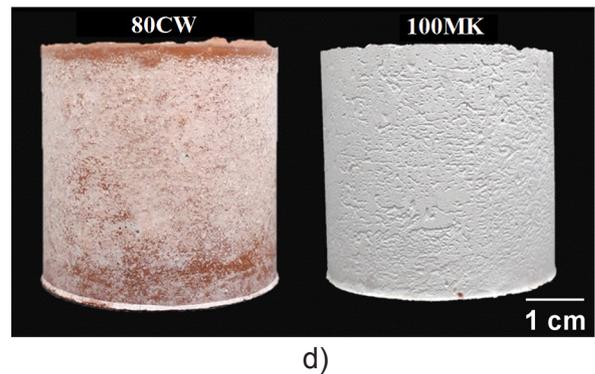
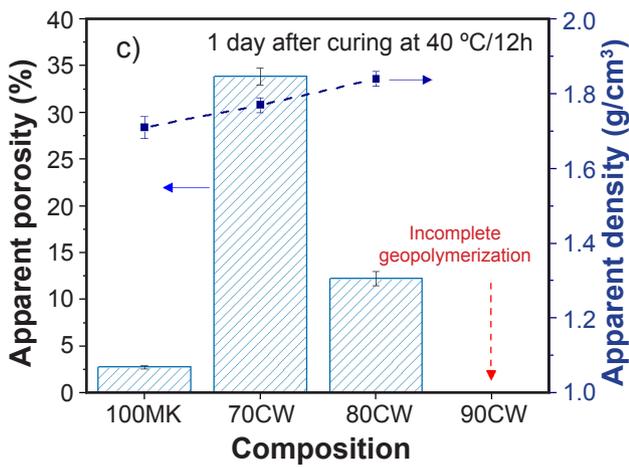
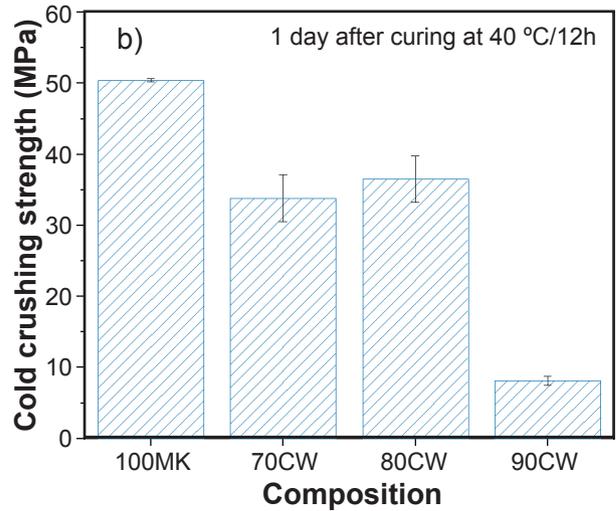
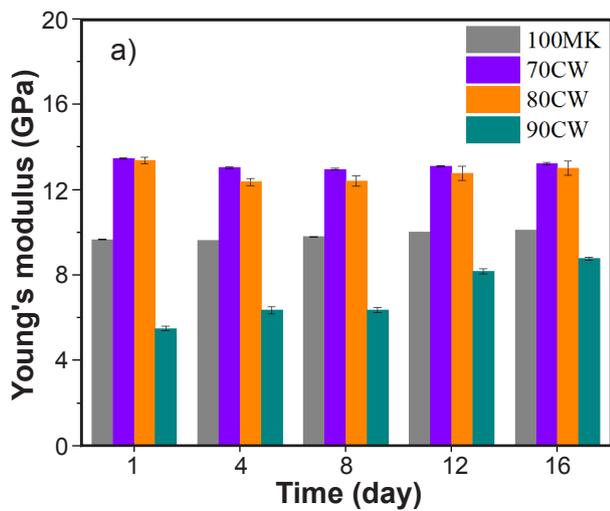


Figure 2: Physico-mechanical properties of the cured geopolymers (40 °C/12 h): a) Young's modulus (E) as a function of time; b) cold crushing strength; c) apparent porosity and density; and d) images of the geopolymer samples (100MK and 80CW) after the demolding step.

composition (90CW, Fig. 2c).

Composites with suitable physico-mechanical properties

could be obtained when replacing 70 and 80 wt% of metakaolin by roof tile waste (Fig. 2). The good performance

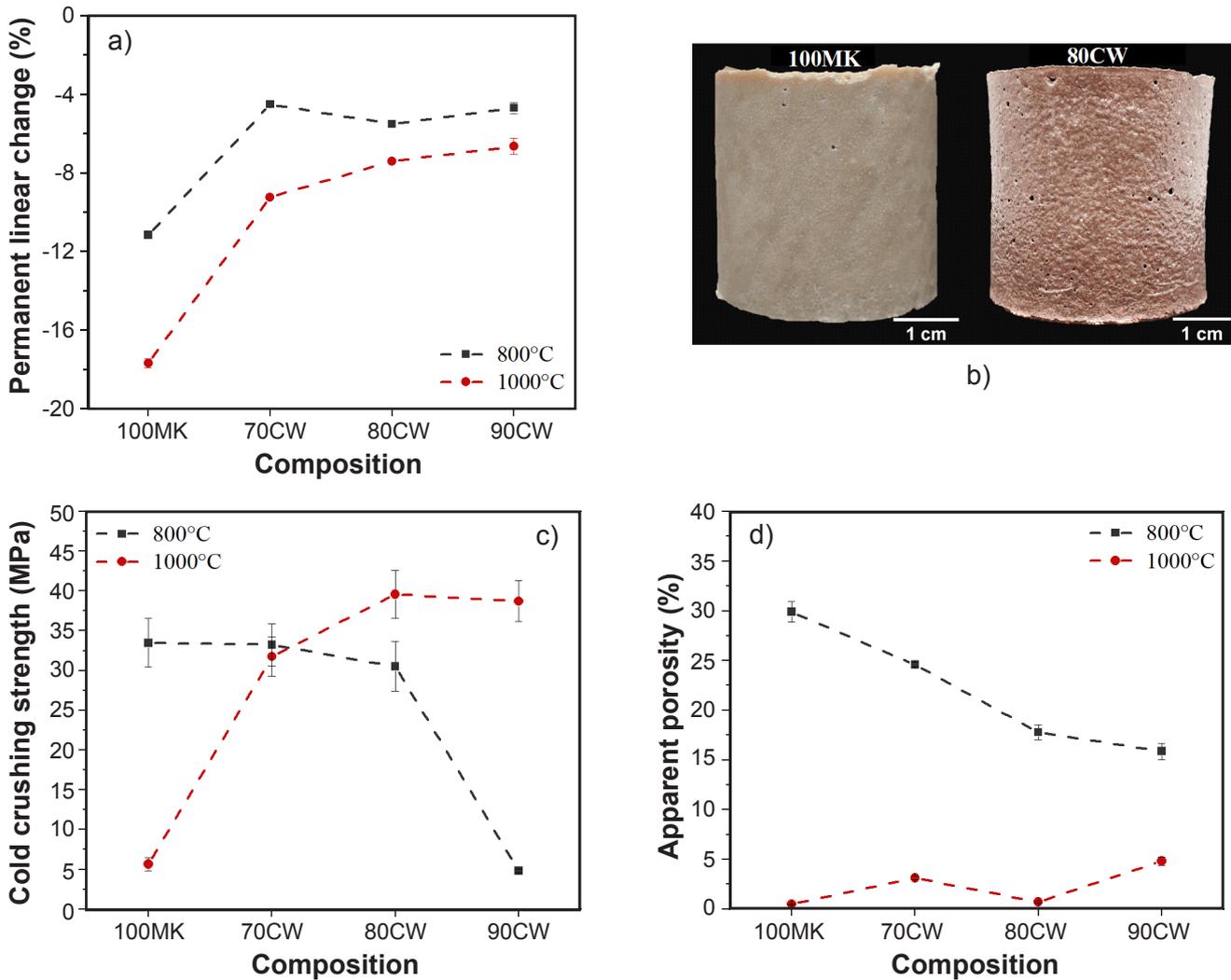


Figure 3: Physico-mechanical properties of the prepared geopolymer composites after firing step at 800 or 1000 °C for 2 h: a) permanent linear change (PLC); b) images of 100MK and 80CW samples after firing at 1000 °C/2 h; c) cold crushing strength (CCS); and d) apparent porosity (AP).

of 70CW and 80CW formulations might be related to: i) the high binding action of the metakaolin-based gel phase, that led to a good cohesion between this compound and the ceramic waste fine particles; and ii) the reduced amount of liquid reagent required during the processing of CW-containing compositions (Table I), as this fact induced some changes in the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  ratio [26, 27]. Consequently, 80CW geopolymer composite showed enhanced stiffness (elastic modulus  $\sim 13.4$  GPa), cold crushing strength (CCS  $\sim 36.5$  MPa), apparent porosity and density (AP  $\sim 12.2\%$  and  $D \sim 1.84$  g/cm<sup>3</sup>, respectively) when compared to 70CW and 90CW compositions. Nevertheless, the reference material (100MK) still presented the best mechanical performance among the analyzed formulations (Fig. 2b, CCS  $\sim 50.4$  MPa) due to the low apparent porosity (2.75%) of the obtained samples (Fig. 2c) and the high density of strong Si-O-Si bonds (Fig. 1b) contained in this microstructure. Fig. 2d also highlights the differences in the surface finishing of 100MK and 80CW samples after the demolding step.

#### Properties of the designed geopolymer composites after firing

Fig. 3a points out that the addition of the ceramic waste to the designed compositions helped adjust the linear shrinkage of the specimens fired up to 1000 °C (changing PLC values from -17.7% to -6.7%). Such a behavior can be associated with the presence of CW particles, as they can favor a better accommodation of the formed liquid phase, and the suitable compatibility between the geopolymeric matrix and this solid waste under the evaluated conditions [7, 28]. The fired samples were also macroscopically uniform and without cracks on their external surfaces, as shown in Fig. 3b.

Distinct trends were identified when analyzing the cold crushing strength behavior of 100MK and 90CW (Fig. 3c). After subjecting the metakaolin-based formulation (100MK) to a heating treatment up to 800 °C, a significant decay of the samples' mechanical strength (33.5 MPa, Fig. 3c) could be detected when compared to the results obtained after

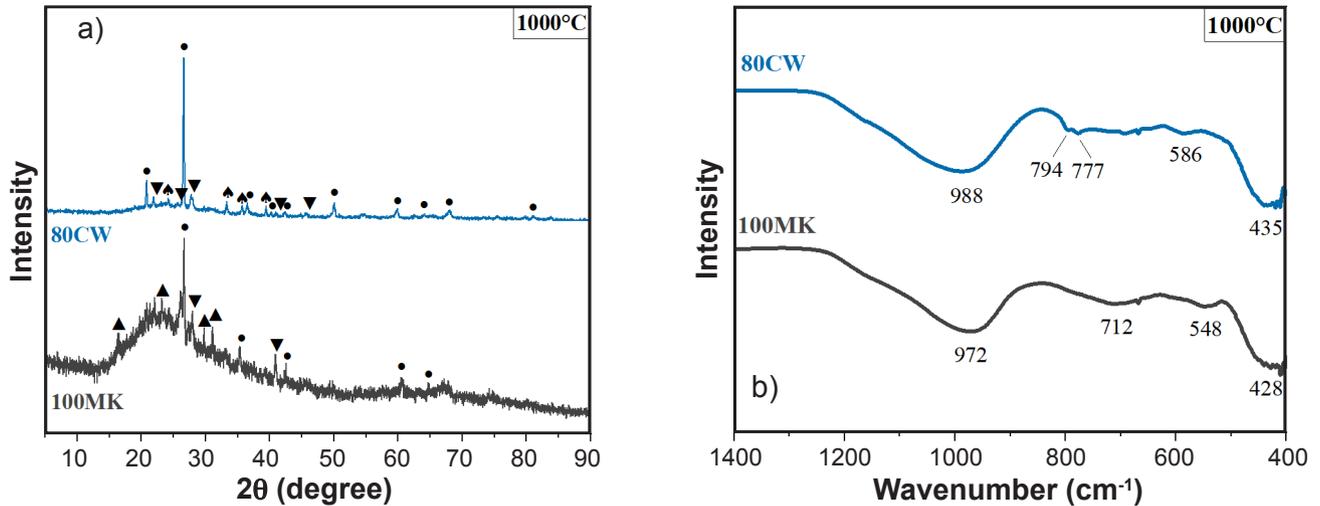


Figure 4: XRD profiles (a) and ATR-FTIR spectra (b) of 100MK and 80CW geopolymers obtained after firing at 1000 °C for 2 h. ● quartz ( $\text{SiO}_2$ , ICDD 01-078-1252); ♠ hematite ( $\text{Fe}_2\text{O}_3$ , ICDD 01-079-1741); ▼ albite ( $\text{NaAlSi}_3\text{O}_8$ , ICDD 01-071-1153); ▲ mullite ( $\text{Al}_{4.984}\text{Si}_{1.016}\text{O}_{9.508}$ , ICDD 01-079-1451).

Table II - Cold crushing strength of metakaolin-based geopolymer composites after firing the samples at 800 or 1000 °C.

Reinforcement	Crushing strength (MPa)		Ref.
	800 °C	1000 °C	
70 wt% of roof tile waste (CW)	33.2	31.8	This study
80 wt% of roof tile waste (CW)	30.5	39.6	
20-60 wt% of cordierite-mullite*	10-15	15-20	[13]
~33.3 wt% of chamotte	-	19.82	[21]
50 wt% of sand	-	4.82	[21]
15 vol% of refractory brick+1 vol% of ceramic fiber	<20	<20	[6]
79.5 wt% of spodumene tailing	-	<35	[23]
50 wt% of cordierite	24.9	-	[12]

\* fly-ash-based.

curing (50.4 MPa, Fig. 2b). Additionally, the geopolymer matrix of this composition was partially converted into a liquid phase when heated up to 1000 °C, which induced a further crystallization of new phases with different structural and thermal features (e.g., albite and mullite, Fig. 4a) and the breaking and/or formation of T-O-T bonds (T= Si or Al, Fig. 4b) [7, 29, 30] in the resulting microstructure. Such transformations led to 100MK specimens with complex microstructures, presenting significant linear shrinkage (Fig. 3a), containing mainly closed pores (as the measured apparent porosity was nearly close to 0%, Fig. 3d) and showing a major drop of their CCS values (changing from 33.5 to 5.6 MPa, Fig. 3c) after firing at 1000 °C for 2 h. On the other hand, the incomplete geopolymerization in 90CW composite resulted in samples with reduced crushing strength after firing at 800 °C (CCS ~4.8 MPa, Fig. 3c), whereas a significant increase of this property (38.7 MPa) was verified after the sintering and densification process of such material at higher temperature (1000 °C). The incorporation of 70 and 80 wt% of the roof tile waste into

the compositions did not significantly affect the mechanical behavior of the geopolymeric matrix (Fig. 3c), and CCS values ranging from 33.5 MPa (70CW) to 30.5 MPa (80CW) could be obtained after the thermal treatment at 800 °C.

Complementary XRD and ATR-FTIR analyses (Fig. 4) showed that 80CW composite did not present major changes in its mineralogical composition (presenting only low-intensity peaks of albite phase combined with hematite and quartz, Fig. 4a) and in Si-O-T bonds (T= Si or Al, located in the wavenumber range around 1000-400  $\text{cm}^{-1}$ , Fig. 4b) after firing at 1000 °C/2 h. Such results confirmed the thermal stability of this material. As indicated in Table II, 70CW and 80CW compositions showed improved and/or similar mechanical performance to other metakaolin-based geopolymeric composites obtained after thermal treatments at 800 or 1000 °C. Such results point out the feasibility of recycling a high amount of the selected roof tile waste in new ceramic products, which may be an alternative manner to promote suitable disposal of this solid waste and allow the development of more sustainable geopolymers.

## CONCLUSIONS

The feasibility of replacing a high amount (70-90 wt%) of metakaolin with roof tile waste (CW) in the production of Na-geopolymer composites was addressed. Based on the obtained results, the following conclusions can be drawn: i) the selected CW proved to be a good material for the design of geopolymer composites with suitable green mechanical strength and improved thermal stability; ii) the reference composition (100MK, waste-free and metakaolin-based geopolymer) presented various phase transformation during heating up to 1000 °C, resulting in liquid phase and crystallization of new phases with different structural and thermal features (e.g., albite and mullite) in the resulting microstructure; therefore, the fired samples showed significant linear shrinkage and a major drop of their mechanical strength (cold crushing strength values varying from 33.5 to 5.6 MPa, after firing at 1000 °C for 2 h); on the other hand, the geopolymer composites containing 70 or 80 wt% of the roof tile waste showed no significative phase/bond changes as a function of temperature, leading to specimens with higher crystallinity (presence of quartz, hematite, and albite in the sintered structure) and improved performance; iii) the incorporation of 80 wt% of the selected ceramic waste into the designed Na-geopolymer proved to be the optimum content to obtain composites with improved crushing strength (CCS ~39.6 MPa), low dimensional changes (PLC ~-7.4%) and high crack resistance (samples with smooth surface and no cracks) after firing at 1000 °C for 2 h; and iv) the recycling of ceramic roof tile waste was successfully achieved in this study, and such strategy may help to mitigate the environmental implications related to the generation of similar solid wastes as well as improve the development of more sustainable geopolymers.

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## REFERENCES

- [1] J. Davidovits, *J. Ceram. Sci. Technol.* **8** (2017) 335.
- [2] P. Duxson, A. Fernández-Jiménez, J.L. Provis, G.C. Lukey, A. Palomo, J.S.J. van Deventer, *J. Mater. Sci.* **42** (2007) 2917.
- [3] S. Qaidi, A. Yahia, B.A. Tayeh, H. Unis, R. Faraj, A. Mohammed, *Mater. Today Sustain.* **20** (2022) 100240.
- [4] P. Duxson, G.C. Lukey, J.S.J. van Deventer, *J. Non. Cryst. Solids* **352** (2006) 5541.
- [5] P. Duxson, G.C. Lukey, J.S.J. van Deventer, *J. Non. Cryst. Solids* **353** (2007) 2186.
- [6] S.A. Bernal, J. Bejarano, C. Garzón, R. Mejía de Gutiérrez, S. Delvasto, E.D. Rodríguez, *Compos. B Eng.* **43** (2012) 1919.
- [7] B.P. Bezerra, M.R. Morelli, A.P. Luz, *Constr. Build. Mater.* **364** (2023) 129989.
- [8] M. Lahoti, K.H. Tan, E.-H. Yang, *Constr. Build. Mater.* **221** (2019) 514.
- [9] G. Masi, W.D.A. Rickard, M.C. Bignozzi, A. van Riessen, *Compos. B Eng.* **76** (2015) 218.
- [10] J.L. Provis, A. Hajimohammadi, C.E. White, S.A. Bernal, R.J. Myers, R.P. Winarski, V. Rose, T.E. Proffen, A. Llobet, J.S.J. van Deventer, *Cem. Concr. Compos.* **36** (2013) 56.
- [11] L. Tian, X. Chen, X. Liu, H. Li, Y. Ge, *Constr. Build. Mater.* **373** (2023) 130755.
- [12] K. Hemra, P. Aungkavattana, *Adv. Powder Technol.* **27** (2016) 1021.
- [13] S. Wattanasiriwech, F.A. Nurgesang, D. Wattanasiriwech, P. Timakul, *Ceram. Int.* **43** (2017) 16063.
- [14] P.N. Lemougna, A. Adediran, J. Yliniemi, A. Ismailov, E. Levanen, P. Tanskanen, P. Kinnunen, J. Roning, M. Illikainen, *Cem. Concr. Compos.* **114** (2020) 103792.
- [15] N. Shehata, O.A. Mohamed, E.T. Sayed, M.A. Abdelkareem, A.G. Olabi, *Sci. Total Environ.* **836** (2022) 155577.
- [16] N. Shehata, E.T. Sayed, M.A. Abdelkareem, *Sci. Total Environ.* **762** (2021) 143166.
- [17] B. Ren, Y. Zhao, H. Bai, S. Kang, T. Zhang, S. Song, *Chemosphere* **267** (2021) 128900.
- [18] T. Kovářík, D. Rieger, J. Kadlec, T. Křenek, L. Kullová, M. Pola, P. Bělský, P. Franče, J. Říha, *Constr. Build. Mater.* **143** (2017) 599.
- [19] J. Tan, J. Cai, J. Li, *Constr. Build. Mater.* **341** (2022) 127771.
- [20] M. Panizza, M. Natali, E. Garbin, V. Ducman, S. Tamburini, *Constr. Build. Mater.* **264** (2020) 120158.
- [21] S. Dadsetan, H. Siad, M. Lachemi, O. Mahmoodi, M. Şahmaran, in "Handb. Sustain. Concr. Ind. Waste Manag.", F. Colangelo, R. Cioffi, I. Farina (Eds.), Woodhead Publ. (2022) 437.
- [22] A.C.C. Trindade, F.A. Silva, H.A. Alcamand, P.H.R. Borges, *Mater. Res.* **20** (2017) 265.
- [23] B. Coppola, C. Tardivat, S. Richaud, J.M. Tulliani, L. Montanaro, P. Palmero, *J. Eur. Ceram. Soc.* **40** (2020) 3314.
- [24] M. Lahoti, K.K. Wong, E.H. Yang, K.H. Tan, *Ceram. Int.* **44** (2018) 5726.
- [25] C. Bai, P. Colombo, *Ceram. Int.* **44** (2018) 16103.
- [26] M. Steveson, K. Sagoe-Crentsil, *J. Mater. Sci.* **40** (2005) 2023.
- [27] K. Juengsuwattananon, F. Winnefeld, P. Chindaprasirt, K. Pimraksa, *Constr. Build. Mater.* **226** (2019) 406.
- [28] A.M. Rashad, G.M.F. Essa, *Cem. Concr. Compos.* **111** (2020) 103617.
- [29] A. Buchwald, M. Vicent, R. Kriegel, C. Kaps, M. Monzó, A. Barba, *Appl. Clay Sci.* **46** (2009) 190.
- [30] D.S.S. Godinho, F. Pelisser, A.M. Bernardin, *Mater. Lett.* **311** (2022) 131625.

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