

Phase transformations and properties evolution of $\text{Ca}(\text{OH})_2$ containing geopolymers as a function of temperature

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Abstract

The composition-processing-structure-properties relationship of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ -based geopolymers containing calcium sources is critical for the design of enhanced ceramic binders. This work evaluated the addition of 1-6 wt% of calcium hydroxide (CH) to a metakaolin-based geopolymer (prepared with NaOH 12 M and colloidal silica suspension) and how it affected the performance of the prepared samples after thermal treatments up to 1000 °C. The setting time, mechanical strength, porosity, density, permanent linear change, and phase and bond type evolution of the specimens with temperature were analyzed. The incorporation of 3 or 6 wt% of CH into the designed composition led to a fast hardening of the mixtures (1.7 h), resulting in geopolymers with high green mechanical strength (18.9 to 23.9 MPa). Nepheline and albite generation in the samples containing 6 wt% of CH resulted in a ceramic with improved cold crushing strength (45.2 MPa) and lower linear shrinkage (-10.5%) when compared to the calcium-free composition.

Keywords: calcium hydroxide, metakaolin, geopolymer, properties, phase evolution.

INTRODUCTION

Inorganic polymers or geopolymers are synthetic materials with environmental benefits and potential properties to be applied as refractory ceramics for intermediate and high-temperature applications [1-4]. The control of the hardening behavior and microstructural rearrangement of such materials is a key factor in obtaining compositions with suitable early-age properties at low curing temperatures (<50 °C). In this sense, some investigations have pointed out that calcium-containing additives might play an important role in the design of metakaolin (MK)-based geopolymers with fast setting time, high packing, and enhanced green mechanical performance [5-10].

The effect of Ca^{2+} ions in the geopolymerization process is still not completely understood and it depends on the intrinsic features of the initial raw materials (selected precursor and activating solution), as well as the overall formulation and synthesis procedure used during the processing steps [8, 11, 12]. Some reaction products are likely to be found in calcium-containing geopolymers [13, 14], such as: i) gel comprising Ca^{2+} ions in its structure; ii) amorphous or crystalline C-S-H phases (where C=CaO, S= SiO_2 , and H= H_2O); iii) calcium aluminates; and iv) calcium aluminosilicates. These compounds are derived from Ca^{2+} and alkaline cations (Na^+ and/or K^+) interactions with silica and aluminum monomers contained in the reactive alkaline medium during the geopolymerization process [5, 13]. For instance, Yip and colleagues [13] reported the coexistence of sodium

aluminosilicate gel and C-S-H phases in metakaolin-based geopolymer containing additions of calcium-rich slags (ground and granulated blast furnace slags - GGBFS). They also stated that the mechanical strength of the studied geopolymers could be enhanced due to the presence of C-S-H gel that filled in the available voids and pores located in the resulting geopolymeric structure. Alonso and Palomo [15] evaluated the influence of the concentration of NaOH aqueous solutions on the reaction products of calcium hydroxide/metakaolin mixtures (1/1 mass ratio). Based on the attained results, the authors pointed out that poor geopolymerization and major formation of C-S-H gel could be detected when using a low alkaline medium (NaOH concentration <5 M), whereas faster MK dissolution and the generation of an amorphous aluminosilicate gel were the main transformations identified for compositions prepared with high alkaline medium (NaOH concentration ≥ 10 M). However, the phase evolution of metakaolin-based geopolymers containing calcium sources after firing at high temperatures has been little explored and it must affect to a greater extent the thermo-mechanical and dimensional stability of these materials.

In this context, this work investigated the effect of adding distinct contents of calcium hydroxide to metakaolin-based geopolymers and how it affected the phase transformations and physico-mechanical properties of the prepared formulations after thermal treatments carried out in the 40-1000 °C temperature range.

EXPERIMENTAL PROCEDURE

The evaluated geopolymers were synthesized using metakaolin (MK, $\text{SiO}_2=61.25$ wt%, $\text{Al}_2\text{O}_3=38.07$ wt%,

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$K_2O=0.53$ wt%, and $CaO=0.15$ wt%, $SiO_2/Al_2O_3 \approx 2.7$ mol/mol, $d_{50}=17.5$ μm , MKHP Ultra, Metacaulim do Brasil, Brazil) and an activating solution (AS, 12 M NaOH + colloidal silica suspension with SiO_2/Na_2O molar ratio=1.4), considering AS/MK mass ratio=0.70. The selected raw materials consisted of NaOH pellets (Scientific Exodus, Brazil) and Levasil CS40-120 ($SiO_2=40$ wt%, Nouryon, Brazil). Furthermore, 1, 3, and 6 wt% of calcium hydroxide (CH, HC07136RA, Scientific Exodus, Brazil) was incorporated into the designed ceramic composition to analyze the effect of the Ca^{2+} ions in the geopolymerization process. The components were processed in a high-energy mixer (Solotest, Brazil) following the procedure described in [16]. The obtained pastes were poured into cylindrical (40x40 mm) and prismatic (150x25x25 mm) molds and cast under vibration (~ 1 min). After that, the samples were covered with plastic film, cured at 40 °C for 12 h, and then fired at 400, 800, or 1000 °C for 2 h.

The setting time and curing behavior of the geopolymeric pastes were evaluated via ultrasonic velocity measurements at room temperature (~ 22 °C) for 24 h and using UltraTest equipment (Ultrasonic Measuring Test System IP-8, Germany). The stiffness evolution of the cured samples with time (1 to 16 days) was also inferred with the impulse excitation technique (ASTM E1876-15) in an RFDA HT1600 device (IMCE, Belgium). Besides that, cold crushing strength, according to ASTM C133 and using a universal testing machine (DL-10000, Emic, Brazil), apparent porosity (ASTM C830, using water as immersion liquid), and permanent linear change (PLC, ASTM C113) measurements were carried out for the investigation of the properties evolution of cured and/or fired specimens (400-1000 °C/2 h). A total of five samples was analyzed for each selected condition and the presented values are the average result with their respective calculated standard deviation.

The structural evolution of the designed compositions was investigated by X-ray diffraction (XRD, D8 Focus, Bruker) using $CuK\alpha$ radiation ($\lambda=1.5418$ Å), nickel filter, 40 mA, 40 mV and step=0.02°, and Fourier transform infrared spectroscopy (FTIR, Spectrum 3, PerkinElmer) using an attenuated total reflectance module (ATR), a scan range of 4000-400 cm^{-1} , 20 scans, and 4 cm^{-1} resolution.

RESULTS AND DISCUSSION

Setting behavior and samples' properties after curing procedure (40 °C)

Fig. 1a points out that the addition of calcium hydroxide (CH) to the geopolymer sped up the stiffening process of the pastes due to the greater availability of Ca^{2+} and OH^- ions in the alkaline medium, which may favor the dissolution of metakaolinite and the formation of Ca-containing gel during the polymerization process [6, 15]. More reactive systems could be obtained when increasing the amount of CH in the mixtures and the setting process of the samples started right after placing the pastes into the molds. According to this

technique, the setting time for the evaluated geopolymers is: G-6CH (~ 1.7 h) < G-3CH (~ 3.1 h) < G-0CH (~ 4.1 h) < G-1CH (~ 4.7 h). Despite their faster hardening, G-3CH and G-6CH compositions still presented a well-packed microstructure, resulting in samples with higher density values [G-6CH (1.71 g/cm^3) > G-3CH (1.66 g/cm^3) > G-0CH (1.56 g/cm^3) > G-1CH (1.54 g/cm^3)]. These results are in tune with the obtained elastic modulus values (Fig. 1b), as the compositions containing CH showed higher stiffness when compared to the reference material (G-0CH). Based on the Young's modulus (E) and cold crushing strength (CCS, Fig. 1c) measurements, the addition of 3 wt% of calcium hydroxide into the geopolymer led to an enhanced performance, as the samples reached E and CCS values of 13.6-14.8 GPa and 23.85 MPa, respectively.

Previous works [5, 6] reported the positive effect of CH in improving the mechanical strength of geopolymers, which was related to the generation of an amorphous Ca-containing geopolymeric matrix that induced the development of dense microstructures. Aiming to investigate this aspect and identify the phases and bonds contained in the evaluated compositions, XRD and FTIR tests were also carried out in this work. Fig. 2a shows that G-0CH and G-6CH presented similar XRD profiles and quartz (derived from the metakaolin) was the only crystalline phase identified in these materials. No crystalline C-S-H hydrated phases could be detected due to the low calcium content in G-6CH composition ($CaO/SiO_2 \sim 0.07$ molar ratio) and, the high-alkaline medium (NaOH 12 M + colloidal silica mix with pH ~ 14) used during the synthesis procedure most likely favored the generation of amorphous aluminosilicate gel (as highlighted in [13-15]) as the major component in the studied formulations. FTIR results (Fig. 2b) indicated the shift of the bands related to vibrations of Si-O-T bonds (T= Si or Al) [11], from ~ 1043 cm^{-1} for the metakaolin to ~ 979 cm^{-1} for the geopolymer, when the geopolymerization reactions took place in both evaluated systems (G-0CH and G-6CH). Characteristic bands of the stretching and bending vibrations of O-H bonds could be observed at 3391 and 1646 cm^{-1} , respectively [14], due to the presence of water in the resulting structure. Besides that, Si-O-Si and Si-O-Al bonds (1000-400 cm^{-1}) [17] and the presence of CO_3^{2-} species (1500-1350 cm^{-1}) [11] were also detected in the cured samples.

Properties of the designed geopolymers after firing

The phase evolution and thermo-mechanical performance of the prepared geopolymers were investigated after the firing step in the 400-1000 °C range. Fig. 3a points out that no significant structural changes could be detected in the FTIR spectra of G-0CH samples and only a small decrease in the intensity of the bands at ~ 979 and ~ 436 cm^{-1} took place after firing this composition at 1000 °C. The latter might be associated with the precipitation of nepheline ($K_{0.24}Na_6Al_{6.24}Si_{9.76}O_{32}$) crystals, as confirmed by the XRD measurements (Fig. 3b). On the other hand, the addition of

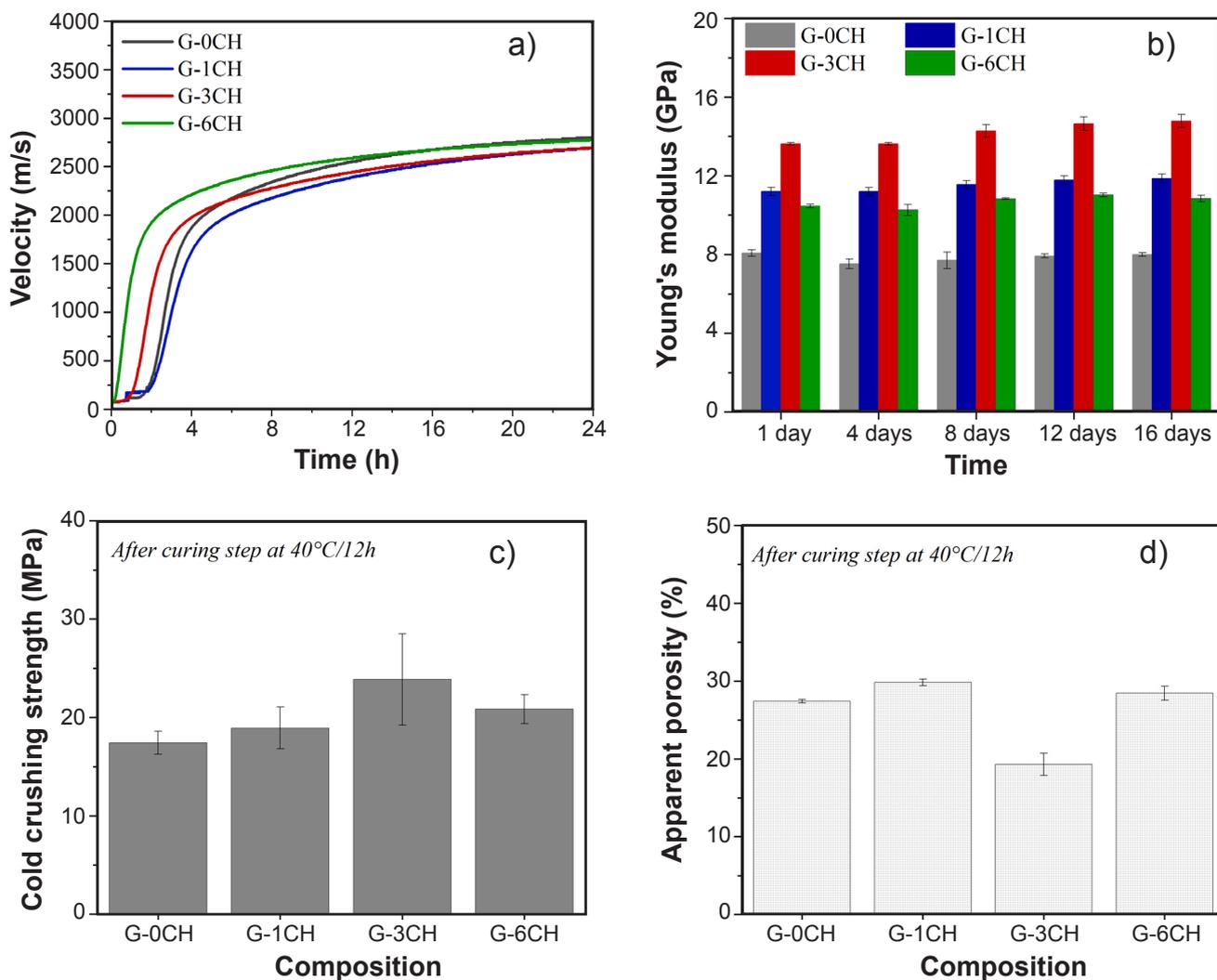


Figure 1: Physico-mechanical properties of the designed geopolymer containing 0-6 wt% of calcium hydroxide (CH): a) propagation velocity of the ultrasonic waves in the fresh pastes as a function of time at room temperature ($\sim 22^\circ\text{C}$); b) Young's modulus evolution of the cured samples at room temperature ($\sim 25^\circ\text{C}$); c) cold crushing strength and d) apparent porosity of the prepared specimens, both after the curing step ($40^\circ\text{C}/12\text{h}$).

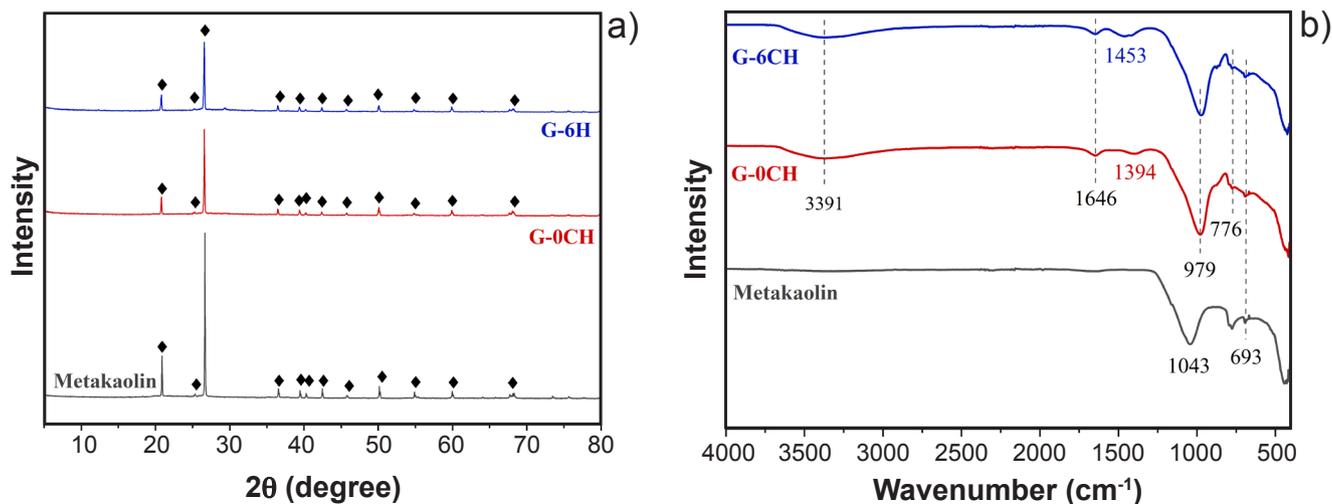


Figure 2: XRD profiles (a) and ATR-FTIR spectra (b) of metakaolin precursor and the evaluated geopolymers (G-0CH and G-6CH) obtained after the curing step ($40^\circ\text{C}/12\text{h}$). \blacklozenge = quartz - SiO_2 (ICSD 01-085-0797).

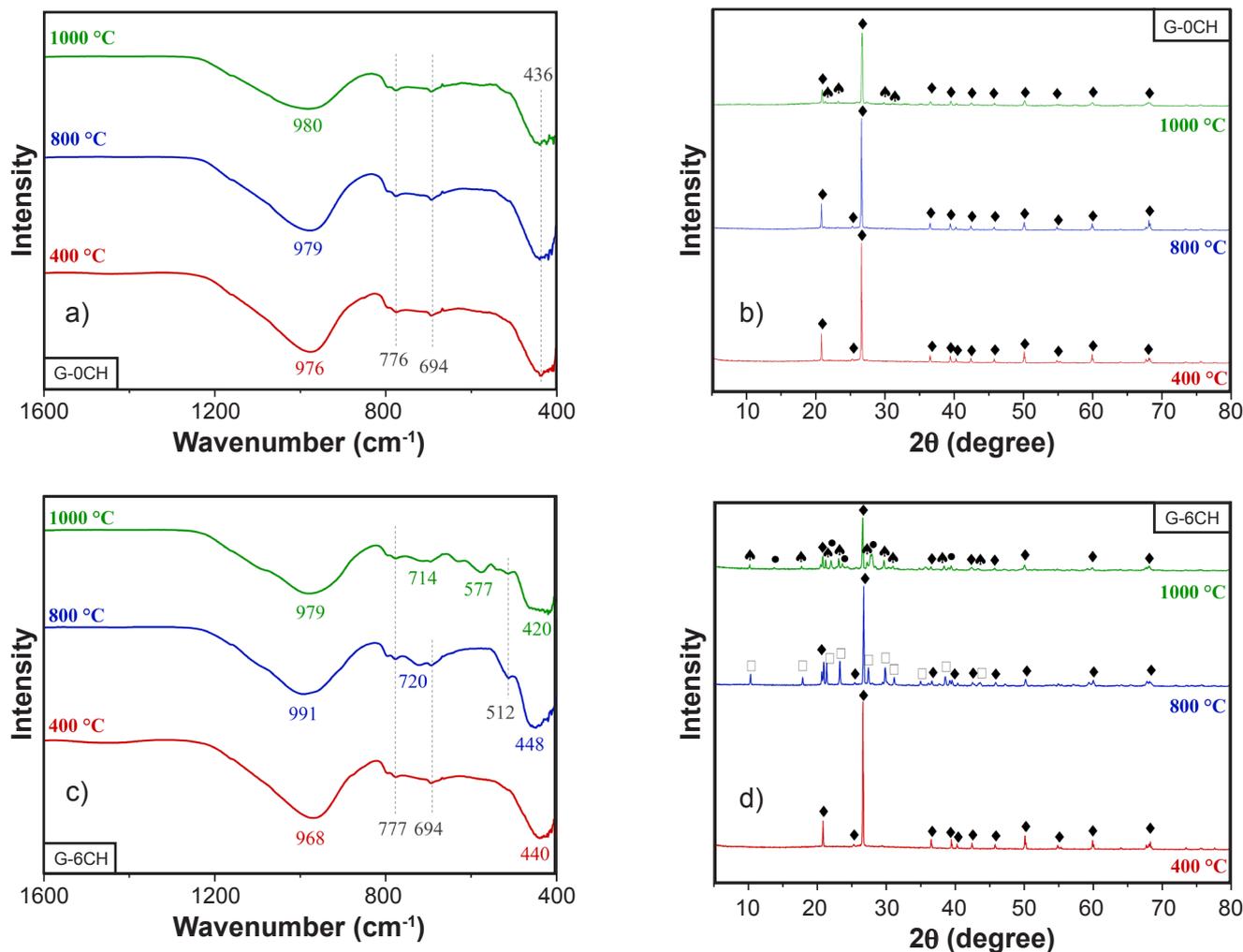


Figure 3: ATR-FTIR and XRD profiles of calcium-free geopolymer, G-0CH (a,b), and the composition containing 6 wt% of calcium hydroxide, G-6CH (c,d), after firing at 400, 800, and 1000 °C/2 h. ◆= quartz - SiO_2 (ICSD 01-085-0457); ♠= nepheline - $\text{K}_{0.24}\text{Na}_6\text{Al}_{6.24}\text{Si}_{9.76}\text{O}_{32}$ (ICSD 01-083-2279); □= $\text{Na}_{1.15}\text{Al}_{1.15}\text{Si}_{0.85}\text{O}_4$ (ICSD 00-049-0007); ●= albite - $\text{NaSi}_3\text{AlO}_8$ (ICSD 00-010-0393).

6 wt% of calcium hydroxide to the evaluated geopolymer (G-6CH) induced some changes in the T-O-T (T= Si or Al) zone of the spectra shown in Fig. 3c. For instance, it can be highlighted that: i) the shift of bands identified at ~ 968 , ~ 694 , and ~ 440 cm^{-1} ; and ii) the formation of new bands at ~ 512 cm^{-1} (800 °C) and 577 cm^{-1} (1000 °C) in Fig. 3c. These changes in the FTIR results were related to the generation of nepheline at 800 °C and albite ($\text{NaSi}_3\text{AlO}_8$) at 1000 °C in G-6CH samples (Fig. 3d). The nepheline and albite crystallization at intermediate temperatures (800 and 1000 °C) could be favored by the selected $(\text{Na}_2\text{O}+\text{K}_2\text{O}+\text{CaO})/\text{Al}_2\text{O}_3$ overall molar ratio (0.7) and the catalytic action of colloidal silica particles that might promote a more efficient interaction among the available species and speed up the precipitation of new compounds. Additionally, the evaluated geopolymers still presented residual quartz (derived from metakaolin) and amorphous components after testing the samples up to 1000 °C (Figs. 3b and 3d).

Fig. 4a points out that all tested geopolymers

(containing 0, 1, 3, or 6 wt% of CH) presented similar shrinkage (approximately -3.6%) after firing at 400 °C, as a result of the water withdrawal (free and physically bonded water). However, a more pronounced shrinkage of the geopolymers could be observed when subjecting them to higher temperatures (Fig. 4a). As reported in [17], liquid phase formation is expected to occur in $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ geopolymers above 600 °C, which explains the reduction of the G-0CH samples' length by approximately -8.5% and -12.4% after firing at 800 and 1000 °C, respectively. Although nepheline crystals can be precipitated in the CH-containing geopolymers at 800 °C (Fig. 3d), liquid formation seems to have a major effect on the dimensional stability of such compositions at this intermediate temperature, resulting in greater shrinkage values (up to -10.8%, Fig. 4a) when compared to the reference material. Nevertheless, an opposite trend was verified after firing the tested geopolymers at 1000 °C, as the calcium-free (G-0CH) samples showed the highest linear shrinkage and a continuous decay of the measured values could be

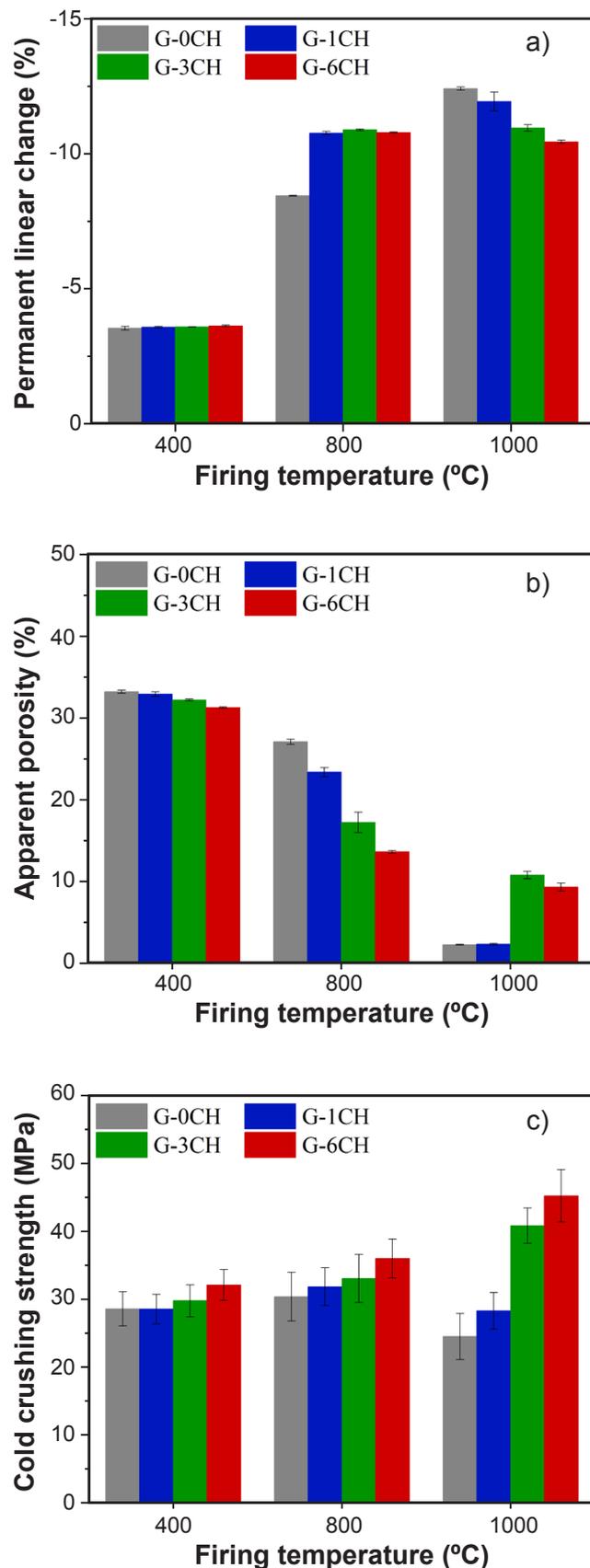


Figure 4: Physico-mechanical properties of the evaluated geopolymers after firing at 400, 800, and 1000 °C/2 h: a) permanent linear change (PLC); b) apparent porosity; and c) cold crushing strength.

observed when raising the CH amount contained in the designed compositions (Fig. 4a). Such a performance may be justified by the more effective precipitation of nepheline and albite crystals in the microstructure of the geopolymers containing greater content of calcium hydroxide.

The densification of the samples' microstructure as a function of the firing temperature became more evident when analyzing the apparent porosity results (Fig. 4b). The significant decrease of the pores content highlights the rearrangement of the phases and the liquid ability to fill in the available voids and flaws contained in these materials. Consequently, an improvement in the cold crushing strength (CCS) results could be observed when increasing the firing temperature and the CH content (Fig. 4c) in the geopolymers. G-6CH presented the best mechanical performance, reaching 45.2 MPa of CCS after firing the specimens at 1000 °C, which represented an increase of 84.5% when compared to G-0CH (CCS ~24.5 MPa).

CONCLUSIONS

This work evaluated the influence of adding calcium hydroxide in metakaolin-based geopolymers and how this additive affected the phase transformations and physico-mechanical properties of the prepared compositions after thermal treatments between 40-1000 °C. According to the obtained results, the following conclusions can be drawn: i) the addition of calcium hydroxide to the geopolymer compositions sped up the curing behavior of the obtained pastes, reducing their setting time from 4.1 to 1.7 h; ii) after the geopolymerization and curing process of the studied compositions, the samples were comprised mainly by amorphous Ca-Na-aluminosilicate gel and residual quartz; no C-S-H hydrates could be identified, which might be related to the limited Ca²⁺ ions content available in reaction medium; G-3CH samples (containing 3 wt% of calcium hydroxide) showed the best performance after curing, reaching Young's modulus of up to 14.8 GPa and mechanical strength of 23.85 MPa after 1 day of curing at 40 °C; and iii) the combination of a colloidal silica-based activating solution, metakaolin and calcium hydroxide in the investigated geopolymer compositions favored the earlier crystallization of nepheline phase at 800 °C and the generation of strong Si-O-Si bonds; G-6CH formulation presented nepheline, albite and residual quartz phases in its microstructure after firing at 1000 °C and dense ceramic specimens with 9.3% of apparent porosity, -10.5% of permanent linear change and improved cold crushing strength (45.2 MPa) could be obtained.

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