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Integrated CO_2 Fixation, Waste Stabilization, and Product Utilization via High-Gravity Carbonation Process Exemplified by Circular Fluidized Bed Fly Ash

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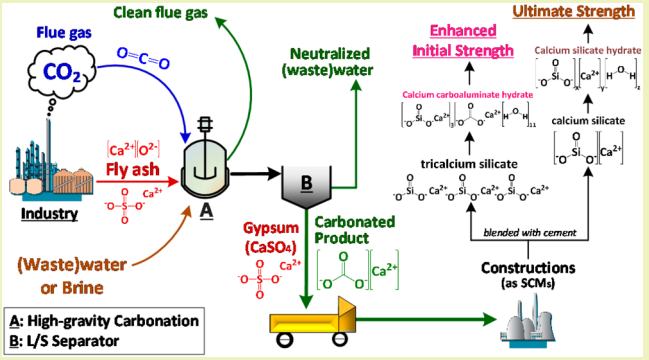
Supporting Information

ABSTRACT: The valorization of industrial solid wastes in civil engineering is one of the main routes for enhancing resource cycle toward environmental and social sustainability. In this study, an integrated approach to capturing CO_2 in flue gas and stabilizing solid wastes for utilization as supplementary cementitious material via a high-gravity carbonation (HiGCarb) process was proposed. The fly ash (FA) generated from a circular fluidized bed boiler in the petrochemical industry was used. The effect of different operating parameters on the carbonation conversion was evaluated by the response surface methodology. The maximal carbonation conversion of FA was 77.2% at a rotation speed of 743 rpm and an L/S ratio of 18.9 at 57.3 °C. In addition, the workability, strength development, and durability of the blended cement with different substitution ratios (i.e., 10%, 15%, and 20%) of carbonated FA were evaluated. The results indicated that cement with carbonated FA exhibited superior properties, e.g., initial compressive strength (3400 psi at 7 d in 10% substitution ratio) and durability (autoclave expansion <0.15%) compared to cement with fresh FA. After HiGCarb, the physico-chemical properties of FA were upgraded, e.g., lower heavy-metal leaching and stabilized volume expansion, which were beneficial to usage as green materials in construction engineering.



KEYWORDS: *HiGCarb, Stabilization, Blended cement, Mineralization, Supplementary cementitious material, Response surface methodology, Compressive strength, Cement chemistry*

INTRODUCTION

Industrial solid wastes, such as fly ash (FA) and steelmaking slag, can be used in civil and construction engineering to increase the sustainability of the environment and society. These materials are generally rich in metal oxides, such as calcium, iron, aluminum, and magnesium oxides. Therefore, a large diversity of utilization can be considered, such as CO_2 adsorbent,[1] lightweight aggregate,[2] supplementary cementitious materials (SCMs),[3] composites,[4] and antibacterial cool pigment.[5] However, some of those solid wastes are classified as hazardous materials because they may contain large amounts of heavy metals[6] and bring air particulate pollution,[7] which might result in severe impacts on the environment and human health. Some of them may contain active species (e.g., free-CaO and free-MgO) so that cement or concrete containing these materials may gradually absorb moisture in the air and cause expansion in the product life cycle. The above-mentioned barriers hinder these materials from widespread applications in construction engineering.

FA generated from a circular fluidized bed (CFB) boiler has been recognized as a pozzolanic constituent and widely used as SCMs or fine aggregates in blended cement.[8,9] Soil modification using fresh FA is also considered to be another utilization approach to increasing strength, enhancing load carrying capacity, and reducing the potential volume change of the soil.[10] Since a significant amount of limestone ($CaCO_3$) was introduced during combustion in the boiler to suppress sulfur-species pollution from petroleum coke, the fresh FA contains a large amount of gypsum ($CaSO_4$) and (free-)calcium oxide (CaO). Therefore, stabilization processes for fresh FA were

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required prior for further utilization in civil engineering.[11,12] Several researches have applied highly pure CO_2 as a curing atmosphere for FA-based cement mortar to eliminate free-CaO content and to enhance initial strength development.[3,12,13]

On the other hand, in recent years, CO_2 emission control in a large-scaled industrial process has also drawn lots of attention due to climate change and global warming issues. To establish a sustainable resource cycle, an integrated multiwaste treatment via high-gravity (HiGCarb) carbonation process has been proposed using CO_2 in flue gas as a chemical to stabilize active components in alkaline solid waste, as shown in eq 1. Since the carbonation is known as a diffusion-controlled reaction, a high-gravity technique has been introduced to enhance the mass transfer between the gas, liquid, and solid phases.[14] The HiGCarb, for instance, using steelmaking slag, exhibited a higher efficiency and a lower operating cost and energy consumption than the traditional fixed bed.[15] Direct use of CO_2 from an emission source also provides a feasible method to achieve CO_2 reduction. In addition, the carbonated product might be able to be utilized as SCMs.[16] However, little research has been done on direct utilization of the carbonated FA from a mineralization process as SCMs in blended cement.

$$CaO_{(s)} + CO_{2(g)} \Leftrightarrow CaCO_{3(s)} \downarrow, \quad \Delta H = -179\ \text{kJ/mol} \tag{1}$$

To the best of our knowledge, this paper is the first one reporting deployment of a HiGCarb process for CO_2 fixation and utilization using FA from a circular fluidized bed boiler. The objectives of this study are to (1) characterize the physico-chemical properties of fresh and carbonated FA, (2) evaluate the effect of different operating factors, including rotation speed, liquid-to-solid ratio, and temperature on carbonation conversion of FA in the HiGCarb process, (3) develop a response surface model of carbonation conversion for locating the potential optimal operating conditions, and (4) investigate the workability, strength development, and durability of blended cement with 10%, 15%, and 20% substitutions of fresh or carbonated FA.

EXPERIMENTAL SECTION

Materials. FA generated from a CFB boiler in a petrochemical industry (Taiwan) was used in this study. Grinding the FA was not required prior to the HiGCarb process because the particle size of the FA was fine enough (e.g., ~15 μm). The physico-chemical properties of ordinary portland cement (OPC) were checked for compliance with ASTM C150 specifications. Graded standard sand (Ottawa sand) following ASTM C778 was used in the mortar specimens. High-pressurized CO_2 with a volumetric concentration of 99% (Ching-Fung Gas, Taipei, Taiwan) was used for all the carbonation experiments.

Characterization. The physico-chemical properties of fresh and carbonated FA were characterized through X-ray fluorescence (XRF), thermogravimetric analysis (TGA), toxicity characteristic leaching procedure (TCLP) tests, scanning electronic microscopy (SEM), and X-ray diffraction (XRD). The chemical properties of FA were analyzed using XRF (PW2430, Phillips) in accordance with ASTM method C114. The carbonation conversion of FA was quantified by TGA (STA600, PerkinElmer, U.S.A.) in accordance with analytical methods reported in the literature.[17−19] In this study, a modified method of thermal analysis for determining the carbonation conversion of alkaline solid wastes was introduced.[20] Qualitative characterization of FA before and after carbonation was carried out using SEM (TM3000, Hitachi, Germany) and XRD (D8 Advance, Bruker, U.S.A.). The diffractometer was equipped with a Cu Kα radiation source operated at 30 kV and 20 mA, with an angular step of 1°/s from 20° to 80°.

Both fresh and carbonated FA were subjected to the TCLP tests for evaluation of the heavy metal leachability, in accordance with NIEA R201.14C.[21] The TCLP was originally developed by the United States Environmental Protection Agency (USEPA) to simulate the worst possible scenario for codisposal of waste and municipal solid waste in a landfill.[22] The standard procedure applies acetic acid solution (pH 2.88 ± 0.05) and acetate buffer solution (pH 4.92 ± 0.05) to simulate the presence of organic compounds leached by acid rain. The concentrations of heavy metals in the solution were analyzed with inductively coupled plasma−optical emission spectroscopy (ICP−OES, ISA JobinYvon JY24, Horiba, Japan).

HiGCarb Process for CO_2 Fixation and Waste Stabilization. An integrated post-treatment process for multiwaste streams of flue gas and solid waste can be achieved by accelerated carbonation. To enhance the reaction efficiency, the HiGCarb process was developed by deploying accelerated carbonation in a rotating packed bed. The FA was well-mixed with tap water to form an FA slurry at designated liquid-to-solid (L/S) ratios. When the experiment began, CO_2 and N_2 gases flew into the HiGCarb process and then the carbonation reaction began. The gas and slurry flow rates of the HiGCarb process were 1.0 and 0.5 L/min, respectively. The FA samples were dried in an oven at 105 °C overnight to eliminate moisture and then analyzed by TGA to evaluate the performance of the carbonation conversion. The evaluation details of the carbonation conversion and CO_2 fixation capacity of FA can be found elsewhere.[17,23]

Response Surface Methodology (RSM). Response surface methodology (RSM) can explore the relationships between several explanatory variables and one (or more) response variables by using a sequence of designed experiments. The experimental variables and responses can be analyzed by a regression procedure using a second-order polynomial equation:

$$y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \varepsilon \tag{2}$$

where y is the response variable; xi and xj are the independent variables; β_0, β_i, β_{ii}, and β_{ij} are incept, linear, quadratic, and interaction constant coefficients, respectively; and ε is the residual. The least-squares estimation was used to determine the model parameters in the approximating polynomial equation with a quadratic model.

In this study, to systematically evaluate the effect of different operating variables on the carbonation conversion of the FA, a statistical model was developed by the RSM. A five-level three-fator central composite design was used for fitting the response surface, leading to 32 experimental data for the RSM analysis. The important factors, including rotation speed (coded as A, range of 550−950 rpm), L/S ratio (B, range of 15−35 mL/g), and temperature (C, range of 20−60 °C) were coded with low and high levels in the D-optimal design.

Carbonated FA as Supplementary Cementitious Materials in Blended Cement. In this study, standard-sized 50 mm blended cement cubes were prepared using fresh or carbonated FA to partially replace OPC at substitution ratios of 10%, 15%, and 20% by weight. A cube pasted with 100% OPC type I (i.e., no FA replacement) was prepared as the control set. The cubes of blended cement were demolded after 24 h and then put into a saturated lime solution for 56 d. The performance of workability, mechanical strength, and durability for differently designed blended cements was evaluated.

The workability of blended cement, including normal consistency (followed CNS 3590[24]), flow test (followed CNS 786[25]), and setting time (followed CNS 786[25]) was evaluated. To maintain consistent workability in cement pastes, a standard flow of 110 ± 5% was maintained by adjusting the quantity of water addition in a blended cement. The CNS 61[26] for OPC type I was utilized to evaluate the feasibility of carbonated FA utilization in the blended cement mortar, where the requirements for minimal compressive strength at 3, 7, and 28 d are 1800, 2800, and 4000 psi, respectively. The durability tests performed for a blended cement included autoclave expansion (followed by CNS 1258[27]) and drying shrinkage (followed by CNS 11056[28]). The CNS specification for portland cement specifies a maximum autoclave expansion of 0.80%.[26]

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RESULTS AND DISCUSSION

Physico-Chemical Properties of Fresh and Carbonated FA. Table 1 presents the physico-chemical characteristics of both fresh and carbonated FA, indicating that the chemical compositions of fresh FA consists mainly of CaO (~62.8%) and SO_3 (~31.0%), as determined by XRF. CaO is not only affecting the pH value of the solution but also affecting the carbonation conversion of FA. The SO_3 composition in the fresh FA is mainly related to $CaSO_4{\cdot}2H_2O$ (gypsum), which had a profound effect on the initial cement chemical as well as mechanical strength. In addition, the contents of MgO, free-CaO, and $Ca(OH)_2$ in the fresh FA were ~0.83%, ~11.4%, and ~3.42%, respectively, where they were generally related to a poor durability of cement mortar (e.g., autoclave expansion). Typically, the MgO content in the cement is limited to less than 6%.[29] After carbonation, both the free-CaO and $Ca(OH)_2$ contents significantly decreased; they were ~0.12% and ~0.14%, respectively. It is reasonable that the dissociation of free-CaO and $Ca(OH)_2$ in the fresh FA occurred after dispersion of the FA into the water. This process would have formed calcium ions, thereby enhancing the alkalinity of the solution, which is actually beneficial to carbonation reaction.[23] Moreover, those active species such as free-CaO and $Ca(OH)_2$ could be effectively reduced after the HiGCarb, which also would improve the cement durability.

Table 1. Physico-Chemical Properties of Fresh and Carbonated Fly Ash (FA) Used in This Study

			Fly ash (FA) from CFB[a]	
categories	items	units	fresh	carbonated
physical properties	density	g/cm^3	2.50	2.44
	specific surface area	cm^2/g	3723	4890
	fineness	cm^2/g	3810	8770
	D (v, 0.5)	μm	16.79	13.19
XRF analysis	SiO_2	%	3.08	2.89
	Al_2O_3	%	1.01	0.98
	Fe_2O_3	%	0.70	0.60
	K_2O	%	0.43	0.33
	Na_2O	%	0.06	0.04
	MgO	%	0.83	1.24
	SO_3	%	31.0	33.0
	CaO	%	62.8	60.1
chemical analysis	free-CaO	%	11.4	0.12
	$Ca(OH)_2$	%	3.42	0.14

[a]CFB: circulating fluidized boiler.

In this study, only calcium species in the FA were assumed to be the major components that participated in the carbonation reaction. Similar estimates of the CO_2 consumption in mortars and concrete were suggested by Steinour.[30] The theoretical sequestration capacity of the FA can be estimated based on eq 3.

$$ThCO_2 = 0.785 \times (CaO - 0.56 \times CaCO_3 - 0.7 \times SO_3) \quad (3)$$

where $ThCO_2$ (g CO_2/g FA) is the theoretical sequestration capacity of the fresh FA, CaO (g CaO/g FA) and SO_3 (g SO_3/g FA) is the weight fraction of CaO and SO_3 in fresh FA measured by XRF, respectively, and $CaCO_3$ (g $CaCO_3$/g FA) is the weight fraction of $CaCO_3$ analyzed by TGA. According to the chemical analysis as shown in Table 1, the theoretical CO_2 fixation capacity was estimated to be 0.323 g CO_2 per gram of fresh FA.

Figure 1 shows the mineralogical characteristics and the SEM images of the fresh and carbonated FA. The mineral

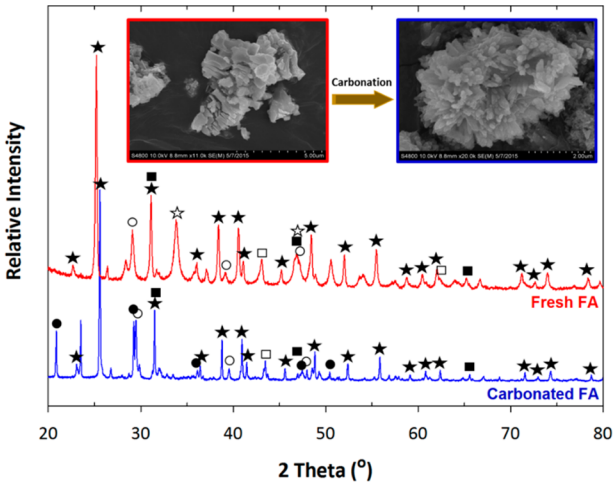

Figure 1. SEM images and XRD patterns of fresh and carbonated fly ash (FA) with peak identification. ☆: $(Ca_3Mg)(SiO_2)_4$ (Merwinite). ★: $CaSO_4$ (Anhydrite). ○: $CaCO_3$ (Calcite). ●: $CaCO_3{\cdot}H_2O$ (Calcite). □: MgO (Periclase). ■: SiO_2 (Stishovite).

compositions of fresh FA include merwinite $[(Ca_3Mg)(SiO_2)_4]$, periclase (MgO), anhydrite $[Ca(SO)_4]$, stishovite (SiO_2), and calcite $(CaCO_3)$, of which $Ca(SO)_4$ is the main phase. Even though $Ca(OH)_2$ was not identified by the XRD, Ca−Mg−Si oxide was present in significant quantities, as indicated by the higher peak intensities in the XRD analysis of the fresh FA. The surface of the fresh FA was smooth in irregularly shapes. In contrast, after carbonation, $(Ca_3Mg)(SiO_2)_4$ was found to be eliminated, instead of the formation of monohydrocalcite $(CaCO_3{\cdot}H_2O)$ and calcite $(CaCO_3)$. The surface of the carbonated FA was uniformly covered with rhombohedral (i.e., calcite) and/or needlelike (i.e., aragonite) crystals, with a size of 1−5 μm. In addition, the formation of the fine $CaCO_3$ precipitates can provide a favorable surface for nucleation and growth of hydration products in cement/concrete,[31] which should be beneficial to the strength development of blended cement. According to the observations of XRD and SEM, it was confirmed that the carbonated products in the FA were mainly calcium carbonates such as monohydrocalcite and calcite.

Table 2 presents the results of the TCLP tests for both fresh and carbonated FA. For the fresh FA, various heavy metals, such as barium (Ba), mercury (Hg), and arsenic (As) could be potentially leached out from the solid matrix. After carbonation, the Ba concentration decreased from 0.076 to 0.058 mg/L, while the leaching concentrations of Hg and As were below the detection limit of ICP-OES. This might be attributed to the formation of carbonate precipitates, thereby decreasing the leachability of heavy metals from the solid matrix. Similar observations found in the literature confirm that the Ba leaching from solid waste should be controlled by the formation of $BaCO_3$.[32] In general, the stabilization mechanisms of heavy metals by carbonation include (1) the formation of metal carbonate precipitates resulting in a reduced leachability of heavy metals,[33] (2) a lowered basicity of solid waste leading to a change in the solubility of mineral compounds due to a shift in

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Table 2. Performance of Toxicity Characteristic Leaching Procedure (TCLP) for Fresh and Carbonated FA

		CFB fly ash		limits regulated in Taiwan		
elements	units	fresh	carbonated	HIW[a]	utilization product	green building[b]
Cd	mg/L	ND < 0.0035	ND < 0.0035	1.0	0.8	0.3
Cu	mg/L	ND < 0.012	ND < 0.012	15.0	12.0	0.15
Pb	mg/L	ND < 0.033	ND < 0.033	5.0	4.0	0.3
Cr^{6+}	mg/L	ND < 0.0034	ND < 0.0034	2.5	0.2	1.5
Hg	mg/L	0.0022	ND < 0.00028	0.2	0.016	0.005
As	mg/L	0.012	ND < 0.00051	5.0	0.4	0.3
Cr	mg/L	ND < 0.044	ND < 0.044	5.0	4.0	–
Se	mg/L	ND < 0.0012	0.009	1.0	0.8	–
Ba	mg/L	0.076	0.058	100	10.0	–

[a]HIW: hazardous industrial wastes. [b]Regulated by Taiwan Architecture & Building Center.

pH (especially for reducing Pb and Zn leaching),[34] and (3) the formation of the polymorph $CaCO_3$, which is beneficial to the uptake of heavy metals, such Ba and Pb.[32] On the basis of the regulations in Taiwan, the carbonated FA should be classified as a nonhazardous industrial waste and considered as a material for green building. It thus suggests that the HiGCarb process can effectively eliminate the leachability of heavy metals, which is beneficial for use as a green material in construction.

Effect of Operating Parameters on Carbonation Conversion of FA. Table S1 of the Supporting Information presents the analysis of variance table for the developed RSM to identify the optimal operation condition for the carbonation conversion. In this study, the developed RSM model was significant because an F-value of 51.77 was obtained, implying there is only a 0.01% chance that a "Model F-statistics" of this large of value could occur due to noise. Figures S1(a) and (b) of the Supporting Information show the normal plot and comparison between predicted and actual values, respectively. The results indicated that there was a dependent relationship between L/S ratio and temperature on the carbonation conversion of the FA in the HiGCarb process. The developed model associated with rotation speed (A), L/S ratio (B), and temperature (C) on the carbonation conversion of FA is presented in eq 4.

$$\delta(\text{coded}) = 72.0 + 1.47 \times A - 0.16 \times B + 4.69 \times C - 4.5 \times B \times C - 6.14 \times A^2 - 3.5 \times B^2 \quad (4)$$

A good fitting of the experimental data to the response surface was observed with an R^2 value of 0.93 and a standard deviation of 0.98%, which indicates that the carbonation conversion of FA could be well predicted by the RSM as expressed in eq 4. The sequences of sensitivity to the carbonation conversion were followed by temperature (positive, highest), rotation speed (positive), and L/S ratio (negative, lowest). As shown in Figure 2, by changing the default values of temperature, different 3D response surface plots based on rotation speed and L/S ratio can be obtained, under which the predicted maximal carbonation conversion of FA was 77.2% at a rotation speed of 743 rpm and an L/S ratio of 18.9 at 57.3 °C.

Workability of Cement Pastes with Carbonated FA. Typically, the water/cement ratio, curing age, and temperature are the main factors affecting cement paste hydration. It is noted that a significant degree of hydration increases with an increase in the water/cement ratio from 0.23 to 0.47, while the changes in the hydration degree become insignificant when the water/cement ratio increases beyond 0.47.[35] Table 3 presents the workability of blended cement pastes, including water demand for normal consistency, flowability, and setting time, with substitution of the fresh or carbonated FA. In this study, the water demands for both fresh and carbonated FA were in the range between 0.26 and 0.29. The results indicate that blended cements with carbonated FA exhibit higher water demand than that with fresh FA because of larger surface areas of the carbonated FA. The water demand of the cement paste is largely dependent on the particle characteristics of the SCM and its portion in the blending. It was confirmed that blended cement with SCM having a higher surface area (e.g., carbonated FA) would demand a large amount of water.

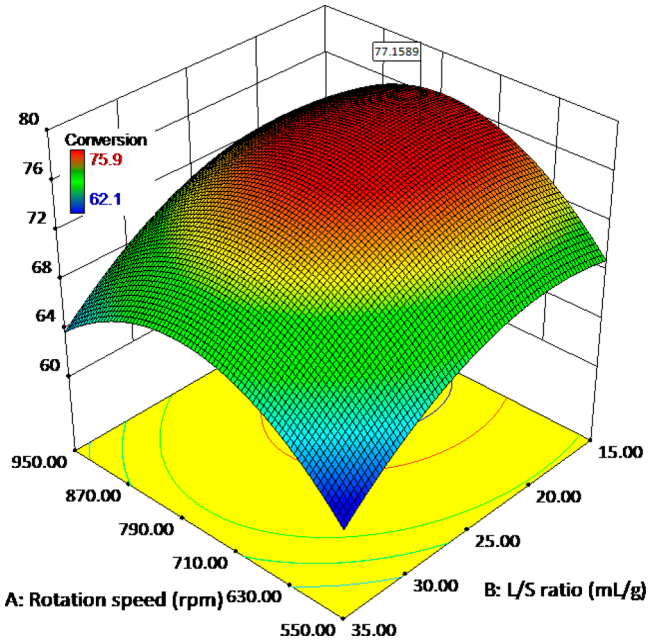

Figure 2. 3D response surface plots for predicting carbonation conversion of FA in the HiGCarb process.

The setting time was found to increase with an increase in substitution ratios in blended cement pastes for both the fresh and carbonated FA. The initial and final setting times of the pure cement were 150 and 250 min, respectively. In contrast, at a substitution ratio of 20%, the setting times for the fresh and carbonated FA were 225 and 320 min, respectively. It is noted that the setting speed is mainly related to the reaction of $3CaO \cdot Al_2O_3$ (C_3A) with water (eq 5), where the reaction immediately hardens the paste (i.e., ~mins).[29] As the FA substitution ratios

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Table 3. Water Demands of Normal Consistency, Flowability, and Setting Time for Cement Pastes with Different Substitution Ratios of Fresh or Carbonated FA

specimens	workability performance			
	normal consistency (mL)[b]	flowability (mL)[c]	initial setting time (min)	final setting time (min)
pure portland cement	165	250	150	250
10% fresh FA	170	270	195	290
10% carbonated FA	180	270	165	260
15% fresh FA	175	280	210	300
15% carbonated FA	185	280	180	270
20% fresh FA	180	290	225	320
20% carbonated FA	190	290	185	290
Limits by regulation in Taiwan[a]	–	105–115%		<375
ASTM C595[42]	–	100–115%	>45	<420

[a]Regulated by CNS 786.[25] [b]Normal consistency water demand (mL/650 g-cement). [c]Flow test water demand (mL/500 g-cement).

increase, the total content of C_3A in the cement pastes decreases since the main compositions of FA are gypsum and calcite, thereby leading to a delay of the exothermic peak. The setting times of all blended cement pastes with up to a 20% substitution ratio of the fresh or carbonated FA met the CNS requirement.

$$C_3A + 6H \rightarrow C_3AH_6 \quad (5)$$

where C, H, and A represent CaO, H_2O, and Al_2O_3, respectively.

In addition, the setting time of the fresh FA was found to be relatively longer than that of the carbonated FA, which could be attributed to the fact that the formation of $CaCO_3$ in carbonated FA can provide additional nucleation sites for hydration reaction, thereby reducing the setting time. It was noted that incorporation of fine pure $CaCO_3$ in the blended cement can reduce set retardation in a ternary blended cement.[31,36−38]

Mechanical Strength of Mortars with Carbonated FA. Figure 3 shows the results of the compressive strength development of tested cement mortars substituted with fresh or carbonated FA as SCMs at various levels of substitution, i.e., 10%, 15%, and 20%. In general, the compressive strength increases continuously within 28 d, while only a slight increase was observed from 28 to 56 d. For both fresh and carbonated FA, only blended cement mortars with a substitution ratio of 10 wt % could meet the CNS technical specification. With an increase in substitution ratio from 10 to 15 wt %, a significant difference in compressive strength after 28 d was observed. As the substitution ratio of either fresh or carbonated FA increases, the compression strength of blended cement decreases due to less OPC amounts in mortars, thereby reducing the available Ca_3SiO_5 (C_3S) and Ca_2SiO_4 (C_2S) contents, which are considered to be the main constituents for strength development in cement. The C_3S hydrates (eq 6) more rapidly with higher hydration heat than C_2S, which would enhance the initial strength development for the first 28 d, while the C_2S

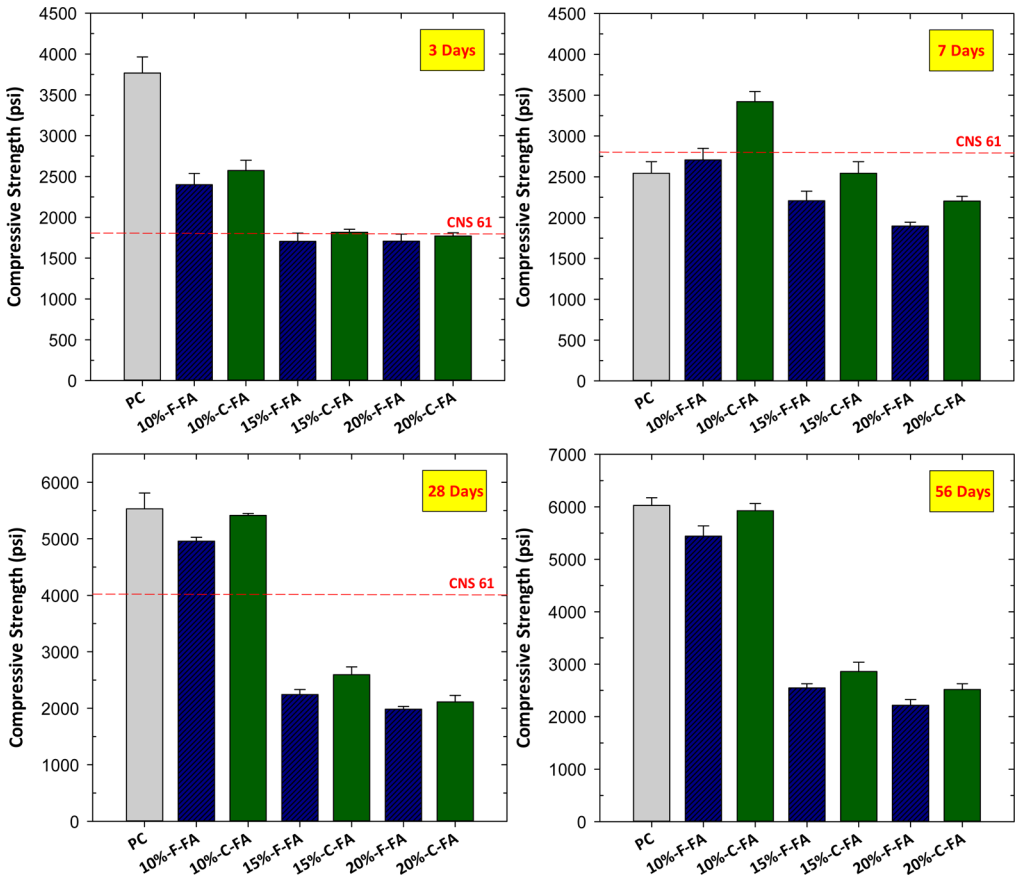

Figure 3. Compressive strength of blended cement with different substitution ratios of fresh (F-) or carbonated (C-) FA for 3, 7, 28, and 56 days, comparable to the CNS-61 requirement in Taiwan.

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hydrates (eq 7) slowly (long-term hydration) and is responsible for the ultimate strength development (usually takes 2 to 3 years for its completion hydration).

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH, \quad \Delta H = 114.16\ \text{kJ/mol} \tag{6}$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH, \quad \Delta H = 38.75\ \text{kJ/mol} \tag{7}$$

where CH represents $Ca(OH)_2$, and $C_3S_2H_3$ represents calcium silicate hydrate (C−S−H colloid), which is a noncrystalline amorphous solid−liquid phase.

The blended cement with the carbonated FA generally exhibited superior compressive strength compared to the fresh FA, especially at early ages. At 7 d, mortar with a 10% substitution ratio of carbonated FA even exhibited higher initial compressive strength than the OPC mortar. This might be attributed to the interaction of C_3A components and the carbonation product ($CaCO_3$), resulting in the formation of calcium carboaluminate hydrate ($C_3A{\cdot}CaCO_3{\cdot}11H$) and $C_3A{\cdot}0.5CaCO_3{\cdot}0.5CH{\cdot}11.5H$, as shown in eq 8.[16] Although the contents of free-CaO and $Ca(OH)_2$ were reduced in the carbonated FA, the exothermic reaction by the carbonation product ($CaCO_3$) would be faster than C_3S, which would enhance hydration heat and form a carboaluminate hydrate for initial strength development.[39]

$$2C_3A + 1.5CaCO_3 + 0.5CH + 22.5H \rightarrow C_3A{\cdot}CaCO_3{\cdot}11H + C_3A{\cdot}0.5CaCO_3{\cdot}0.5CH{\cdot}11.5H \tag{8}$$

On the other hand, although the C_3A content in cement (typically ∼10% in clinker) contributes little to the strength of concrete, the C_3A hydration will result in a great amount of hardening heat (eq 5). This might lead to a negative effect on the strength after 28 d by weakening the cement matrix bond with microcrack formation due to its high thermal expansion of air and water in the mortar.[40] The C_3A easily reacts with sulfates (e.g., gypsum) and water to form ettringite (eq 9). With the great amount of $CaSO_4{\cdot}2H_2O$ (noted as $C\check{S}{\cdot}2H$) in FA, the formed ettringite can cover the C_3A crystal to prevent C_3A from further hydration. This could improve the strength development and prolong the setting time of blended cement (as discussed in the Workability of Cement Pastes with Carbonated FA section). In this study, the highest initial compressive strength for both fresh and carbonated FA was at 10% substitution ratio, where the SO_3 content in blended cement was in a range between 3.1% and 3.3%.

$$C_3A + 3(C\check{S}{\cdot}2H) + 26H \rightarrow C_3A{\cdot}3C\check{S}{\cdot}32H\,(\text{ettringite}), \quad \Delta H = 364.76\ \text{kJ/mol} \tag{9}$$

In some circumstances, the formed ettringite could further react with the uncovered C_3A to form monosulfate (AFm). In the presence of $CaCO_3$ (i.e., carbonated FA), this reaction can be delayed and reduced due to the formation of monocarboaluminate, as shown in eq 10. A similar observation was also found in the literature,[41] which indicated that the formation of ettringite was accelerated by $CaCO_3$ at the very beginning of hydration (e.g., 30 min).

$$3(C_3A{\cdot}C\check{S}{\cdot}12H)\,(\text{AFm}) + 2CaCO_3 + 18H \rightarrow 2(C_3A{\cdot}CaCO_3{\cdot}11H) + C_3A{\cdot}3C\check{S}{\cdot}32H\,(\text{ettringite}) \tag{10}$$

Aside from the aforementioned chemical enhancement, physical improvement due to the highly fine particle size of the carbonated FA (i.e., a fineness of 8770 cm^2/g) could result in (1) high surface area providing activate sites for epitaxial crystallization of the C_3S hydration product, such as C−S−H and (2) microfiller into free spaces between clinker grains. Similar observations were found in the literature for pastes containing $CaCO_3$, either as a chemical reagent or as a limestone constituent.[16,40] This suggests that the use of carbonated FA as SCM in blended cement mortar can enhance the mechanical properties to a greater degree than the use of fresh FA.

Durability of Mortars with Carbonated FA. Figure 4 shows the soundness of blended cement mortars with the fresh

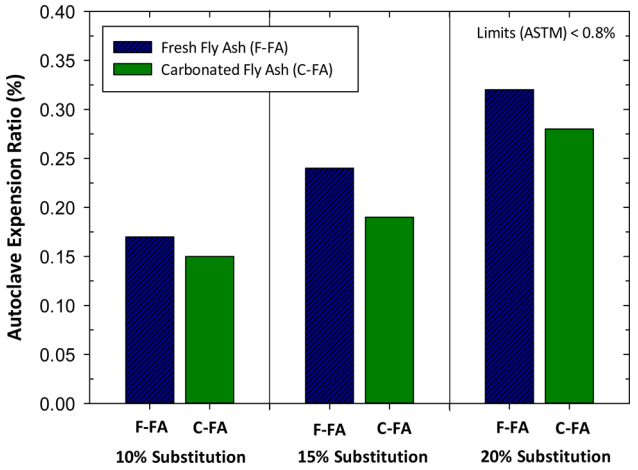

Figure 4. Autoclave expansion ratio (soundness) of cement mortars blended with different substitution ratios of fresh (F-) and carbonated (C-) FA.

or carbonated FA through the autoclave expansion test, which indicated that the expansion capacity of the blended cement mortar increased with an increase in substitution ratio of the FA due to higher free-CaO contents in mortar. The maximal expansions for the fresh and carbonated FA were around 0.325% and 0.275% in the case of 20% substitution ratio, which met the ASTM requirement (i.e., <0.8%).[42] In all cases of using the carbonated FA in the blended cement, the expansion increment could be successfully stabilized, which is comparable to that using fresh FA. This was attributed to the elimination of the reactive free-CaO content in the carbonated FA with relatively stable compounds (e.g., $CaCO_3$). Similar observations could be found in the literature that the durability of the cement mixtures was greatly enhanced by employing either pure limestone powder[43] or carbonated materials[15,44] in blended cement.

Figure 5 displays that the drying shrinkage of blended cement mortars is comparable to the OPC mortar, by which it indicates the volume change due to water loss by evaporation in a specimen when the blended cement is exposed to a dry environment. The results revealed that the drying shrinkage of all specimens increased rapidly within the first 7 d and gradually reached a steady state up to 42 d. The drying shrinkages of all

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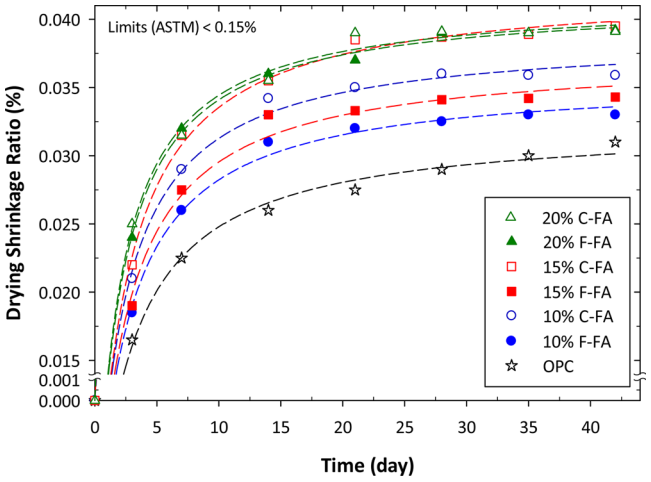

Figure 5. Drying shrinkage of blended cement with different substitution ratios of fresh (F-) or carbonated (C-) FA (cured in air and exposed a dry environment at 23 °C).

the blended cement mortars containing FA were higher than that of the OPC control within 42 d. However, no significant damage was observed in the blended cement with up to a 20% substitution ratio of the fresh or carbonated FA. All specimens met the ASTM requirement for blended cement with low heat of hydration, i.e., a maximal shrinkage of 0.15%.[42] Based on the above evidences, it suggests that the carbonated FA should be a suitable SCM in blended cement due to its excellent durability.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b00014.

Information as mentioned in the text. (PDF)

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Notes

The authors declare no competing financial interest.

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