

Strength Development of Alkali-Activated Fly Ash Exposed to a Carbon Dioxide-Rich Environment at an Early Age

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ABSTRACT

The development of a binder system with a lower carbon footprint as an alternative to Portland cement has been intensely researched. In the present study, alkali-activated fly ash exposed to carbon dioxide at an early age was characterized in compressive strength tests and by MIP, XRD and FT-IR analyses. The compressive strength of carbonated specimens experienced a dramatic increase in comparison to uncarbonated specimens. The microstructural densification of the carbonated specimens was evidenced by MIP. The XRD pattern showed peaks assigned to nahcolite, indicating that the pH was lower in the carbonated specimens. Under the carbon dioxide-rich environment, the aluminosilicate gel reached a more Si-rich state, which improved the mechanical properties of the alkali-activated fly ash.

Key words : Fly ash, Alkaline activation, Geopolymer, Carbonation, Strength development

1. Introduction

The development of a binder system with a lower CO₂ footprint as an alternative to Portland cement is an area of intense research at present. The focus has been on blended cements, i.e., mixtures of clinker minerals and supplementary materials, and on clinker-free systems.^{1,2)} Geopolymer among these types of new binder systems is a class of alkali-activated material that offers satisfactory performance comparable to those by existing systems.³⁾

Constraints which arise with the adoption of geopolymer include a deficit of in-depth knowledge of the material behavior under different physicochemical conditions.⁴⁾ Studies conducted so far have enabled the visualization of the reaction process, from the activation of the aluminosilicate gel precursor, to the formation of the gel, while the durability aspects of the material remain relatively unclear.⁵⁾ In particular, a carbon source in geopolymer was reported to reduce the activation degree of the precursor, which in turn reduces the strength development rate.⁶⁾ This phenomenon was further supported in Bernal et al. (2013), who offered evidence of structural degradation in alkali-activated fly ash exposed to CO₂ at an early age.⁷⁾ The current understanding of geopolymer exposed to carbonation is limited to the identification of the mechanism governing the structural integrity of the material despite the fact that the geopolymeric gel itself is unharmed.

This study investigates the strength development of

alkali-activated fly ash exposed to a CO₂-rich environment at an early age. Fly ash activated by a solution with a silicate modulus of 1.0 exposed to CO₂ after 24 h of initial curing was characterized by compressive strength tests and multi-technical analyses.

2. Experimental Procedure

2.1 Materials and specimen preparation

The geopolymer precursor used in this study was a Class F fly ash from the Hadong thermal power plant of Korea Southern Power Co., Ltd. The chemical composition of the fly ash is given in Table 1. The alkali-activator was produced by a mixture of a 9M sodium hydroxide (NaOH) solution and a sodium silicate solution (Korean Industrial Standards KS Grade-3; SiO₂ = 29 wt%, Na₂O = 10 wt%, H₂O = 61 wt%, specific gravity = 1.38) at a weight ratio of 1:1 to reach a silicate modulus (SiO₂/Na₂O) of 1.0. The 9M NaOH solution was prepared by dissolving solid NaOH pellets in distilled water. Pastes were produced by a mixture of the fly ash and the activator at a liquid-to-solid ratio of 0.5 by weight.

The fly ash and the activator were mechanically stirred in a mixer for five minutes and were then placed into a cubic mold 50 × 50 × 50 mm in size. The mold was sealed in a plastic bag and placed in an oven at 80 °C for the initial 24 h. After the initial setting, the following exposure condition was applied: (a) specimens were demolded and sealed in a plastic bag to prevent carbonation and (b) specimens were demolded and placed in an accelerated carbonation chamber to expose them to an atmospheric CO₂ concentration of 10% until the designated test day. Note that “uncarbonated specimens” refer to the former, while “carbonated speci-

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Table 1. Chemical Composition of the Fly Ash Used in this Study

(wt%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	P ₂ O ₅	TiO ₂	K ₂ O	SO ₃	LOI*
Fly ash	57.0	21.0	10.0	4.8	1.3	1.5	1.5	1.4	1.0	2.71

*Loss on ignition

mens” refer to the latter throughout this paper. The temperature and humidity were 20°C and 65%, respectively, and were identical for both exposure conditions.

2.2 Test procedures

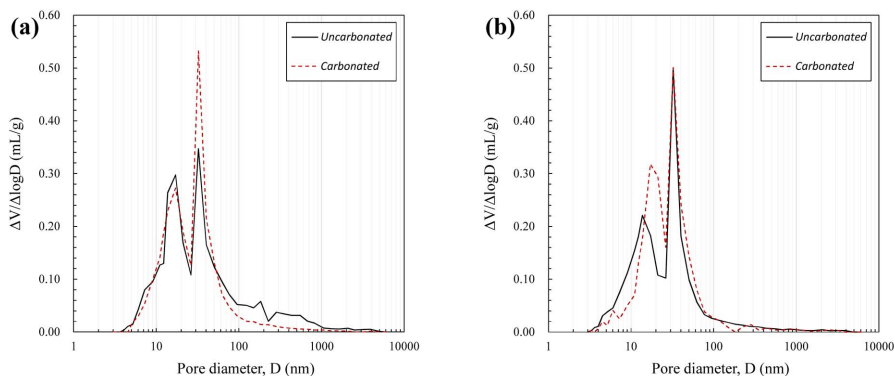
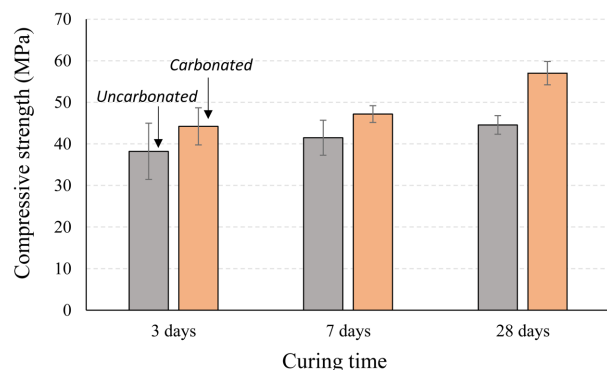
The influence of carbonation on the alkali-activated fly ash was determined by examining the mechanical properties and the gel state. The mechanical properties of the uncarbonated and carbonated specimens were analyzed by compressive strength tests and by mercury intrusion porosimetry (MIP), while the gel chemistry was analyzed by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). Cubic samples were used for the compressive strength test. Fractured samples were used for the MIP analysis, while powdered samples passing a 100 μm sieve were used for the XRD and FT-IR analyses.

Compressive strength tests were carried out using a 500 kN universal testing machine at a loading speed of 0.02 mm/s. The strength was averaged from three replicates. The MIP analysis was conducted using an Autopore VI 9520 machine (Micromeritics Corp.) in the pressure range of 30 to 60,000 psia to detect a pore diameter range of 3 to 6,000 nm. The XRD analysis was conducted using a Rigaku D/MAX 2500H instrument with CuKα radiation at 40 kV and 100 mA. A step size of 0.010° and a scan speed of 2°/min in a 2θ range of 5-45° were adopted as the experimental conditions. The FT-IR spectra were collected using Nicolet 6700 device (Thermo) in a spectral range of 3600-600 cm⁻¹ and at a spectral resolution of 0.09 cm⁻¹.

3. Results

3.1 Compressive strength

The compressive strength levels of the uncarbonated and carbonated specimens at 3, 7 and 28 days are shown in Fig. 1.

**Fig. 2.** MIP test result for uncarbonated and carbonated alkali-activated fly ash. Log differential intrusion curve and cumulative volume of mercury intruded as a function of the pore diameter at (a) 3 days and (b) 28 days.**Fig. 1.** Compressive strength of carbonated and uncarbonated alkali-activated fly ash geopolymer as a function of curing time. Error bars indicate one standard deviation either side of the mean.

Both specimens showed an increase in the strength as a function of time. The compressive strength values of the uncarbonated specimens were 38.2, 41.5 and 44.6 MPa at 3, 7 and 28 days, while those of the carbonated specimen were 44.2, 47.2 and 57.0 MPa, respectively. The difference in the strength at 28 days was the most distinctive, i.e., 12.47 MPa, which corresponds to an increase of 28% compared to that of the uncarbonated specimen. This suggests that the strength of the alkali-activated fly ash is significantly enhanced by exposure to a CO₂-rich environment.

3.2 Porosity

The log differential intrusion curve obtained from the MIP tests is shown in Fig. 2. The median pore diameter, average pore diameter, porosity, and cumulative volume of mercury extruded during the depressurization are summarized in Table 2. It was noted that carbonation did not cause any sig-

Table 2. Summary of the MIP Test Results

Age	3 days		28 days	
	Uncarbonated	Carbonated	Uncarbonated	Carbonated
Exposure condition				
Median pore diameter (nm)	33.3	32.1	31.8	31.8
Average pore diameter (nm)	24.0	22.9	20.0	24.0
Porosity (%)	39.9	32.8	40.4	32.8

nificant change in the median pore diameter. Similarly, the average pore diameter was not noticeably altered by carbonation. While the median pore diameter and average pore diameter in the alkali-activated fly ash remained mostly unchanged by carbonation, the porosity was significantly reduced by carbonation at 3 and 28 days. The porosity of the uncarbonated specimen was 39.9% and 40.4% at 3 and 28 days, respectively, while that of the carbonated specimen was 32.8% at 3 and 28 days, thereafter showing a remarkable decrease. A possible conclusion drawn from this observation is the capability of carbonation to densify the microstructure of alkali-activated fly ash. Meanwhile, it is important to note that porosity measurements via MIP can be influenced considerably by the complex pore structure of the geopolymer and by the ink-bottle effect.^{8,9} Furthermore, alkali-activated fly ash reportedly does not undergo densification as a function of the curing time and does not gain in strength, unlike hydration of Portland cement which consumes water and densifies the microstructure.⁹

3.3 XRD

The XRD patterns of the raw fly ash, and the uncarbonated and carbonated alkali-activated fly ash samples are shown in Fig. 3. Peaks corresponding to mullite, quartz and hematite were observed in the raw fly ash, as shown in

Figs. 3 (a) and (b). These peaks remained in the alkali-activated fly ash regardless of the age of the specimen or exposure to carbonation, as they were unreactive crystalline phases present in the fly ash. Meanwhile, it can be observed in Fig. 3 (b) that peaks corresponding to nahcolite only began to appear in the carbonated specimen at 28 days. Nahcolite is a carbonate mineral with a chemical composition of sodium bicarbonate (NaHCO_3), which is soluble in water.¹⁰ The formation of nahcolite and sodium carbonate heptahydrate, the efflorescence produced when alkali-activated fly ash is exposed to an atmosphere, reportedly has a detrimental effect on the strength development of alkali-activated fly ash.^{6,7,11} Specifically, the formation of nahcolite reportedly occurs in conjunction with a decline in the strength of alkali-activated fly ash according to previous studies.^{7,11} This indicates that the correlation between the formation of nahcolite and the enhanced strength is unclear.

3.4 Gel structure

The FT-IR spectra of the uncarbonated and carbonated alkali-activated fly ash samples are shown in Fig. 4; the main spectral regions of interest are labelled above the spectra. Region 1 labelled in Figs. 4 (a) and (b) is assigned to the aluminosilicate ring and cage structures.¹² A peak in this

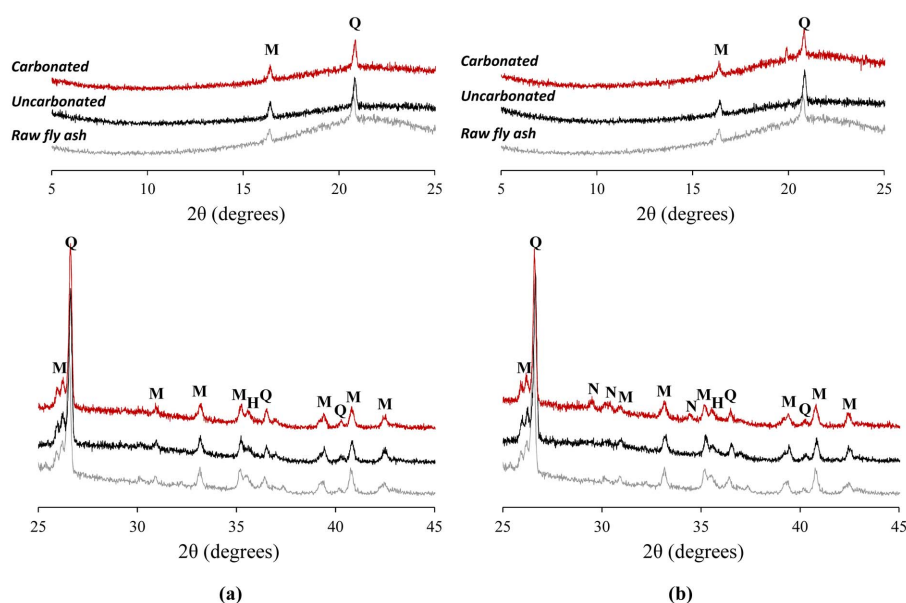


Fig. 3. XRD patterns of the raw fly ash, carbonated and uncarbonated alkali-activated fly ash at the age of (a) 3 days and (b) 28 days. M: Mullite, Q: Quartz, H: Hematite, N: Nahcolite.

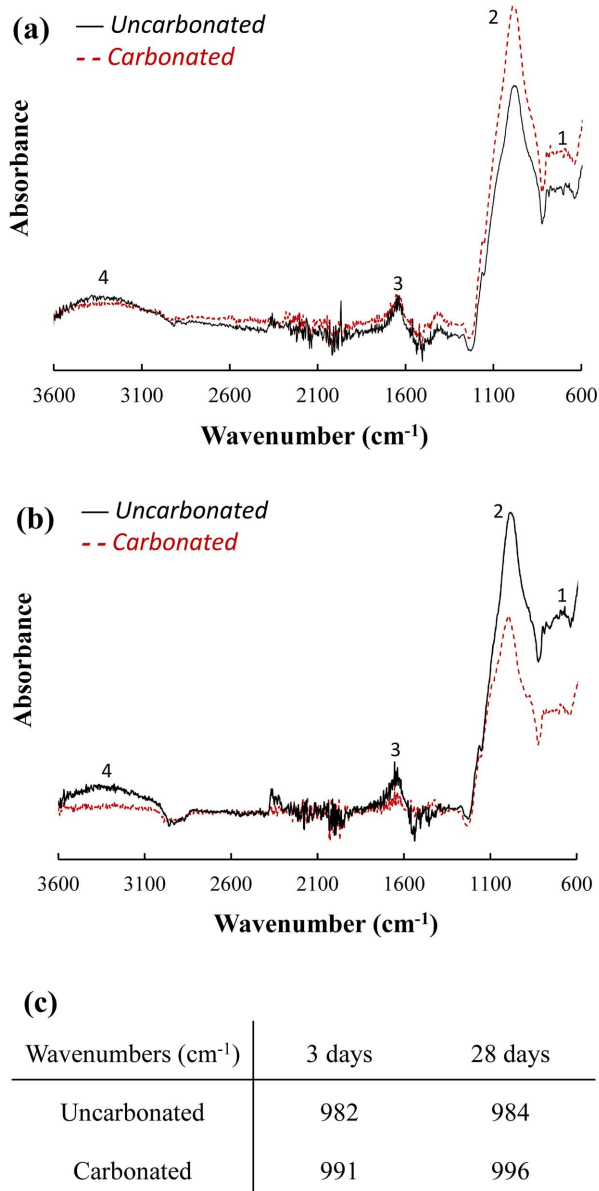


Fig. 4. FT-IR spectra of the carbonated and uncarbonated alkali-activated fly ash at the ages of (a) 3 days and (b) 28 days, and (c) summarized peak position of the main band.

region was visible only in the uncarbonated specimen at 28 days, centered at 670 cm⁻¹. This sharp peak indicates the crystalline or semi-crystalline structure of zeolite typically observed in alkali-activated fly ash.¹³⁾ This indicates that carbonation reduced the aging of the aluminosilicate gel, which tends to crystallize as zeolite species.

Region 2 is assigned to the asymmetric stretching vibration of Si-O-T, where T is tetrahedral Si or Al appearing at 1000-980 cm⁻¹.¹³⁾ The peak position of the band in this region is summarized in Fig. 4 (c). While this peak position generally shifted toward lower wavenumbers (i.e., for the uncarbonated specimen it is 981.95 cm⁻¹ to 984.05 cm⁻¹ from

3 days to 28 days), the peak position of the carbonated specimen appeared at lower wavenumbers. It is generally accepted that the shift of this peak toward lower wavenumbers can be attributed to the substitution of Al in Si-O-T with Si, which reduces the bond angle and therefore decreases the molecular vibrational force constant.^{14,15)} It is important to note that the spectrum of the carbonated specimen in this region was relatively broader toward lower wavenumbers, showing a shoulder-like spectrum at 1050 cm⁻¹ (Fig. 4 (b)).

Regions 3 and 4 are assigned to the bending vibration and stretching vibration of H-O-H.¹³⁾ The peak intensity in these regions is reduced as the reactivity increases.¹⁶⁾ A reduction of the peak intensity of the carbonated specimen in these regions may indicate higher polymerization, but it may have also been caused by the unsealed condition or by exposure to an atmosphere which evaporated moisture from the specimen.

4. Discussions

The results obtained in this study provide new insight into the influence of carbonation on alkali-activated fly ash exposed to carbonation at an early age. Specifically, carbonation brought an enhancement in the mechanical properties of alkali-activated fly ash. The observation of this phenomenon can be elucidated by the chemistry of the aluminosilicate gel.

4.1 Mechanical properties

The compressive strength of the carbonated specimens was higher at all ages, and the difference in the uncarbonated and carbonated specimens was highest at 28 days (Fig. 1). Such an enhancement in the mechanical properties was correlated with the porosity as measured by MIP (Table 2). The porosity of the carbonated specimens was much lower than that of the uncarbonated specimens; therefore, the higher compressive strength of the carbonated specimens is plausible. Meanwhile, the increase in the strength at all ages could not be correlated with the pore properties (i.e., the median pore diameter, average pore diameter and porosity) remaining almost unaltered regardless of the age. In particular, the correlation between the strength development of alkali-activated fly ash and its porosity change is reported to be unclear, which necessitates a closer look at what occurs in the gel during exposure to accelerated carbonation.⁹⁾

4.2 Gel chemistry of aluminosilicate gel

The carbonate product nahcolite as detected by XRD indicates that the pH level in the carbonated specimen was lower. The formation of nahcolite may correspond to a decrease in the porosity of the carbonated specimens, but this cannot serve to explain the improvement in the mechanical properties.

The gel state analyzed by FT-IR in Fig. 4 provides more

useful information about the chemistry of the aluminosilicate gel. The carbonated specimen generally had a peak assigned to the main band of tetrahedral silicate at lower wavenumbers, indicating that the gel state in the carbonated specimens was potentially more mature (Si-rich). A shift of the peak position toward lower wavenumbers as a function of time and the carbonated specimens showing the peak at lower wavenumbers appear to be to some extent reasonable evidence that explains the mechanical improvement in the carbonated specimens.⁵⁾ The optimum Si/Al ratio of the gel which yields the highest strength depends on the precursor, while this value tended to be less than 2 in previous studies. A higher value is usually well correlated with the strength.⁵⁾

A previous study of the carbonation of the alkali-activated fly ash system reported common degradation in the mechanical properties due mainly to lower degree of activation.⁶⁾ A recent study conducted by Bernal *et al.* (2013) also reported a similar observation, whereas the gel chemistry was not significantly altered and the aluminosilicate gel remained unharmed by exposure to carbonation.⁷⁾ The major difference among the present and these earlier studies is the curing and exposure condition. The initial curing appears to play a vital role in enabling a sufficient degree of reaction to proceed for strength development before exposure to carbonation. That is, the gel state can be more Si-rich in the carbonated specimen despite the fact that the degree of reaction in such a system may be lower after a sufficient amount of reaction has occurred. This in turn may provide a higher degree of strength development in the alkali-activated fly ash system. Although a Si-rich state of the gel and a densified microstructure were proposed to contribute to development in the higher strength in alkali-activated fly ash exposed to a CO₂-rich environment, the two mechanisms should be considered separately as covering a correlation requires further study.

5. Conclusions

This study investigated the strength development of alkali-activated fly ash exposed to a CO₂-rich environment at an early age. The fly ash activated by a solution with a silicate modulus of 1.0 exposed to CO₂ after 24 h of initial curing was characterized by the compressive strength and by MIP, XRD and FT-IR analyses. The main conclusions extracted from this work are given below.

Alkali-activated fly ash exposed to a CO₂-rich environment at an early age can undergo a strength enhancement such that its strength will exceed the mechanical strength of an unexposed specimen.

The microstructure of the carbonated specimen was more densified, which may correspond to the higher strength development.

A carbonation product was detected in the XRD analysis, indicating that the pH was lower in the carbonated specimen, but its correlation with the strength enhancement is

less likely.

The aluminosilicate gel of the carbonated specimen was in more Si-rich state in comparison to that of the uncarbonated specimen. This is the main contributor to the development of the strength.

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