

INFLUENCE OF SODIUM HYDROXIDE REDUCTION THROUGH CARBONATION CURING AND SODIUM SILICATE ENRICHMENT ON ONE-PART FA-GGBS GEOPOLYMER

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ABSTRACT

This study examines the effects of reduced sodium hydroxide content, increased sodium silicate usage, ground granulated blast furnace slag incorporation, and carbonation curing on one-part fly ash-based geopolymers. Silica-rich activator systems improved compressive strength and reduced porosity through enhanced gel formation and matrix densification. High-silica mixtures showed minimized carbonation-related strength loss, while carbonation curing refined the pore structure. Sodium based carbonate contributed positively to performance, whereas calcium-based carbonate played a minor role.

Keywords: Geopolymer, Carbonation Curing, GGBS, Fly ash

1. INTRODUCTION

Fly ash (FA) based geopolymers have attracted significant attention as a sustainable and low-CO₂ alternative to ordinary Portland cement (OPC), owing to their lower embodied energy, reduced greenhouse gas emissions, and utilization of industrial by-products. The binding mechanism of FA-based geopolymers relies on the alkali activation of aluminosilicate precursors, leading to the formation of a three-dimensional N–A–S–H gel network that provides mechanical strength and durability [1].

Despite these advantages, the widespread application of FA-based geopolymers is still hindered by technical and practical limitations. From a material performance perspective, FA geopolymers often exhibit relatively low early-age strength and high porosity. From a practical standpoint, conventional FA geopolymer systems typically require elevated-temperature heat curing to achieve sufficient strength, involve complex mixing procedures, and rely on highly alkaline liquid activators particularly sodium hydroxide (NaOH) which pose safety, handling, and environmental concerns [1]. These challenges significantly limit their feasibility for large-scale construction applications.

To overcome these limitations, the incorporation of ground granulated blast furnace slag (GGBS) and the application of carbonation curing have been proposed as effective strategies. The addition of GGBS introduces reactive calcium into the system, promoting the formation of C–A–S–H gel, which can significantly enhance early-age strength and enable ambient curing without external heat supply. In parallel, carbonation curing has emerged as a promising technique for geopolymer systems, as it can densify the pore structure and potentially improve total porosity through the formation of carbonate reaction products[2].

In recent years, the concept of one-part geopolymers also referred to as “just-add-water”

geopolymers has gained increasing interest due to its simplicity and improved safety. In this approach, alkaline activators are introduced in solid (powder) form rather than as corrosive alkaline solutions, thereby simplifying the mixing process and reducing health risks. Conventionally, geopolymer activation relies on a combination of sodium silicate (Na₂SiO₃) and sodium hydroxide, however, the high alkalinity associated with NaOH remains a major drawback. Reducing or partially eliminating NaOH while increasing the contribution of sodium silicate represents a promising pathway toward safer and more practical geopolymer formulations [2].

Although previous studies have independently examined the effects of GGBS incorporation, carbonation curing, and alternative alkaline activator compositions, a comprehensive understanding of their combined effects in one-part FA-based geopolymer systems remains limited. In particular, the synergistic role of reduced NaOH content, increased Na₂SiO₃ usage, GGBS addition, and carbonation curing in achieving acceptable mechanical performance, pore structure refinement, and practical applicability has not yet been fully clarified.

Therefore, this study aims to systematically investigate the combined effects of (i) reducing NaOH content by predominantly using sodium silicate-based solid activators, (ii) incorporating GGBS to enable ambient curing and enhance strength, and (iii) applying carbonation curing to densify the matrix and improve pore characteristics in a one-part FA-based geopolymer system. The overarching objective is to develop a simplified, safer, and more practical geopolymer binder that eliminates heat curing, reduces reliance on hazardous alkaline solutions, and delivers competitive performance for sustainable construction applications.

2. TEST PROGRAMS

2.1 Materials

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This study primarily utilizes industrial by-products as active fillers, including low calcium FA JIS Class II ($\text{SiO}_2=62.04\%$, $\text{Al}_2\text{O}_3=25.50\%$, $\text{CaO}=3.96\%$, $\text{SO}_3=0.73\%$), and GGBS ($\text{SiO}_2=33.66\%$, $\text{Al}_2\text{O}_3=13.19\%$, $\text{CaO}=45.21\%$, $\text{SO}_3=2.09\%$, $\text{SSA}=4020 \text{ cm}^2/\text{g}$)

A one-part geopolymer system was prepared using solid alkaline activators comprising anhydrous sodium silicate (Na_2SiO_3 , $\text{Na}_2\text{O} \cdot n\text{SiO}_2$ with $n = 0.9\text{--}1.1$; and sodium hydroxide (NaOH) flakes with $\geq 99\%$ purity. To reduce the use of highly caustic NaOH , the activator formulation primarily relied on sodium silicate with reduced NaOH content. Fine aggregate (maximum particle size 2.5 mm) was used for mortar specimen.

2.2 Methods

(1) Mix design

The mix proportions were designed by fixing key parameters to ensure consistency among all mixtures. The water-to-binder ratio was maintained at 0.40, while the activator-to-binder ratio was fixed at 0.12. The alkalinity level was controlled by fixing the Na_2O -to-binder ratio at 0.06. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio was maintained within the range of 2.3–2.7 to promote stable geopolymer gel formation.

For mortar mixtures, the binder-to-sand ratio was fixed at 1. The binder consisted of fixed proportions of FA and GGBS. All other mix parameters were kept constant to isolate the effects of GGBS incorporation and curing conditions as shown in Table 1

Table 1 Selected Parameter

W/B	Activator/B	$\text{Na}_2\text{O/B}$	$\text{SiO}_2/\text{Al}_2\text{O}_3$	B/Sand
0.4	0.12-0.17	0.06	2.39-2.64	1

B=Binder

Table 2 summarizes the mix proportions with a fixed binder composition of 80% FA and 20% GGBS, while the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio was varied from 70/30 to 100/0 to examine the effect of reducing NaOH and increasing sodium silicate on geopolymer performance

Table 2 Mix Proportion

Mix	FA	GGBS	Na_2SiO_3	NaOH	Activator /B	$\text{SiO}_2/\text{Al}_2\text{O}_3$
1	80	20	70	30	0.12	2.39
2			80	20	0.14	2.46
3			90	10	0.15	2.54
4			100	0	0.17	2.64

(Ratio is % by weight)

(2) Mixing Procedure

All mixtures were prepared following geopolymer mixing approach. First, FA, GGBS, and solid alkaline activators were dry-mixed in a laboratory mixer for approximately 2–3 minutes to ensure homogeneity. Subsequently, the predetermined amount of water was gradually added, and mixing was continued for an additional 3–5 minutes until a uniform and workable paste or mortar was obtained.

The fresh mixture was then cast into steel molds. Then, the specimens were compacted using a vibration

table to remove entrapped air and sealed to prevent moisture loss during the initial setting period.

(3) Specimen preparation

Paste specimens were demoulded and sectioned into square pieces ($\approx 40 \times 40 \times 5 \text{ mm}$) to facilitate CO_2 penetration throughout the material. These pieces were subsequently exposed to either air or carbonation curing

For mortar specimens, fine sand was added to the same binder-activator mixture to prepare the mortar, which was then cast and demoulded. The demoulded specimens were subsequently exposed to either air or carbonation curing under the same conditions as the paste specimens. All paste and mortar specimens were maintained under their respective curing conditions without alteration until testing.

(4) Curing Condition

Two distinct curing regimes were employed in this study. The first, air curing (A), served as the control condition and was conducted under ambient laboratory conditions (20°C , 60% relative humidity). The second, carbonation curing (C), was performed in a controlled environmental chamber maintained at a CO_2 concentration of 20%, a temperature of 20°C , and a relative humidity of 60%

(5) Experiment Setup

Compressive strength was determined in accordance with JIS R 5201:2015 using $40 \times 40 \times 160 \text{ mm}$ mortar specimens, and the reported values represent the average of three specimens per mix. Total porosity was measured using the Archimedes method with average of six specimens per mix.

Microstructural characterization was performed on paste specimens. XRD analysis was conducted using a Bruker D2 PHASER (LYNXEYE) over a 2θ range of $5^\circ\text{--}60^\circ$ with a 0.025° step size. TGA/DTG was carried out using a Netzsch analyzer on approximately 50 mg of powder ($<150 \mu\text{m}$), heated from 25 to 1000°C at $20^\circ\text{C}/\text{min}$ under a nitrogen atmosphere ($150 \text{ mL}/\text{min}$), using Al_2O_3 as the reference

The experimental program evaluated the combined effects of reduced NaOH content, increased Na_2SiO_3 usage, GGBS incorporation, and carbonation curing on one-part FA-based geopolymers by comparing air-cured and carbonation-cured specimens in terms of compressive strength, porosity, and microstructure.

3. RESULTS AND DISCUSSION

3.1 Compressive Strength

Fig.1 compares the compressive strength of specimens subjected to air curing and carbonation curing at 28 days. The x-axis represents the percentage of Na_2SiO_3 (bottom axis) and the corresponding NaOH content (top axis), which are inversely proportional.

Under air curing, compressive strength increases consistently with increasing Na_2SiO_3 content. The highest strength is obtained at 100% Na_2SiO_3 , followed by 90%, 80%, and 70%, with the 70% mixture exhibiting the lowest strength. The overall strength gain from 70% to 100% Na_2SiO_3 is approximately 41.7% (From 44.1 to 62.5MPa) A similar increasing trend is observed for carbonation-cured specimens. In this case, the mixture

with 100% Na_2SiO_3 also shows the highest compressive strength, followed by 90% and 80%, while the 70% mixture again exhibits the lowest value. The total strength increase across this range is approximately 121.3% (From 27.7 to 61.3 MPa)

These results indicate that increasing Na_2SiO_3 content while reducing NaOH enhances compressive strength. This behavior is attributed to the increased availability of soluble silica, which promotes gel formation and enhances gel cross-linking within the matrix. This interpretation is consistent with the microstructural analysis results (XRD, TGA/DTG) and is discussed further in the subsequent section.

A comparison between air curing and carbonation curing reveals an overall reduction in compressive strength after carbonation. As shown in Fig.2 the greatest strength loss occurs in the mixture with 70% Na_2SiO_3 , (37.2%) whereas the reduction progressively decreases for 80% and 90%, with the 100% Na_2SiO_3 mixture exhibiting only a minor strength decrease (1.8%). The strength reduction after carbonation is primarily associated with decalcification and alkaline carbonation of the binding gels (C-A-S-H and N-A-S-H), which partially transform into carbonation products, as confirmed by the microstructural analysis. (XRD, TGA/DTG) [3].

Nevertheless, increasing Na_2SiO_3 content effectively mitigates carbonation-induced strength loss. The minimal reduction observed in the 100% Na_2SiO_3 mixture suggests that high silica mixtures provide enhanced carbonation resistance, likely due to the formation of a denser and more stable gel network resulting from the higher silica availability.

3.2 Porosity

Fig.3 presents the porosity results of specimens subjected to air curing and carbonation curing. For both curing regimes, porosity decreases with increasing Na_2SiO_3 content and the corresponding reduction in NaOH content.

Under air curing, the highest porosity is observed in the specimen containing 70% Na_2SiO_3 , with a value of approximately 25.9%. As the Na_2SiO_3 content increases to 80%, 90%, and 100%, porosity gradually decreases. The overall reduction in porosity between the 70% and 100% Na_2SiO_3 mixtures is approximately 3–5%. This reduction is attributed to the increased availability of soluble silica, which enhances gel formation [4] and results in a denser matrix with reduced pore volume.

In the case of carbonation curing, all specimens exhibit lower porosity compared to their air-cured counterparts. The highest porosity under carbonation curing is again observed in the specimen with 70% of Na_2SiO_3 , measuring approximately 22.9%, followed by a progressive decrease with increasing Na_2SiO_3 content, consistent with the trend observed under air curing. The further reduction in porosity under carbonation curing is associated with the precipitation of stable carbonation products, such as calcium- and sodium-based carbonates, within the pore network. These products form through reactions between CO_2 and sodium- and calcium-bearing

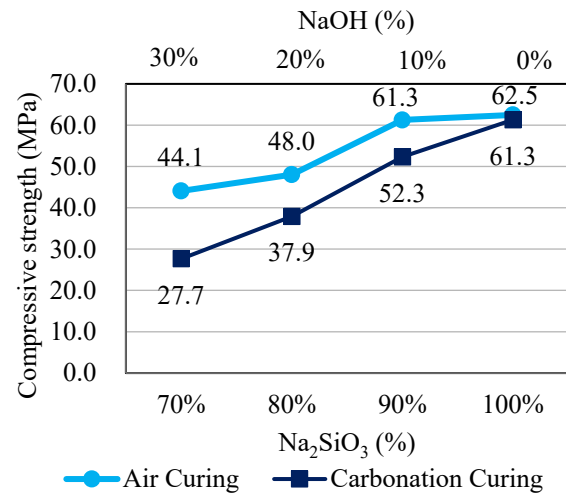


Fig.1 Compressive strength at 28 day-curing

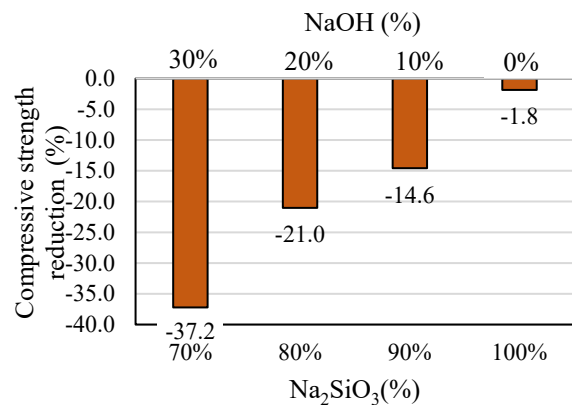


Fig.2 Percentage reduction in compressive strength due to carbonation curing (Relative to air curing)

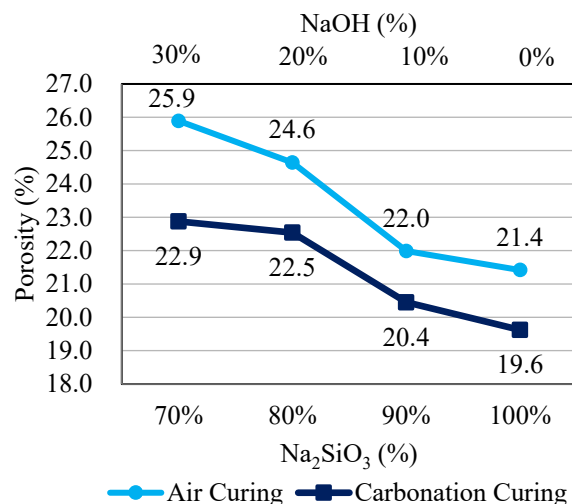


Fig.3 Porosity at 28 day-curing

species originating from GGBS and, to a lesser extent, the geopolymer gel. The resulting carbonate phases partially fill voids and refine capillary pores, leading to a more compact and dense microstructure [4]. This mechanism is discussed in detail in the microstructural analysis section (XRD and TGA/DTG).

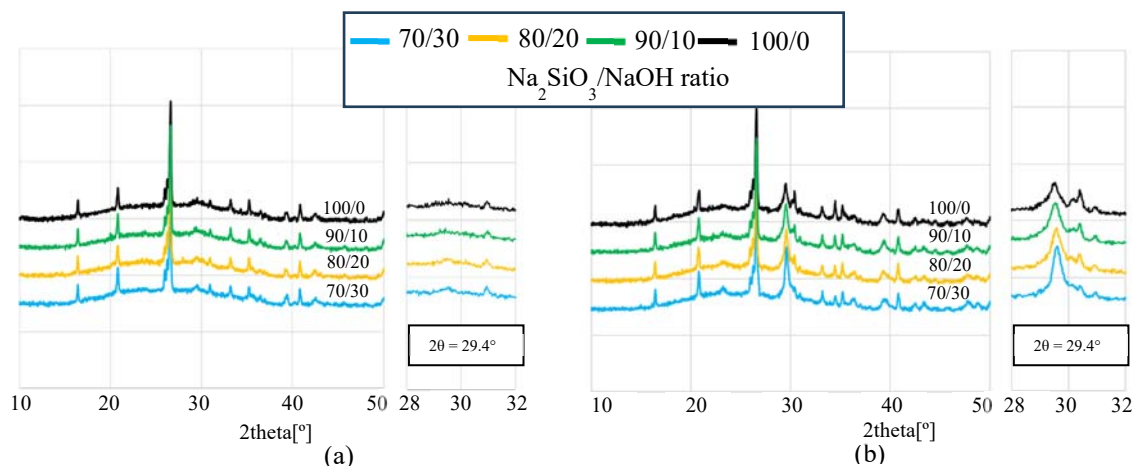


Fig.4 XRD patterns of all specimens at 28 curing (a) air curing (b) carbonation curing

Although carbonation curing reduced total porosity compared with air curing, it did not improve compressive strength, instead, carbonated specimens exhibited lower strength. This suggests that pore refinement was offset by chemical degradation of the geopolymer gel, including C–A–S–H decalcification and alkali carbonation of N–A–S–H. Therefore, strength development is governed primarily by gel integrity rather than total porosity

3.3 X-ray diffraction (XRD)

The XRD patterns of all specimens under air curing and carbonation curing are presented in Fig.4(a) and Fig.4(b), respectively. Under air curing, the XRD patterns of all mixtures exhibit very similar characteristics, making clear differentiation between specimens difficult. A comparable trend is also observed for the carbonation-cured specimens, where the overall diffraction patterns remain largely similar across all mixtures.

However, a notable distinction under carbonation curing is observed at the diffraction peak located at approximately $2\theta=29.4^\circ$ (Fig.4(b)). This peak is attributed to the formation of calcite (CaCO_3), a typical carbonation product formed through the reaction between CO_2 and calcium-bearing phases derived primarily from GGBS. As shown in Fig.4(b), the specimen containing 70% Na_2SiO_3 exhibits the most pronounced calcite peak, while the peak intensity gradually decreases with increasing Na_2SiO_3 content (80% and 90%), with the lowest intensity observed for the specimen containing 100% Na_2SiO_3 . [5]

Although XRD is not strictly quantitative, these results suggest that mixtures with lower Na_2SiO_3 content tend to promote greater calcite formation compared to those with higher Na_2SiO_3 content. This behavior is attributed to enhanced formation of aluminosilicate and calcium-containing gels in high silica mixtures. Calcium is preferentially incorporated into the gel rather than being available for carbonation reactions leading to calcite formation. Consequently, increased gel formation reduces calcite content, as supported by the TGA/DTG.

3.4 Thermogravimetric analysis (TGA)

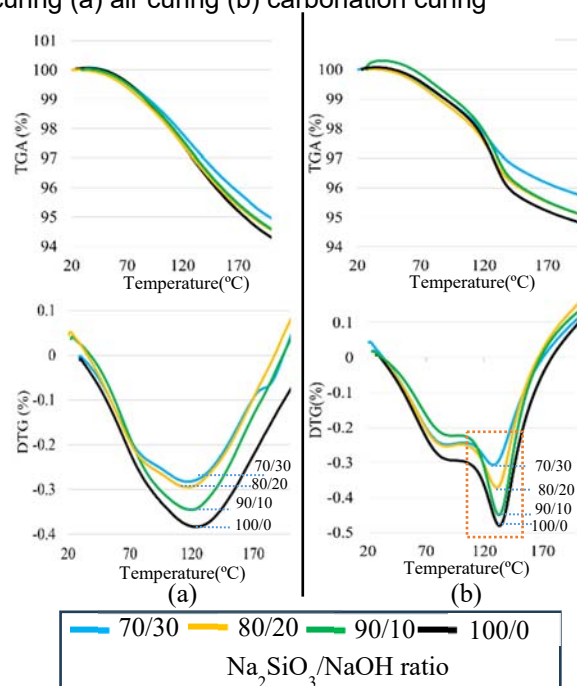


Fig.5 TGA/DTG at 28 day-curing in temperature range 20–200°C (a) Air Curing (b) Carbonation curing

Thermogravimetric analysis reveals key differences in the thermal behavior of specimens containing different $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio. For comparative analysis, two main temperature ranges are considered: Section 1 (20–200 °C) and Section 2 (550–850 °C), which are associated with gel dehydration and decomposition of carbonated products respectively.

(1) Temperature Range of 20–200 °C (Section 1)

Fig.5 illustrates the TGA/DTG results within the temperature range of 20–200 °C for air curing (Fig. 5(a)) and carbonation curing (Fig.5(b)). The thermal events observed in this range are primarily attributed to the dehydration of physically and chemically bound water within the geopolymer matrix. This includes the release of bound water from reaction gels such as C–A–S–H and N–A–S–H, as well as the decomposition of sodium bicarbonate (NaHCO_3) formed during carbonation curing [6].

In both curing systems, a prominent mass loss is observed around 130°C, which corresponds to the dehydration of gel water, resulting in the formation of anhydrous gel phases and water vapor. The depth of the peak at 130°C can be used as a qualitative indicator of gel quantity[6]. Specimens with higher Na₂SiO₃ content exhibit more pronounced downward DTG peaks in this region, with the 100% Na₂SiO₃ mixture showing the highest intensity. This trend indicates that increasing Na₂SiO₃ content enhances geopolymerization due to the higher availability of soluble silica, leading to increased gel formation.

These observations are consistent with the XRD results. The TGA results indicate that specimens with higher Na₂SiO₃ content exhibited greater gel dominance. The increased gel content suggests that calcium was preferentially incorporated into C–A–S–H-type gels rather than being available for carbonation reactions that form calcium carbonate, which explains the reduced calcite peak observed in the XRD patterns.

For carbonation-cured specimens, an additional dominant downward DTG peak appears at approximately 110–180 °C (Fig. 5(b)), attributed to the decomposition of sodium bicarbonate (NaHCO₃) [6]. Specimens with higher Na₂SiO₃ content show stronger peaks in this range, indicating increased formation of sodium-based carbonation products.

Fig.6 presents the mass loss percentage of all specimens in temperature range 20–200°C (Section 1) under both curing conditions. Within each curing system, mass loss increases with increasing Na₂SiO₃ content, further confirming the increased gel content in high silica mixtures. The specimen containing 100% Na₂SiO₃ exhibits the highest mass loss in both air curing and carbonation curing. However, when comparing air-cured and carbonation-cured specimens, a reduction in mass loss is observed after carbonation for all mixtures. This reduction indicates partial gel decomposition or transformation into carbonation products during CO₂ exposure.

Moreover, Fig.7 shows that specimens with lower Na₂SiO₃ content experience greater gel loss after carbonation. The specimen containing 70% Na₂SiO₃ exhibits the highest reduction in mass loss (13.9%), which is consistent with its lowest compressive strength and higher porosity.

A clear relationship can therefore be established between gel formation, compressive strength, and porosity. As shown in Fig.1, increasing Na₂SiO₃ content leads to higher compressive strength, with the 100% Na₂SiO₃ mixture exhibiting the highest strength, followed by 90%, 80%, and 70%. This behavior is attributed to enhanced gel formation, particularly C–A–S–H, which contributes to a denser and stronger matrix [1]. Similarly, porosity decreases with increasing Na₂SiO₃ content (Fig.3), with the lowest porosity observed in the 100% Na₂SiO₃ specimen and the highest in the 70% Na₂SiO₃ specimen. This reduction in porosity is associated with increased gel formation, which refines capillary pores and densifies the microstructure. Overall, gel quantity plays a critical role in governing both mechanical performance and pore structure.

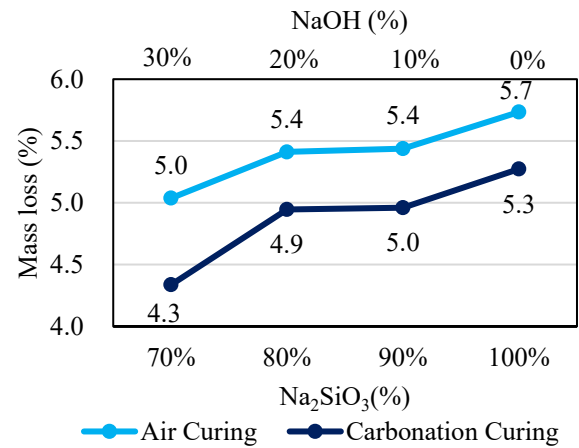


Fig.6 Mass loss (%) in temperature range 20–200°C

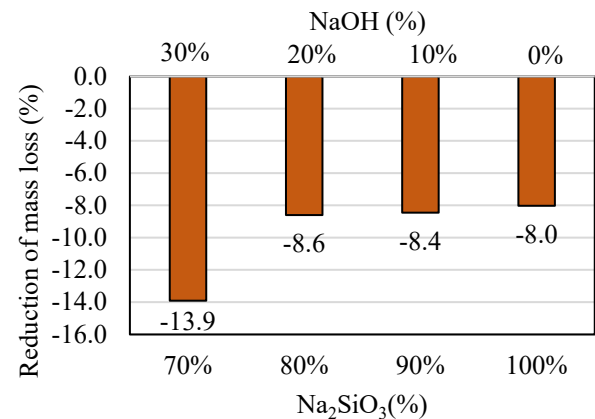


Fig.7 Percentage reduction in mass loss (%) due to carbonation curing (Relative to air curing) in temperature range 20–200°C

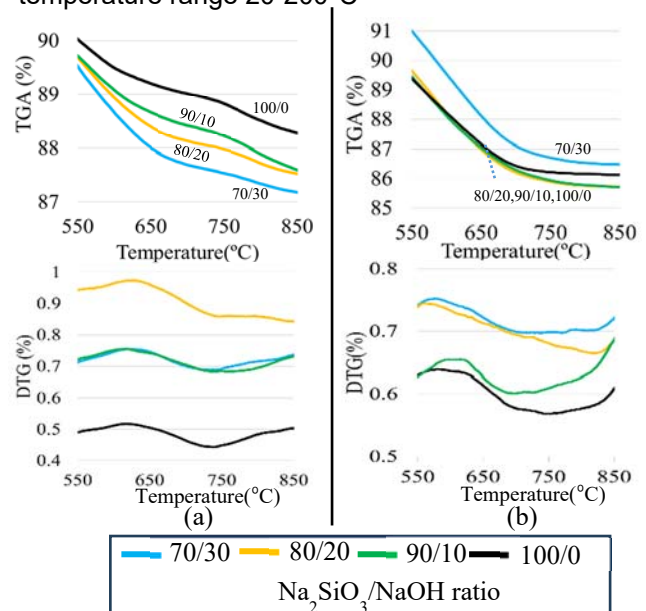


Fig.8 TGA/DTG at 28 day-curing in temperature range 550–850°C (a) Air Curing (b) Carbonation curing

(2) Temperature Range of 550–850 °C (Section 2)

Fig.8 presents the TGA/DTG results within the temperature range of 550–850 °C for both air-cured and carbonation-cured specimens. In both curing conditions,

the thermal curves of all mixtures exhibit similar profiles. However, carbonation-cured specimens display more pronounced decomposition features within this range.

Decomposition occurs within the temperature range of approximately 550–700°C. This is mainly associated with the decomposition of sodium carbonate (Na_2CO_3), which forms as a secondary product from sodium bicarbonate decomposition, releasing Na_2O and CO_2 . Previous studies have also reported partial decomposition of calcium carbonate (CaCO_3) within this temperature range [6].

At higher temperatures (700–850 °C), mass loss is mainly attributed to CaCO_3 decarbonation [6]. The overlapping decomposition ranges of Na_2CO_3 and CaCO_3 ($\approx 550\text{--}850$ °C) make it difficult to distinguish or quantify their individual contributions using TGA/DTG alone.

Nevertheless, the mass loss observed in Section 2 under carbonation curing can be attributed to the decomposition of carbonate phases, including Na_2CO_3 and CaCO_3 . Fig.9 compares the mass loss percentage in Section 2 (550-850°C) for both curing systems. Carbonation-cured specimens exhibit a higher mass loss than air-cured specimens, confirming the formation of carbonation products during CO_2 exposure.

Furthermore, Fig.10 shows that specimens with lower Na_2SiO_3 content exhibit greater mass loss in this temperature range, indicating higher carbonate formation especially in Calcite. The specimen containing 70% Na_2SiO_3 shows the highest increase in mass loss after carbonation (93.4%), followed by 80%, 90%, and 100% Na_2SiO_3 . This trend is consistent with the XRD results, which showed the strongest calcite peak for the 70% Na_2SiO_3 specimen, confirming that lower-silica systems are more susceptible to carbonation-induced calcium carbonate formation.

4. CONCLUSIONS

This study examined the effects of increasing sodium silicate content and carbonation curing on one-part FA-GGBS based geopolymers with reduced NaOH. The results highlight the importance of silica-rich activator systems in controlling strength development, pore structure, and carbonation behavior. The main conclusions are as follows:

- (1) Higher sodium silicate content resulted in increased compressive strength, lower porosity, and greater gel formation.
- (2) High-silica mixtures showed minimized carbonation-related strength loss, associated with a denser geopolymer matrix.
- (3) Porosity was further reduced under carbonation curing, particularly in high silica mixtures, due to matrix densification and carbonation product formation.
- (4) The combined presence of high-silica mixtures and the formation of sodium bicarbonate during carbonation contributed positively to strength and porosity, while calcium carbonate played a minor role in this system.

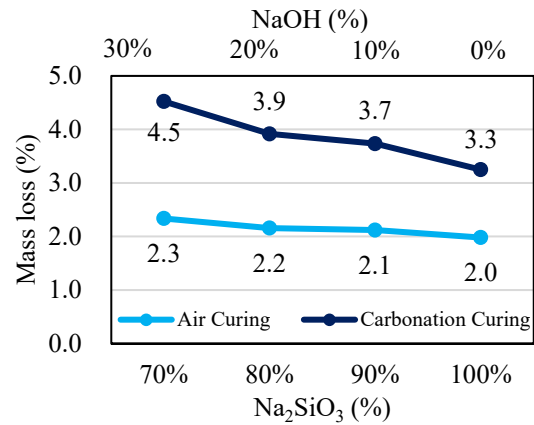


Fig 9. Mass loss (%) in temperature range 550-850°C

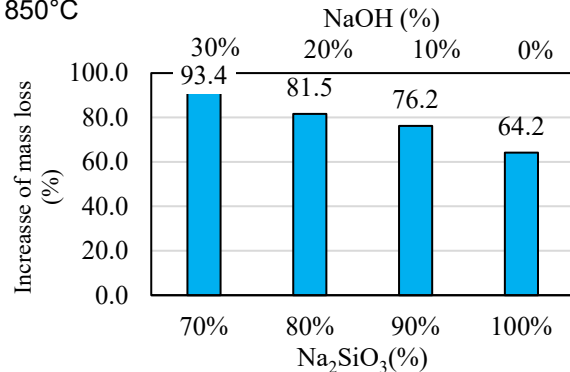


Fig.10 Percentage increase in mass loss (%) due to carbonation curing (Relative to air curing) in temperature range 550-850°C

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