Accelerated Carbonation Assessment of High-Volume Fly Ash Concrete

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Abstract

The issue of concrete carbonation has gained importance in recent years due to the increase use in supplementary cementing materials (SCMs) in concrete mixtures. While there is general agreement that concrete carbonation progresses at maximum at a relative humidity of about 60%, the rate may differ in the case of cements blended with SCMs, especially with high-volume fly ash replacements. In this study, the effect of high-volume fly ash concrete exposed to low ambient relative humidity (RH) conditions (57%) and accelerated carbonation (4% CO_2) is investigated. Twenty-three concrete mixtures were produced varying in cementitious contents (310, 340, 370, and 400 kg/m^3), water-to-cementitious materials ratio (0.45 and 0.50), and fly ash content (0%, 15%, 30%, and 50%) using a low and high-calcium fly ash. The specimens were allowed 1 and 7 days of moist curing and monitored for their carbonation rate and depth through phenolphthalein measurements up to 105 days of exposure. The accelerated carbonation test results indicated that increasing the addition of fly ash also led to increasing the depth of carbonation. Mixtures incorporating high-calcium fly ash were also observed to be more resistant against carbonation than low-calcium fly ash due to the higher calcium oxide (CaO) content. However, mixtures incorporating high-volume additions (50%) specimens were fully carbonated regardless of the type of fly ash used. It was evident that the increase in the duration of moist curing from 1 day to 7 days had a positive effect, reducing the carbonation depth for both plain and blended fly ash concrete mixes, however, this effect was minimal in high-volume fly ash mixtures. The results demonstrated that the water-to-cementitious ratio (W/CM) had a more dramatic impact on carbonation resistance than the curing age for mixtures incorporating 30% or less fly ash replacement, whereas those mixtures incorporating 50% showed minor differences regardless of curing age or W/CM. Based on the compressive strength results, carbonation depth appeared to decrease with increase in compressive strength, but this correlation was not significant.

1. Introduction

The need for innovative infrastructures and urban housing is enormous and the burden of fulfilling these necessities is heavily reliant on the concrete industry. In order to meet these expectations, more than 4.1 billion metric tons of ordinary portland cement (OPC) are mass-produced every year contributing approximately 3.4 billion metric tons of CO_2 [1]. These emissions are estimated to add up to 7% of the total emissions from all sources indicating the enormity of the impact on environment [2]. Hence, the construction industry is under an immense burden to decrease these emissions, and to seek alternatives to produce reliable materials having identical properties as cement [3]. One of the most popular methods in which to alleviate the environmental impact on cement production and reduce emissions is by increasing the use of supplementary cementing materials (SCMs) in concrete mixtures [4].

Utilization of SCMs such as fly ash and blast furnace slag presents many advantages, such as improving fresh and hardened properties, minimizing thermal cracking, and resisting chemical threats such as alkali-silica reaction, sulfate attack, and chloride penetration [5]. Typically, these properties are enhanced by using more SCMs, provided that the concrete is proportioned, placed, and cured appropriately. On the one hand, however, the carbonation resistance of such cementitious systems is typically found to be reduced with high volume SCM substitutions [6]-[11]. Inclusion of SCMs in concrete can reduce the calcium hydroxide (CH) content due to the pozzolanic reactivity which can decrease the alkalinity level required for steel protection. In particular, fly ash can reduce the pH level further accelerating the carbonation rate and depth which produces high risk for corrosion [12]. Hence, researchers have found that an increase in replacement by fly ash has a negative effect on the depth of carbonation. It is one of the few cases where high dosages of SCMs do not improve the durability of reinforced concrete structures.

The corrosion of reinforcing steel in concrete is considered one of the most serious problems considering the durability of the structure. It is the main reason for the degradation of reinforced concrete structures throughout the world as it negatively impacts its service life [13]. In reinforced concrete structures, the surface of the steel rebar is normally protected from corrosion by a thin passive layer of iron oxide formed by the high alkalinity (pH ≈ 13) of the concrete's pore structure [14]. This phenomenon will protect the steel from corrosion indefinitely unless the passive film is destroyed either by the presence of an excessive amount of chlorides at the location of the steel, or by the reduction of the pore

solution pH as a result of the carbonation process. While in North America chloride-induced corrosion has been the leading cause of corrosion [15], in recent years there has been increased concern over carbonation-induced corrosion for blended cement-based concrete mixtures, especially those incorporating higher levels of SCMS replacements [16] [17] [18].

Carbonation is a physico-chemical process that arises from the chemical reaction between carbon dioxide (CO_2) from the environment and calcium bearing hydrates such as CH, calcium silicate hydrate (C-S-H), ettringite (AFt) and monosulfate (AFm), lowering the alkalinity of the concrete. When atmospheric CO_2 penetrates in the hardened concrete, it dissolves in the pore water to form carbonic acid and further reacts with hydrates to form calcium carbonate [10]. If the carbonation front reaches the surface of the steel reinforcement, corrosion can initiate if sufficient moisture and oxygen are present, resulting in the development of cracks, rust stains, and spalls of concrete cover [11]. The progression of carbonation in cementitious systems however, is extremely slow and may take years to obtain sufficient results. Consequently, the majority of researchers adopt an accelerated carbonation method—increasing CO_2 concentrations and optimizing relative humidity (RH) conditions—to hasten the process and assess the carbonation resistance of concrete.

Carbonation of Fly Ash Concrete

While the mechanisms of degradation are well-known in plain cement systems, recent studies have focused on the effects of fly ash replacement on carbonation depth. In a research conducted by Khunthongkeaw *et al*. [11], they concluded that fly ash containing higher calcium oxide (CaO) content tends to have lower carbonation depths as compared with low CaO fly ash. Another research carried out by Sanjuán *et al*. [19] confirms that the partial addition of high CaO content fly ash to the OPC offers a good resistance against carbonation. Considering the claims made in the above research, calcium oxide (CaO) content in fly ash is believed to have an influence on the carbonation.

Relative humidity (RH) is also an important parameter to be considered while studying accelerated carbonation in a controlled environment. It is generally agreed that a RH of approximately 40% - 85% is required for carbonation to progress in concrete. Concrete being a porous material allows the internal water to saturate in its pores, leaving no space for CO_2 to occupy. Due to this, the ingress of CO_2 inside the concrete is limited and subsequently the resistance against carbonation is increased [20]. In the case of fly ash concrete, it was observed that higher relative humidity improves the resistance against carbonation. This pattern can be validated from a study performed where specimens were allowed to moist cure for 1 day and then moved to a controlled environment (20°C and 65% RH). Carbonation was observed to decrease when relative humidity was increased from 65% to 80% and 90% RH. It was also observed that the significant effect of lack of moist curing time provided to the specimens was

compensated by increasing the relative humidity [21].

Multiple researchers suggest the importance of moist curing and its effect on the carbonation depths of fly ash concrete. If the concrete is adequately cured, it significantly reduces the large pores inside the concrete making it less penetrable. In a research study on concrete incorporating high volumes of fly ash, the results suggested that with an increase in the moist curing period from 7 to 28 days, the carbonation depth was observed to decrease. However, the effect was not substantial when the curing period was further prolonged from 28 to 91 days [22]. Contrasting results were found in a study which indicated that 90 days curing had a positive effect against carbonation of fly ash concrete in comparison with 28 days curing [23]. In a study of fly ash concrete subjected to accelerated carbonation, it was clearly evident that the longer the specimens are allowed to moist cure before placing in the accelerated carbonation chamber, the less carbonation depth that was observed [24]. This emphasizes the importance of moist curing conditions before exposure to the CO_2 infused environment. However, it is not uncommon for many concrete structures to experience insufficiently curing periods prior to exposure to ambient conditions.

A linear relationship was found between porosity and carbonation depths indicating that the carbonation value increases as porosity increases [24]. It can be predicted that denser concrete mixtures would be more resistant against the threat of carbonation since a lower porosity exists, which will slow the ingress of CO_2. This was supported by research done by Bouzoubaa *et al*. [12] suggesting that an increase in w/cm ratio will increase the coefficient of carbonation both at 3 and 7 days of curing. Similar results were observed in a research suggesting the lower w/cm ratio mixtures offer better resistance against carbonation due to its denser pore structure [11]. Fly ash concrete with higher w/cm ratios tends to have higher carbonation depth due to the lack of calcium hydroxide content in the fly ash [25]. A similar trend was observed in a research where three w/cm ratios (0.35, 0.50, and 0.65) were considered. An increase in carbonation depth was observed with an increase in w/cm ratio for specimens exposed in an accelerated carbonation chamber with a 75% relative humidity [26].

While the carbonation resistance of concrete in natural environments is the most reliable method, accelerated tests are used to assess carbonation resistance of concrete. Moreover, while parameters used in such tests can vary among researchers, employing a concentration of 3% - 4% CO_2 and a 50% - 60% RH seems to be appropriate for accelerated tests that can develop many linear relationship of carbonation depths between the two methods [27] [28] [29]. However, accelerated carbonation performed at these lower RH conditions may underestimate the carbonation resistance of concrete mixtures with high-volume SCM substitutions. In this paper, several mixture combinations incorporating a high- and low-calcium fly ash and exposed to accelerated carbonation conditions (57% RH and 4% CO_2) are investigated. The influence of cementitious contents, W/CM, curing age and clinker replacement with up to 50% fly ash on carbonation depth and rate is presented influence.

2. Materials and Experimental Method

2.1. Materials Used

The cement used for this study was the Type I/II Ordinary Portland Cement (OPC) which conforms to the ASTM C150 specifications [30]. In this study, two fly ashes were used in the majority of the mixtures including a low-calcium (LC) and high-calcium (HC) fly ash. The two fly ashes conform to the ASTM C618 [31] and were procured from plants in Texas, USA. The compositions of all cementitious materials used are given in Table 1, together with the calculated Bogue composition for the OPC.

The coarse and fine aggregates used for this research were of crushed and manufactured limestone for the coarse and fine aggregate, respectively. The materials were procured from a local source in central Texas. The physical properties are highlighted in Table 2.

2.2. Mixture Proportions

A total of 23 concrete mixtures were produced with the concretes divided into

Table 1. Chemical properties of cementitious materials.

	OPC (%)	LC (%)	HC (%)
SiO_2	20.8	41.05	49.40
CaO	63.62	20.69	2.99
Al_2O_3	4.4	17.80	22.02
Fe_2O_3	4.3	3.84	1.04
SO_3	2.9	1.29	0.79
MgO	1.1	3.63	12.64
Na_2O	0.11	1.89	0.75
K_2O	0.67	0.62	1.52
Na_2O_e	0.551	-	-
LOI	1.6	-	-
$SiO_2 + Al_2O_3 + Fe_2O_3$	-	62.69	72.46
C_3S	58		
C_2S	18		
C_3A	5		
C_4AF	13		

Table 2. Physical properties of aggregates.

Aggregates	Bulk specific gravity (OD)	Bulk specific gravity (SSD)	Apparent specific gravity	Absorption (%)	Dry rodded unit weight (kg/m^3)
Manufactured Sand	2.55	2.61	2.73	2.63	1819.64
Coarse Aggregate	2.52	2.58	2.68	2.44	1574.89

three series of mixtures designated LC, HC, and CONT each varying in water-to-binder (W/binder) contents (0.50 and 0.45) and total cementitious contents (310, 340, 370, and 400 kg/m³). The first two series consisted of mixtures with either a low-calcium (LC) or high-calcium (HC) fly ash used as a cement clinker replacement ranging from 15% to 50% at 15% intervals by mass of total cementitious content. Lastly, a final series included control mixture (CONT) with no SCMs replacement utilizing the Type I/II OPC with varying cementitious contents. The mixture proportions together with fresh concrete properties are given in Table 3.

Table 3. Concrete mixture proportions.

| Mix ID	Mix Series	W/binder	SCM Replacement (%)	Mix Proportions (kg/m³)		Fresh Properties		
				OPC	SCM	Slump (mm)	Air (%)	Density (kg/m³)
LC-1			15	263.5	46.5	50	2.3	2390
LC-2			30	217	93	80	1.9	2380
LC-3		0.50	50	155	155	100	1.8	2390
LC-4			30	238	102	190	2.4	2325
LC-5	LC		30	259	111	210	2.6	2340
LC-6			15	289	51	50	1.9	2400
LC-7		0.45	30	238	102	80	2.2	2400
LC-8			15	314.5	55.5	130	1.4	2410
LC-9			30	259	111	150	1.3	2425
HC-1			15	263.5	46.5	80	3.0	2350
HC-2			30	217	93	80	2.0	2410
HC-3		0.50	50	155	155	110	2.5	2370
HC-4			15	238	102	160	2.4	2320
HC-5	HC		30	259	111	190	2.4	2310
HC-6			15	289	51	40	2.0	2420
HC-7		0.45	30	238	102	70	2.1	2420
HC-8			15	314.5	55.5	140	2.4	2370
HC-9			30	259	111	180	2.2	2370
CONT-1			-	310	-	70	3.5	2345
CONT-2		0.50	-	340	-	100	2.1	2370
CONT-3	CONT		-	370	-	200	3.1	2320
CONT-4			-	370	-	70	2.1	2410
CONT-5		0.45	-	400	-	120	2.5	2380

2.3. Mixing Procedure

For mixing, the mixer was initially cleaned by rinsing and draining the water. Aggregating batching was done by mixing the aggregates well in the mixer for approximately five minutes to ensure uniformity. Coarse aggregates were added first and were allowed to mix for three minutes, following by fine aggregates for two minutes. Approximately 70% of the total water was added and mixed for another three minutes. Subsequently, the cementitious materials were added and allowed to mix for five minutes following by the remaining water for another three minutes. The mixture was allowed to rest for another three minutes after removing from the mixer. The mixing procedure was followed in accordance with ASTM C192 [32].

2.4. Accelerated Carbonation Setup

The carbonation chamber was large enough to accommodate 50 prisms when specimens were placed vertically. One mechanical fan was placed in the chamber to ensure air circulation. A humidity probe placed inside the chamber provided information of the humidity conditions inside throughout the test using a data acquisition system. The prisms were positioned in the chamber in such a manner that all specimens were spaced at a minimum of 5 mm between prisms and chamber walls as shown in Figure 1. For this experiment, the RH of the chamber was controlled and monitored at 57% ± 5% through the use of an industrial dehumidifier attached to the chamber; the dehumidifier reduces the humidity in the enclosed environment by removing water vapor from the air through ventilation ducts and were attached in such a way that the inflow and outflow of CO_2 through the system was maintained throughout the test. Lastly, the CO_2 level inside the chamber was adjusted and maintained at 4.0% ± 0.5% by volume through the use of a gas regulator and oxygen tank attached to a solenoid valve that would trigger the system to adjust when levels were beyond the threshold. A digital display was placed above the carbon tank which indicated the CO_2 level and the temperature inside the carbonation chamber. Figure 2 demonstrates the entire accelerated carbonation setup.
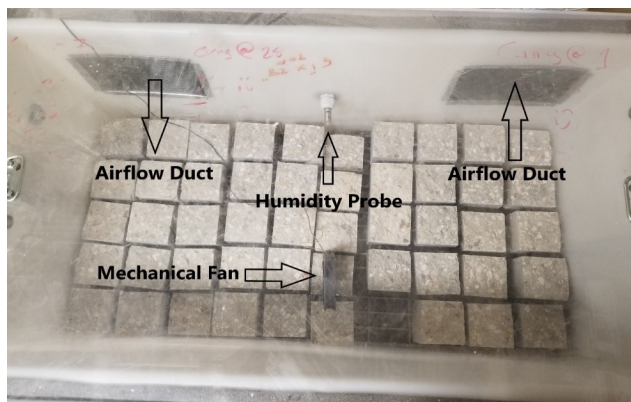
Figure 1. Accelerated carbonation chamber.

Figure 2. Accelerated carbonation setup.

2.5. Preparation and Casting of Test Specimens

Each mixture included a set of 100×200 mm concrete cylinders for determining compressive strength at various ages, and prismatic specimens of $100 \times 100 \times 350$ mm ($4 \times 4 \times 14$ inches) to determine the carbonation depth under accelerated conditions. For carbonation test, a pair of specimens were prepared per mix and demolded after being stored at $23°C \pm 3°C$ ($73°F \pm 5°F$) under wet burlap and plastic for 24 hours. Thereafter, one prism per concrete mix was immediately prepared for transfer to the carbonation chamber, while the second prism was placed in a moist curing chamber for additional 6 days (7-day total moist cure) to explore the influence of curing age on the rate of carbonation. In the case of compression testing, twelve 100×200 mm (4×8 inches) cylinders were cast per mix and standard procedure according to ASTM C31 was followed for making the specimens. The cylinders were allowed to cure in the laboratory at $23°C \pm 3°C$ ($73°F \pm 5°F$) under wet burlap and plastic for 24 hours prior to being demolded. Thereafter, samples were transferred to the moist curing chamber and tested after desired age of curing was obtained (2, 7, 28, and 90 days).

2.6. Accelerated Carbonation Test

Following an initial 1 day and 7 days of moist curing, the carbonation prisms were allowed to air dry in a controlled environment (23°C, 50% RH) for a minimum of 3 hours to allow removal of moisture from the concrete as well as easier control of the relative humidity in the chamber during testing; the short drying period minimized the length and curing age for which each specimen was intended to be subjected to (1 and 7-day moist cure) prior to testing. While it is likely the specimens were still in relatively saturated conditions upon placement into the chamber, the attached dehumidifier allowed for faster control of the relative humidity conditions to reach equilibrium between the specimens and surrounding environment. The prisms were then vertically placed into the car-

bonation chamber with CO_2 level of 4.0% ± 0.5% by volume, temperature of 23˚C ± 2˚C, and relative humidity (RH) of 57% ± 5%.

For each specimen, the age at which the carbonation depth was measured was 28, 56, 63, 70, and 105 days of exposure to CO_2. An approximately 50 mm thick slice was cut off the prism at each stage of testing with a mechanical cutting device which left a freshly broken surface. The split slice is then brushed and the depth of carbonation was determined by spraying the freshly fractured surface with a 0.5% phenolphthalein solution. Following 1 h ± 5 min, a picture of the colored surface was taken and the carbonation depth was determined with a ruler at 5 equidistant points on each of the four sides of the slice giving a total of twenty measurement points (see Figure 3). Measurements were not made within 15 mm of the corners. If the measurement falls to an aggregate, it is extrapolated on both sides of this aggregate. The average carbonation depth for each side was calculated and the average carbonation depth of the concrete mix is reported.

3. Results and Discussion

3.1. Carbonation Assessment Based on Type of Fly Ash

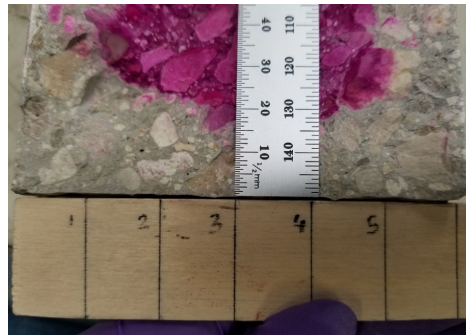Figure 4 and Figure 5 demonstrate the carbonation patterns for specimens with

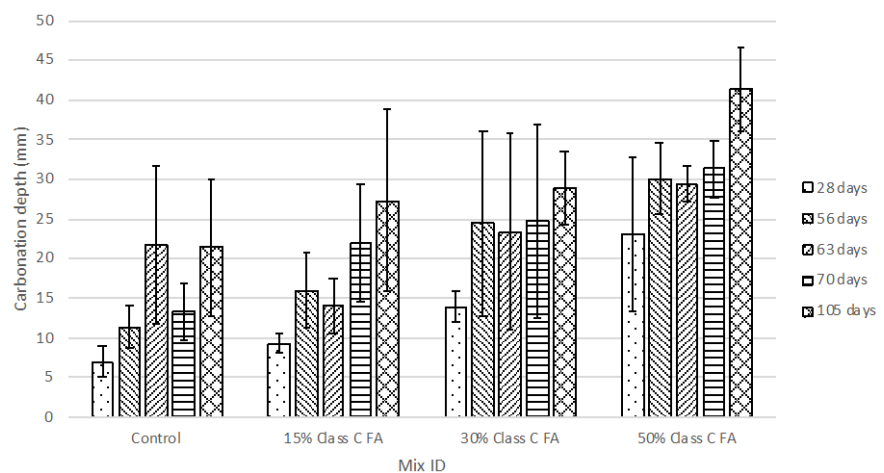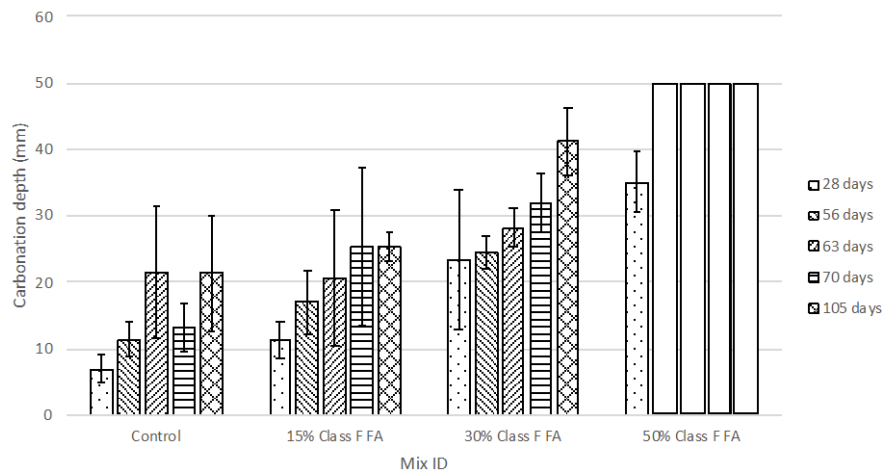

Figure 3. Carbonation depth recording method.

Figure 4. Comparison of high-calcium fly ash specimens with control (7-day curing).

Figure 5. Comparison of low-calcium fly ash specimens with control (7-day curing). *white bars indicate fully carbonated specimens.

and without low- and high-calcium fly ash at 0.50 w/cm ratio moist cured for 7 days, respectively. Based on the information obtained, it is noticeable that carbonation depths increase with time of exposure to CO_2 for all mixtures. However, the carbonation depth over time was more dramatic with increasing amounts of fly ash, especially for mixtures incorporating 50% fly ash. For mixtures incorporating low-calcium fly ash, the rate of CO_2 ingress was more pronounced when compared to high-calcium fly ash concretes. In fact, mixtures incorporating low-calcium fly ash at 50% replacement had such a detrimental effect that specimens were fully carbonated by no later than 56 days of exposure (see **Figure 5**). It can be clearly inferred that high-calcium fly ash is more resistant against carbonation as compared to low-calcium fly ash. This is likely attributed to the higher calcium oxide (CaO) content present in the chemical composition of high-calcium fly ash. The CaO present in the hydrated cement paste will be transferred into $CaCO_3$ upon carbonation from CO_2 exposure. Consequently, carbonation rate of concrete is mainly governed by the CO_2 buffer or binding capacity from the availability of calcium bearing hydrated per unit volume of the cement paste as suggested by Leemann *et al.* [27]. Hence, the extent of chemical interaction (and binding of CO_2) will be reduced compared with OPC concrete [21]. Additionally, the lower portlandite content provides an initial lower pH in the pores solution, in which typically lead to more rapid carbonation of other calcium-bearing hydrates such as calcium silicate hydrates [10] [33]. While the carbonation rate for fly ash mixtures is likely to decrease with increasing curing time, the results demonstrate that the carbonation rate at an early age is significantly faster in insufficiently cured high-volume SCM concrete. The longer the moist curing period for concrete, the higher the degree of hydration of the cement and the lower the porosity and permeability of the concrete is [29].

In general, for mixtures incorporating high-calcium fly ash, the results show that the average carbonation depth across all ages increased by 18%, 54%, and 108% for 15%, 30%, and 50% fly ash replacement in comparison to the control.

On the other hand, mixture including low-calcium fly ash showed an increase of 33%, 100%, and 214% for 15%, 20%, and 50% fly ash replacements in comparison to the control (note that 50% low-calcium fly ash mixtures were fully carbonated by 56 days of exposure).

3.2. Assessment Based on Moist Curing

It was also observed that specimens with 1-day moist curing are more prone to carbonation ingress as compared with 7-day moist curing specimens. **Figure 6** and **Figure 7** describe the effect of 1-day and 7-day moist curing on both low- and high-calcium F fly ashes at different cementitious material contents, and it is evident that longer moist curing period helps the concrete to improve resistance against carbonation. Because the carbonation is related to permeability of concrete, higher carbonation should be expected in inadequately cured concrete, with or without fly ash [7]. Moreover, increasing levels of fly ash, i.e. greater than 30%, significantly increase the rate of carbonation. Several such cases were tested, and it can be clearly inferred that specimens with 1-day moist curing highlight more carbonation depth as compared to specimens with 7 days of moist curing regardless of w/cm ratio or cementitious materials content.
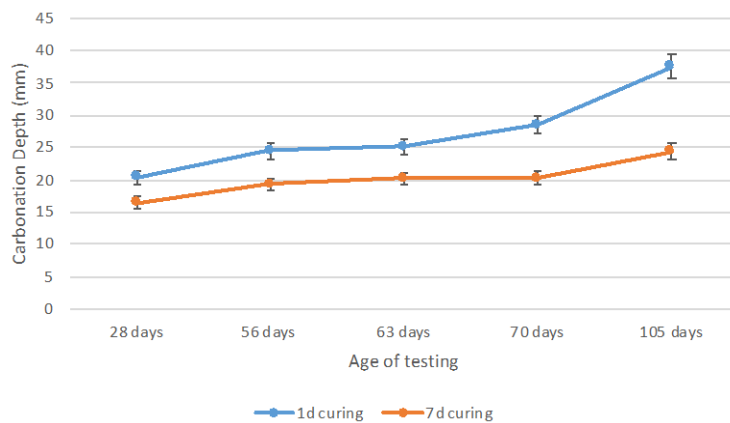
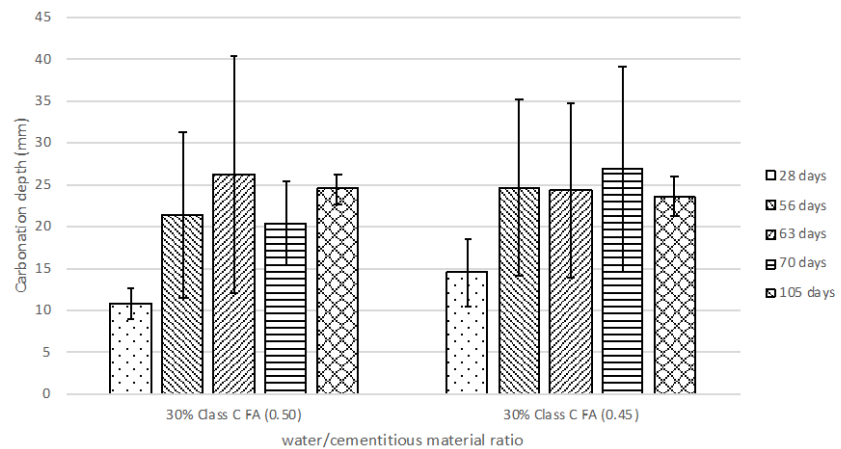**Figure 6.** Comparison between 1-day and 7-day curing for high-calcium fly ash.
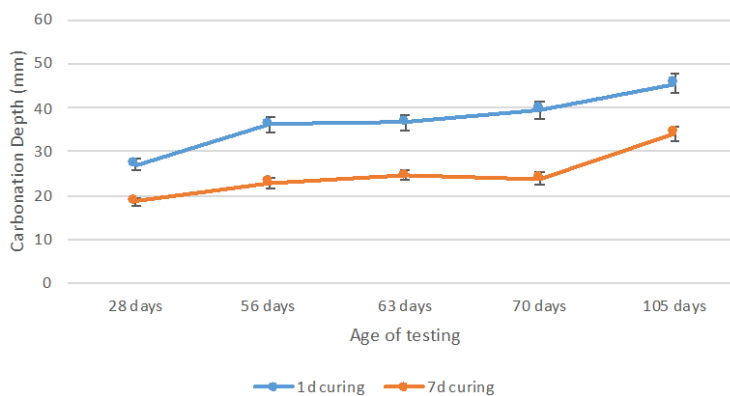
Figure 7. Comparison between 1-day and 7-day curing for low-calcium fly ash.

## 3.3. Comparison Based on Water-Cementitious Materials Ratio

Previous studies suggested that with a decrease in water-cementitious material ratio the carbonation depth will also decrease since the concrete will be denser and less permeable. In the present study, a comparison between low- and high-calcium fly ashes consisting of 0.50 and 0.45 w/cm ratio is demonstrated in **Figure 8** and **Figure 9**. In both cases, 0.5 w/cm ratio specimens indicated higher carbonation depths than 0.45 w/cm ratio specimens with 7-day moist curing. However, this pattern was not consistent throughout all days of testing. Low-calcium fly ash specimens followed an identical trend however the difference between 0.50 and 0.45 w/cm ratio specimens was not significant.

## 3.4. Comparison Based on Amount of Cementitious Material

A comparison between different cementitious contents was made at a given w/cm ratio and fly ash replacement. **Figure 10** and **Figure 11** indicate the comparison between specimens consisting of 340, 370 and 400 kg/m^3 at 0.50 w/cm
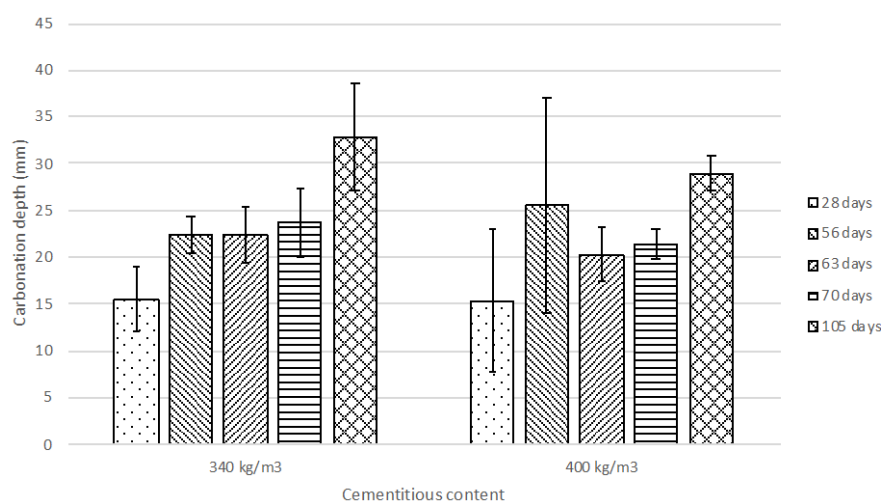

Figure 8. Comparison between 0.50 and 0.45 w/cm ratio for high-calcium fly ash (7-day curing).
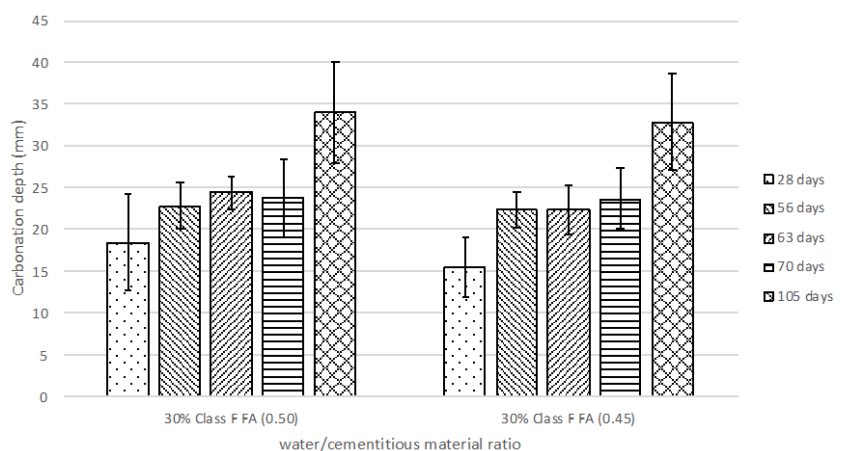
Figure 9. Comparison between 0.50 and 0.45 w/cm ratio for low-calcium fly ash (7-day curing).
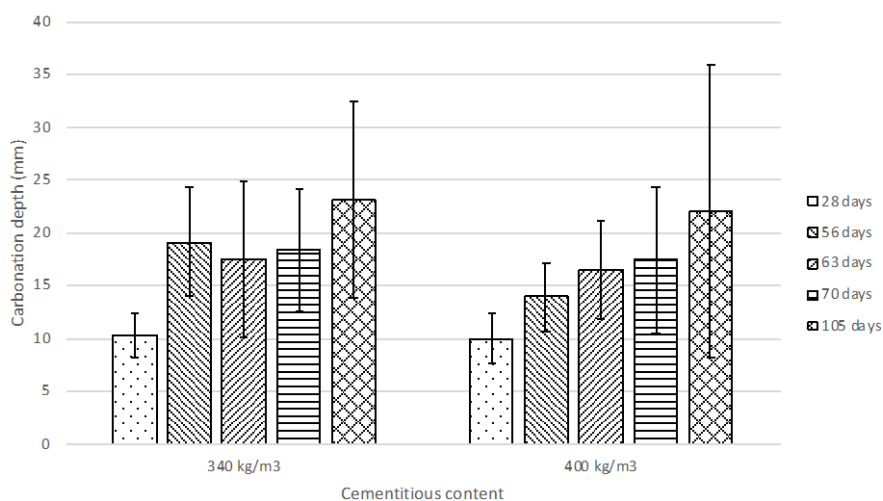
Figure 10. Comparison between 340 and 400 kg/m^3 cementitious content for high-calcium fly ash at 0.45 w/cm (7-day curing).

Figure 11. Comparison between 340 and 370 kg/m^3 cementitious content for low-calcium fly ash at 0.5 w/cm (7-day curing).

ratio after 7 days of moist curing. The results indicated a slight decrease in the carbonation depth earlier on however, little significance was observed between the mixtures with extended exposure time in. This pattern was observed in the majority of the cases in which mixtures with increasing total cementitious content, a slight decrease in the carbonation depth was observed. This may be attributed to the availability of the calcium hydroxide (Ca(OH)$_2$) content per unit volume of the cement paste in each mixture, especially with increasing clinker content. As a result, the binding capacity and thus, chemical reactivity with CO$_2$ is increased [27].

4. Conclusions and Recommendations

The following conclusions can be drawn from the present study.
  1) Regardless of the type of fly ash used, the depth of accelerated carbonation

increased with an increase in fly ash content. High-calcium fly ash was more resistant against the threat of carbonation as compared to low-calcium fly ash.

2) The depth of accelerated carbonation decreased as the moist curing period increased from 1 to 7 days.

3) Accelerated carbonation was decreased with a decrease in water-cementitious material ratio from 0.5 to 0.45 in case of control mixes. However, no clear pattern was observed in case of fly ash concrete mixes.

4) Cementitious content did not seem to affect the carbonation severely and no fixed pattern can be determined from the results for control mixes. In the case of low- and class high-calcium fly ashes, increase in cementitious content seemed to have a positive effect against carbonation. Effect of phase transformation [34] [35] [36] on carbonation process can be studied in future.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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