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# Shrinkage and carbonation of alkali-activated calcined clay-ground granulated blast furnace slag (GGBFS) concrete



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## ABSTRACT

This research investigates the influence of alkaline concentration and calcium content on the shrinkage mechanisms, carbonation resistance and reinforcement corrosion of alkali-activated concrete system composed of calcined clay and ground granulated blast furnace slag (GGBFS). An increase in Na<sub>2</sub>O% led to an improvement in the mechanical performance, pore structure refinement, reducing both accelerated and natural carbonation. However, the increase in alkaline concentration generated a greater shrinkage for mixtures with a higher proportion of GGBFS; the opposite was observed for mixtures with calcined clay as the dominant precursor. The results of 1-year of total shrinkage shows that the concrete containing high calcined clay and Na<sub>2</sub>O contents demonstrated the best performance. Importantly, there was no evidence of reinforcement corrosion observed after the carbonation front had reached the steel-concrete interface following 2 % CO<sub>2</sub> accelerated carbonation exposure. This was attributed to the high pH values measured in the carbonated region of the alkali-activated concrete.

# 1. Introduction

The growing need for environmentally-friendly concretes has stimulated the advancement of a class of substitute binders referred to as alkali-activated binders. These binders are produced by reacting materials rich in alumina and silica with alkaline activators, such as sodium hydroxide and sodium silicate solution. They are generated through the chemical reaction of solid precursors, including fly ash, GGBFS, and calcined clay, with alkaline solutions. When GGBFS, a material that contains a considerable amount of calcium, is used as the raw material for alkali activation, it often leads to the formation of C-A-S-H (calcium aluminium silicate hydrate) compounds [1]. These compounds can be activated with moderate alkalinity and contribute to the development of a dense matrix within the concrete structure [2]. On the other hand, lowcalcium systems like fly ash, metakaolin and calcined clays usually result in N-A-S-H (sodium aluminium silicate hydrate) gels. However, these gels are activated in exposure to highly alkaline environments [1]. Blended systems of GGBFS and low-calcium precursors can contain both N-A-S-H and C-A-S-H gels, with higher calcium content leading to increased shrinkage [3-5].

Despite their mechanical advantages over OPC binders, alkali-

activated binders face challenges like significant shrinkage, which can be 2-4 times higher than OPC binders [2]. The issue of shrinkage is more noticeable and pronounced in alkali-activated GGBFS systems compared to other low-calcium alkali-activated composite systems like fly ash and metakaolin [2,6]. In alkali-activated composite systems, the reduction in size is primarily caused by two factors: autogenous shrinkage and drying shrinkage. Autogenous shrinkage occurs due to water loss within the material during the hydration process, leading to capillary stress formation. Drying shrinkage happens when moisture evaporates into the surrounding environment. Both mechanisms contribute to a decrease in the volume of alkali-activated composites [6]. The combination of autogenous shrinkage and drying shrinkage is referred to as total shrinkage. Increased levels of alkali concentration in alkali-activated binders have been associated with high drying shrinkage, with higher concentrations of Na<sub>2</sub>O leading to a gradual increase in drying shrinkage [7].

Another significant challenge in the field of alkali-activated concrete (AAC) is carbonation, which poses a substantial risk to their long-term durability. For conventional concretes, carbonation involves the reaction between carbon dioxide from the air and the Portland cement paste, leading to detrimental degradation that can significantly impact the

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durability of civil infrastructures. Extensive research has been conducted to understand the mechanisms and consequences of this reaction on Portland cement structures [8]. One particularly damaging consequence of concrete carbonation is the dissolution of portlandite (Ca (OH)<sub>2</sub>), an important source of hydroxide ions serving as a buffer to counteract neutralization caused by carbonation [9]. The consumption of portlandite reduces the pore solution pH below 9, resulting in the corrosion of steel bars in reinforced concrete due to the breakdown of the passivation layer at the steel-concrete interface [10]. Previous studies showed that alkali-activated concrete demonstrates less resistance to carbonation compared to ordinary Portland cement concrete [11,12]. Several factors have been identified as influential in affecting the carbonation process in AAC including the type and composition of precursors, concentration and type of activators, silicate modulus and exposure conditions including both natural and accelerated carbonation [12].

The alkalinity of the pore solution, influenced by the concentration and type of alkali, and the partial concentration of carbon dioxide significantly affect both carbonation rate and pH decrease in accelerated carbonation tests [13]. Bernal et al. [3] found that under natural carbonation conditions, the formation of natron (Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O) is favoured, while under accelerated carbonation testing with CO<sub>2</sub> concentrations ranging from 1 % to 100 %, nahcolite tends to form instead. It was also observed that accelerated carbonation testing may underestimate the service life of geopolymer binders. Therefore, measuring resistance to carbonation through accelerated tests at high levels of CO2 concentration might not be suitable for evaluating geopolymer binder durability [3]. According to a study conducted by Badar et al. [14], the effects of accelerated carbonation on the corrosion process of steel rebar in geopolymer concretes were evaluated using electrochemical measurements. The results showed that geopolymer concretes prepared with fly ash low in calcium content are better suited for producing durable concrete for structural applications exposed to carbonating environments. These materials demonstrated properties that mitigate the risk of reinforcement corrosion induced by carbonation in concrete. Babaee et al. [13] conducted a study to examine the carbonation behaviour of low-calcium fly ash-based geopolymer binders by varying the concentration of alkaline solution. Based on the analysis of pH and electrochemical properties of the reinforcement electrode incorporated in alkali-activated fly ash, Babaee et al. [13] determined that there was no evidence of depassivation taking place, even when subjected to accelerated carbonation (or natural exposure conditions).

Recent interest has grown in using low-calcium precursors combined with GGBFS to mitigate drawbacks like efflorescence, extended setting time, and poor workability. However, high GGBFS content can lead to reduced setting time and increased surface cracking due to shrinkage [6]. The alkali-activated fly ash GGBFS concretes exhibited the significantly high drying shrinkage in comparison with standards for OPCbased concretes [15]. There has been growing interest in using a combination of calcined clay and GGBFS as the novel precursor in alkaliactivated concretes in recent years [16-18]. The combination of lowgrade calcined clay and GGBFS in geopolymer concretes has demonstrated potential for enhancing the mechanical properties of the concrete. Rakhimova et al. [19] reported that a combination of GGBFS and calcined clay, which consisted of 60 % amorphous phase of kaolinite/ montmorillonite, exhibited favourable quality as a secondary precursor in blended alkali-activate systems. Gomes et al. [16] conducted a study on alkali-activated mortars utilizing a low-grade calcined clay combined with GGBFS. The findings demonstrate that the increase in GGBFS content greatly influenced the mortar properties due to the presence of Ca-rich phases like C-(A)-S-H/C-(N)-A-S-H, which resulted in improved microstructure densification. Furthermore, the increase of GGBFS content in the mix composition led to an increase in pH leading to enhanced resistance against carbonation. Nonetheless, the findings of this study did not provide a clear understanding regarding the potential risks of reinforcement depassivation or progression to corrosion due to the

significant carbonation depth observed in accelerated tests and a potential decrease in pH value. With the growing use of calcined clay in the construction materials industry, understanding the behaviour of an alkali-activated precursor containing calcined clay and GGBFS, particularly in terms of shrinkage development and carbonation, remains a research gap that needs to be addressed to accelerate the adoption of this precursor.

This study examines the influence of alkaline concentration and calcium content on both shrinkage mechanisms and resistance to carbonation in a binary alkali-activated concrete system consisting of calcined clay and GGBFS. The aim is to understand how variations in these parameters affect the performance characteristics of this type of concrete mixture in natural conditions. Furthermore, the condition of steel bars after accelerated carbonation was visually investigated. This assessment aimed to evaluate the durability of the passive film when exposed to carbon dioxide over an extended period.

## 2. Materials and methods

## 2.1. Raw materials

The calcined clay was obtained from Argeco through industrial flash calcination techniques. This specific type of clay can be classified as lowgrade due to its kaolinite content accounting for 55 wt%. On the other hand, the GGBFS used in this study originated from Australian Steel Mill Services, located in Port Kembla, New South Wales, Australia. The chemical compositions of calcined clay and GGBFS measured by X-ray Fluorescence (XRF) (Table 1). Fig. 1 exhibits the crystalline components of calcined clay and GGBFS, which primarily consist of calcite, quartz, kaolinite, and certain zeolite minerals. The alkaline activator for the calcined clay-GGBFS alkali-activated concrete was composed by mixing sodium silicate solution (Chem-Supply, Port Adelaide SA, Australia - $Na_2O = 9.1$  %,  $SiO_2 = 28.9$  % and Weight Ratio ( $SiO_2$ :  $Na_2O$ ) 3.16–3.26) with sodium hydroxide pellets (NaOH) with purity: 98 %, specific gravity: 2.13 g/cm<sup>3</sup> and pH: 14. The sand has a specific gravity of 2.65 and water absorption of 3.5 % while the coarse aggregate (10 mm basalt) has water absorption of 1.79 %.

## 2.2. Alkali-activated concrete mix design and testing procedures

The alkali-activated concrete mix was designed according to Table 2. NaOH pellets and sodium silicate solutions were mixed in proportions to form alkaline solutions in different Na<sub>2</sub>O percentages (8 % and 10 %) and constant activator modulus (Ms = SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio) equal to 1.5. The alkaline solution was prepared 24 h prior to usage. The samples were mixed in an electric Pan-drum mixer. Afterwards, fresh concrete was poured into different molds and vibrated on a vibrating table to remove trapped air. After 1 day, all concrete samples were demoulded, sealed and transferred to a controlled room with a temperature of 23  $\pm$  2 °C.

## 3. Experimental program

## 3.1. Compressive strength

The compressive strength of the alkali-activated concrete made from calcined clay and GGBFS was evaluated after 1, 3, 7, 14 and 28 days of curing. The testing method used three cylinders for each testing date, following the guidelines outlined by ASTM C39 [20]. The compression testing was conducted using a Universal Hydraulic Test Frame (UH-500kN XR).

## 3.2. Total and autogenous shrinkage

Concrete prisms with a dimension of 280 mm  $\times$  75 mm  $\times$  75 mm were fabricated to monitor the evolution of autogenous and total

#### Table 1

Chemical compositions of Calcined clay and GGBFS (% by weight).

	SiO2	Al2O3	Fe2O3	CaO	MgO	Na2O	K2O	TiO2	SO3	(LOI)
Calcined clay	70.42	22.34	2.34	0.49	0.16	0.1	0.19	1.1	0.02	1.76
GGBFS	31.52	12.22	1.14	44.53	4.62	0.21	0.33	1.03	3.23	0.79



Fig. 1. XRD patterns of Calcined clay and GGBFS.

# Table 2

Alkali-activated	concrete ex	perimental	design	mixes
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Mixing <sup>(1)</sup>	GGBFS (%)	Activator modulus (M <sub>S</sub> )	Activator concentration $Na_2O\% = Na_2O/(CC + GGBFS)$ (%)	Total Binder (kg∕ m³)	Coarse/fine aggregate ratio	Water/solid
70CC/30S-8	30	1.5	8	400	1.9	0.45
70CC/30S-	30	1.5	10	400	1.9	0.45
10						0.45
50CC/50S-8	50	1.5	8	400	1.9	0.45
50CC/50S-	50	1.5	10	400	1.9	
10						

\*Note 1: CC: Calcined clay, S: Ground Granulated Blast-furnace Slag.

\*Note 2: Water: free water + water in silicate solution. Solid: Binder + solid in silicate solution (SiO<sub>2</sub> and Na<sub>2</sub>O) + NaOH pellet.

shrinkage over a period of 365 days (Fig. 2). The measurement of shrinkage strain was conducted using a digital gauge meter with an accuracy level of  $\pm 1~\mu\text{m/m}.$  After 24 h of casting, the reference lengths of concrete prisms were measured shortly after being removed from their molds to determine total shrinkage. Total shrinkage was monitored in this study by exposing unsealed specimens to a controlled environment of a temperature of 23  $\pm$  2 °C and relative humidity (RH) of 50  $\pm$ 3 % immediately after demolding. Measurements for autogenous shrinkage were taken after wrapping the specimens by a self-adhesive waterproof aluminium foil and storing them in an environmental chamber at a constant temperature of 23  $\pm$  2 °C. The aluminium foil aimed to prevent moisture loss throughout the experimental period. The shrinkage value is the average of shrinkage measurements in three prisms. A standardized protocol, known as the "Simplified procedure for the determination of autogenous shrinkage," outlined in European Standard EN 12390-16 [21], was employed for this purpose. The weight of specimens subjected to the autogenous shrinkage was monitored, and it exhibited negligible variation over the entire test duration. This observation suggests that the self-adhesive aluminium foil effectively maintained a tight seal, ensuring minimal moisture loss during testing.

#### 3.3. Natural and accelerated carbonation test

Accelerated carbonation test and natural carbonation was performed with samples of 50 mm thickness concrete discs cut from the middle part of three identical 100  $\times$  200 mm cylinders. The samples were sealed one day after casting and cured for 28 days, then the samples were unpacked and stored for two weeks in a controlled room at a constant temperature of 23  $\pm$  2 °C and 50  $\pm$  3 % RH until transferred to the carbonation chamber. For accelerated carbonation, specimens were placed in a carbonation chamber at 2 % CO2 concentration, 23 °C and 50 % relative humidity. The carbonation depth was measured after 2-8 weeks of exposure. For natural carbonation, the specimens were kept for 365 days in the controlled room at 0.03 % CO2 concentration with the same temperature and RH. The depth of carbonation was measured by applying 1 % solution of phenolphthalein in alcohol to the surface of a split concrete specimens. The carbonation depth is the average depth of three concrete discs for each test. For the accelerated and natural carbonation test, two OPC concretes with 40 % replacement of OPC by GGBFS were prepared for comparison. The first one called OPC- S50 (50 MPa grade) and the second one OPC-S40 (40 MPa grade). The two mixes were submitted to the same exposure conditions as the alkali activated



Fig. 2. Autogenous and total shrinkage prisms of alkali-activated concretes.

## concretes.

## 3.4. Pore structure study by $N_2$ adsorption

The pore size distribution and porosity of the hardened alkaliactivated pastes were evaluated at 28 days of curing. The paste compositions used for testing followed the same proportions as outlined in Table 2, but without coarse and fine aggregate. The alkali-activated pastes were prepared and cured under sealed conditions until 28 days. It should be noted that the pore structure was assessed only on uncarbonated samples. Prior to conducting the experiment, the paste samples were immersed in isopropanol for one hour to stop the hydration and then vacuum-dried at 40 °C for 30 min [22]. Crushed and ground samples were utilized and then screened using a sieve with a particle size of 75 µm. Approximately 1 g of sample was used for the analysis. To assess the distribution of pore sizes, the nitrogen adsorption technique was utilized. The pore size distributions (PSDs) of the samples were calculated using the Barrett-Joyner-Halenda (BJH) method with the Kelvin model of pore filling [23]. Previous studies have indicated that analyzing PSDs based on desorption branches of isotherms is an appropriate approach. The range of mesopores with a width between 2 and 50 nm was determined to be the most accurate in terms of pore size distribution by employing the BJH method [24,25].

## 3.5. Pore solution extraction and pH measurements

The pH profiles were determined utilizing a combination of the powder suspension technique and pore solution extraction method [13]. The method used to extract pore solution from the alkali-activated pastes at 28 days was based on a procedure described in the previous studies [13,26]. The extraction process involved using high pressure

over 350 MPa to obtain the pore fluid from uncarbonated and sealed paste samples. Cylindrical paste samples with dimensions of 35 mm diameter and 70 mm height were utilized for this purpose (Fig. 3). At 28 days, the paste specimen was removed from the mould and placed in the centre of a pore extraction device. High pressure, exceeding 350 MPa, was able to extract the pore solution from the hardened paste specimens. Barneyback and Diamond indicated that the pore solution extraction method is suitable for paste specimens even after extended hydration periods [27]. Following the extraction, the pH value of the obtained solution was determined using a calibrated pH meter with an accuracy level of  $\pm 0.01$ . After a period of 28 days, it was not possible to acquire an adequate quantity of pore solution from the unsealed and carbonated samples due to the exposure to RH of 50 %. Consequently, for carbonated specimens, the powder suspension technique was employed after this duration. To execute the powder suspension method, samples of alkali-activated pastes powder at 1 mm intervals up to a depth of 5 mm in the specimens were collected using a profile grinder. The collected powder was then mixed with deionized water in a solid-to-liquid ratio of 1:1 for 5 min on a magnetic stirrer. The pH value of the obtained solution was determined using the calibrated pH meter. Three pH value measurements were performed to determine the average pH values of paste samples.

## 3.6. X-ray diffraction (XRD) analysis

The mineralogical composition of the composite material was assessed through XRD analysis. A Bruker D8 Discover diffractometer was used to examine a finely powdered paste derived from samples that had been aged for 28 and 365 days for natural exposure and also those subjected to an 8-week accelerated carbonation process. The paste was prepared using the same concrete mixing composition, without coarse and fine aggregates, as described in Section 3.4 and 3.5. The paste was ground into powder using a mortar and pestle. After that, the paste powder was screened through a 75  $\mu$ m sieve prior to XRD analysis. The XRD measurements were carried out at standard settings with an electrical current of 20 mA and voltage of 40 kV. Scanning took place over a range of angles (20) spanning from 5° to 80°, however only the 20° to 65° 20 was studied.

## 3.7. Fourier-transform infrared spectroscopy (FTIR) analysis

The FTIR analysis was also used to identify the hydration products for different ages and exposed to natural or accelerated carbonation of the paste powder. The FTIR spectra were collected by a Perkin Elmer Frontier IR spectrophotometer. The spectrophotometer was equipped with a 3 mm diameter diamond/ZnSe crystal. The absorption spectrum was measured with a resolution of 2 cm<sup>-1</sup> and 32 accumulations from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> per spectrum. The band between 650 cm<sup>-1</sup> and 1800 cm<sup>-1</sup> was the only considered for analyzing the results since the reaction products appeared at this range.

## 3.8. Carbonation-induced reinforcement corrosion

Two concrete mixes, namely 50CC/50S-10 and 70CC/30S-10 in Table 2, were used to cast the reinforced concrete specimens to investigate the reinforcement corrosion. In previous studies [13,28–30], researchers have utilized a similar approach to evaluate the corrosion of steel in reinforced concrete and geopolymer samples. The schematic details of the sample subjected to accelerated carbonation followed by electrochemical measurements are illustrated in Fig. 4. Round steel bars of 12 mm diameter with normal ductility were embedded into the concrete. To ensure accurate corrosion measurements, any existing rust on the reinforcing bars was carefully removed using a gentle wirebrushing technique. The embedded bars, which had a length of 50 mm and machined ends, underwent welding at one side to attach a copper wire. To facilitate the reinforcing bars attachment, acrylic tubes



Fig. 3. Extraction of pore solution from alkali-activated pastes.



Fig. 4. Reinforced alkali-activated specimen configuration, adapted from Nguyen and Castel [29].

were installed at both ends of the bars. In addition, acrylic tube was filled with silicone sealant to prevent the direct ingress of CO2 to the steel bar. Total 18 reinforced concrete specimens, including 9 specimens for each 50CC/50S-10 and 70CC/30S-10 mix, were fabricated in this study.

One day after casting, the samples were removed and carefully wrapped before being placed in a controlled room at the temperature of 23  $\pm$  2 °C and RH of 50  $\pm$  3 % until 28 days. Subsequently, the wrapped samples were unwrapped and sealed using aluminium tapes around

their edges at the top and bottom sides, ensuring the diffusion of  $CO_2$  through the circumference surfaces (Fig. 4). After that, the specimens were exposed to the controlled room for a period of two weeks. Subsequently, the specimens were then moved to a carbonation chamber with the same condition of accelerated carbonation ( $CO_2 2 \%$ ) as described in the section 3.3. Samples exposed to accelerated carbonation for a duration of up to 134 days. The carbonation depth was measured by phenolphthalein spraying test. After exposure to accelerated carbonation, the reinforced specimens were subjected to wetting and drying

cycles for over 300 days. Each cycle consisted of one week in distilled water followed by two weeks of drying in a controlled room. In addition, the water was not renewed throughout the entire experimental duration to minimise any excessive ions leaching. The containers were kept closed at all times to prevent water evaporation affecting the water level. At the end of the wetting/drying cycles (314 days), the specimens were split, and the steel bars were extracted for visual inspection aiming to assess the level of corrosion.

## 4. Results and discussion

## 4.1. Compressive strength

Fig. 5 shows the compressive strengths of the calcined clay – GBBFS activated alkali concretes cured at 23  $\pm$  2 °C up to 28 days with Ms. (SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio) equal to 1.5 and two different activator concentrations (Na2O% = 8,10). At day 1, the compressive strength of the samples ranged from 14.4 to 31.6 MPa for those in the group consisting of 70 % calcined clay (70CC30S) with concentrations of 8 M and 10 M respectively. Similarly, in the group containing a mixture of 50 % calcined clay (50CC50S), compressive strengths were found to be around 17.4 to 26.6 MPa when using Na<sub>2</sub>O concentrations of 8 % and 10 % respectively. The compressive strength of the concrete samples showed a consistent pattern for both the 3-day and 7-day age. As the concentration of activator Na2O% increased, there was a tendency for an increase in compressive strength. However, this effect appeared to be more pronounced in samples with higher amounts of calcined clay, such as the 70CC30S-10 mixture which achieved a compressive strength of 43.9 MPa after 7 days, compared to only reaching 37.7 MPa for the 50CC50S-10 mixture.

At 14-day, comparable strengths were observed for both mixes' groups with varying concentrations of  $Na_2O$  - approximately 30 MPa and 45 MPa for dosages of 8 % and 10 %, respectively. For the concentration equal to 8 %, both mixes, 50CC50S and 70CC30S, still showed compressive strengths close to 30 MPa at 28-day age, with a slight increase for the mixture with a higher proportion of GGBFS (50CC50S-8) with reached 34 MPa. The mechanical performance increased with Na2O% of 10 %, reaching about 54.7 MPa for the sample with 50 % calcined clay (50CC50S) and 50.3 MPa for the mixture with

70 % calcined clay (70CC 30S) at 28 days. This can be explained by the fact that a fixed Ms. requires a certain amount of SiO<sub>2</sub> to satisfy the balance/reaction of the solution. Thus, increasing Na<sub>2</sub>O% brings more soluble silicate species into the system, which is necessary to form the reaction products, affecting the chemical composition and resulting in this extended mechanical property [31]. The increase in molar concentration, coupled with the presence of calcium, results in the formation of C-A-S-H instead of N-A- S-H. This process continues until all available Ca<sup>2+</sup> within the system is consumed [32], which likely occurred with the mixture containing 10 % Na<sub>2</sub>O. Furthermore, the compressive strength of 50CC50S-10 and 70CC30S-10 was higher than that of 100 % alkali-activated slag, as reported in previous studies [33,34], indicating the positive effects of calcined clay in the alkaliactivated slag system.

# 4.2. Total and autogenous shrinkage

Shrinkage poses a significant challenge in alkali-activated materials. The level of drying shrinkage observed in alkali-activated compositions can be approximately three times higher than that experienced by ordinary Portland cement concrete specimens cured under ambient conditions with a temperature of 23 °C and relative humidity of 50 % [6,35]. Unlike other alkali-activated concretes containing high GGBFS content [36,37], no microcracking was observed on the surface of alkaliactivated calcined clay-GGBFS concretes, as presented in Fig. 6. Fig. 6 (b) shows an example of microscopic analysis to confirm the absence of microcracks on the specimens.

Fig. 7 illustrates the evolution of the total shrinkage in all concrete samples after demoulding for a duration of one year. Within the initial 30-day period, concretes consisting of 70 % calcined clay (70CC30S-8 and 70CC30S-10) exhibited similar total shrinkage value, measuring around  $-430 \,\mu$ m/m. Meanwhile, concrete mixtures with a composition ratio of 50 % calcined clay to slag (50CC50S-8) experienced slightly higher total shrinkage at approximately  $-500 \,\mu$ m/m. Notably, 50CC50S-10 samples showed the highest level during this initial phase with the total shrinkage value at roughly about  $-533 \,\mu$ m/m. Zhang et al. [38] carried out a study with OPC concrete blended with GGBFS under the same testing conditions. At 30 days of measurement, the concretes with 32 MPa grade with 100 % OPC and 40 % replacement of GGBFS



Fig. 5. Compressive strength development up to 28 days of alkali-activated concretes.



Fig. 6. No crack or microcrack was observed in the alkali-activated calcined clay GGBFS concretes after 1 year. a) Shrinkage specimen b) An example of microscopic observation (10× magnification.



Fig. 7. Total shrinkage development of alkali-activated concretes up to 365 days.

showed values around -380 and  $-400\,\mu\text{m/m},$  respectively. Meanwhile, the 50 MPa grade concrete made with 100 % OPC and 40 % GGBFS showed values around  $-650\,\mu\text{m/m}.$ 

In the long-term, up to 365 days, it was observed that the mix 70CC30S-10 exhibited a value of total shrinkage of around  $-620 \,\mu\text{m/m}$ , which is the lowest value recorded among all mixes after one year. An important observation is that, after 150 days, total shrinkage remained almost constant (Fig. 7). On the other hand, specimens with lower activator concentrations such as 70CC30-8 and those with equal proportions of calcined clay and GGBFS (i.e., 50CC50S-8 and 50CC50S-10) showed higher total shrinkage values after a duration of 365 days, reaching approximately –766  $\mu m/m,$  –782  $\mu m/m,$  and – 844  $\mu m/m$ respectively. Unlike alkali-activated concretes using only GGBFS, systems that utilize low calcium precursors exhibit lower total shrinkage with higher concentrations of alkali activator. Some studies involving fly ash and metakaolin [6,39] have shown that an increase in the concentration of activators can lead to a reduction in shrinkage, up until a certain threshold is reached. This phenomenon results in the formation of a compact and robust geopolymeric matrix, which leads to enhanced compressive strength and lower shrinkage values. Nguyen et al. [24], in their work with OPC and LC3 concrete, showed that up to 100 days of measurement of total shrinkage, the reference samples (45 MPa grade) with 100 % OPC and the LC3 sample (replacement 30 % calcined clay +14 % limestone) presented values around  $-600 \ \mu\text{m/m}$ , similar to the values of samples 70CC30S-10 at 100 and 365 days. The use of calcined clay resulted in a significant reduction in the shrinkage compared to 100

% slag alkali-activated materials. Specifically, Collins and Sanjayan [35] reported that the drying shrinkage of alkali-activated slag was more than three times higher than that of OPC specimens after more than 300 days of exposure to 23 °C and 50 % RH.

The development of autogenous shrinkage of alkali-activated calcined clay/GGBFS concretes is presented in Fig. 8. The variation of autogenous shrinkage is specifically highlighted from day 1 to day 15, as shown in Fig. 8 (a). In this figure, negative values indicate shrinking behaviour while positive values present expansion or swelling tendencies of the concrete samples. Notably, it was observed that greater expansions occurred in the mixes containing a higher proportion (70%) of calcined clay (70CC30S group) compared to those of 50CC50S group. Specifically, after one day, 70CC30S-8 concrete exhibited the highest value recorded at approximately 3 µm/m. Only 70CC30S-10 concrete exhibited an expansion from day 5 to day 8. Further research is required to explain this expansion in relation with the calcined clay content and the activator concentration. Lolli et al. [40] observed that metakaolin geopolymers exhibit chemical expansion instead of shrinkage during the first three days. Peak levels of expansion were observed within the first 10 days, which can be attributed to N-A-S-H precipitation and densification. This expansive behaviour is distinct to sodium-based geopolymers derived from metakaolin, as low-calcium alkali-activated pastes primarily made of fly ash and GGBFS do not display any swelling at all [40,41]. Long-term autogenous shrinkage, measured up to 365 days (Fig. 7(b)), revealed that concretes containing a higher proportion of GGBFS (50CC50S) exhibited higher autogenous shrinkage compared to the 70CC30S concretes. Specifically, after one year, the 70CC30S-8 and 70CC30S-10 concretes displayed autogenous shrinkage values of  $-279 \ \mu m/m$  and  $-188 \ \mu m/m$  respectively. Conversely, the corresponding values for the 50CC50S-8 and 50CC50S-10 concretes were significantly higher at approximately  $-544 \ \mu m/m$  and  $-613 \ \mu m/m$ respectively. These high autogenous shrinkage values have also been previously reported in studies with alkali activated slag (AAS) with more than 100 days of measurements [42-44]. Autogenous shrinkage could account for 30 %-70 % of the total shrinkage of AAS mortar depending on the activator composition [42,44]. These findings could potentially be connected to the primary type of gel (N-A-S-H or C-A-S-H) present in each composition as well as its microstructural enhancement and pore size distribution, which will be further examined in the subsequent sections. A previous study indicates that C-A-S-H possesses a notably higher filling capacity in comparison to the N-A-S-H gel [26]. In a recent study by Nguyen et al. [24] on OPC and LC3 concretes, the authors observed that after 100 days of measuring autogenous shrinkage, the reference samples with 100 % OPC (45 MPa grade) and the LC3 concrete (45 MPa grade with a replacement of 30 % calcined clay and 14 % limestone), showed values around  $-180~\mu\text{m/m}$  and - 275  $\mu\text{m/m}$ respectively. These values were higher than those recorded for samples labeled as 70CC30S-8 and 70CC30S-10 at the same time point.



Fig. 8. Autogenous shrinkage development of alkali-activated concretes up to a)15 days b) 365 days.

# 4.3. Pore structure study by $N_2$ adsorption

The sizes of the pores can be categorized into different groups: micropores, small capillary or gel pores, medium capillary pores, and large capillary pores. Micropores have a size ranging between 0.5 nm to 2.5 nm. Small capillary or gel pores size ranging from 2.5 nm to 10 nm. The size of medium capillary pores falls within the range of 10 nm to 50 nm while large capillary pores are in the range of 50 nm to 10  $\mu$ m [45]. Fig. 9 displays the pore size distribution of alkali-activated calcined clay/GGBFS pastes after 28 days of curing. The analysis revealed that variations in the precursor proportions and Na<sub>2</sub>O% concentrations led to

distinct impacts on the pore size distribution of alkali-activated pastes.

Fig. 9 demonstrates a greater concentration of micropores and gel pores in specimens with high GGBFS content, with the specimen 50CC50S-10 having the highest amount of micropores and gel pores and the lowest large capillary pores content, which can be attributed to the refinement of the pore structure with the increase of the Na<sub>2</sub>O%. In the meantime, the blends containing 70 % calcined clay (70CC30S) demonstrated comparable amounts of micropores and gel pores. However, the mixture with a lower sodium concentration (70CC30S-8) exhibited a greater volume of medium and large capillary sections, exhibiting the highest cumulative pore volume among all mixes.



Fig. 9. Pore size distribution of alkali-activated calcined clay/GGBFS pastes determined by nitrogen adsorption and BJH method.

The autogenous shrinkage of alkali-activated materials can be affected by micropores, gel pores, and medium capillary pores. Pores with sizes less than 50 nm have the ability to create capillary pressure, leading to a significant increase in the self-desiccation process within the microstructure [24,46]. This observation elucidates the reason behind the high autogenous shrinkage values (Fig. 7 (b)) observed in the two mixes with the highest percentages of GGBFS (50CC50S-8 and 50CC50S-10) compared to of 70CC30S group. This can be attributed to a significant proportion of smaller- sized pores, specifically those with a diameter below 50 nm, in 50CC50S-8 and 50CC50S-10 pastes. It is reported that smaller pores tend to experience higher levels of capillary pressure compared to larger ones. This indicates that pore characteristics play a significant role in determining the overall shrinkage behaviour and associated stresses within these materials [5]. Moreover, the higher number of large pores and some changes in the microstructure over 1 year (will be discussed in following sections) on sample 70CC30S-8 may be linked to higher drying shrinkage when compared to sample 70CC30S-10.

The pore size distribution in Fig. 9 is not consistent with the compressive strength presented in Fig. 5. Specifically, 50CC50S-8 exhibits a pore size distribution similar to 50CC50S-10, yet its compressive strength is lower than that of 50CC50S-10, as shown in Fig. 5. This discrepancy can be attributed to the limitation of N<sub>2</sub> adsorption, which measures pore widths only in the range of 2 nm - 100 nm. Pores in the meso- and micro-scale range (100 nm to 10 µm), which significantly influence the mechanical properties of alkali-activated materials [47,48], are beyond the measurement capability of N<sub>2</sub> adsorption. In addition, it is expected that the porosity of calcined clay-GGBFS alkali-activated materials will be altered by carbonation. The change in porosity due to carbonation and its influence on steel corrosion will be investigated in a future study.

## 4.4. Accelerated carbonation and natural carbonation test

Table 3 and Fig. 10 show the carbonation depth and photos of the phenolphthalein indicator results for accelerated and natural carbonation. The carbonation depths shown are the average values of 15 to 20 measurements at least 10 mm away from the sample edge. Overall, both proportion of precursors and increase in the concentration of the alkaline solution influenced the carbonation mechanism of the samples.

For the accelerated carbonation (Table 3), the carbonation depths in the first week for the mixes 70CC30S-8, 70CC30S-10, 50CC50S-8 and 50CC50S-10 were respectively,  $10.1 \pm 1.03$ ,  $9.5 \pm 1.99$ ,  $6.1 \pm 0.56$  and  $6.3 \pm 0.79$  mm, indicating a decrease in carbonation depth with an increase in the alkaline solution concentration. In week 2, 70CC30S-8 concrete exhibited an approximately 50 % increase compared to week 1, while other mixtures displayed smaller increments. This occurrence may be attributed to the initial carbonation of the pore solution, suggesting that this particular mixture contains a lower quantity of Na<sup>+</sup> ions in its pore solution compared to the others mixes. It is consistent with a previous study by Pouhet and Cyr [10], which reports that 97 % of the pore solution was carbonated in the accelerated carbonation of geopolymers with 100 % pure metakaolin. Khan and Castel [49] also observed a similar trend of high carbonation depth for mixes with fly ash and GGBFS. Furthermore, the increased presence of macrospores presented in Fig. 8 within these samples facilitates CO<sub>2</sub> diffusion, consequently accelerating the carbonation process. The carbonation depth of the samples 70CC30S-10, 50CC50S-8 and 50CC50S-10 significantly increased after 6 weeks of accelerated carbonation, reaching carbonation depths of approximately 17.2  $\pm$  1.11, 16.6  $\pm$  1.47 and 16.5  $\pm$ 0.87 mm respectively (Table 3). On the other hand, sample 70CC30S-8 only showed a slight increase by 13 %, compared to its carbonation depth at week 2. It is possible that this minimal increase can be attributed to the almost complete carbonation of its pore solution during the first two weeks. After 8 weeks, the accelerated carbonation process resulted in complete carbonation in the 70CC30S-8 samples (Fig. 10).

## Table 3

Accelerated and natural carbonation depth of the alkali-activated concrete mixes.

Mix Reference	Carbonation depth Accelerated	mm (average)		Carbonation depth mm (average) Natural		
	1 week	2 weeks	6 weeks	8 weeks	6 months	12 months
70CC30S-8	$10.1\pm1.0$	$19.3\pm1.5$	$22.2\pm1.0$	Full carbonated	$13.1\pm2.4$	$17.91 \pm 1.3$
50CC50S-8	$9.5\pm2.0$	$11.0\pm1.1$	$17.2\pm1.1$	$20.4\pm1.7$	$9.9\pm1.3$	$13.79\pm0.9$
70CC30S-10	$6.1\pm0.6$	$10.5\pm1.9$	$16.6\pm1.5$	$17.8 \pm 1.5$	$10.2\pm1.6$	$12.63 \pm 1.1$
50CC50S-10	$6.3\pm0.9$	$10.3\pm1.3$	$16.5\pm0.9$	$17.1 \pm 1.3$	$8.4\pm1.0$	$11.75\pm1.4$
OPC-S40	$3.47 \pm 1.1$	-	-	$10.66\pm1.8$	$4.34\pm1.5$	$4.46\pm1.6$
OPC-S50	$1.19\pm0.9$	-	-	$7.15\pm2.1$	$\textbf{2.88} \pm \textbf{0.9}$	$3.95 \pm 1.1$

# Accelerated carbonation

OPC-S40





OPC-S50





Natural carbonation

70CC/30S-8

50CC/50S-8

70CC/30S-10



Fig. 10. Phenolphthalein indicator test results at 8 weeks exposed to 2 % CO<sub>2</sub> accelerated carbonation (Top) and 12 months natural carbonation (Bottom) of the alkali-activated and OPC/GGBFS concrete mixes.

On the other hand, the 50CC50S-8 samples experienced an increase of approximately 15.7 % in their carbonation depth. The mixes with an alkaline concentration of 10 (70CC30S-10 and 50CC50S-10) exhibited only a slight increase compared to week six, reaching depths of carbonation at around approximately  $17.8 \pm 1.49$  and  $17.1 \pm 1.25$  mm, respectively. The two reference concretes, with a 40 % substitution of OPC by GGBFS, exhibited varying carbonation depths. The OPC-S50 (50 MPa grade) recorded a carbonation depth of approximately 7.15 mm after 8 weeks under accelerated carbonation. In contrast, the OPC- S40 (40 MPa grade) demonstrated a marginally greater depth at about 10.66 mm.

The natural carbonation observed after six months followed a similar pattern to the accelerated carbonation (Table 3). The mixture 70CC30S-8 still exhibited the highest depth of carbonation, at approximately 13.1  $\pm$  2.39 mm. However, the specimen containing a higher percentage of GGBFS and an equal Na<sub>2</sub>O concentration (50CC50S-8) displayed lower levels of carbonation with depths around 9.9  $\pm$  1.33 mm. The carbonation depth of 70CC30S- 10 concrete was comparable to those of 50CC50S-8 concrete at approximately  $10.2 \pm 1.57$  mm. Interestingly, it was noted that the mixture 50CC50S-10 had the lowest carbonation front penetration after six months, exhibiting a depth around  $8.4 \pm 1.03$ mm. After one year of exposure to natural carbonation, the 70CC30S-8 mixture maintained its position with the highest level of carbonation depth (17.91  $\pm$  1.33 mm). Following by the mix 50CC50S-8 which exhibited a carbonation depth of approximately 13.79  $\pm$  0.85 mm. In comparison, mixtures containing higher activator concentration (70CC30S-10 and 50CC50S-10 concretes) demonstrated lower values of carbonation depth, at around 12.63  $\pm$  1.11 mm and 11.75  $\pm$  1.40 mm, respectively. These findings align with previous studies of the authors conducted on mortar and using the same precursors material [16]. The carbonation mechanism of this material is influenced by the concentration of alkali present in the pore solution, alongside the quantity of calcium in its precursors.

## 4.5. pH measurements

## Fig. 11 shows the pH measurement of pore solution at 28 days and

leachate results of accelerated/natural carbonation. For all uncarbonated geopolymer specimens at 28 days using the leachate powder suspension methodology, a pH ranging from 12.49 to 12.63 was observed. In contrast, applying the pore solution extraction method revealed a slight elevation in all samples, with the lowest recorded value being 12.7, on mix 70CC30S-8. Mixtures with higher activator concentration (70CC30S-10 and 50CC50S-10) showed a higher pH for the pore solution measurement, 12.81 and 12.97, respectively. After 28 days, the samples were exposed to dry conditions with a RH of 50  $\pm$  3 % under both accelerated and natural carbonation. As a result, it was not possible to extract the pore solution from these samples. Therefore, only the powder suspension method was utilized to measure the pH values after 28 days. It is worth noting that while the values obtained through this method may not be accurate pH values of the pore solution, however, they do reflect the overall trend of pH variation at different depths over time [13].

After 6 months of exposure under natural carbonation, all specimens presented a considerable drop in their pH values, approximate 1.6 for the specimens with the highest percentage of calcined clay (70CC/30S-8 and 70CC/30S-10) and close to 1.9 for the specimens with the highest percentage of GGBFS (50CC/50S-8 and 50CC/50S-10). After one year of exposure to natural carbonation, the pH levels of the specimens remained constant with minimal fluctuations. The decrease in pH in the samples after 6 months can be attributed to the presence of carbonated phases in the pore solution, along with the concentration of calcium, leading to the formation of CaCO<sub>3</sub>. It is important to note that even with the pH drop, all mixtures maintained pH values higher than 10.5, reducing the possible corrosion risk of steel bars which normally occurs at values close to 9. Pouhet and Cyr [10] reported that this drop in pH under natural conditions in 100 % metakaolin geopolymer occurred due to carbonation of the pore solution and generation of Na<sub>2</sub>CO<sub>3</sub> in the first weeks and bicarbonate formation after 6 months, resulting in a drop in pH from 12 at 14 days to a stable value of 10.5 after 6 months of exposure. This phenomenon is further discussed in the next section, where more detailed information about pore solution carbonation will be provided.



In terms of accelerated carbonation, it is evident that the pH values

Mix Reference

Fig. 11. pH measurement of pore solution at 28 days and leachate results of accelerated/natural carbonation of AAC mixes.

experienced a significant decrease, similar to natural carbonation condition. However, despite this decline, pH remained above the critical range for steel bars depassivation (with a pH level around 9). Therefore, drawing conclusions solely based on the carbonation depth from phenolphthalein indicator test results as shown in Table 3 and Fig. 10 can lead to an incorrect evaluation of the durability of reinforced geopolymer concrete structure. For instance, sample 70CC/30S-8 was 100 % carbonated after 8 weeks under accelerated carbonation, however the samples had a pH above 10.83, which was higher than both mixes with more GGBFS and higher Na2O concentration (50CC/50S-8 and 50CC/ 50S-10). The discrepancy between phenolphthalein spraying test (Fig. 9) and pH values (Fig. 10) is further discussed in Section 4.8. Previous studies have indicated that the utilization of accelerated carbonation may not be the most effective method for assessing carbonation in alkali-activated materials. This is primarily due to the fact that high CO<sub>2</sub> concentration in accelerated carbonation led to a shift towards equilibrium phases, resulting in rapid rates of carbonation and significantly low pH values below 10 [6,19]. A more thorough evaluation of the accelerated carbonation condition, pH reduction and its potential impact on the corrosion of steel bars will be provided in the following sections.

## 4.6. X-ray diffraction (XRD) analysis

The XRD analyses of uncarbonated alkali-activated blends containing calcined clay and GGBFS after 28 days are shown in Fig. 12. The crystalline spectra of the mixtures revealed prominent peaks corresponding to quartz, indicating the presence of calcined clay as confirmed by XRD analyses of the raw calcined clay, which is illustrated in Fig. 1. Interestingly, all samples also exhibited distinct peaks at angles of  $20.9^{\circ}$ 20,  $39.5^{\circ}$  20, and  $45.9^{\circ}$  20 indicative of kaolinite in their XRD patterns. Furthermore, zeolites from the faujasite family were detected in the specimens due to metakaolin dissolution. The XRD patterns of all samples displayed a broad peak at around  $26^{\circ}$  20 and  $36^{\circ}$  20, indicating the presence of an amorphous phase associated with C-A-S-H gel formation. Fig. 12 reveals that increasing the amount of GGBFS or the Na2O concentration results in higher intensity of this peak. This phenomenon can be attributed to the dissolution of calcium hydroxide from GGBFS followed by the formation of additional C-A-S-H gel. This finding aligns with the porosity results, which indicate that increasing the Na<sub>2</sub>O concentration from 8 % to 10 % resulted in a more pronounced refinement in the pore size distribution for samples containing higher amounts of calcined clay (70CC30S-10). This can be attributed to greater dissolution of the precursor, leading to an increased formation of additional C-A-S-H gel. Small peaks of calcite and Gaylussite (Na<sub>2</sub>Ca(CO<sub>3</sub>)) were detected, which relates to calcite from GGBFS and the initial exposure of the samples to  $CO_2$  during sample preparation.

After undergoing accelerated carbonation for 8 weeks, the XRD patterns of mixtures containing carbonated alkali-activated calcined clay and GGBFS display changes, as shown in Fig. 13. The analysis indicates a clear rise in the intensity of the calcite peak overlapping C-(A)-S-H after the process of accelerated carbonation. Additionally, other forms of calcium carbonate such as aragonite and vaterite become noticeable. After undergoing the accelerated carbonation process, peaks corresponding to sodium bicarbonate compounds - Nahcolite (NaHCO<sub>3</sub>) were detected. Additionally, the occurrence of carbonate minerals containing both sodium and calcium such as Gaylussite (Na<sub>2</sub>Ca(CO<sub>3</sub>)) were observed. The presence of these carbonates indicated the occurrence of the carbonation process in the calcined clay-GGBFS alkaliactivated materials. However, due to the high peaks from quartz originating from the calcined clay, peaks related to these carbonates appeared only small in Fig. 1. As shown in Fig. 13, the presence of calcium carbonate peaks in all specimens suggests that the C-A-S-H/N-A-S-H phases experienced a decalcification during the accelerated carbonation. These peaks correspond to aragonite at  $26.2^{\circ}$  20 and  $52.5^{\circ}$ 20, as well as vaterite at  $27.2^{\circ}$  20 degrees. The intensity of these peaks is higher in samples with higher GGBFS content including 50CC50S-8 and 50CC50S-10 mixes. Additionally, there was also an observed overlap between a peak corresponding to calcite and C-A-S-H peak at 29.5° 20. However, this overlapping peak was less pronounced in the mix 50CC50S-10 mixture suggesting a smaller decalcification of the C-A-S-H gel. Previous studies have revealed that accelerated carbonation tests conducted on alkali-activated slag binders let to the formation of trona (Na<sub>3</sub>H(CO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O) as the main phase, whereas for metakaolin systems, calcite has been found to be the dominant phase [50]. Trona formation was not observed in this study. Bernal et al. [50] highlighted that the



Fig. 12. XRD diffractograms of 28 days uncarbonated alkali-activated calcined clay/GGBFS.



Fig. 13. XRD diffractograms of 8-week accelerated carbonated of alkali-activated calcined clay/GGBFS.

introduction of 10 wt% metakaolin into the GGBFS binder systems effectively prevented trona formation. This was likely due to the presence of dissolved alumina, which could bind with sodium in alumino-silicate gels and reduce alkali availability as much alumina is introduced to the system. Almost all samples revealed the presence of gaylussite (33.2° 20) and nahcolite (31.2° 20 and 36.1° 20). However, nahcolite was detected with lower intensity in the samples containing higher proportions of calcined clay such as 70CC30S-8 and 70CC30S-10.

Fig. 14 shows the XRD patterns of specimens exposed to 12 months of natural carbonation. In general, natural carbonation after one year led to a change in the structure of the composites, showing phases related to both, carbonation of the pore solution and the geopolymeric gel, but

with much lower intensities than those presented in the accelerated carbonation (Fig. 13). Compared to accelerated carbonation, samples under natural conditions showed reduced or no peaks relative to calcium carbonate phases such as aragonite and vaterite. Except for 70CC30S-8 concrete, all mixes had reduced peaks of aragonite at  $26.2^{\circ} 2\theta$  and  $52.5^{\circ} 2\theta$ , as well as vaterite at  $27.2^{\circ} 2\theta$ . No nahcolite peak was identified at  $31.2^{\circ} 2\theta$  and the peak at  $36.1^{\circ} 2\theta$  showed a considerable decrease in intensity (with the exception of mix 70CC30S-8). The main difference observed was in the 70CC30S-8 mix, which after a year exposed to natural carbonation showed high calcite peaks compared to the other mixes. In Fig. 14, the 70CC30S-8 mix continues to show a lower broad ramp related to the C-A-S-H gel at 28 days (Fig. 12) compared to the



Fig. 14. XRD diffractograms of 12 months natural carbonation alkali-activated calcined clay/GGBFS.

other mixes and strongly indicates a dominance of N-A-S-H gel on its structure after one year under natural carbonation conditions. This aligns with findings related to the depth of natural carbonation (Fig. 10) and other studies involving natural carbonation using low calcium fly ash blended with GGBFS [26], where for high proportions of fly ash in the mix, the prevailing N-A-S-H gel reaction resulted in a higher presence of unbound  $Ca^{2+}$  ions within the pore solution. The interaction between the available  $Ca^{2+}$  ions and  $CO_2$  lead to the precipitation of calcium carbonate (CaCO<sub>3</sub>) within the saturated pore solution, concurrently forming sodium carbonate (Na2CO3) phases. This phenomenon was followed by the decomposition of remaining C-A-S-H in calcite type gel. However, no changes were made to the N-A-S-H gel structure, thus showing that N-A-S-H does not react with CO2 in natural conditions [26]. The enhanced decomposition of C-A-S-H and subsequent generation of Na<sub>2</sub>CO<sub>3</sub> phases could potentially account for the intriguing disparity observed between sample 70CC30S-8, which exhibited a higher total shrinkage (following one year of exposure to identical conditions as the samples undergoing natural carbonation), and sample 70CC30S-10. In a related study by Nedeljković et al. [26], focusing on natural carbonation of fly ash-GGBFS systems, it was reported that the removal of calcium ions from the gel interlayers and gel sheet layers during carbonation leads to a reduction in gels' size due to the molecular restructuring of the gels. This results in a reduction in the paste volume and a concurrent increase in the final porosity, which is distinct from the carbonation of ordinary Portland cement (OPC) pastes.

#### 4.7. FTIR analysis

The FTIR spectra for both non-carbonated and carbonated samples within the infrared range of 650 to 1800 cm<sup>-1</sup> are presented from Figs. 15 to 17. Generally, the FTIR findings is consistent with the XRD analysis. Fig. 15 shows the results of uncarbonated samples up to 28 days. The initial and most prominent peak within the spectrum, situated approximately at 964–976 cm<sup>-1</sup>, corresponds to the asymmetric vibration of Si-O-T (T = Si or Al), indicative of the binder gel (C-A-S-H, N-A-S-(H)) characteristics [51,52]. Mixtures 50CC50S-8 and 50CC50S-10 exhibited identical wavenumbers (964 cm<sup>-1</sup>), implying that the increase of alkaline concentration from 8 to 10 did not yield any

noticeable alteration in their primary phase. Nonetheless, the mixtures containing the highest levels of calcined clay (70CC30S group) displayed a distinct pattern. Specifically, in the case of the 70CC30S-10 mixture, increasing the Na<sub>2</sub>O concentration from 8 % to 10 % led to a noticeable downward shift in the Si-O-T asymmetric band, from 976 cm<sup>-1</sup> to 970 cm<sup>-1</sup>. As noted in a previous study [16], this leftward shift is indicative of a heightened formation of C-A-S-H over N-A-S-H. The peak identified at 1515 cm<sup>-1</sup> corresponds to the stretching vibrations of the O-C-O bond. This spectral feature is linked to initial carbonate formation, arising from the initial interaction between alkali sodium hydroxide and atmospheric CO2 diffused onto the surface of the alkaliactivated material [53]. The strength of these bands decreased with a higher Na<sub>2</sub>O content, which might be associated with a greater incorporation of Na<sup>+</sup> ions within the geopolymer structure, alongside improved mechanical strength. The wide bands detected in all FTIR spectra around 1683 cm<sup>-1</sup> correspond to the stretching (-OH) and bending (H-O-H) vibrations of water molecules bound within the hydrated products generated during alkaline activation [54]. The intensity of these bands decreased as the Na<sub>2</sub>O concentration was reduced, a trend that might be associated with mechanical strength values at 28 days (Fig. 5).

Fig. 16 presents the outcomes for accelerated carbonation at 2 and 8 weeks, as well as natural carbonation over one year, of samples in 70CC30S group. The vibration involving bending out-of-plane vibration  $(v2-CO_3^{2-})$  corresponds to both calcite and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) due to the carbonation process [55,56]. Notably, only the 70CC30S-8 mixture (under natural condition) exhibited notable peaks corresponding to calcite and sodium carbonate phases around 864 cm<sup>-1</sup>, a finding that aligns with the outcomes observed during XRD natural carbonation (Fig. 14). Fig. 15 and Fig. 16 show the Si–O–T (where T = Al, Si) band undergoes a shift from lower to higher wavenumbers (970  $\rightarrow$  987 cm<sup>-1</sup>) from 28 days uncarbonated condition to an 8-week period under accelerated carbonation for the 70CC30S-10 mix. This shift presents the polymerization of the silicate gel, attributed to the decalcification of the principal reaction product (C-A-S-H/N-A-S-H gel). The specimen 70CC30S-8 followed the same trend after 8 weeks under accelerated carbonation shifting from lower to higher wavenumbers (976  $\rightarrow$  993 cm<sup>-1</sup>). Fig. 16 illustrates that from the 28-day non-carbonated condition



Fig. 15. FTIR spectra of (a) 28 days uncarbonated alkali-activated calcined clay/GGBFS.



Fig. 16. FTIR spectra of 2-8 weeks accelerated carbonation and 12 months natural carbonation 70CC30S group.



Fig. 17. FTIR spectra of 2-8 weeks accelerated carbonation and 12 months natural carbonation 50CC50S group.

(Fig. 15) to 1 year under natural carbonation, there was no alteration in the wavenumber for the 70CC30S-10 sample. This negligible variation indicates that there was no decomposition of the aluminosilicate gel in these samples. In contrast, 70CC30S-8 paste exhibited a slight increase (976  $\rightarrow$  980 cm<sup>-1</sup>) in wavenumber. Both specimens displayed significantly lower intensities for this peak compared to those detected under accelerated conditions. This indicates that the decomposition of the aluminosilicate gel is limited to samples exposed to high concentrations

of CO2. Fig. 16 also shows, the stretching vibration (v3-CO<sub>3</sub><sup>2</sup>) observed at 1505 cm<sup>-1</sup>, involving O–C–O bonds and linked to the carbonated groups and the increase of calcium carbonate for the accelerated condition in 70CC30S-8 and 70CC30S-10 samples. In the natural carbonation, both samples exhibited reduced intensities in comparison to the accelerated carbonation, with 70CC30S-10 sample displaying the least intensity. The bands detected around 1673 and 1651 cm<sup>-1</sup> correspond to the stretching (-OH) and bending (H-O-H) vibrations of water

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molecules bound within the hydrated products from accelerated and natural carbonation respectively.

Fig. 17 displays the results of accelerated carbonation at 2 and 8 weeks, as well as natural carbonation over a period of 1 year of samples in 50CC50S group. In contrast to the 70CC30S group, the vibration involving bending out-of-plane vibration ( $v2-CO_3^{--}$ ) corresponds to both calcite and sodium carbonate (Na2CO3), can be clearly identified in mixes 50CC50S-8 and 50CC50S-10 under accelerated carbonation conditions both in week 2 and 8. No peaks related to these phases were detected in the natural exposure condition after 1 year for both mixes. Furthermore, Fig. 15 and Fig. 17 demonstrate that the Si–O–T (where T = Al, Si) band exhibits a shift from lower to higher wavenumbers during the transition from a 28-day non-carbonated state to an 8-week period under accelerated carbonation for both mixtures (50CC50S-8 and 50CC50S-10). This shift indicates the polymerization of the silicate gel, attributed to the decomposition of C-A-S-H gel. Fig. 17 further shows

that the transition from the 28-day non-carbonated state (Fig. 15) to 1 year under natural carbonation did not lead to any wavenumber alteration for the 50CC50S group, exhibiting that there is no decomposition of the aluminosilicate gel in these samples. Consequently, the decomposition of the aluminosilicate gel appears to occur in samples exposed to high concentrations of CO<sub>2</sub>. The behaviour of the functional group around 1500 cm<sup>-1</sup>, involving O-C-O bonds (v3-CO<sub>3</sub><sup>2-</sup>), exhibited a contrasting trend between the 50CC50S and 70CC30S mixes during accelerated carbonation. Within the 70CC30S group, increasing the activator concentration did not affect the peak intensity or wavenumber for this group when evaluated at 2 weeks and 8 weeks. However, in the case of the 50CC50S group, an elevation in alkaline Na<sub>2</sub>O concentration led to changes in wavenumbers as the samples exposed to an extended period of accelerated carbonation. For instance, in sample 50CC50S-10, the shift in wavenumbers occurred between the week 2 and week 8 of accelerated carbonation, transitioning from lower to higher values



**Fig. 18**. Carbonation depth of specimens after 56 days accelerated carbonation 2 % CO<sub>2</sub> (a): 70CC30S-10 and (b): 50CC50S-10; Carbonation depth of specimens after 314 days including accelerated carbonation 2 % CO<sub>2</sub> and wetting/drying cycles (c): 70CC30S-10 and (d): 50CC50S-10.

 $(1491 \rightarrow 1515 \text{ cm}^{-1})$ . Conversely, the sample with lower Na<sub>2</sub>O concentration (50CC50S-8) experienced a shift from higher to lower wavenumbers (1513  $\rightarrow$  1507 cm<sup>-1</sup>). Consequently, 50CC50S group characterized by a higher proportion of GGBFS (and consequently increased calcium content in the mixture), increasing the alkaline concentration led to diverse outcomes, giving rise to distinct forms of calcium carbonates during accelerated carbonation. This phenomenon aligns with the findings in the XRD results (Fig. 12), where the specimens with the highest Na<sub>2</sub>O concentration (50CC50S-10) exhibit higher aragonite (CaCO<sub>3</sub>) formation (at 26.2°  $2\theta$  and 52.5°  $2\theta$ ), while the presence of calcite (CaCO<sub>3</sub>) overlapping with the C-A-S- H gel is more pronounced at 29.5° 2 $\theta$  for 50CC50S-8. During natural carbonation, the 50CC50S group (Fig. 17) follows a pattern similar to the 70CC30S group (Fig. 16). In both cases, the samples demonstrate decreased intensities in comparison to accelerated carbonation, with sample 50CC50S-10 showing the lowest intensity. The bands identified at approximately 1600 and 1700  $\rm cm^{-1}$  correspond to the stretching (-OH) and bending (H-O-H) vibrations of water molecules within the hydrated products. resulting from both accelerated and natural carbonation processes. This trend aligned with the behaviour observed in the 70CC30S samples, although there were notable intensity differences between the 50CC50S-8 and 50CC50S-10 samples from week 2 to week 8 of the accelerated carbonation.

## 4.8. Carbonation-induced reinforcement corrosion

Fig. 18 presents the carbonation depth carbonated specimens of 70CC30S-10 and 50CC50S-10 mixes after 56 days of accelerated carbonation and the end of wetting/drying cycles. From Fig. 18, from the phenolphthalein indicator, it is obvious that the carbonation depth reached the steel-concrete interface in both 70CC30S-10 and 50CC50S-10 specimens after 8 weeks in exposure to accelerated carbonation.

The visual inspection was conducted on steel bars extracted from the 70CC30S-10 and 50CC50S-10 following accelerated the periods of carbonation and wetting/drying cycles at 314 days. Examples of steel bar condition are shown in Fig. 19. In general, no corrosion was observed on any of the steel bars as presented in Fig. 18 (c)(d) and Fig. 19. The steel bars were in good condition compared to a severely corroded steel bar from a previous study [29], which was exposed to the same wetting/drying cycles after the carbonation depth reached the steel bar, as shown in Fig. 19(c). This is consistent with the reduction of pH values in the previous section (Fig. 10). After carbonation, the pH values remained higher than 10.5, preventing the depassivation of steel bars in carbonated calcined clay-GGBFS alkali-activated concretes. Accurately measuring the carbonation depth in alkali-activated concrete is challenging due to the high solubility and mobility of sodium carbonate [57]. Phenolphthalein is colourless when the pore solution pH is below 9. Then, it turns to a light pink when the pH values are higher than 9 [13]. Additionally, measuring carbonation depth in alkali-activated calcined clay and GGBFS concretes was even more difficult due to the concrete's red colour, which originated from the calcined clay. The light pink colour of the phenolphthalein indicator overlapping with the redish colour of the concrete can be observed in Fig. 18(c) and (d). In a previous study relating to alkali-activated fly ash/slag mortar [17,58], pH values in similar accelerated carbonation exposure were estimated higher than 10 in the carbonated regions. Authors estimated pH values to be around 10.5 near the steel bars after carbonation in this study, which is consistent with previous studies and with the pH values reported in Fig. 11. The insignificant increase of carbonation depth between 8 weeks of accelerated carbonation (56 days) and end of wetting/drying cycles (314 days) was observed in Fig. 18. Consequently, although accelerated carbonation is widely utilized in OPC-based concretes, carbonation depth from accelerated carbonation can significantly overestimate the carbonation in calcined clay-GGBFS alkali-activated concretes due to the carbonation of the pore solution. The calcined clay-GGBFS alkali-activated concrete could maintain the passivity of reinforcement when the



**Fig. 19.** Examples of steel bars after accelerated carbonation and wetting/ drying cycles. (a) and (b): steel bars in this study. (c): a steel bar with severe corrosion in a previous study [29] exposed to the same wetting/drying cycles after carbonation depth reaching the steel-concrete interface.

carbonation depth, measured by phenolphthalein solution, reaching the steel bars level. A detailed electro-chemical investigation will be carried out in the future to explain the observations reported in this paper.

## 5. Conclusions

The conducted experimental investigation aimed to understand the relationship among alkaline concentration, calcium content, and their collective impact on shrinkage mechanisms and carbonation resistance (natural and accelerated) within a binary alkali-activated concrete system comprising calcined clay and GGBFS. In addition, the condition of steel bars after accelerated carbonation was visually investigated. The outcomes of this whole analysis have led to several significant findings relating to how these materials react to the previously mentioned detrimental processes:

 Increasing Na<sub>2</sub>O content to 10 % improved mechanical performance, with 28-day compressive strengths of 54.7 MPa (50CC50S-10) and 50.3 MPa (70CC30S-10). The higher Na<sub>2</sub>O levels enhanced soluble silicate species, improving mechanical properties by promoting C-A-S-H formation.

- Over a year, the 70CC30S-10 mixture showed the lowest total shrinkage at around  $-620 \ \mu\text{m/m}$ , similar to previous studies on 50 MPa OPC blended concretes with GGBFS or calcined clay. In contrast, mixes with lower activator concentrations, like 70CC30–8, 50CC50S-8, and 50CC50S-10, had higher shrinkage values of  $-766 \ \mu\text{m/m}$ ,  $-782 \ \mu\text{m/m}$ , and  $-844 \ \mu\text{m/m}$ , respectively. Regarding autogenous shrinkage, concretes with 70 % calcined clay (70CC30S) showed more expansion in the first 15 days compared to those with a 50–50 blend (50CC50S). Over 365 days, formulations with more GGBFS (50CC50S) had higher long-term autogenous shrinkage than 70CC30S-group.
- Notably, 50CC50S mixes had higher cumulative micropores and gel pores, refined pore structure and decreasing larger capillary pores content, explaining the increased autogenous shrinkage for this group. Conversely, 70 % calcined clay blends (70CC30S group) exhibit comparable small pores, while 70CC30S-8 demonstrates higher median-large capillary pores and cumulative pore volume content, relating to an increasing total shrinkage compared to 70CC30S-10.
- Following an 8-week period, accelerated carbonation led to the complete carbonation of the 70CC30S-8 samples, potentially due to the fast pore solution carbonation. This suggests a lower Na<sup>+</sup> alkali quantity in this mixture's pore solution compared to others. The group with alkaline concentration of 10 (70CC30S-10 and 50CC50S-10) showed carbonation depths of 17.8  $\pm$  1.49 mm and 17.1  $\pm$  1.25 mm, respectively. After a year of natural carbonation exposure, the 70CC30S-8 blend maintained the highest carbonation depth, followed by mix 50CC50S-8. Conversely, mixtures with an activator concentration of 10 (70CC30S-10) exhibited lower carbonation depths.
- Regarding accelerated carbonation, there was a notable decrease in pH values similar to that observed in natural carbonation. Despite this decline, pH levels remained above the critical range for steel bars depassivation (around pH 9). Therefore, solely relying on phenol-phthalein indicator test outcomes for assessing accelerated carbonation values can lead to misleading conclusions. For instance, although sample 70CC/30S-8 was entirely carbonated after 8 weeks in accelerated carbonation, its pH still exceeded 10.83.
- The XRD analysis of non-carbonated samples revealed peaks corresponding to kaolinite, zeolites, quartz, and an amorphous phase associated with C-A-S-H gel formation. Enhanced intensity was observed with increased GGBFS content or Na2O concentration. This observation aligns with porosity results, indicating a more pronounced pore size distribution refinement for higher calcined clay content (70CC30S-10) upon increasing Na<sub>2</sub>O concentration from 8 % to 10 %. Small peaks of calcite and Gaylussite (Na<sub>2</sub>Ca(CO<sub>3</sub>)) were also detected, the former attributed to GGBFS-related calcite and the latter to initial CO<sub>2</sub> exposure during sample preparation.
- XRD patterns after 8 weeks of accelerated carbonation showed intensified calcite peaks along with emerging forms of calcium carbonate like aragonite and vaterite. Sodium bicarbonate compounds, including Nahcolite, were present, along with sodium calcium carbonate minerals like Gaylussite. Calcium carbonate peaks in all samples indicated the decalcification of alumisilicate gel phases, particularly noticeable in specimens with higher GGBFS and calcium content, such as 50CC50S-8 and 50CC50S-10 mixes.
- After 12 months of natural carbonation, XRD patterns showed structural changes in the composites, with phases linked to pore solution carbonation and geopolymeric gel, though less intense than in accelerated carbonation. Peaks for calcium carbonate phases like aragonite and vaterite were reduced or absent, except in 70CC30S-8, which had high calcite peaks and lower C-A-S-H gel, indicating N-A-S-H gel dominance. The interaction of unbound Ca<sup>2+</sup> ions with CO<sub>2</sub> led to calcium carbonate (CaCO<sub>3</sub>) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>)

formation, explaining the higher shrinkage in 70CC30S-8 compared to 70CC30S-10.

- FTIR results confirmed the XRD findings. In uncarbonated 70CC30S mixes, increasing Na<sub>2</sub>O from 8 % to 10 % caused a significant shift in the Si-O-T band, indicating more C-A-S-H formation over N-A-S-H. The v2-CO<sub>3</sub><sup>2-</sup> vibration, linked to calcite and Na<sub>2</sub>CO<sub>3</sub> from carbonation, appeared only in the 70CC30S-8 mix during natural carbonation and in all 50CC50 mixes during accelerated carbonation. Changes in alkaline concentration affected the O-C-O bond group (v3-CO<sub>3</sub><sup>2-</sup>) in 50CC50S mixes, showing diverse calcium carbonate forms during accelerated carbonation in GGBFS-rich samples.

The visual inspection of steel bars indicated that alkali-activated calcined clay/GGBFS concretes could maintain the passivity of reinforcement despite the carbonation front reaching the steel-concrete interface. Therefore, the durability of calcined clay-GGBFS alkali-activated reinforced concrete against carbonation cannot be determined solely from the carbonation depth measured using the phenolphthalein indicator test. This can be attributed to the pH values remaining higher than about 10 after carbonation, likely to prevent the depassivation of reinforcement in calcined clay-GGBFS alkali-activated concrete. A detailed electro-chemical investigation will be carried out in the future to explain the observations reported in this paper.

## CRediT authorship contribution statement

Samuel De Carvalho Gomes: Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Quang Dieu Nguyen: Writing – review & editing, Writing – original draft, Visualization, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Wengui Li: Writing – review & editing, Supervision, Investigation. Arnaud Castel: Writing – review & editing, Supervision, Resources, Project administration, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Data availability

Data will be made available on request.

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