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ORIGINAL ARTICLE

Preliminary study of the effect of carbonation curing on geopolymers

Estudo preliminar do efeito da cura por carbonatação em geopolímeros

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Abstract: Carbonation curing differs from weathering carbonation since it is performed intentionally at the early ages of cement hydration. This cure involves applying different levels of CO_2 (5% to 99%) to concrete for a short period of time, usually followed by conventional hydration. The objective of this article was to evaluate the carbonation curing in metakaolin-based geopolymer concretes, activated with NaOH and Na_2SiO_3, and compare them with Portland cement (PC) concrete. The following tests were applied: determination of pH, carbonation depth, water absorption by immersion, void index, and compressive strength. The results showed that after the carbonation curing, the geopolymer concrete had compressive strength and carbonation depth equivalent to the concrete with PC, but with a lower absorbed CO_2 content. Although this type of cement absorbs less CO_2 but is more sensitive to carbonation. The effect on the void ratio was not remarkable. Furthermore, the alkalinity of concretes can be partially recovered after subsequent curing by water immersion.

Keywords: carbonation curing, geopolymer, metakaolin, carbon dioxide.

Resumo: A cura por carbonatação difere da carbonatação por intemperismo, pois é realizada intencionalmente nas primeiras idades de hidratação do cimento. Essa cura envolve a aplicação de diferentes níveis de CO_2 (5% a 99%) ao concreto por um curto período de tempo, geralmente seguido de hidratação convencional. O objetivo deste artigo foi avaliar a cura da carbonatação em concretos geopolímeros à base de metacaulim, ativados com NaOH e Na_2SiO_3, e compará-los com o concreto de cimento Portland (CP). Foram aplicados os seguintes testes: determinação do pH, profundidade de carbonatação, absorção de água por imersão, índice de vazios e resistência à compressão. Os resultados mostraram que após a cura da carbonatação, o concreto geopolimérico apresentou resistência à compressão e profundidade de carbonatação equivalentes ao concreto com CP, porém com menor teor de CO_2 absorvido. Portanto, este tipo de cimento absorve menos CO_2, mas é mais sensível à carbonatação. O efeito na taxa de vazios não foi notável. Além disso, a alcalinidade dos concretos pode ser parcialmente recuperada após a cura subsequente por imersão em água.

Palavras-chave: cura de carbonatação, geopolímero, metacaulim, dióxido de carbono.

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1 INTRODUCTION

Curing by carbonation is a process carried out in the first hours of hydration of cementitious materials and can be applied with different concentrations of CO_2, ranging from 5% to 99.9% [1]-[8]. This process is different from weathering carbonation, which occurs in the hardened cement paste and is associated with the action of CO_2 in the atmosphere, impairing the passivation of the reinforcements. In the case of carbonation curing, CO_2 is intentionally introduced to react with the hydrated and non-hydrated cement phases at early ages. Thus, carbonation curing was developed to accelerate strength increase, promote CO_2 sequestration and convert more stable phases in concrete [4], [9], [10].

Carbonation curing is usually performed within the first 24 hours after mixing and casting the cementitious materials, for a short period (on the scale of hours or a few days), followed by conventional curing to complete the chemical reactions. Conventional curing (exposure to humid environments) is usually executed after carbonation curing to allow subsequent hydration of the cement grains [2], [3], [7].

Therefore, at least three distinct steps are defined for carbonation curing. The first is the preconditioning of the material for controlled removal of surface-free water. The second step is the actual exposure to CO_2 to form a layer of carbonated phases on the most superficial surface of the materials. The third step is post-conditioning to allow additional hydration of unreacted phases. Despite the reduced pH in the carbonate zone right after the carbonation curing process [8], the core alkalinity is kept high to allow passivation and prevent steel corrosion when the technique is applied to reinforced concrete structures. In this situation, the carbonation cure should be limited to the first millimeters of the material, not compromising its protection against corrosion [10]-[13]. In general, the main applications of carbonation curing are related to the production of non-reinforced cement-based materials, as precast elements and concrete blocks [10], [14], [15].

Carbon dioxide from carbonation curing can react with different anhydrous and hydrated phases of Portland cement [12], [13]. In the short term, the reaction of CO_2 with tricalcium silicate (C_3S) and dicalcium silicate (C_2S) in the presence of water produces calcium silicate hydrate (C-S-H) and calcium carbonate ($CaCO_3$) according to Equations 1 and 2 [7]. Carbon dioxide can also react with the hydrated phases of cement, such as $Ca(OH)_2$, C-S-H, and ettringite [1], [3], [7], [10] according to Equations 3, 4 and 5. A denser layer with a remarkable amount of $CaCO_3$ is formed after carbonation curing, with carbonate being less soluble than $Ca(OH)_2$ [1]. This technique contributed to the reduction of porosity and permeability of the materials, in addition to increasing the penetration resistance of chloride ions and other durability benefits [1]-[5], [10], [16], [17]. Equações estão ok. Apenas a legenda de indicação do "C-S-H" da Equação (1) ficou deslocada, pois deve estar alinhada com o composto 3CaO·2SiO2·3H2O. Igualmente para a equação (4), onde o "Carbonate" e "Gypsum" deve ficar um mais par

$$\underset{C_3S}{2\left(3CaO\cdot SiO_2\right)} + 3CO_2 + 3H_2O \rightarrow \underset{C-S-H}{3CaO\cdot 2SiO_2\cdot 3H_2O} + \underset{Carbonate}{3CaCO_3} \tag{1}$$

$$\underset{C_2S}{2\left(2CaO\cdot SiO_2\right)} + CO_2 + 3H_2O \rightarrow \underset{C-S-H}{3CaO\cdot 2SiO_2\cdot 3H_2O} + \underset{Carbonate}{CaCO_3} \tag{2}$$

$$\underset{Portlandite}{Ca\left(OH\right)_2} + CO_2 \rightarrow \underset{Carbonate}{CaCO_3} + H_2O \tag{3}$$

$$\underset{Ettringite}{3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O} + 3CO_2 \rightarrow \underset{Carbonate}{3CaCO_3} + \underset{Gypsum}{3CaSO_4\cdot 2H_2O} \tag{4}$$

$$\underset{C-S-H}{3CaO\cdot 2SiO_2\cdot 3H_2O} + 3CO_2 \rightarrow \underset{Carbonate}{3CaCO_3} + 2SiO_2 + 3H_2O \tag{5}$$

On the other hand, information on carbonation curing is needed for low calcium content materials. The study of the application of this technique in geopolymers is an evident lack in the literature. Few references [18]-[21] on the carbonation of geopolymers are found in the literature.

Geopolymer is an inorganic material obtained from the reaction between aluminosilicates and alkaline activators. The main aluminosilicate precursors used are kaolin, metakaolin, rice husk ash, and volcanic rock dust, depending on the study region. These precursors can also be obtained from industrial waste sources, such as fly ash and slag [22].

The most commonly used alkaline activators are potassium hydroxides, sodium hydroxides, phosphoric acids, potassium silicates, sodium silicates, or a mixture of these components [23]-[25].

The reactive amorphous silico-aluminous materials dissolve in the tetrahedral form of AlO_4^{4-} and SiO_4^{4-} rapidly by hydrolysis to form the Si-O-Si and Si-O-Al oligomers when they come into contact with the alkaline solution (pH > 13.0) (Equations 6 and 7). By polycondensation, this material forms a resistant three-dimensional structure, giving rise to a polymeric chain [23], [25]. The main product of this interaction is the amorphous N-A-S-H gel (hydrated sodium aluminosilicate) (Equation 8) [26], but the presence of zeolites is also indicated in the literature [27].

$$Al_2O_3 + 3H_2O + 2OH^- \rightarrow 2\left[Al\left(OH\right)_4\right]^- \tag{6}$$

$$SiO_2 + 2OH^- \rightarrow \left[SiO_2\left(OH\right)_2\right]^{2-} \tag{7}$$

$$Al_2O_3 \cdot 2SiO_2 + 2OH^- + 2Na^+ + H_2O \rightarrow \underset{N-A-S-H}{2NaAlSiO_4 \cdot H_2O} \tag{8}$$

The combination of different aluminosilicate materials, chemical activators, curing procedures, and additives produces different geopolymer cements, but generally with good mechanical properties and adequate durability, in addition to environmental benefits [22]. The most common applications of geopolymers are in airport floors, marine structures, repair mortars, sidewalks, roof tiles, cycle paths, precast slabs, concrete pipes, railway sleepers, and tunnel segments [25], [28]-[30].

Given the particularities of geopolymer materials, this article aimed to evaluate the carbonation curing of metakaolin-based geopolymer concretes, activated with NaOH and Na_2SiO_3. A comparison was made with a reference concrete (ordinary Portland cement), with equivalent compressive strengths. This is a preliminary study, to understand the initial behavior of geopolymer concretes after carbonation curing, focusing on the determination of pH, carbonation depth, water absorption by immersion, void index, and compressive strength. Subsequently, other studies are currently being performed by these authors to evaluate the durability of this material in aggressive environments.

2 MATERIALS AND EXPERIMENTAL PROGRAM

2.1 Materials

Commercial metakaolin composed of quartz (40.03%), illite (27.54%), kaolinite (22.78%), and microclinium (9.66%) was used in this study as a source of aluminosilicate. The alkaline activators were produced using a sodium hydroxide (NaOH ≈ 99%) and sodium silicate (Na_2SiO_3) solution. The proportion of materials for the composition of the geopolymer was 45.28% metakaolin, 4.82% NaOH, and 50.0% Na_2SiO_3. Therefore, a molar ratio (Na_2SiO_3 / NaOH) of 1.60 was used, with a content of 23% Na_2O in relation to metakaolin and alkaline solids-to-metakaolin ratio of 0.62.

Ordinary Portland cement (CEM I) was used in conventional concretes for comparison with geopolymer concretes. Table 1 shows the characteristics of the aggregates (fine and coarse) used in both concretes.

Table 1. Characterization of fine and coarse aggregates.

Property	Fine	Coarse
Specific gravity (g/cm^3)	2.64	2.90
Bulk density (g/cm^3)	1.64	1.45
#200 sieve fineness (%)	0.63	1.00
Fineness module	2.01	2.64
Maximum size (mm)	4.75	9.50

Cubic specimens (75 mm edge) of concrete were casted for the tests. Some initial parameters were defined for casting the concrete. The compressive strength at 28 days should be around 25 MPa (usual strength in conventional concrete) and the expected carbonation depth after carbonation curing should be 8-15 mm (excessive values can compromise the passivation of reinforcements regarding corrosion). In this way, some concrete mixtures were initially tested, until finding the mixture that met these parameters.

The proportion defined for Portland cement concrete (PC concrete) was 1: 2.03: 2.47: 0.55 (cement: sand: gravel: water). Similar proportions of fine and coarse aggregates were used for the production of geopolymer concrete (GEO concrete). However, the water-to-metakaolin ratio was 0.74.

2.2 Methods

After casting the concrete (GEO and PC), the specimens were cured by two different methods: carbonation curing (C) and conventional curing (N). The carbonation curing consisted of three controlled steps, according to Table 2. In Step 1, the pre-conditioning aimed to partially remove free water from the pores to facilitate the entry of CO_2. In this phase, the thermal curing of the geopolymers (6 h) was necessary to allow the penetration of CO_2, since samples pre-conditioned at room temperature showed a water loss of less than 1.0%, making it impossible for carbon dioxide to enter in GEO concrete, according to Figure 1.

In Step 2, the cubes were placed in a hermetically sealed steel chamber (500 x 500 mm in size) with a CO_2 cylinder with a pressure regulator. This phase allows the controlled entry of CO_2 into the concrete. Before injecting carbon dioxide, the oxygen inside the chamber was aspirated with a vacuum pump for 5 minutes. Finally, in Step 3 (additional curing), the specimens were stored in a curing chamber to complete the chemical reactions.

Table 2. Carbonation curing steps.

Concrete	Step 1: preconditioning	Step 2: carbonation	Step 3: additional curing
GEO	4 h in mold (T = 50 ± 5) °C; 2 h out of the mold (T = 50 ± 5) °C; 18 h (T = 25 ± 5) ºC, (RH = 45 ± 5) %	6 h, 15 Psi ≈ 99% CO_2 (T = 25 ± 5) ºC, ambient RH	27 days (T = 25 ± 5) °C, ambient RH
PC	6 h in mold (T = 25 ± 5) °C; 18 h (T = 25 ± 5) ºC, (RH = 50 ± 5) %	6 h, 15 Psi ≈ 99% CO_2 (T = 25 ± 5) ºC, ambient RH	27 days (T = 25 ± 5) °C, (RH = 95 ± 5) %

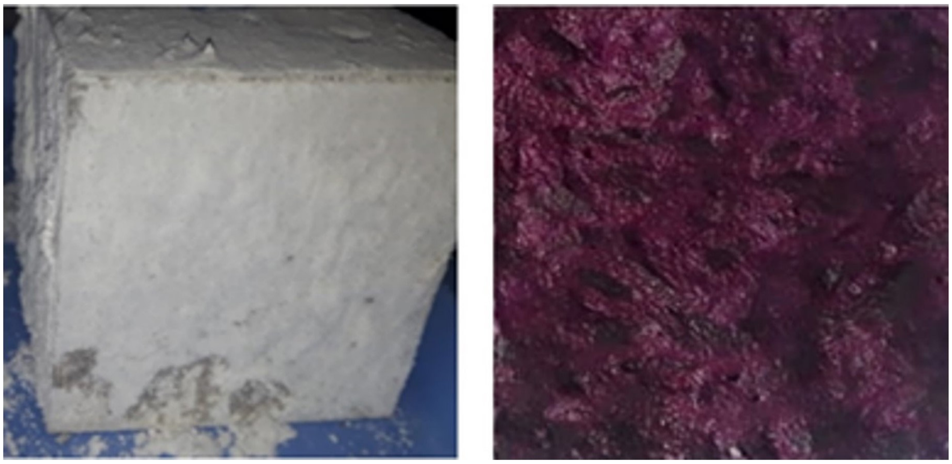

Figure 1. External carbonation (right) and zero carbonation depth in geopolymer concrete (left) without thermal curing.

Conventional curing (N) of PC concrete was performed for 28 days, similar to Step 3. Conventional curing (N) of GEO concrete was initially composed of thermal curing (50 ± 5) °C for 6 hours, similar to Step 1, followed by curing for 28 days, as per Step 3.

After carbonation (Step 2), some specimens were immediately sectioned into two parts and a phenolphthalein solution was sprayed across the cross-section. The measurement of carbonation depth was performed with a digital caliper, with a precision of 0.001 mm. 24 carbonation depth points were measured per specimen to calculate the average depth. An estimate of the carbonation area was also made using photographs of the specimens treated in software. The percentage of CO_2 uptake in the concretes was expressed in % using as reference the mass of the concrete before carbonation, according to Zhang and Shao [16]. During the carbonation process, the concrete gains mass with the penetration of CO_2 at the same time that it loses water during the reactions. For this reason, water from the inner walls of the chamber was collected with absorbent paper and the value included in the final concrete mass.

The suspension method called *ex-situ* leaching [10] was used to determine the pH of the concretes. Fragments of the specimens were manually ground into granulometry passing through a 0.30 mm sieve. 3 grams of powder were extracted from the samples and mixed with 10 grams of distilled water. A digital pH meter was used in this solution to determine the pH of the concretes.

The water absorption by immersion and the void index of the concretes were determined at 28 days using three specimens per condition. ASTM C140 [31] procedures were applied for these tests. Compressive strengths were determined according to ASTM C109 [32]. This test was performed before (end of Step 1) and after (end of Step 2) the specimens entered the carbonation chamber and after 28 days of additional curing (end of Step 3). Three specimens were selected per condition [7]. A universal press with a capacity of 100 tf was used. Finally, the statistical analysis of the experimental data was performed using analysis of variance (ANOVA) and Tukey's test, with a significance level of 5%.

Microstructure analyzes were performed on carbonated and non-carbonated specimens after step 2 (exposure to the carbonation chamber). The concrete samples were manually pulverized and the material that passed the 100 sieve (0.15 mm) was separated for X-ray diffraction (XRD) testing. The test was carried out between 5º and 75º 2θ, with an angular step of 3º per minute in an X-ray diffractometer model Miniflex 600, Rigaku, with X-ray generator tubes (Kα of Cu λ= 0.154 nm) and voltage of 40kV.

3 RESULTS AND DISCUSSIONS

The mass loss of GEO and PC concretes due to the release of free water during the preconditioning phase (step 1) was 13.1% and 32.9%, respectively (Table 3). The smallest loss of water in the geopolymers during the preconditioning phase is mainly associated with the Na_2SiO_3 activator since about 73% of the water used in the mixtures comes from sodium silicate. Thus, the higher density of the alkaline activator (≈ 1.576 g/ml) in relation to water (≈ 1.0 g/ml) may have interfered with the water loss of the GEO concrete at this stage.

Table 3. Results of preconditioning and carbonation in the concretes.

Property	GEO-C		PC-C		Statistical analysis	
	Average	%	Average	%	*p*-value	Significance level
Water loss (g) during step 1	9.00 ± 0.59	13.1	32.77 ± 4.18	32.9	4.64E-14	Significant
Mass increase (g) after 6 hours of carbonation, step 2	9.59 ± 1.01	0.85	22.7 ± 2.23	2.14	1.05E-10	Significant
Carbonation depth (mm)	10.1 ± 2.11	-	9.10 ± 1.54	-	0.074	Non-significant
Carbonated area (mm^2)	2556.35 ± 283.94	45.40	2335.17 ± 182.08	41.50	0.319	Non-significant

An increase in mass was observed in the concretes after the period inside the carbonation chamber (6 hours, 15 Psi). PC concrete showed a 2.5 times greater mass increase than GEO concrete. This increase in mass is due to the incorporation of CO_2 into the internal structure of the concrete, forming carbonates ($CaCO_3$ or Na_2CO_3).

The greater loss of water during Step 1 in PC concrete may have influenced the pore network of the material, facilitating the ingress of CO_2. This gas reacted with the hydrated ($Ca(OH)_2$ and C-S-H) and non-hydrated (C_3S and C_2S) phases of this cement, resulting in a greater mass increase for PC concrete. Moreover, the higher amount of calcium (Ca^{2+}) in Portland cement can also increase the CO_2 uptake [19], [33], justifying the greater mass gain observed.

Figure 2 shows the carbonation depth and carbonation area of GEO and PC concretes. The carbonation depth of the geopolymers was around 10.1 mm and the carbonated area was around 45.4%. In Portland cement, a depth close to 9.1 mm and a carbonated area of 41.5% were obtained. Non-carbonated (conventional curing) samples were also used for comparison in Figure 2.

According to Figure 2, the carbonation depth and the carbonated area in the concretes were similar. Although the colorimetric technique with phenolphthalein is merely qualitative, the results show that concrete with metakaolin-based geopolymers may have a greater capacity to absorb CO_2, measured by mass increase (Table 3), during carbonation curing compared to the Portland cement concrete. Thus, the lower absorbed CO_2 content (by mass) produced an equivalent carbonation depth in the geopolymer compared to the PC concrete. However, other techniques to really measure the amount of products formed by carbonation curing must be performed to quantify this information.

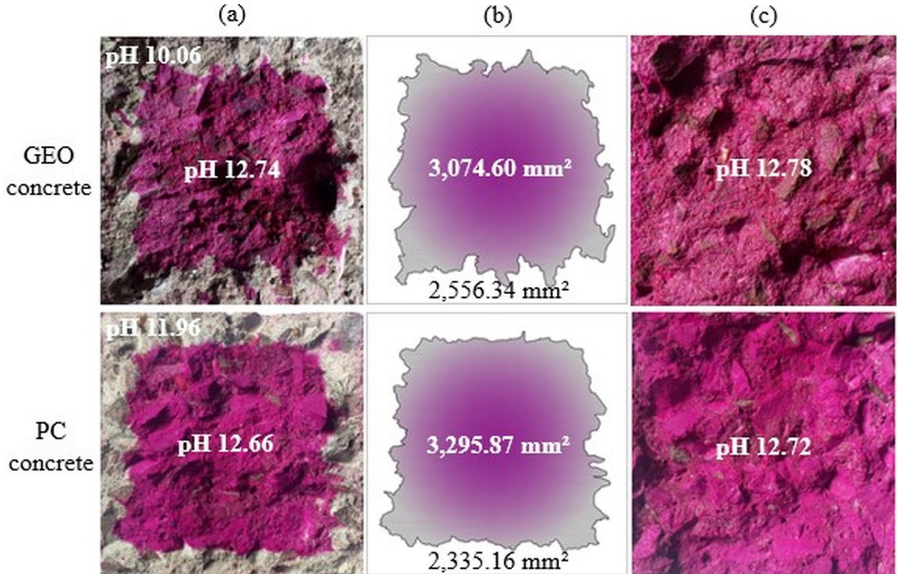

Figure 2. Carbonation of GEO and PC concretes: (a) carbonation depth; (b) carbonated area; (c) non-carbonated (reference) samples.

The binding capacity of geopolymer with CO_2 is associated with the type and proportion of alkaline activators used in the geopolymer formulation since carbonation depends on the availability of alkali for the formation of sodium carbonates. The aluminosilicate gel can substantially capture sodium (Na^+) in the structure and reduce the carbonate content during carbonation, as discussed in Nedeljković et al. [19].

According to Figure 2, the pH of the core (innermost region and therefore not carbonated) of the specimens right after the carbonation step (step 2) was similar to the reference concrete (≈ 12.7). This demonstrates that the core is maintained at a high pH, therefore, there is no risk of steel corrosion if the technique is used in reinforced concrete structures. However, the surface pH showed a slight reduction, being more evident in the GEO concrete (from 12.74 to 10.06).

Figure 3 (XRD results) shows the presence of Na_2CO_3 phases in the GEO-C sample and $CaCO_3$ in the PC-C sample, both extracted from the concrete surface (0-5 mm). The identification of these peaks is supported by other studies [34]-[37]. Therefore, the formation of carbonates ($CaCO_3$ in Portland cement) and (Na_2CO_3 in the geopolymer) can reduce the pH of the concrete.

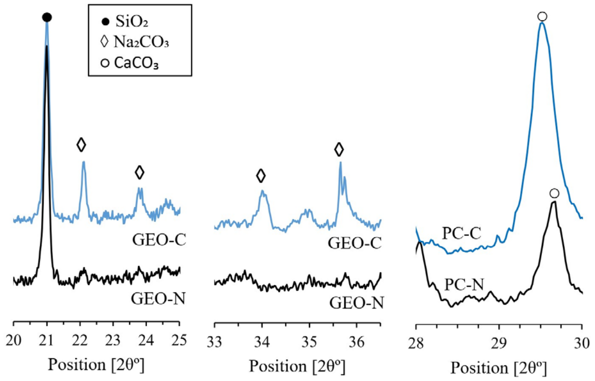

Figure 3. Result of X-ray diffraction of the concrete surface after Step 2.

Table 4 and Figure 4 show the results of water absorption by immersion and void index of the concretes after 28 days of carbonation curing (GEO-C and PC-C) and conventional curing (GEO-N and PC-N). These results support the discussions made so far.

Table 4. Results of water absorption by immersion and void ratio of concretes.

Properties	Average (%)			
	GEO-N	GEO-C	PC-N	PC-C
Water absorption by immersion	11.09 ± 0.47	10.93 ± 0.43	7.33 ± 0.26	6.33 ± 0.05
Void index	22.86 ± 0.84	22.32 ± 0.67	16.75 ± 0.48	14.59 ± 0.20

Properties	Statistical analysis	*p*-value	Significance level
	Comparative		
Water absorption by immersion	GEO-N – GEO-C	0.7001	Non-significant
	PC-N – PC-C	0.0030	Significant
	GEO-C – PC-C	5,20E-02	Significant
	GEO-N – PC-N	0.0002	Significant
Void index	GEO-N – GEO-C	0.4368	Non-significant
	PC-N – PC-C	0.0004	Significant
	GEO-C – PC-C	4,38E-02	Significant
	GEO-N – PC-N	0.0019	Significant

The immersion water absorption and void ratio of GEO concrete was significantly higher compared to PC concrete, regardless of the curing process used. Similar behavior was found in the literature. Albidah et al. [38] obtained three times higher water absorption in metakaolin-based geopolymer compared to Portland cement concrete for the same water-to-binder ratio. According to these authors, the porosity of geopolymer concrete can vary greatly depending on the molar ratio between alkaline activators (NaOH and Na_2SiO_3), the ratio between solid activators and precursor (metakaolin), the water-to-binder ratio, and the proportion of aggregates during the formulation of the concrete.

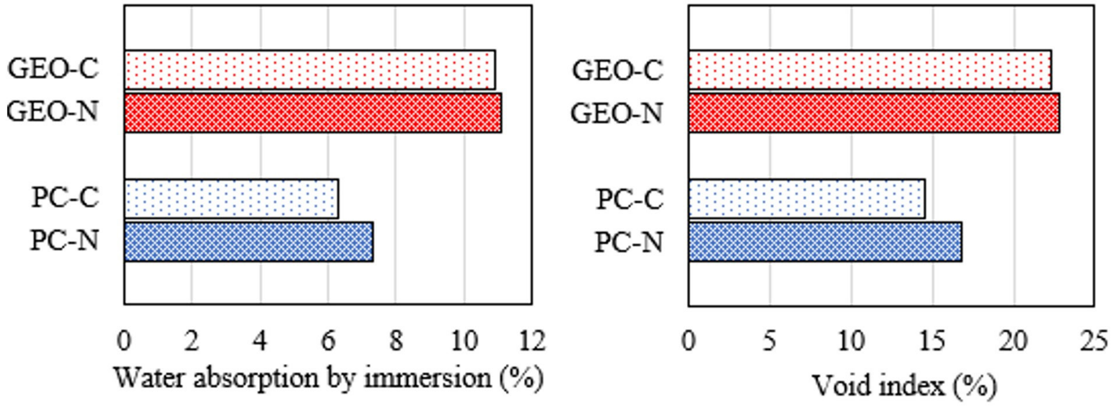

Figure 4. Water absorption by immersion and void index of the concretes.

According to Albidah et al. [38], there is an ideal alkali solids-to-metakaolin content to produce a geopolymer concrete with lower water absorption. These authors found water absorption of 6.6% and 7.0% for an alkaline solids-to-metakaolin ratio of 0.21 and 0.41, respectively. Thus, the authors showed that proportions between 0.25 and 0.37 are indicated for absorption values between 5.5% and 4.7%. The present article used an alkaline solids-to-metakaolin ratio of 0.62, which may have favored the greater water absorption of GEO concrete. Also, sodium silicate can re-dissolve the newly formed reaction phases of geopolymers, breaking chemical bonds and weakening the structure of the material, resulting in increased porosity and water absorption, as discussed by Zhang et al. [39].

Also, according to Puertas et al. [33], the higher content of Na_2SiO_3 used in the activation of activated alkali cement (from slag) resulted in considerable shrinkage during curing and crack formation. Thus, the water absorption observed in the geopolymer concrete of this study may have been influenced by the content of sodium silicate used for alkaline activation. According to Figure 4, the effect of carbonation curing in reducing the permeability of concrete (water absorption and void index) was greater in Portland cement concrete, although a slight reduction in this property was noted for GEO concrete as well, but not statistically significant. This indicates that the formation of sodium carbonate

(Na_2CO_3) due to carbonation curing in geopolymer concrete showed difficulty in promoting pore refinement, unlike what occurred in Portland cement-based material, which predominantly forms calcium carbonate ($CaCO_3$). According to Bernal et al. [40], the sodium carbonate resulting from the carbonation of geopolymers binds to a large amount of water, making it more voluminous and with a greater capacity to fill and block pores. Therefore, the low CO_2 absorption may indicate that a smaller amount of Na_2CO_3 was produced during carbonation and, for this reason, the void index of the geopolymer concrete remained close to the reference concrete (non-carbonated).

The significant reduction in water absorption and void index of carbonated PC concrete compared to reference concrete (PC-N) is associated with the filling of voids due to the formation of $CaCO_3$, partially blocking the pores and reducing the possibility of the entry of substances into the material. This result agrees with other research [2]-[5], [10].

Despite the higher water absorption and void index (Figure 4), GEO concrete had higher compressive strength than PC concrete. Table 5 and Figure 5 shows the compressive strength of the concretes before and after entering the carbonation chamber (Step 2), and after the additional 27 days of curing, totaling 28 days of age (Step 3). The (N) specimens are the reference samples, which have not been carbonated.

Table 5. Results of compressive strength of concrete.

Age	**Compressive strength (MPa)**			
	GEO-N	**GEO-C**	**PC-N**	**PC-C**
24 h	-	25.84 ± 0.66	-	13.25 ± 0.63
30 h	17.74 ± 1.37	26.93 ± 2.32	16.98 ± 0.73	15.50 ± 1.76
28 days	39.08 ± 3.84	26.89 ± 3.05	34.85 ± 2.75	26.44 ± 1.00

Properties	**Specimens**	**Statistical analysis**		**Significance level**
		Comparative	***p*-value**	
Compressive strength	(N)	GEO-N-30 h – GEO-N-28 d	0.0008	Significant
		PC-N-30 h - PC-N-28 d	0.0004	Significant
		GEO-N-30 h – PC-N-30 h	0.4418	Non-significant
		GEO-N-28 d – PC-N-28 d	0.1960	Non-significant
	(C)	GEO-C-24 h - GEO-C-30 h	0.4787	Non-significant
		GEO-C-30 h - GEO-C-28 d	0.9876	Non-significant
		PC-C-24 h - PC-C-30 h	0.3647	Non-significant
		PC-C-30 h - PC-C-28 d	0.0047	Significant
		GEO-C-24 h – PC-C-24 h	7.35E-5	Significant
		GEO-C-30 h – PC-C-30 h	0.0068	Significant
		GEO-C-28 d – PC-C-28 d	0.8204	Non-significant
	(N) *vs* (C)	GEO-N-30 h - GEO-C-30 h	0.0040	Significant
		PC-N-30 h - PC-C-30 h	0.2948	Non-significant
		GEO-N-28 d - GEO-C-28 d	0.0126	Significant
		PC-N-28 d - PC-C-28 d	0.0075	Significant

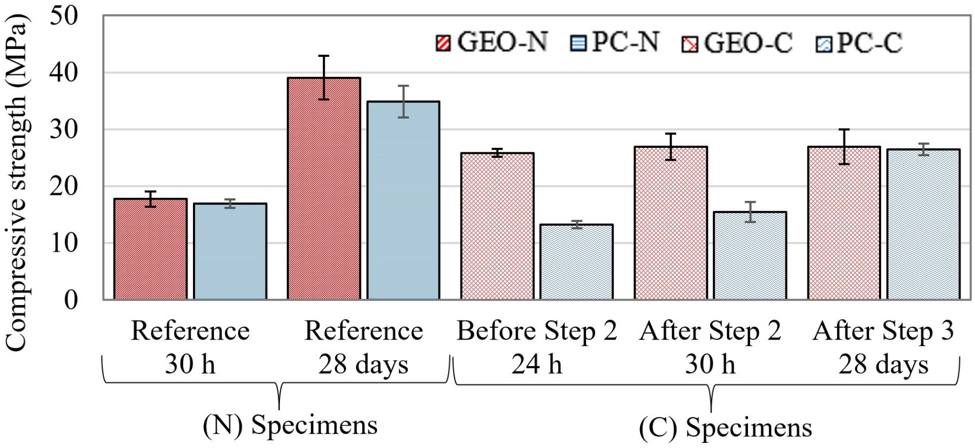

Figure 5. Compressive strength of concrete at different ages.

According to ANOVA and Tukey's test, there was no significant difference in the compressive strength of GEO concrete before and after carbonation curing and also in relation to the additional 27 days of curing (28 days of age). On the other hand, the variation in compressive strength of PC concrete was considerable after subsequent curing. Despite the differences observed between the GEO-C and PC-C concretes before and after stage 2 of curing by carbonation, at the end of the process (28 days) both mixtures showed equivalent resistance. In addition, there were also important differences in the compressive strength between the carbonated (C) and non-carbonated (N) specimens, except for the PC sample (30 h) as shown in Table 5. The strength of the reference samples (GEO-N and PC-N) was similar and the resistance increased significantly up to 28 days in both studied concretes.

The higher strength of the geopolymer in the initial preconditioning step (24 h) was provided by the thermal curing in the samples that were cured by carbonation - (C) specimens - since the higher temperature accelerates the polymerization reactions and, consequently, increases the initial resistance [23], [27]. After Step 2 (exposure to CO_2 for 6 hours), a slight increase in compressive strength (about 4.2%) was observed in the geopolymer. The binding capacity of CO_2 can be associated with this behavior, due to the lower absorption of carbon dioxide during carbonation curing (Table 3 and Figure 2).

The increase in compressive strength in PC concrete after Step 2 was 17%. This increase reinforces previous results. The formation of $CaCO_3$ during carbonation curing clogged the pores and increased the density of the concrete, increasing compressive strength. These results agree with the reduction in water absorption (Figure 4) and the higher CO_2 uptake of PC concrete compared to GEO concrete. Thus, once again the results indicate that the effect of carbonation curing is greater in concretes with Portland cement.

The increase in compressive strength (70.5%) after additional curing occurred only in PC concrete. This increase is associated with the formation of the C-S-H gel mixed with $CaCO_3$ from carbonation during the 27 days of additional curing [1], [12]. In general, the mechanical strength of concrete is concentrated in the solid part of the material. Compressive strength decreases linearly with increasing porosity [41]. This means that porosity and resistance are inversely proportional, that is, a reduction in porosity can result in an increase in resistance and vice versa. Therefore, filling the capillary voids with carbonates after the carbonation curing process refines the pores of the concrete and increases the solid part, resulting in increased mechanical strength.

Figure 6 shows the GEO and PC concretes after 27 days of additional curing (step 3). Different shades of pink color were identified on the surfaces of the samples. This demonstrates that the alkalinity of the carbonated region was partially restored after further curing. Partial pH recovery of concretes after the additional curing step during carbonation curing was indicated in other studies with Portland cement [10], but no similar study was found for geopolymers. Therefore, these results are innovative and visually indicate that the alkalinity of the carbonated region can be partially recovered in the geopolymers in a similar way to Portland cement concrete.

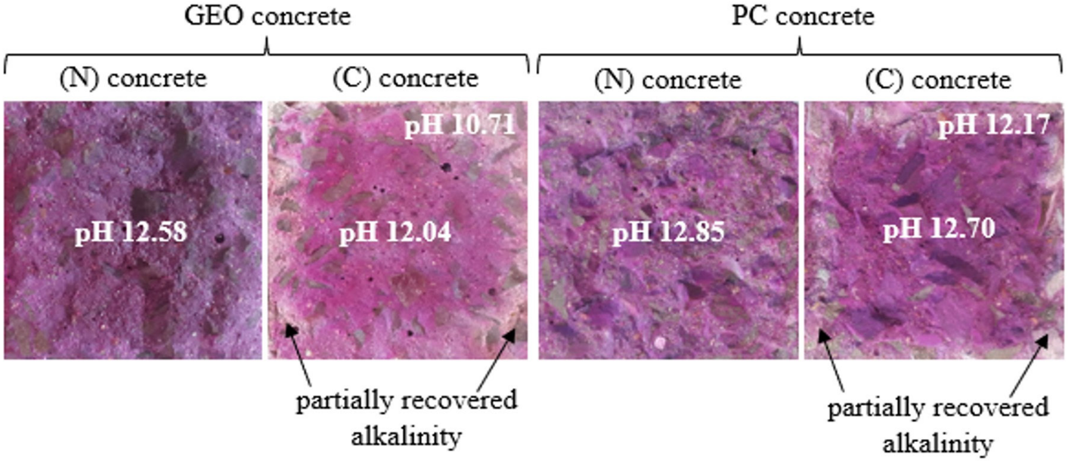

Figure 6. Partial pH recovery after step 3.

According to Figure 6, a slight increase in surface pH value was observed in GEO (≈ 10.71) and PC (≈ 12.17) concretes. Despite the lower pH of the geopolymer concerning the reference concrete, Robayo-Salazar et al. [21]

discussed that the steel remains passivated with a pH close to 10.7, offering no risk of corrosion of the reinforcement. Values close to 10.5 were also indicated by Pouhet and Cyr [18]. The increase in pH reinforces that the alkalinity of the carbonated samples was partially recovered, demonstrated by the light pink color obtained by the phenolphthalein colorimetric test. Moreover, pH values around 11.3 to 12.5 have been reported by other studies [10], [16] involving Portland cement after additional curing.

4 CONCLUSIONS

The following conclusions were obtained from the execution of this study:

- The metakaolin-based geopolymer concrete showed depth and extent of carbonation similar to Portland cement concrete. However, the GEO concrete requires thermal curing preconditioning to release water from the mixture and unblock the pores for CO_2 penetration. Also, PC concrete showed a 2.5 times greater mass increase than GEO concrete during carbonation curing. Therefore, concretes with metakaolin-based geopolymers may have a greater capacity to bind CO_2 during carbonation curing compared to Portland cement concrete, since less CO_2 was absorbed by the geopolymers and similar carbonation depth was observed.
- During carbonation curing, the surface pH was reduced. Moreover, the alkalinity of the carbonated region was partially restored after further conventional curing. Although other studies have shown that the pH of Portland cement concrete can be partially recovered after the additional curing step during carbonation curing, this article showed that this effect also occurs in geopolymer concrete.
- Carbonation curing in geopolymer concrete showed difficulty in promoting pore refinement. Also, there was no significant difference in the compressive strength of GEO concrete before and after carbonation curing. Even so, the compressive strength of geopolymer concrete was higher than the compressive strength of Portland cement concrete.
- The variation in the compressive strength of PC concrete was significant after the additional curing. The increase in compressive strength in PC concrete after Step 2 was 17%. This increase reinforces that the formation of $CaCO_3$ during carbonation curing clogged the pores and increased the density of the concrete, increasing compressive strength. These results agree with the reduction in water absorption by immersion and the higher CO_2 absorption of PC concrete compared to GEO concrete. Thus, the results indicate that the effect of carbonation curing is greater in concretes with Portland cement.

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