Effect of Type and Content of Fly Ash on Carbonation of Mortars

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Abstract

This article deals with the carbonation of mortar, which incorporates two types of fly ash that have different CaO content. Carbonation depths of mortar, measured from the exposure in real environment and in accelerated carbonation chamber were investigated. The experiments revealed that the decreased water to binder ratio and content of fly ash, or the increased period of curing in water, led to better carbonation resistance. For a given replacement level of fly ash, mortar incorporating higher CaO fly ash exhibited a better carbonation resistance. A longer initial curing period resulted in lower carbonation depth, especially when mortar was incorporated by fly ash or had a high w/b. The analysis showed that there is a strong relationship between carbonation depth and compressive strength. The relation was found to be linear and its slope was dependent on the length of curing.

1. Introduction

Carbonation is one of the durability problems that occurs when carbon dioxide reacts, in the presence of moisture, with calcium hydroxide in concrete. Although carbonation is not harmful to plain concrete, the reaction affects the amount of calcium hydroxide in concrete, which is the product of the hydration reaction. It also reduces the alkalinity of the concrete pore water. Thus, the corrosion protection of reinforcing steel by high alkalinity can be destroyed. It is obvious that for reinforced concrete structures, the onset of reinforcement corrosion is considered as one of the important stages for determining the service life of the structure.

Based on published materials, there are few literatures that could report the effect of type of fly ash. Furthermore, researches on the effect of fly ash are continuing. For instance, Ho and Lewis [1], Wee et al. [2], and Papadakis [3] reported an increase in carbonation rates when the cement was partially replaced by fly ash. Malhotra et al. [4] reported the test results of ten-year outdoor exposure of high strength/high performance concrete specimens (w/b = 0.27 to 0.29) that the carbonation depth of concrete incorporating 57% of fly ash was negligible. Atis [5] reported that fly ash concrete made with 50% replacement, which has much lower w/b than the cement-only concrete, showed lower or comparable carbonation depth when compared with the cement-only concrete. In addition, the test results from various sources cited in Wesche [6] showed that concretes of equal strength with and without fly ash have similar carbonation resistance levels.

Hence, in this study, experimental investigations on the effect of type and content of fly ash as well as paste content, water to binder ratio, and curing period on carbonation depth were carried out. Carbonation depths of mortar were measured from the exposure in real environment and in the accelerated carbonation chamber. The relationship between the carbonation depths in the two environments was investigated. In addition, an attempt was made to relate carbonation depth in a real environment to the compressive strength of the tested mortars.

2. Experimental Program

2.1 Materials

Ordinary Portland cement type 1 (OPC) and two types of lignite fly ash (FA1 and FA2) were used. Chemical compositions and physical properties of the materials are shown in **Table 1.** The fine aggregate was river sand with the fineness modulus and the specific gravity in SSD condition of 3.12 and 2.62, respectively. The aggregate complied with the requirement of ASTM C33 and had the minimum void ratio of 0.36.

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2.2 Mixture proportion and specimen preparation for normal exposure carbonation test

Twenty-four mixtures of mortars were proportioned by varying paste content (ratio of paste volume to the void volume of compacted aggregate phase of 1.2 and 1.4), water to binder ratio (0.5 and 0.6), and replacement percentage of fly ash (0%, 10%, 30%, and 50%). The ratio of paste volume to void content of compacted aggregate phase (γ) is defined as

$$\gamma = \frac{V_p}{V_{void}} \qquad (1)$$

where V_p is the volume of paste in the unit volume (1 m^3) of fresh concrete and V_{void} is the volume of the void in the densely compacted total aggregate (fine and coarse aggregates) in the unit bulk volume (1 m^3) of the aggregate. The volume of paste can be derived as

$$V_p = V_c + V_f + V_w + V_{air} \qquad (2)$$

where V_c, V_f, V_w, and V_{air} are the volumes of cement, fly ash, water, and air, respectively, in a unit volume (1 m^3) of concrete mixture (m^3). The mixture proportions of mortar are summarized in **Table 2**.

Table 1 Properties of cementitious materials

	Cement	FA1	FA2
Chemical composition (%)			
Silicon dioxide	20.99	45.88	33.13
Aluminum oxide	5.18	26.20	26.89
Iron oxide	3.20	10.94	11.96
Calcium oxide	64.63	8.28	15.07
Magnesium oxide	1.30	2.83	2.94
Sulfur trioxide	2.61	1.04	1.63
Insoluble residue	0.13	-	-
Sodium oxide	0.04	0.9	1.42
Potassium oxide	0.40	2.78	3.33
Titanium dioxide	0.25	0.51	0.52
Phosphorus pentaoxide	0.05	0.1	0.16
Free lime	0.75	0.18	-
Gypsum content	5.60	-	-
Physical properties			
Specific gravity (g/cm^3)	3.15	2.03	2.13
Loss on ignition (%)	1.17	0.17	0.04
Blaine fineness (cm^2/g)	3150	3460	3430
Water requirement (%)	100	95.6	90.2

Table 2 Mixture proportion of mortar for the normal exposure carbonation test and carbonation coefficients

Mix	γ	Type	w/b	%r	Cement (kg/m^3)	Fly ash (kg/m^3)	Water (kg/m^3)	Sand (kg/m^3)	K (mm/month$^{0.5}$)
N1	1.2	-	0.50	0	504	0	252	1488	0.57
N2	1.2	FA1	0.50	10	443	49	247	1488	0.62
N3	1.2	FA1	0.50	30	329	141	238	1488	1.05
N4	1.2	FA1	0.50	50	225	225	230	1488	2.29
N5	1.2	FA2	0.50	10	443	49	247	1488	0.62
N6	1.2	FA2	0.50	30	329	141	238	1488	1.06
N7	1.2	FA2	0.50	50	225	225	230	1488	2.06
N8	1.4	-	0.40	0	675	0	270	1300	0.25
N9	1.4	FA1	0.40	10	591	66	264	1300	0.42
N10	1.4	FA1	0.40	30	437	187	253	1300	0.66
N11	1.4	FA1	0.40	50	297	297	243	1300	1.34
N12	1.4	FA2	0.40	10	591	66	264	1300	0.34
N13	1.4	FA2	0.40	30	437	187	253	1300	0.57
N14	1.4	FA2	0.40	50	297	297	243	1300	1.27
N15	1.4	-	0.50	0	592	0	296	1300	0.58
N16	1.4	FA1	0.50	10	520	58	290	1300	0.78
N17	1.4	FA1	0.50	30	386	165	280	1300	1.13
N18	1.4	FA1	0.50	50	264	264	270	1300	2.10
N19	1.4	FA2	0.50	10	520	58	290	1300	0.72
N20	1.4	FA2	0.50	30	386	165	280	1300	1.06
N21	1.4	FA2	0.50	50	264	264	270	1300	1.98

For each mixture, 50 mm cubes were cast and demolded after 24 hours. All specimens were moist-cured for 28 days before being exposed to a real environment (normal exposure) for exposure periods of 3, 6, 12, and 18 months. The location within the city of Bangkok, Thailand was selected as the real environment. The annual average relative humidity and temperature recorded by the Meteorological Department were 72.5% and 28.9°C, respectively. The average concentration of CO_2 recorded by the authors was 625 ppm. At the age of measurement, specimens were tested for carbonation depth in the laboratory. These specimens were split and cleaned. The depth of carbonation was determined by spraying 1% of phenolphthalein in the solution of 70% ethyl alcohol on a freshly broken surface [7]. The phenolphthalein solution is colorless and used as an acid-base indicator. The color of the solution changes into purple when the pH is higher than approximately nine. Therefore, when the solution is sprayed on a broken surface, the carbonated portion is uncolored (concrete color) and the non-carbonated portion is purple.

2.3 Mixture proportion and specimen preparation for accelerated carbonation test

To investigate the effect of partial replacement of OPC with fly ash, plain OPC mortar mixtures having w/b = 0.3 (Binder:Sand = 1:1) and 0.5 (Binder:Sand = 1:2) were selected as reference mixtures. The replacement percentages of fly ash were 10 and 30%. For each mixture, 50 mm cubes specimens were cast for testing the compressive strength, total permeability void, and carbonation depth. The specimens were demolded 24 hours after casting and then cured in water for 7, 14, and 28 days. The mixture proportions for accelerated carbonation test are summarized in **Table 3**.

(i) Compressive strength

After the curing periods of 7, 14, and 28 days, the cube specimens were tested for compressive strength. The test procedure was in accordance with ASTM C39.

(ii) Total Permeable void

The total permeable void was measured to study the effect of fly ash on the total porosity of mortar. The test procedure was in accordance with ASTM C642. After being moist-cured for 28 days, the specimens were dried in an oven at a temperature of 105±2 °C for 24 hours. Then, the oven-dried mass was determined (W_1). After that, specimens were boiled for five hours to saturate the specimens and evacuate the entrapped air bubbles in the specimens. The saturated surface-dried mass in air (W_2) and apparent mass in water (W_3) were determined. The volume of permeable voids was calculated as follows:

$$V = \frac{W_2 - W_1}{W_2 - W_3} \times 100 \tag{3}$$

where V is the amount of permeable voids (%)

(iii) Carbonation depth

Specimens were cured in water for a period of 7, 14, and 28 days before they were stored in an accelerated carbonation chamber for a period of one and two months. The environment in the chamber had a CO_2 concentration of 4% (40,000 ppm). Temperature and relative humidity were controlled at 40°C and 55%, respectively.

Table 3 Mixture proportion of mortar for accelerated exposure carbonation test

Type	w/b	%r	C (kg/m^3)	FA (kg/m^3)	Water (kg/m^3)	Sand (kg/m^3)
-	0.3	0	980	0	294	980
FA1	0.3	10	868	96	289	964
FA1	0.3	30	652	280	280	932
FA2	0.3	10	869	97	290	966
FA2	0.3	30	654	280	280	934
-	0.5	0	553	0	277	1383
FA1	0.5	10	493	55	274	1370
FA1	0.5	30	376	161	269	1343
FA2	0.5	10	493	55	274	1370
FA2	0.5	30	376	161	269	1343

3. Results and Discussion

3.1 Normal exposure carbonation tests

(i) Carbonation coefficient

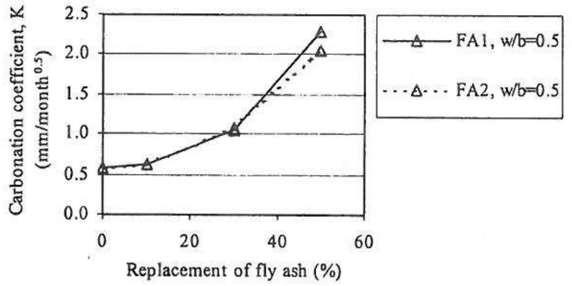
In the study, carbonation depth measured from mortar until 18 months of exposure was used for estimating the corresponding carbonation coefficient (K). K is inversely proportional to the carbonation resistance of mortar and was estimated by using the empirical relationship as follows:

$$X_c = K\sqrt{t} \tag{4}$$

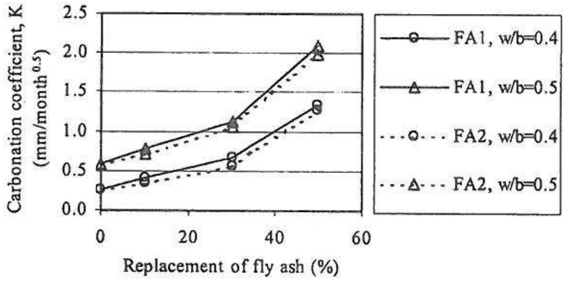
where X_c is the carbonation depth (mm). t is the period of exposure to real environment (month). K is the corresponding carbonation coefficient (mm/month$^{0.5}$). The linear formulation in Eq. (2) has been adopted by numerous researchers [2, 8, 9]. The values of the carbonation coefficient for the mixtures investigated in real environment are listed in **Table 2**.

(ii) Effect of type and replacement of fly ash

Figs. 1(a and b) shows the effect of type and replacement of fly ash on the estimated carbonation coefficient. It was found that the carbonation coefficient increased along with an increase in the replacement percentage of fly ash, which is consistent with the trend of concrete observed by numerous researchers [1, 3, 10]. This increment is drastic when the replacement level is higher than 30%. At the replacement level of 50%, it was about four or five times higher than that of Portland cement alone. This is possibly due to the dominating effect of reduction in $Ca(OH)_2$, by the pozzolanic reaction and by the reduction of cement content over the effect of pore refinement.



(a)



(b)

Fig. 1 Carbonation coefficient & replacement of fly ash; (a) $\gamma = 1.2$, (b) $\gamma = 1.4$

It is also observed that at similar fly ash replacement percentage, the carbonation coefficient of mixture incorporating FA1 (CaO = 8%) is generally higher than that of FA2 (CaO = 15%). This is partly because the tested mortars with high CaO fly ash (FA2) exhibit a lower porosity than those with low CaO fly ash (FA1). In addition to the lower porosity, higher calcium oxide content in FA2 can provide some amount of $Ca(OH)_2$, which results in slowing down of the movement of the carbonation front. **Fig. 2** shows that for a given fly ash replacement level, the 28-day porosity of mortar mixture incorporating FA2 is larger than that of the FA1 mortar. **Fig. 3** shows that at the same fly ash replacement level, the amount of $Ca(OH)_2$, tested by thermogravimetric analysis, in a mixture incorporating FA2 is generally higher that that of FA1 (specimens were cured for 28 days and carbonated for 28 days). The porosity and the amount of $Ca(OH)_2$ of the FA1 mortar were expected to be higher and lower, respectively than those of the FA2 mortar at all ages.

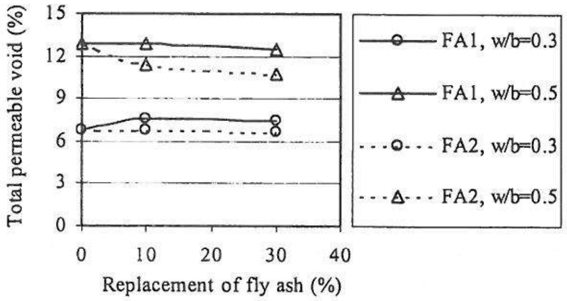


Fig. 2 Total permeable void & replacement of fly ash (at age of 28 days)

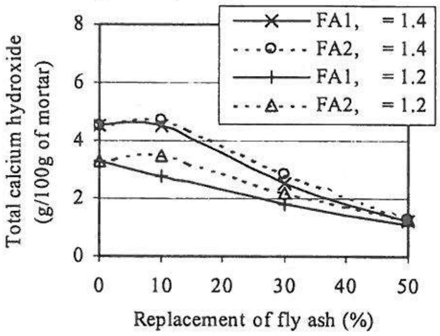


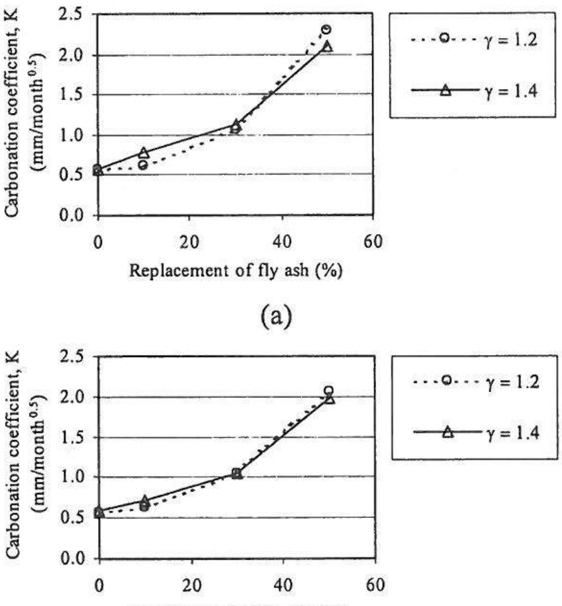
Fig. 3 Total $Ca(OH)_2$ & replacement of fly ash (cured and carbonated for 28 days)

(iii) Effect of water to binder ratio

Effect of w/b on the estimated carbonation coefficient of fly ash mortar is also presented in **Fig. 1(b)**. It is evident that for a given fly ash replacement level, a higher w/b led to a greater carbonation coefficient, possibly due to the pore structure densification. This finding is clearly in agreement with numerous researchers [10, 11, 12] and, as confirmed by **Fig. 2**, a lower w/b led to lower porosity of mixture.

(iv) Effect of paste content

Influence of paste content on the depth of carbonation is studied by comparing mixtures with different values of ratio paste content to the total compacted aggregate phase (γ) of 1.2 and 1.4. The comparisons are shown in **Figs. 4 (a and b)**. However, it is observed that for a given water to binder ratio and a fly ash replacement percentage, there is insignificant influence of the γ value. This finding is corroborated by those reported by Russell et al. [13] and Loo et al. [14] that by comparing mixtures with the same w/b, effect of cement content on the rate of carbonation is insignificant. It should be noted that, for a constant w/c, the cement content of the mixture represents paste content. This may be, therefore, concluded that the volume of paste and aggregate slightly affects the carbonation resistance of the mixture, although CO_2 has to diffuse through the interconnected capillary pores within paste matrix. Carbonation resistance of mixtures is more dominantly affected by the quality of paste than by the amount of paste.



(a)

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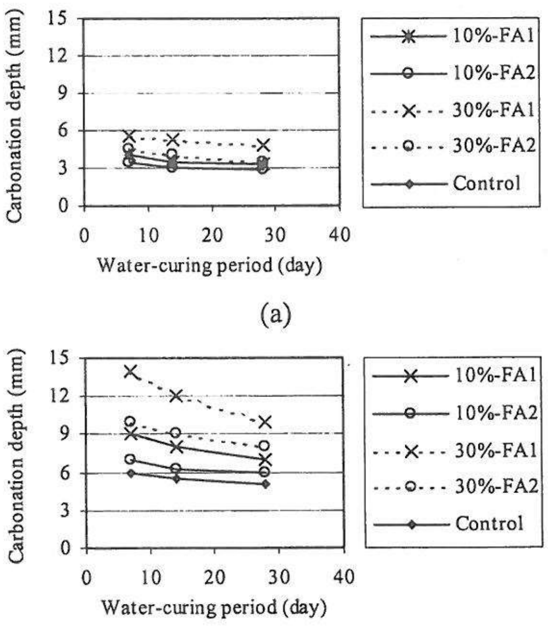
Fig. 4 Effect of paste content on carbonation coefficient; (a) FA1, (b) FA2



(a)

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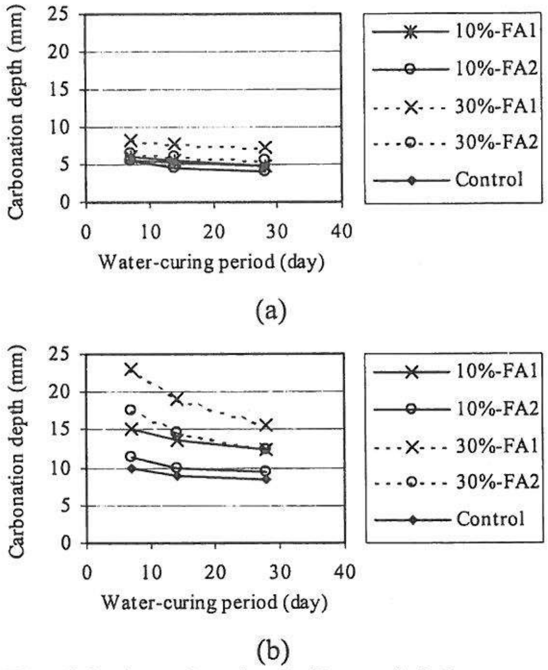
Fig. 5 Carbonation depth (1 month) & water-curing period; (a) w/b = 0.3, (b) w/b = 0.5



(a)

(b)

Fig. 6 Carbonation depth (2 months) & water-curing period; (a) w/b = 0.3, (b) w/b = 0.5

3.2 Accelerated carbonation tests

(i) Effect of curing period

Figs. 5 and 6 illustrate the relationships between the carbonation depth and water-curing period for the mortar specimens carbonated for one and two months, respectively. The result reveals that an increase in the water-curing period increases the carbonation resistance. This finding is consistent with the trend of concrete observed by various researchers [15, 16, 17]. However, for the mortar specimens which have a w/b of 0.3 [**Figs. 5(a) and 6(a)**], the effect of extension of curing period is insignificant, especially for the cement-only specimens. When the length of curing was extended from 7 to 28 days, the carbonation depth was reduced only about one millimeter. The reduction of carbonation depth due to extended curing period is more significant for the mortar specimens having a w/b of 0.5 [**Figs. 5(b) and 6(b)**], especially when fly ash is incorporated. This is because the low w/b mortar has low porosity, which causes difficulty for cured water to reach the inner portion of the mortar. From **Figs. 5(b) and 6(b)**, it is also observed that the differences between carbonation depth of the control mortar and those of the fly ash-mixed mortar are smaller when the curing period is extended. This phenomenon implies that sufficient curing is essential for mortars with fly ash. This is due to the slow rate of cement hydration by retardation of fly ash at an early age and the pore refinement by pozzolanic reaction at a later age. However, extending the curing period beyond 14 days results in less of an effect on carbonation depth than the extension done at earlier ages.

(ii) Relationship between compressive strength and carbonation depth

An attempt was made to relate the carbonation depth of mortars carbonated for one month in the accelerated carbonation chamber to the 28-day compressive strength of the same mortars. The relationships are shown in **Figs. 7(a-c)**. It is observed that there is a strong relation between the 28-day compressive strength and the carbonation depth of mortars. The depth of carbonation decreases with an increase in compressive strength. This finding appears to be logical since both the diffusivity of the hardened cement paste and its compressive strength are significantly controlled by its porosity. This corresponds to the trend of concrete observed by various researchers [14, 17, 18]. The statistical analysis in **Figs. 7(a-c)** shows that linear equations can be drawn to relate carbonation depth with 28-day compressive strength of the tested mortars (x is the compressive strength and y is the carbonation depth). The slopes of the relationships depend on the curing duration. Therefore, it is possible to estimate the depth of carbonation tested by the accelerated method from its 28-day compressive strength and water-curing period.

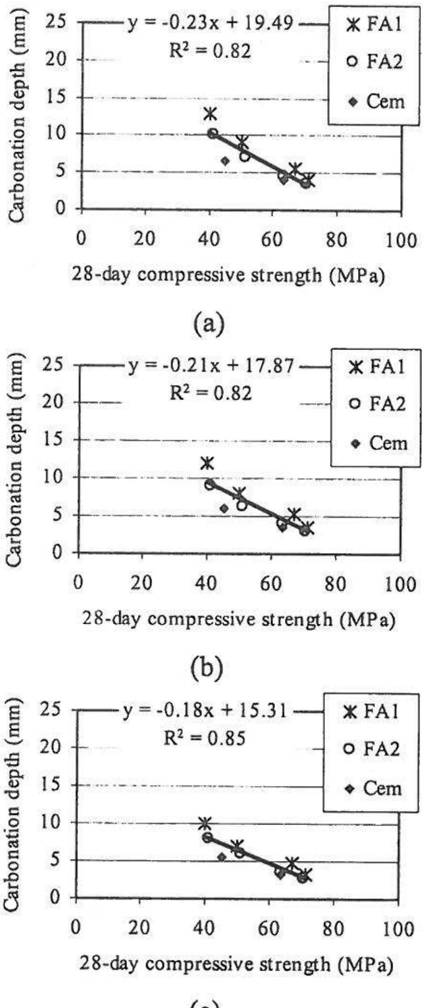


Fig. 7 Carbonation depth & 28-day compressive strength; (a) curing = 7 days, (b) curing = 14 days, (c) curing = 28 days

(iii) Relationship between values of carbonation depth in accelerated and real environment

Generally, the rate of carbonation in the real environment is slow due to low CO_2 concentration level in the atmosphere. Hence, the accelerated carbonation test methodology is a practical method to assess the carbonation resistance of mixtures within a reasonably short time. An attempt was made to relate the carbonation depths of mortar exposed to a real environment (normal exposure) to the carbonation depth of mortar with the same w/b carbonated in the accelerated carbonation chamber for one month (accelerated carbonation depth). The relationship is shown in **Fig. 8**. The analytical result reveals that there is a strong relation between the carbonation depths of mortar carbonated in a real and in an accelerated environment. The relationship was found to be linear and the slope depended on the exposure period. Therefore, it is possible to estimate the depth of carbonation of mortar exposed in a real environment from the depth of carbonation obtained from the accelerated carbonation test. It is noted that from the discussion in previous section, the accelerated carbonation depth could be estimated from the 28-day compressive strength and water-curing period. Therefore, it is possible to estimate the carbonation depth in a real environment from the 28-day compressive strength and water-curing period too.

The extension of the works done in this paper to concrete is underway. The study carried out on concrete will be useful for the mix design considering carbonation as well as for estimating the carbonation depth of actual concrete structures constructed using the designed concrete. As an example of durability design, proper thickness of concrete covers based on the designed service life can then be specified.

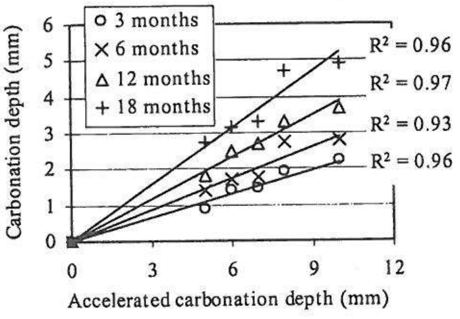


Fig. 8 Relationship between normal and accelerated carbonation depth

4. Conclusions

On the basis of the results investigated in this study, the following conclusion can be made.

1. It was confirmed that a lower w/b led to a slower rate of carbonation. In addition, it was also observed that for a constant w/b, the carbonation resistance changed insignificantly with the paste content.

2. It was found that carbonation depth increases in proportion to the replacement level of fly ash, especially at a high replacement level. However, when small amount of fly ash was incorporated in the binder (10%), carbonation depth slightly increased, or was in some cases, equivalent to the cement-only mixtures. In addition, for a given replacement percentage, mortar incorporating high CaO fly ash exhibited higher carbonation resistance than that of the low CaO fly ash mortar.

3. Regarding the test results, carbonation resistance can be increased by extending the curing period. However, for a mixture with a low w/b, influence of extending the curing duration was not significant. Adequate curing is essential for fly ash mixtures that have a high w/b, especially at a high replacement level.

4. There was a strong relation between carbonation depth and 28-day compressive strength of the tested fly ash mortars. The statistical trend was found to be linear and the slopes of the relationship were dependent upon the length of curing.

5. There was also a strong relation between the depth of carbonation obtained from the tests in real environment and the depth of carbonation derived from the accelerated carbonation chamber. The slope of the relationship was found to depend on the exposure period.

5. Acknowledgements

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References

[1] Ho DWS, Lewis RK. Carbonation of Concrete and its Prediction. Cement and Concrete Research 1987; 17: 489-504.

[2] Wee TH, Suryavanshi AK, Logendran D. Pore Structure Controlling the Carbonation of A Hardened Cement Matrix Blended with Mineral Admixture. Advances in Cement Reserch 1999; 11(2): 81-95.

[3] Papadakis VG. Effect of Supplementary Cementing Materials on Concrete Resistance against Carbonation and Chloride Ingress. Cement and Concrete Reserch 2000; 30: 291-299.

[4] Malhotra VM, Zhang MH, Read PH, Ryell J. Longterm Mechanical Properties and Durability Characteristics of High-strength/ High-performance Concrete Incorporating Supplementary Cementing Materials under Outdoor Exposure Conditions. ACI Material Journal 2000; 97(5): 518-525.

[5] Atis CD. Accelerated Carbonation and Testing of Concrete Made with Fly Ash. Construction and Building Materials 2002 (article in press).

[6] Wesche K. Fly Ash in Concrete: Properties and Performance, TC67-FAB. RILEM, 1991.

[7] RILEM Committee CPC-18. Measurement of Hardened Concrete Carbonation Depth, TC14-CPC. RILEM, 1988.

[8] Papadakis VG, Vayenas CG, Fardis MN. Experimental Investigation and Mathematical Modelling of the Concrete Carbonation Problem. Chemical Enginnering Science 1991; 46(5/6): 1333-1338.

[9] Castro P, Sanjuan MA, Ganesca J. Carbonation of Concrete in Mexico Gulf. Building and Environment 2000; 35: 145-149.

[10] Sulapha P, Wong SF, Wee TH, Swaddiwudhipong S. Carbonation of Concrete Containing Mineral Admixtures. Journal of Material in Civil Engineering 2003; 15(2): 134-143.

[11] Uomoto T, Takada Y. Factors Affecting Concrete Carbonation Rate. In: Nagataki S, Nireki T, Tomosawa F, editor. Durability of Building Materials and Components 6. E & FN Spon, 1993. p. 1133-1141, 1993.

[12] Roy SK, Poh KB, Northwood DC. Durability of Concrete-Accelerated Carbonation and Weathering Studies. Building and Environment 1999; 34: 597-606.

[13] Russell D, Basheer PAM, Rankin GIB, Long AE. Effect of Relative Humidity and Air Permeability on Prediction of the Rate of Carbonation of Concrete. Structures and Building 2001; 146: 319-326, 2001.

[14] Loo YH, Chin MS, Tam CT, Ong KCG. A Carbonation Prediction Model for Accelerated Carbonation Testing of Concrete. Magazine of Concrete Reserch 1994; 46: 191-200.

[15] Fattuhi NI. Concrete Carbonation as Influenced by Curing Regime. Cement and Concrete Research 1988; 18: 426-430.

[16] Balayssac JP, Detriche CH, Grandet J. Effect of Curing Upon Carbonation of Concrete. Construction and Building Materials 1995; 9(2): 91-95.

[17] Parrott LJ. Some Effects of Cement and Curing Upon Carbonation and Reinforcement Corrosion in Concrete. Materials and Structures 1996; 29: 164-173.

[18] Chi JM, Huang R, Yang CC. Effects of Carbonation on Mechanical Properties and Durability of Concrete Using Accelerated Testing Method. Journal of Marine Science and Technology 2002; 10(1): 14-20.

[19] Khan MI, Lynsdale CJ. Strength, Permeability, and Carbonation of High-Performance Concrete. Cement and Concrete Research 2002; 32: 123-131.