

ポスター発表 | [共通セッション] International Session (国際セッション)

■ 2025年9月11日(木) 9:00 ~ 10:20 ■ Uo (熊本城ホール)

## Concrete Durability and Performance

座長：朱 晓旭（清水建設）

[11AM1-Uo-13] The influence of carbonation curing on chemical characteristics of fly ash and GGBS-based geopolymers

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キーワード：Carbonation Curing、Geopolymer、GGBS

FA-GGBS geopolymers are sustainable cement alternatives. Carbonation curing captures CO<sub>2</sub> enhancing its performance. It alters phase composition, microstructure, and sodium interactions, forming new reaction products. Comparing carbonated and non-carbonated specimens helps justify carbonation curing, predict performance, and optimize conditions. XRD, FTIR, and TG/DTA analyses to reveal phase transformations, functional group interactions, and thermal stability changes

## The influence of carbonation curing on chemical characteristics of fly ash and GGBS-based geopolymers

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### 1. INTRODUCTION

Fly ash (FA) and ground granulated blast furnace slag (GGBS) geopolymers are sustainable alternatives to traditional cement. Carbonation curing captures CO<sub>2</sub> from cement production, offering an eco-friendly approach while enhancing fly ash geopolymer performance. According to Mahfoud, E. et al. (2024), it can support carbonation can enhance fly ash geopolymer properties, particularly by reducing porosity. However, the interaction between carbonation and alkali-activated systems, especially in calcium-rich geopolymers, is unclear. Understanding its impact on microstructure is key to optimizing performance. Carbonation curing possibly modifies the phase composition, microstructure, and sodium-rich interactions within the alkaline matrix, leading to the formation of new reaction products. Therefore, investigating the differences between carbonated and non-carbonated specimens is crucial for understanding the chemical changes that occur. This knowledge can help scientifically justify the use of carbonation curing, predict material performance, optimize curing conditions, and provide insights into chemical transformations and their role in material sustainability. Chemical analyses, including XRD, FTIR, and TG/DTA analyses were conducted to investigate carbonation products in FA-GGBS geopolymers. These techniques reveal phase transformations, functional group interactions, and thermal stability changes, offering insights into the roles of FA and GGBS in carbonation and their impact on geopolymer properties.

### 2. METHODOLOGY

Fly ash (FA) and GGBS were used as binders. Paste specimens underwent one day of heat curing (60°C, 99% RH), followed by either air curing (20°C, 60% RH) or carbonation curing (20% CO<sub>2</sub>, 20°C, 60% RH) for 28 days. The mix design is shown in Table 1.

### 3. RESULTS AND DISCUSSION

#### 3.1 X-ray diffraction (XRD)

Fig.1 shows the spectra of all specimen types (both carbonated (C) and air-curing pastes (A)) exhibit major halo (hump) between 2θ = 25° and 30°, and minor peaks related to quartz (Q) and mullite (M) throughout graphs. This is linked to the formation of an amorphous geopolymer network, a key feature of geopolymerization. The presence of Q and M in all specimens, regardless of carbonation, suggests these crystalline phases naturally form during geopolymerization, aligning with existing research. (Mahfoud, E., et al, 2024)

XRD reveals carbonation's impact on crystalline phases. Fig.2 shows the significant observation is the presence of a distinct peak at 2θ = 29.4° in the carbonated FA80 and FA70 specimens, which is difficult to detect in the carbonated FA100 specimens. This peak is indicative

Table 1: Mix design

	A/W	Binder mix proportion (%)	
		FA	GGBS
Alkaline concentration	0.12	100	0
		80	20
		70	30

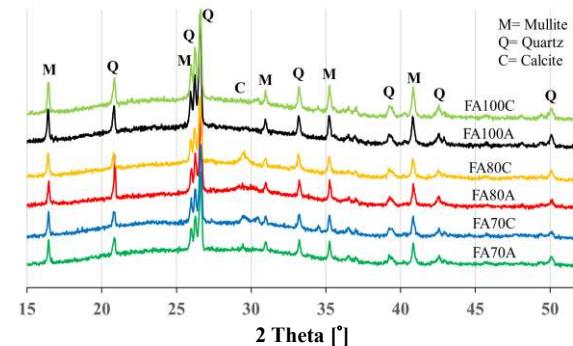


Fig 1. XRD patterns of all specimens at 28 curing days

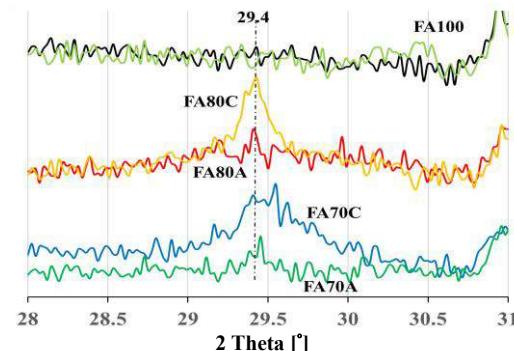


Fig.2 XRD peak at 2θ = 29.4° of 28 curing day specimen

of calcite (CaCO<sub>3</sub>) formation, suggesting that carbonation primarily affects the calcium-rich phases contributed by GGBS. This confirms that GGBS plays a significant role in promoting carbonation, leading to the formation of calcium carbonate in geopolymer pastes. However, in FA100, does not exhibit a pronounced peak at 2θ = 29.4°, suggesting that calcite (CaCO<sub>3</sub>) formation is minimal due to the absence of calcium.

#### 3.2 Fourier transform infrared spectroscopy (FTIR)

Fig. 3 presents the FTIR spectra of pastes at 28-day curing, comparing carbonation curing (C) and air curing (A). The results confirm carbonation product formation, indicated by distinct peaks. Generally, in fly-ash-based geopolymers, Si–O and Al–O bending vibrations (500–800 cm<sup>-1</sup>) and asymmetric Si–O–Si and Si–O–Al stretching vibrations (900–1200 cm<sup>-1</sup>) reflect silicate phases and the polymerization of C–A–S–H and N–A–S–H gels. A key observation is the pronounced 1452 cm<sup>-1</sup> peak in carbonated FA80 and FA70, linked to C–O bond stretching in carbonates, primarily as calcite,

Keywords: Fly-Ash, GGBS, Carbonation curing, JSCE Annual Conference

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due to GGBS-derived calcium. This peak is much weaker in FA100, indicating limited calcium carbonate formation, aligning with XRD findings. Furthermore, the carbonation process influences both GGBS and non-GGBS specimens, as evidenced by the appearance of a hump peak around  $2300\text{ cm}^{-1}$ , which corresponds to the C–O bond stretching vibration. This suggests the formation of  $\text{CO}_2$ -derived carbonated products across all mixtures. This hump peak can be detection of sodium carbonate ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , natron) and sodium bicarbonate in the form of trona ( $\text{Na}_2(\text{CO}_3)_2 \cdot \text{NaH}(\text{CO}_3) \cdot 2\text{H}_2\text{O}$ ) (Mahfoud, E., et al,2024). It can highlight the interaction between carbonation and the sodium-rich alkali-activated system. This suggests that carbonation reactions occur not only with calcium-containing phases but also within the sodium-rich environment, influencing the mineralogical composition of the geopolymers.

### 3.3 Thermogravimetric analysis (TGA)

Fig 4. Shows the thermogravimetric analysis results demonstrate that the addition of GGBS leads to increased mass loss between  $25^\circ\text{C}$  and  $200^\circ\text{C}$ . The DTG spectrum reveals a pronounced peak around  $130^\circ\text{C}$  in all specimens, particularly in those containing GGBS, which is associated with the dehydration of geopolymers and the decomposition of sodium bicarbonate (NaHcolite) formed during carbonation. According to Alexander et al.(2022), this first peak (around  $130^\circ\text{C}$ ) is primarily attributed to the dehydration and decarbonation of sodium bicarbonate ( $\text{NaHCO}_3$ ), which decomposes between  $100^\circ\text{C}$  and  $180^\circ\text{C}$  to form sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), water ( $\text{H}_2\text{O}$ ), and carbon dioxide ( $\text{CO}_2$ ). In this temperature range, due to the presence of carbonated products, all carbonated specimens exhibit a slightly higher peak. At higher temperatures, carbonated specimens exhibit distinct thermal events around  $\sim 450^\circ\text{C}$  and  $\sim 700^\circ\text{C}$ , corresponding to the decarbonation of carbonated phases. The peak at approximately  $450^\circ\text{C}$  is associated with the decarbonation of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), formed from the decomposition of sodium bicarbonate, as previously explained. Additionally, Mahfoud, E., et al. (2024) suggest that certain calcium carbonates ( $\text{CaCO}_3$ ) can decompose at relatively lower temperatures ( $450\text{--}700^\circ\text{C}$ ) if they exist in an unstable phase, possibly originating from FA. This behavior is particularly evident in GGBS-containing specimens (Fig.4a)(FA70,FA80),which exhibit greater mass loss compared to FA100, indicating that GGBS plays a significant role in carbonation by contributing calcium, which promotes carbonate formation. Furthermore, the peak observed at  $\sim 700^\circ\text{C}$  onward corresponds primarily to the decarbonation of calcium carbonate in GGBS-containing mixtures, with a minor contribution from sodium carbonate. This aligns with XRD and FTIR findings, further reinforcing the impact of GGBS on carbonation reactions. The TGA results clearly show that FA80 and FA70 exhibit greater mass loss than FA100, confirming that GGBS enhances the extent of carbonation. Additionally, The DTG spectrum shows a peak around  $900^\circ\text{C}$  in GGBS-containing specimens, indicating high-temperature transformation of calcium-rich phases

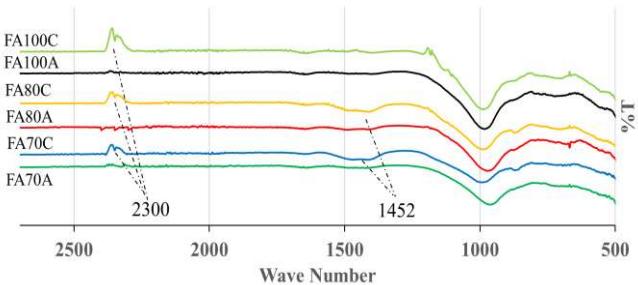


Fig 3. FTIR pattern of all specimens at 28 curing days

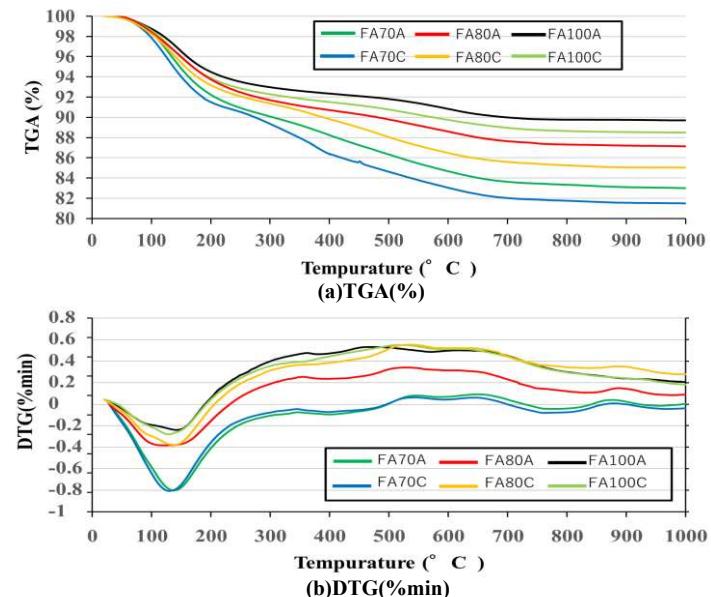


Fig.4 TGA pattern of all specimens at 28 curing days.

and the formation of a new calcium-associated phase, distinguishing them from non-GGBS specimens.

## 4. CONCLUSIONS

The combined XRD, FTIR, and TG/DTA analyses provide a comprehensive understanding of carbonation behavior in FA-GGBS geopolymers. The incorporation of GGBS enhances carbonation by supplying calcium, leading to increased carbonate formation and distinct thermal decomposition events. Meanwhile, FA100 demonstrates a different carbonation pathway, primarily influenced by sodium-based reactions within the alkali-activated matrix. The presence of sodium bicarbonate and sodium carbonate across all specimens suggests that carbonation occurs through interactions with both calcium- and sodium-rich phases. These findings highlight the role of precursor composition in governing carbonation reactions, which has implications for optimizing the performance of geopolymers in structural applications.

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