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STUDIES ON THE INCORPORATION OF GEOPOLYMER WITH GGBS ADDITION THROUGH THE INFLUENCE OF CARBONATION CURING

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ABSTRACT: This study explores the incorporation of fly-ash geopolymer mortar through the incorporation of Ground Granulated Blast Furnace Slag (GGBS) and carbonation curing. The purpose of this study is to promote it as a competitive alternative to traditional cement products. Utilizing fly ash as the basis material, mixing with different weight percentages of GGBS (0%, 20%, and 30%). Evaluating compressive strength, porosity, autogenous shrinkage, accelerated carbonation, and efflorescence susceptibility of the specimens. Although GGBS enhances microstructure and early strength, it presents concerning issues including efflorescence, increased shrinkage, and Ca^{2+} induced expansion. Carbonation curing, on the other hand, significantly mitigates these problems; it can prevent gypsum formation-related expansion or cracking and reduce porosity by more than 10% in FA100 (without GGBS) specimens and double in FA70 (with 30% GGBS addition) specimens. The findings possibly suggest that fly-ash geopolymer mortar serves as an excellent replacement for traditional cement-based materials since the combination of GGBS and carbonation curing improves both its mechanical qualities and environmental sustainability.

Keywords: Fly-ash, GGBS, Geopolymer, Carbonation curing

1. INTRODUCTION

In recent years, Japan has declared its commitment to achieving carbon neutrality by 2050 as part of its efforts toward a sustainable and decarbonized society, aligning with the Sustainable Development Goals (SDGs). The concrete industry, however, is a significant contributor to CO_2 emissions, primarily due to the calcination of clinker in cement production. To address this, Japanese cement manufacturers have made substantial environmental strides by improving the production rate of ordinary Portland cement (OPC) and by actively incorporating by-products from other industries as raw materials and fuels. The use of blended cements, which partially replace OPC with ground granulated blast furnace slag (GGBS) and fly ash (FA), has also significantly contributed to CO_2 reduction. In the field of civil engineering, however, obtaining additional CO_2 reductions will necessitate innovative strategies beyond conventional techniques. This is where geopolymers (GP), which completely eliminate the use of cement, have garnered attention [1].

GP is a class of hardened materials formed by the polycondensation reaction (polymerization) of aluminosilicate powders with alkaline activators [1]. There are several distinct types of GP, and the raw materials utilized greatly affect their characteristics. In countries such as China, where metakaolin (MK) is readily produced, MK-based GP is being investigated as a high-performance material. On the other hand, Japan and other nations are investigating the application of FA-GGBS-based GP as environmentally friendly materials in order to exploit industrial by-products and lower CO_2 emissions. [2]

The reasons for the difficulty of using them are the high levels of impurities and inconsistent quality of industrial by-products such as GGBS and FA. Additionally, GP research is still in its infancy worldwide, leaving numerous problems unresolved and few effective concrete admixtures established. Moreover, there is no standardized mix design method; it is challenging to use the results of previous studies because of the different parameters. As a new material, GP lacks long-term performance data, and practical examples of their application are scarce. Consequently, as research on FA-GGBS-based GP has progressed in Japan, a number of difficulties have surfaced. [1]

To address these challenges, this research focuses on the investigation of this corporation, enhances understanding, and explores potential solutions. Among them, the direct utilization of FA, heat, and CO_2 emissions was considered to achieve suitable performance and utilize industrial by-products. This approach also explored the potential for carbonating GP products to improve the properties of GP through carbonation curing.

Carbonation curing is a process used in concrete and GP construction where carbon dioxide (CO_2) is introduced to accelerate the curing and hardening of the material. In the process, calcium hydroxide

($Ca(OH)_2$) in the concrete or GP combines with CO_2 to generate calcium carbonate ($CaCO_3$), which aids in the material's densification and strengthening [3].

The study suggests that this could enable the efficient production of low-cost, high-performance, and stable GP products. Therefore, this research primarily focuses on the carbonation curing of GP, speculating on the mechanisms of carbonation reactions and verifying the feasibility of this approach.

2. RESEARCH SIGNIFICANCE

This study emphasizes the significance of environmentally friendly construction by studying the enhancement of fly ash-based geopolymer with GGBS (FA-GGBS GP) through carbonation curing. The goal of this study is to enhance material performance, including durability, workability, and mechanical qualities. This advancement eliminates the impact on the environment and promotes eco-friendly activities by providing practical and affordable substitutes. The results support innovation in the building sector and encourage the application of more eco-friendly and effective building materials and methods.

3. MATERIALS AND METHODS

3.1 Materials

This study uses fly ash (FA, JIS Type II) and ground granulated blast furnace slag (GGBS, Blaine fineness 6000) as active fillers, activated with JIS 3sodium silicate (water glass) and 95% pure sodium hydroxide. Chemical compositions are shown in Tables 1 and 2, with GGBS added to FA in amounts up to 30% for its reactivity. GGBS replacement percentages ranged from 0% to 30%. The top limit of 30% was chosen because it was initially observed that specimens with a 30% GGBS addition demonstrated rapid hardening, which could potentially complicate the experimental procedures This study utilizes dry sand to mortar specimens with dimensions of 40 mm x 40 mm x 160 mm were cast, then heat-cured for a minimum of one day at 60°C.


(a) (b)

Fig. 1 (a) Na_2SiO_3 Solution Barrel (b) NaOH pellets barrel

3.2 Experiment setup

3.2.1 Selection of parameters

Experimental parameters were selected to evaluate their impact on the compressive strength and workability of GP. Key factors included the ratios of water glass to sodium hydroxide, liquid to solid, slag to total cementitious material (slag content), alkali solution to FA/GGBS binder (L/B), and curing method. In Japan, parameters are expressed as sodium-to-silica molar ratios (Si/A), sodium ion concentration, and alkali activator-to-water ratios (A/W) (Harada et al., 2012). Preliminary tests used established parameters, focusing on mixtures with L/B = 0.5, Paste/Sand = 1:1, and Si/A = 0.4–0.7 for optimal GP strength and workability [4].

Preliminary tests were conducted to examine key parameters. Compressive strength tests at 28 days showed that A/W ratios above 0.16 produced viscous, unworkable mixtures, while those between 0.12 and 0.15 were workable. Higher alkaline concentrations improved strength, with optimal Si/A ratios between 0.5 and 0.6. Based on these findings, further tests will use the optimized parameters outlined in Table 3.

Table 3 Parameters

L/B	Sp/Ss	Si/A	A/W
0.5	1:1	0.6	0.12/0.15

3.2.2 Preparation of the Test Specimen and mix design.

In geopolymer (GP) preparation, the liquid component must be mixed in advance, with sodium hydroxide and sodium silicate requiring a reaction time of 4–12 hours to avoid anomalies or precipitation, with this study using 4 hours as the standard. [5,6]

The alkali stimulant was prioritized in the formulas used in the calculating procedure, which use the L/B and Sp/Ss ratios to determine the total mass per cubic meter. The Si/A molar mass ratio of the stimulant was selected, and the water was used to adjust the Na^+ concentration (A/W) and the Si^{4+}/Na^+ ratio using SH and a water glass. In relation to the overall mass of the alkali stimulant, this calculated the increased amounts of water glass, SH, and water in the binder. The formulae listed in Table 4 were used to prepare the GP mortar specimens for this study.

Table 1 Chemical composition of active fillers (wt.%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	P_2O_5	Na_2O	K_2O	MnO	MgO	SO_3	Tio_2	SrO
FA	62.04	25.50	4.28	3.96	0.31	0.46	0	0	1.27	0.73	1.33	0.12
GGBS	34.11	15.36	0.83	35.99	0	0.40	0.62	1.07	6.58	2.50	2.41	0.12

Table 2 Chemical composition of Na_2SiO_3 Solution

Na_2SiO_3 Solution	SiO_2%	Na_2O%	Molar ratio	Specific gravity (15°C)	Viscosity (mPa・s)	Fe%	Water-insolubles (%)
	27.5-29.5	11.3-12.3	2.4-2.5	1.43-1.46	100-150	0.02 or less	0.2 or less

Table 4 Mix proportions.

	GGBS (%)*	A/W	Unit Amount (kg/m^3)		
			JIS3 Na_2SiO_3 Solution	NaOH	Water
FA100	0%	0.12	213.6	39.4	106
FA80	20%				
FA70	30%				
FA100 HA	0%	0.15	247.6	45.7	68
FA80HA	20%				
FA70HA	30%				

Note: L/B = 0.5,Si/A=0.6, HA = High Alkaline Stimulant, *GGBS (% by weight)

3.2.3 Consideration of carbonation curing method.

The timing of carbonation curing significantly affects the polycondensation reaction of GP [7]. This study evaluates four methods:

1. Pre-Heating Carbonation: This method involves initiating carbonation curing simultaneously with heat curing at the early stage of the GP's polycondensation reaction, shortly after the material has been cast.
2. Post-Heating Carbonation: In this approach, carbonation curing is applied after one day of heat curing, at a point when the GP's polycondensation reaction is nearly complete.
3. Pre-Room Temperature Carbonation: Here, carbonation curing is carried out at room temperature immediately after the commencement of the GP's polycondensation reaction, shortly after casting.
4. Post-Room Temperature Carbonation: This method applies carbonation curing at room temperature once the GP's polycondensation reaction has advanced to an intermediate stage between the previous three methods, specifically when air curing is complete and the material is ready for demolding.Carbonation chambers (Fig.2) maintained 60% humidity and 5% CO_2 concentration; for room temperature, this study utilizes the constant temperature-humidity chamber with the constant temperature at 20°C shown in Fig. 3. And a heat-curing chamber with the heated condition set to 60°C.

Fig. 2 Carbonation chamber.

Fig. 3 Constant temperature and humidity chamber.

Results showed that pre-heating carbonation caused defects and low strength, while pre- and post-room temperature carbonation delayed curing and caused cracking. Post-heating carbonation, applied after heat curing, allowed complete polycondensation and produced consistent strength, making it the optimal method. Thus, only post-heating carbonation will be discussed in this study.

Throughout this experiment, various specimens were cast using the mix proportions in Table 4 and primarily subjected to both carbonation and air curing as outlined in Table 5. FA type II and GGBS were used as active fillers, with sodium hydroxide and sodium silicate as alkaline activators.

Table 5 The primary curing methods employed throughout this study.

Curing method	Curing process
Air Curing	1 day of heating curing → Demolding→ Ambient air curing (room temperature)
Post-Heating Carbonation	1 day of heating curing → Demolding→6 days of carbonation curing at room temperature→ Ambient air curing (room temperature)

3.2.4 Overview of experimental program

The experimental program assessed the effects of GGBS addition and carbonation curing on GP mortar using standardized tests, including compressive strength (JIS A1108), pH measurements in an accelerated carbonation test (JIS A1153), porosity (JIS R2205), shrinkage (JIS A1129), and elevated Ca^{2+} effects through dry-wet cycles (JIS A6204). These tests offered insights into the mechanical performance, durability, and dimensional stability of GP mortar.

To measure compressive strength, carbonation depth, porosity, shrinkage, and dry-wet cycle effects, GP mortar specimens (Fig. 5) underwent one day of heat curing. After demolding, they were subjected to air curing or carbonation curing (20°C, 60% humidity, 5% CO_2 concentration).

Fig. 5 GP Mortar specimens

4. RESULTS AND DISCUSSION

In this study, air-curing and carbonation-curing were selected to be the main considerations, with the primary curing methods employed throughout this study illustrated in Table 5. The studies and comparative analyses between these two methods were conducted. To clearly investigate the impact of carbonation curing and GGBS incorporation on the enhancement of GP.

4.1 Consideration of pH measurement during accelerated carbonation test

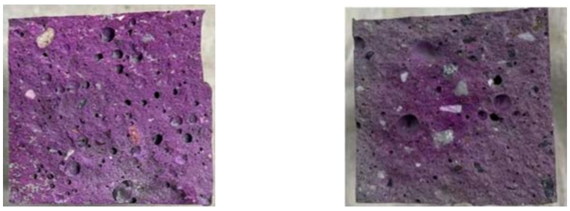
4.1.1 Overview of test outcomes

Figure 7 presents the results of the pH measurement through an accelerated carbonation test using phenolphthalein (also referred to as phenolphthalein test) on GP specimens after 6 days of carbonation curing. From these results, it is evident that the coloration of the air-cured and carbonation-cured specimens differs significantly, indicating that carbon dioxide has reacted with the GP specimens. Additionally, it was observed that higher alkali content (HA) results in a darker coloration.

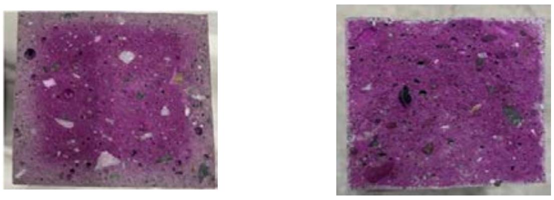
4.1.2 Role of CO_2 Reaction, Alkali Content, and pH in Carbonation Curing

Figure 7, moreover, shows a comparison between FA100 and FA70 specimens, suggesting that the reaction processes between CO_2 and GP differ. For FA70, the reaction process is similar to that of conventional mortar, with clearly distinguishable regions of rapid reaction and unreacted or slower-reacting areas. There is a distinct boundary between these regions, with the central unreacted or slow-reacting area remaining very dark in color.

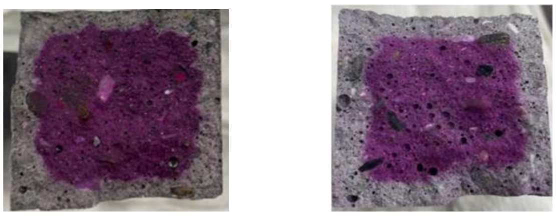
However, in the case of FA100 specimens, this phenomenon was not observed, and the overall color of the carbonation-cured specimen, both at the surface and the core became lighter compared to the air-cured specimen. Furthermore, regardless of the alkali content, whether low or high, the boundary between the reacted and unreacted regions was indistinguishable, and although the outer layer lightened, some color remained.



FA100(Air-Curing) FA100(Carbonation curing)



FA100 HA (Carbonation curing) FA70 (Air curing)

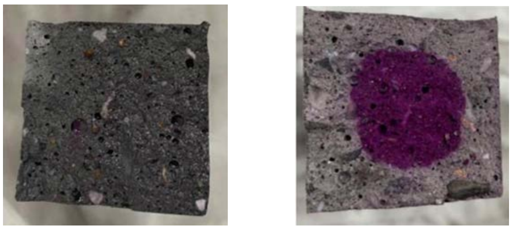


FA70 (Carbonation curing) FA70HA (Carbonation curing)

Fig. 7 phenolphthalein test results (6 days of carbonation curing)

Figure 8 illustrates the results of the phenolphthalein test conducted on GP specimens after 20 days of carbonation curing. The FA100 specimen exhibited almost no coloration, while the core of the FA70 specimen remained very dark. This suggests that the addition of GGBS altered the internal structure of the GP, thereby changing the CO_2 transport pathways.

Based on the coloration observed in the FA100 specimen, it can be inferred that CO_2 penetration likely reached the core, suggesting a continuous transport pathway. In contrast, the transport pathway in the FA70 specimen may be discontinuous or obstructed.



FA100 (Carbonation curing) FA70 (Carbonation curing)

Fig. 8 Phenolphthalein test results (20 days of carbonation curing)

Moreover, as shown in Table 6, this phenomenon could be attributed to the fact that the initial products formed after carbonation in the FA100 specimen remain highly alkaline, Table 6 illustrates the surface pH of GP specimens with the same mix design after 6 days of carbonation curing. Although the pH decreases after carbonation, it still remains highly alkaline. According to Yamazaki et al. [8], the formation of sodium bicarbonate was detected, and the pH of the product is above 11. This suggests that, in addition to the formation of other carbonate compounds, the specimen still retains the ability to exhibit coloration. The concentration gradient of this product likely caused the blurred boundary observed in the phenolphthalein test. However, as carbonation progresses further and the pH continues to decrease, this product is likely to decompose, resulting in the loss of coloration, as observed in the entire FA100 specimen.

Unlike the typical circular coloration patterns observed in conventional concrete, the phenolphthalein coloration in GP may exhibit a square-shaped pattern. This is likely due to the uneven distribution of alkalis and the unique microstructure within GP. The hydration products of GGBS and FA may form distinct gel structures and pore distribution patterns at the micro level. These differences could alter the CO_2 transport and the distribution patterns of alkali metal ions (such as sodium and potassium) within the concrete, which in turn may affect the reaction pattern when the phenolphthalein indicator comes into contact with the concrete surface. [8]

Table 6 Surface PH at 6 days curing

Specimen type	Surface PH
FA100 (Air Curing)	12.7
FA100 (Carbonation Curing)	11.2
FA80 (Air Curing)	12.2
FA80 (Carbonation Curing)	9.5
FA70 (Air Curing)	12,2
FA70 (Carbonation Curing)	9.2

4.2 Investigation on GP Porosity

This section will investigate the impact of Carbonation Curing, GGBS Incorporation, and Alkaline Concentration on GP Porosity

4.2.1 Effect of Carbonation Curing on Porosity Reduction

The influence of carbonation curing on the porosity of FA-GGBS GP mortar is evident from Fig. 9, which presents porosity data at 7 days of age. The specimens subjected to carbonation curing exhibited consistently lower porosity across all material proportions (70%, 80%, 100%) compared to those cured in air, highlighting the beneficial effects of carbonation on reducing voids within the GP matrix. There are some research states that this curing method effectively converts Ca^{2+} to $CaCO_3$, filling voids and improving the overall durability of the GP [9]

4.2.2 Impact of GGBS Incorporation on GP Porosity

In addition to carbonation curing, the incorporation of GGBS and adjustments in the alkali-to-water (A/W) ratio were also observed to influence porosity. As shown in Fig. 10, GP generally exhibits more large air voids and fewer small voids compared to ordinary concrete. According to Neville (2012), the void ratio in cement mortar is around 15% and increases in concrete, highlighting the importance of reducing the void ratio in GP. Fig. 9 shows that adding GGBS and increasing the A/W ratio effectively reduces the void ratio [10]. This significant reduction is attributed to the combined effects of GGBS and carbonation, where GGBS not only acts as a micro-filler but also enhances the reaction environment, facilitating the formation of dense carbonation products. [11-13].

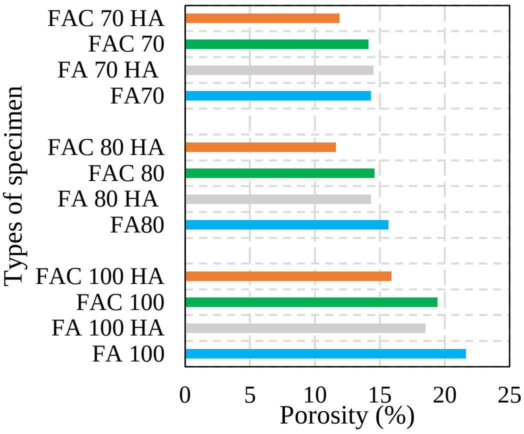
For instance, as shown in Fig. 9 and Fig. 10, the addition of GGBS combined with high alkaline concentration resulted in a notable decrease in porosity, particularly in the FA70 and FA70 HA samples, which exhibited approximately 6% lower porosity than FA100 and FA100 HA. It is evident to demonstrate that GGBS accelerates the GP's hydration, leading to more consistent hydration and fewer unreacted particles, which reduces capillary voids and total porosity by increasing density and fineness [14]. GGBS not only acts as a micro-filler but also enhances the reaction environment, facilitating the formation of dense carbonation products. [9,15]

4.2.3 Combined Effects of Carbonation Curing and Alkaline Concentration on Porosity

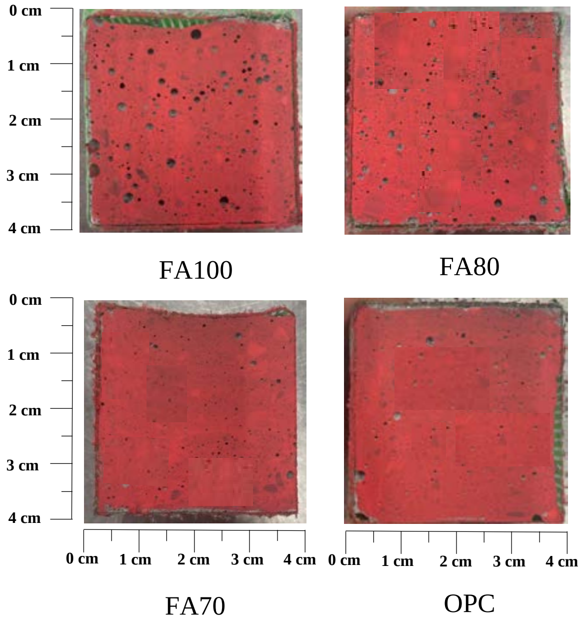
The alkaline environment, strengthened by a higher A/W ratio, further supports the carbonation process by promoting the dissolution of silicates and aluminates from both FA and GGBS. This leads to the formation of additional hydration products, such as C-S-H and C-A-S-H gels, which are crucial in reducing porosity. When carbonation curing is applied, these effects are enhanced, resulting in even fewer unreacted particles and voids and, consequently, a denser GP structure. [13,16]

Figure 9 also shows that the high alkaline (HA) curing condition generally results in lower porosity than the FA samples but exhibits slightly higher porosity compared to the FAC samples. This indicates that while high alkaline curing positively influences the microstructure by reducing voids, carbonation curing appears to have a more significant impact on reducing porosity. The combined effects of carbonation and high alkaline curing are particularly evident in reducing porosity, thus contributing to a denser microstructure. [14,15]

It may be concluded that carbonation curing significantly densifies FA-GGBS GP mortars by reducing porosity and increasing strength through the formation of stable carbonate phases, which fill voids and refine the pore structure. GGBS incorporation and alkaline adjustments further enhance this effect, making carbonation curing an effective method to improve GP microstructure.



Note: C = Carbonation curing. HA=High alkaline.
Fig. 9 Void ratio of GP mortar at 14 days



FA100 FA80

FA70 OPC

Fig.10 Images of porosity

4.3 Strength consideration

This section will investigate the Impact of Carbonation and Non-Carbonation Curing on strength, studying Influence of GGBS Incorporation and Alkaline Concentration

4.3.1 Compressive Strength and Microstructural Development

The compressive strength of the FA-GGBS GP mixtures at 28 days of age is shown in Fig. 11. The data unambiguously show that the compressive strength of FA-GGBS GP can be greatly increased by raising the GGBS content, maximizing the alkali-to-water ratio (A/W), and utilizing heat curing. These improvements in strength reflect the promotion of polycondensation reactions, which are essential for enhancing the mechanical properties of the GP. This finding is in line with other studies, such as those by Lee van Deventer [17], which reported that heat-cured GP samples achieved high early strength within 1 to 3 days, whereas air-cured samples exhibited a more gradual strength increase, reaching moderate levels by 28 days.

Through a variety of methods, the addition of GGBS is essential to improving the strength of GP matrices. The GP network is strengthened when GGBS interacts with alkaline activators to create additional hydration products, such as calcium-aluminosilicate-hydrate (C-A-S-H) gel. Additionally, the microstructure's density is also increased by GGBS through its role in filling pores and decreasing voids. The fine particles of GGBS act as nucleation sites, promoting further hydration reactions. The increased calcium content of GGBS in FA-based GPs improves alkali activation, resulting in more sustained and enhanced reactions. [3,5,18]

Despite these improvements, Fig. 11 also reveals that for FA100 (without GGBS), even with optimal Si/A and L/B ratios and adequate aggregate content, the compressive strength remains lower than that of conventional silicate cement. This suggests that the inclusion of GGBS and the application of heat curing are essential for achieving the desired performance in GP mixtures.

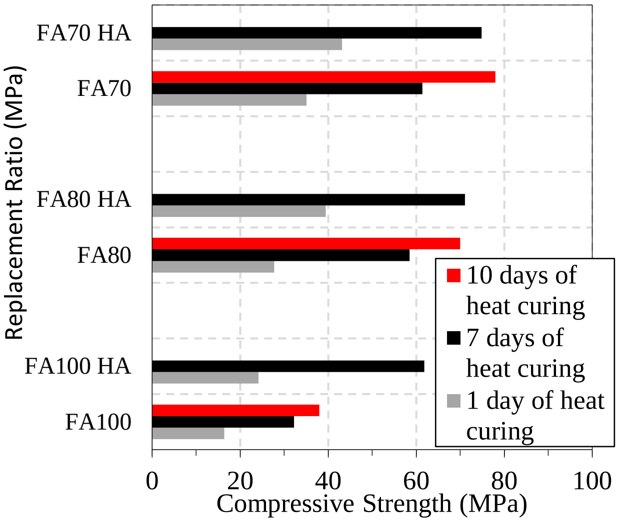


Fig. 11 Compressive Strength at 28 Day

4.3.2 Impact of Carbonation Curing on Strength.

Figure 12 illustrates the strength development of GP mixtures under carbonation curing and non-carbonation curing. The findings indicate that after 14 days, strength development almost stops. Reactions inside FA-GGBS GP can be further catalyzed by continuous heat curing in a high-temperature environment.

For GGBS-blended specimens, compressive strength at 7 days is similar across all curing methods. However, carbonation curing appears to halt strength development after 7 days, likely due to the carbonation of the alkaline activators, which reduces pH and disrupts polycondensation [19]

In the case of carbonation-cured FA100, specimens aged up to 42 days resulted in higher compressive strength compared to air-cured specimens. There is a possible explanation for the strength gain is the densification of the microstructure that occurs by the production of carbonation products [3].

The findings imply that, although the precise mechanisms are currently unknown, the presence of carbonation products may have strengthened the FA100 specimens' strength after day 7. It is speculated that these products could assist with the microstructure become denser [20]. On the other hand, carbonation products seem to reduce the initial strength of specimens that were combined with GGBS. This may be due to the reaction between CO_2 and the C-A-S-H gel, leading to the formation of $CaCO_3$ [21,22]. Additionally, when comparing subsequent strength development, it is likely that the residual alkaline activators within the specimens were also reacted due to the carbonation process [19].

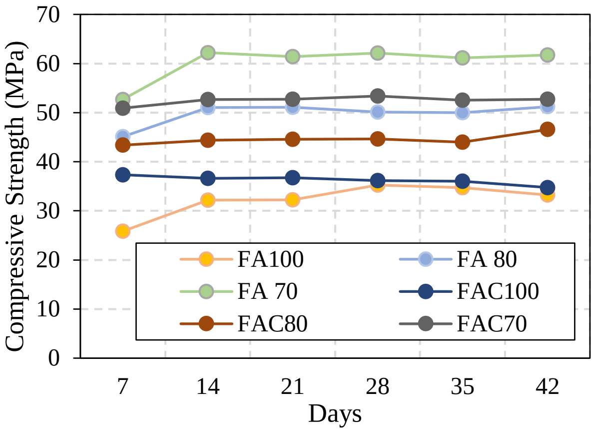
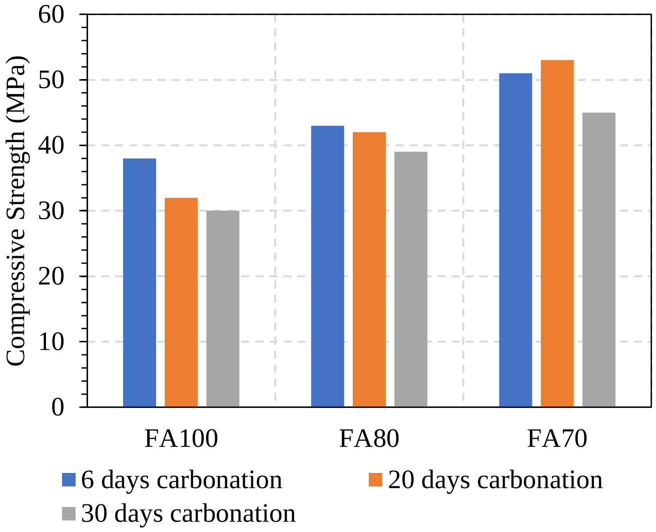


Fig. 12 Strength development up to 42 days

Furthermore, Fig. 13 presents the compressive strength measurements following a 30-day extension of the carbonation curing period. The data reveal that prolonged carbonation results in a reduction in the compressive strength of geopolymer mortar. This decline in strength, particularly in specimens containing GGBS, can likely be attributed to the degradation of the C-A-S-H gel. As previously discussed, the breakdown of this gel is a potential cause of the strength loss. Interestingly, even the FA100 specimens, which contain very low calcium (Ca^{2+}) content and minimal C-A-S-H gel, also exhibited a decline in strength. Initially, carbonation leads to the densification of the matrix due to the formation of carbonation products, which temporarily enhances strength. However, with extended carbonation, the reduction in pH possibly destabilizes these carbonation products, weakening the material and contributing to the observed decrease in strength [21,22]

It is reasonable to suggest that GGBS incorporation, alkaline content, and the combined impacts of carbonation and non-carbonation curing greatly affect the compressive strength and microstructural development of FA-GGBS GP mixes. While carbonation curing has the potential to enhance strength by densifying the microstructure, extended carbonation can lead to strength reduction, particularly in GGBS-blended specimens due to the decomposition of C-A-S-H gel. The results emphasize the complex relationship between polycondensation processes and carbonation, suggesting that carbonation curing should be applied with caution, especially in practical applications. [23]



carbonation curing)

4.4 Shrinkage Behaviour and Mass Change rate

This section will investigate the Influence of carbonation curing, GGBS Incorporation and alkaline concentration on shrinkage behavior and mass change rate

4.4.1 Impact of Carbonation and Non-Carbonation Curing on Shrinkage

Figure 14 presents the autogenous shrinkage data for FA-GGBS GP specimens, highlighting the significant role that GGBS plays in influencing shrinkage behavior. The results indicate that GGBS incorporation markedly increases shrinkage, with a clear correlation between the amount of GGBS added and the extent of shrinkage observed. For instance, the FA70 mix exhibits nearly four times the shrinkage of the FA100 mix. The shrinkage is more significant in the mixtures with 70% fly ash (FA70 and FA70HA) compared to those with 100% fly ash (FA100 and FA100HA). High alkaline concentration (HA) seems to very slightly reduce the shrinkage in both FA100 and FA70 mixtures, as seen in the comparison between FA100 vs FA100HA and FA70 vs FA70HA. Shrinkage increases more rapidly during the first 7 to 14 days, after which it begins to stabilize, particularly in the HA samples. This suggests that GGBS content significantly dictates the magnitude of shrinkage in GP mixtures. The research from [24,25] also support this suggestion.

The increased shrinkage in GGBS-rich mixtures can be attributed to the differential reactivity between GGBS and FA. GGBS hydrates more rapidly than FA, leading to the early formation of hydration products that initially cause volume expansion as they fill the pores within the FA-GGBS GP matrix [26]. However, as hydration progresses and water evaporates, the volume previously occupied by hydration products contracts, resulting in increased autogenous shrinkage. This phenomenon, often referred to as the "hydration-induced Poisson effect" [27], is particularly pronounced in GGBS-rich mixtures.

Additionally, the incorporation of GGBS alters the pore structure of the FA-GGBS GP, potentially obstruct capillary action, it may contribute to increased autogenous shrinkage. This impact can also limit water evaporation, further increased shrinkage [28]. The differential reactivity between GGBS and FA influences the nature and rate of hydration products, thereby affecting shrinkage behavior. Excessive shrinkage, as noted by Mehta and Monteiro [29], can lead to detachment at the interface with reinforcing bars, reducing the protective benefits of GP concrete and raising concerns on its reinforced structural application. [24,25]

Figure 15 compares the shrinkage measurements for specimens subjected to air curing and carbonation curing. The results reveal that, in specimens without GGBS, carbonation has a negligible impact on shrinkage. However, for specimens containing GGBS, carbonation leads to a noticeable reduction in shrinkage. The graph illustrates the shrinkage behavior of fly ash GP mixtures with varying GGBS content and the effect of carbonation. It shows that carbonation-cured samples (FAC100, FAC80, FAC70) consistently exhibit lower shrinkage compared to non-carbonated counterparts (FA100, FA80, FA70). FA100 shows the lowest shrinkage. Adding 20% GGBS in FA80 increase shrinkage, with further reduction in its carbonation-cured specimens. Similarly, FA70 with 30% GGBS increase shrinkage, and FAC70 shows even greater improvement over time.

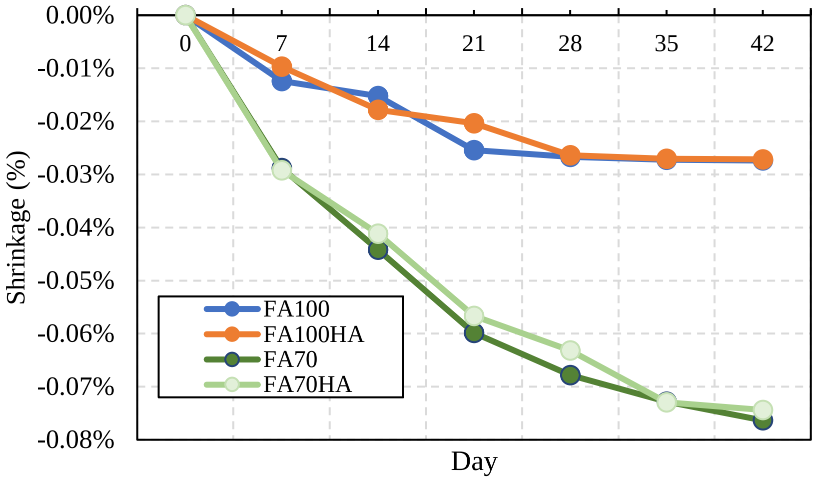


Fig. 14 Shrinkage Behavior in Different Fly Ash Content and Alkaline Concentration

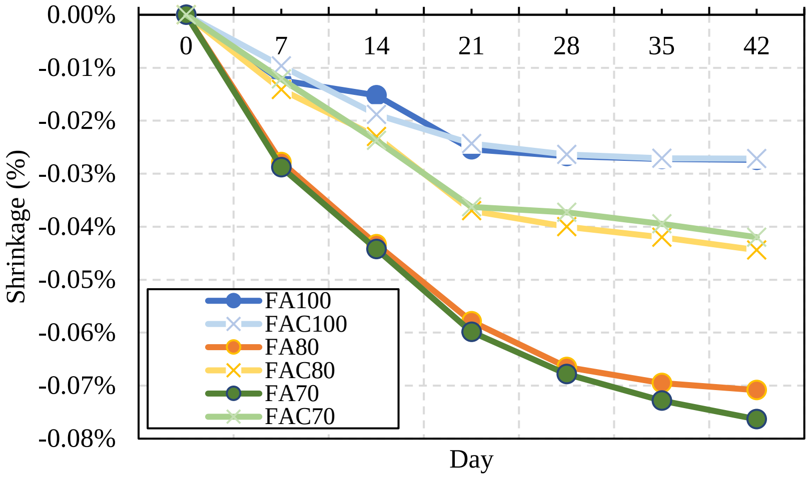


Fig. 15 Shrinkage Behavior of specimens subjected to non-carbonation curing and carbonation curing.

This reduction in shrinkage can be attributed to the effect of carbonation on the GP matrix's pH. Carbonation decreases the pH, which in turn halts the hydration reactions driven by the alkali activators, leading to a reduction in shrinkage. [25, 27].

4.4.2 Mechanism of Carbonation-Induced Shrinkage Reduction

Figure 16 illustrates the difference in mass change rates between specimens subjected to air curing and carbonation curing. It can calculate by following equation (1),

Difference in mass change rate = Air curing mass change rate – Carbonation curing mass change rate = moisture dissipation difference rate – amount of CO_2 fixation (1).

This difference, as described by equation (1), can also refer to be considered to be the sum of the disparity in moisture loss and the mass of CO_2 fixed during carbonation. In FA100 specimens, the comparable shrinkage results between air-cured and carbonation-cured specimens suggest that the moisture loss rate is similar in both cases. Consequently, the difference in mass change rate can be attributed to the amount of CO_2 fixed. The data indicate that CO_2 fixation peaked at 8 days of curing and then gradually declined. This trend, when considered alongside the strength data, suggests that CO_2 was initially fixed as carbonation compounds. However, as carbonation progressed and pH decreased, these compounds dissolved, releasing CO_2. [25]

In specimens containing GGBS, the formation of $CaCO_3$ during carbonation leads to densification of the microstructure, which influences moisture loss rates. Therefore, the difference in mass change rate cannot be solely attributed to CO_2 fixation. However, as carbonation progresses, the difference in mass change rate remains stable, likely due to the stable formation of $CaCO_3$. During carbonation, CO_2 reacts with Ca^{2+} to form $CaCO_3$, which remains stable and does not decompose even as the pH decreases. From these results, it can be concluded that carbonation suppresses shrinkage in GGBS-containing specimens, as free Ca^{2+} and CO_2 are stably bound as $CaCO_3$ [25,27]

It can be said that adding GGBS to FA-based GP mixtures increases autogenous shrinkage due to GGBS's rapid hydration, which alters pore structure and enhances shrinkage. However, carbonation curing reduces shrinkage in GGBS-rich mixtures by forming stable $CaCO_3$ that densifies the microstructure and lowers moisture loss. Carbonation also decreases pH, stopping alkali-driven hydration reactions, further reducing shrinkage. These findings suggest that carbonation curing effectively controls shrinkage in GGBS-incorporated GP systems, improving their durability in reinforced structures. [24,25,27]

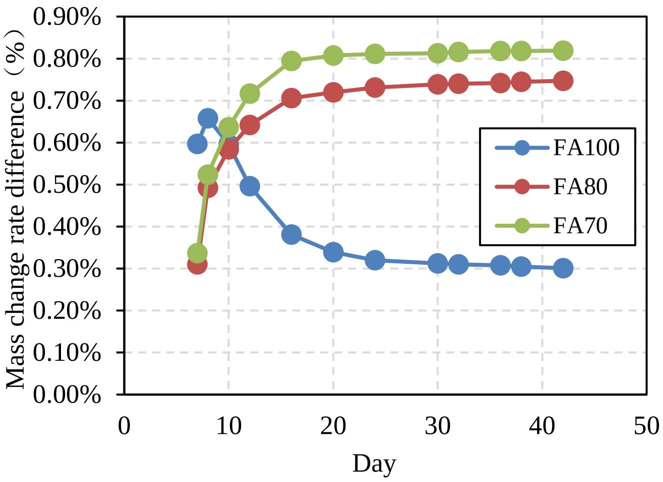


Fig. 16 Difference in mass change rates between specimens subjected to air curing and carbonation curing in FA100, FA80 and FA70.

4.5 Dry-wet cycle test evaluation

The incorporation of GGBS in GP concrete introduces both benefits and drawbacks, particularly concerning the presence of calcium ions (Ca^{2+}) and their interactions during curing processes. GGBS, rich in Ca^{2+}, can cause efflorescence, internal expansion, and cracking, all of which negatively impact the long-term stability and strength of GP concrete. The curing methods employed also have an impact on these problems, with carbonation curing offering a potential approach to lessen some of the difficulties. [30,31]

4.5.1 Impact of GGBS Incorporation: Challenges with Ca^{2+} in GP Concrete

The addition of GGBS to FA-based GP mortar has a major effect on the material's behavior due to the high Ca^{2+} content. When Ca^{2+} reacts with sulfates, expanding phases such as sulfoaluminate compounds or calcium sulfate (gypsum) can be formed. According to Duxson et al.[3], these substances absorb water and cause volumetric expansion, which weakens the GP's resistance to sulfates and results in internal expansion, cracking, and decreased structural integrity. The long-term stability of FA-GGBS GP is greatly threatened by the creation of these expansive phases, which are caused by the presence of Ca^{2+} as in Fig. 17.

Fig.17 Image of Efflorescence. (FA70)

Furthermore, efflorescence, a process where soluble calcium salts migrate to the surface and form as white crystalline layers upon water evaporation, can be caused by the presence of these salts in the GP matrix. This efflorescence not only affects the aesthetic appearance of the concrete but also indicates ongoing chemical reactions that could further degrade the material over time [31]. Moreover, environmental issues are also raised by the possible leakage of Ca^{2+} into the environment, as this could have an impact on nearby soil or water supplies. Therefore, addressing the challenges posed by free Ca^{2+} in FA-GGBS GP is crucial for the material's application in construction. [32]

4.5.2 Role of Carbonation Curing in Mitigating Ca^{2+}-Related Challenges

Carbonation curing has been explored as a potential method to mitigate the adverse effects of Ca^{2+} in GP concrete. During carbonation, CO_2 reacts with Ca^{2+} to form $CaCO_3$, which can help stabilize the material and reduce the risks associated with internal expansion and efflorescence [21]. In the dry-wet cycling test, where specimens underwent alternating cycles of drying and immersion in a 5% sodium sulfate solution, carbonation-cured specimens demonstrated superior resistance to sulfate attack compared to those subjected to air curing. [33]

The results for FA70 after two cycles are shown in Fig. 18. Air-cured specimens showed a white layer on the surface, suggesting efflorescence and possible continuous sulfate reactions. In contrast, no such layer formed in those that underwent carbonation curing, indicating that carbonation effectively inhibits the production of expansive gypsum and lowers the risk of sulfate attack-induced cracking. [34]

Moreover, carbonation curing appears to enhance the overall resistance of GP concrete to aggressive environments. The formation of stable $CaCO_3$ through carbonation could help densify the microstructure, reducing porosity and limiting the ingress of harmful agents, such as sulfates. This improved resistance to sulfate environments highlights the potential of carbonation curing as a method for enhancing the durability of GGBS-containing GP concrete. [30]

It is possible to state that while the incorporation of GGBS in GP concrete offers benefits such as increased strength, it also introduces problems associated with the presence of Ca^{2+}, such as efflorescence, internal expansion, and cracking. Carbonation curing offers an effective method to address these problems by stabilizing Ca^{2+} as $CaCO_3$, strengthening the material's resilience to sulfate attack, and lowering shrinkage.

(a)

(b)

Fig. 18 Results of Dry-Wet Cycles ((a) Air Curing, (b) Carbonation Curing)

5. CONCLUSION

In this study, it may be proposed that various challenges associated with the research on GP were addressed by first establishing a unified set of parameters. Specimens with various compositions and curing conditions were created to evaluate these challenges. Subsequently, various approaches were explored, aiming to lessen these problems, and carbonation curing was shown to be the most practical way. The effects of different compositions and curing methods were compared, it may be possible to lead to the following conclusions:

1. The results of the phenolphthalein experiment suggest that the rate and type of CO_2 reactions, as well as the CO_2 transport pathways, are likely to vary depending on the GGBS content in the GP.
2. The porosity may indicate that the reaction products of CO_2 differ depending on the type of GP, with a higher likelihood of amorphous products being formed.
3. The results of the compressive strength tests and pH measurements suggest that the initial strength remains high even after carbonation, indicating that residual alkaline activators may have reacted during the carbonation process.
4. Shrinkage measurements possibly demonstrated that carbonation reduces shrinkage in GGBS-blended GP.
5. Through the dry-wet cycle tests, it may be possible to confirm that post-carbonation specimens exhibited greater stability. No expansion or cracking due to gypsum formation was observed.

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