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Carbonation rates of concretes containing high volume of pozzolanic materials

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Abstract

The project studies the influence of fly ash and slag replacement on the carbonation rate of the concrete. The experimental work includes samples of pure Portland cement concrete (CEM I 42,5 R), blast-furnace slag concrete (CEM III-B), and fly ash blended concrete. To reveal the effect of curing on carbonation rate, the concretes were exposed to various submerged curing periods during their early ages. After that, the samples were subsequently exposed in the climate room controlling 20 °C and 50% RH until the testing date when the samples had an age of 5 months. Then, the accelerated carbonation test controlling the carbon dioxide concentration of 3% by volume, with 65% relative humidity were started to perform. The depth of carbonation can be observed by spraying a phenolphthalein solution on the fresh broken concrete surface. Finally, according to Fick's law of diffusion theoretical equations are proposed as a guild for estimating the carbonation rate of fly ash and blast-furnace slag concretes exposed under natural conditions from the results from accelerated carbonation tests.

Keywords: Acceleration; Carbonation; Corrosion; Fly ash; Granulated blast-furnace slag

1. Introduction

Corrosion due to carbonation normally occurs on reinforced concrete structure especially in urban area which usually has a high concentration of carbon dioxide, emitted from vehicles or industrial factories, in the atmospheric air. The mechanism of carbonation consists of gaseous diffusion combined with chemical reaction. Carbon dioxide in the atmosphere diffuses through the empty pore of concrete and reacts with the hydration products, which is known as a carbonation process. Carbonation of concrete is commonly defined as the chemical reaction between carbon dioxide present in the atmosphere and the cement hydration products such as $Ca(OH)_2$, C–S–H, C–A–H. Among all mentioned phases, the reaction with $Ca(OH)_2$, which buffers the pH, characterized by the irreversible chemical reaction, plays the most important role in de-passivating phenomena.

The effect of pozzolanic replacement on carbonation depth of concrete concerns both binding capacity of CO_2 and porosity. Pozzolanic concretes have long been considered to be less capable of resisting carbonation than Portland cements owing to their lower portlandite content [1]. In pozzolan concrete, the quantity of $Ca(OH)_2$ will be significantly reduced by the lower quantity of Portland cement (PC) and consumption by pozzolanic reaction. Hence, the extent of chemical interaction (and binding of CO_2) will be reduced compared to PC concrete [2].

In the porosity aspect, owing to slow rate of pozzolanic reaction compared with the hydration of PC, carbonation of pozzolana-containing cements is greater when the curing time is shorter [3], 7 days for example [4], i.e. when the permeability of pozzolanic cement pastes is significantly higher than that of the equivalent Portland cement pastes. Since carbonation is related to permeability of concrete, higher carbonation should be expected in inadequately cured fly ash concretes [5].

In this study, experimental investigation on the influences of pozzolanic replacement and curing period on carbonation resistance of concrete was carried out. A tentative model for estimating the carbonation depth of concrete under natural

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Table 1
Mix proportions in kg per cubic meter of concrete

Mix no.	Mixture	CEM I 42,5 R (kg/m^3)	CEM III-B (kg/m^3)	Fly ash (kg/m^3)	Water (kg/m^3)	Total aggregate (kg/m^3)	w/c+f	w/c+$k\cdot$f[a]
1	CEM I 0.42	350	–	–	147	1800	0.42	0.42
2	CEM I 0.60	350	–	–	210	1800	0.60	0.60
3	CEM I +25FA	262.5	–	87.5	178.5	1800	0.51	0.60
4	CEM I +50FA	175	–	175	147	1800	0.42	0.60
5	CEM III	–	350	–	210	1800	0.60	0.60
6	CEM III +50FA	–	175	175	147	1800	0.42	0.60

[a] k=0.40.

exposure was proposed based on the results from accelerated tests.

2. Experimental investigation

The six concrete mixtures were designed to investigate the influence of the degree of replacement of PC by pozzolana on the carbonation behaviour of concrete. Controlling parameters are the weight of total binder content of 350 kg/m^3 and total aggregate content of 1800 kg/m^3. Two types of cement, CEM I 42,5R and blast-furnace slag cement CEM III-B, were used in the experimental program. The fly ash replacements up to 50% by weight were performed in the investigation. The porosity of the concrete in terms of water content was controlled by two factors namely, water to total binder ratio (w/b) and effective water to binder ratio (w/c+$k\cdot$f). The k-value is mentioned in the design guild of fly ash concrete for adjusting the amount of fly ash that is really reactive in the mixture [1]. According to EN 206:2002 [6], the k-factor of *0.40* which is for the concrete exposed atmospheric air environment was used throughout this study. The mix proportions in one cubic meter of all concrete are shown in Table 1.

One day after mixing, the hardened concrete samples were cured 3, 7, and 28 days under water at 20 °C and subsequently exposed in the climate room controlling 20 °C and 50% RH until the testing date. The accelerated carbonation tests were started when the samples had the age of 5 months.

The carbonation process of concrete under natural conditions is rather slow due to the low concentration of carbon dioxide in the environment which is only about 0.03–0.04% by volume. The process may last more than several ten years in a good quality concrete. In the experimental works, it is desirable to accelerate the process to shorten the duration of testing to predict long term performance under natural conditions. The acceleration can be performed either by increasing the concentration of carbon dioxide in the exposed environment or increasing the atmospheric pressure. Nevertheless, under the conventional condition, the penetration of carbon dioxide into concrete processes by the gas diffusion due to the difference in the carbon dioxide concentration between those in the atmosphere and inside the concrete pores. Therefore, to clarify the behaviour of real carbonation process, the accelerated carbonation was conducted by increasing the concentration of carbon dioxide in the environment. The accelerated carbonation which provides the carbon dioxide concentration of 3% by volume, with 65% relative humidity controlled by NH_4NO_3 solution (NH_4NO_3 in water=1.9:1 by weight) was set up in this study. The inlet flow of gas was held constant at the rate of 100 cm^3/min.

The depth of carbonation through the circumference of the cylindrical sample was observed by the associate of phenolphthalein indicator. The standard 20-cm long (10-cm diameter) cylinders were cut into three pieces of 6-cm thick samples using a machine saw. The two cut surfaces of all samples were both coated with epoxy, and only the circumference surfaces are opened to expose the accelerated carbonation environment. When the samples reach the carbonated age to be tested, the samples were half-broken along the diameter, and then the broken surfaces were sprayed with phenolphthalein indicator. Measurements of the depth of carbonation were performed at 3 points along each side, and the 6 values thus obtained finally averaged.

3. Theoretical background and experimental results

Fig. 1(a–c) shows the relationship between carbonation depth and carbonation period for concretes which have submerged curing periods of 3, 7 and 28 days, respectively. The depths of carbonation were observed after the period of 1, 4 and 9 weeks of 3% CO_2 by volume accelerated carbonation aging.

As generally known, carbonation depth in a given concrete progresses with exposure duration. However, the rate of carbonation reduces with respect to time period, and is usually considered as proportional to the square root of exposure period. Even in the case of accelerated carbonation conditions, the depths of carbonation are in proportion to the square root of exposure time like the case of natural indoor exposure conditions and natural outdoor exposure condition under a shelter [7,8].

According to square root theory, the depth of carbonation, x, can be considered related to the exposure duration, t, in accord with the second law of Fick as shown in following equation:

$$x = k\sqrt{t}. \qquad (1)$$

The other approach for determining carbonation coefficient is done according to the law of diffusion. Diffusion is the transport of gas or liquid through the porous media in a function of the concentration gradient. In the case, where a concrete is subjected to CO_2, carbon dioxide ingression into the concrete pores with the concentration gradient of the exposed CO_2 in the environment as the driving force. According to Fick's first law of diffusion, the amount of CO_2 ingress into concrete is simply demonstrated as shown in the following equation

$$J = -D\left(\frac{\partial c}{\partial x}\right)_t \qquad (2)$$

where J is a carbon dioxide flux (g/m^2 s), D is a diffusion coefficient (m^2/s), c is a CO_2 concentration (g/m^3), and x is a depth of penetration (m).

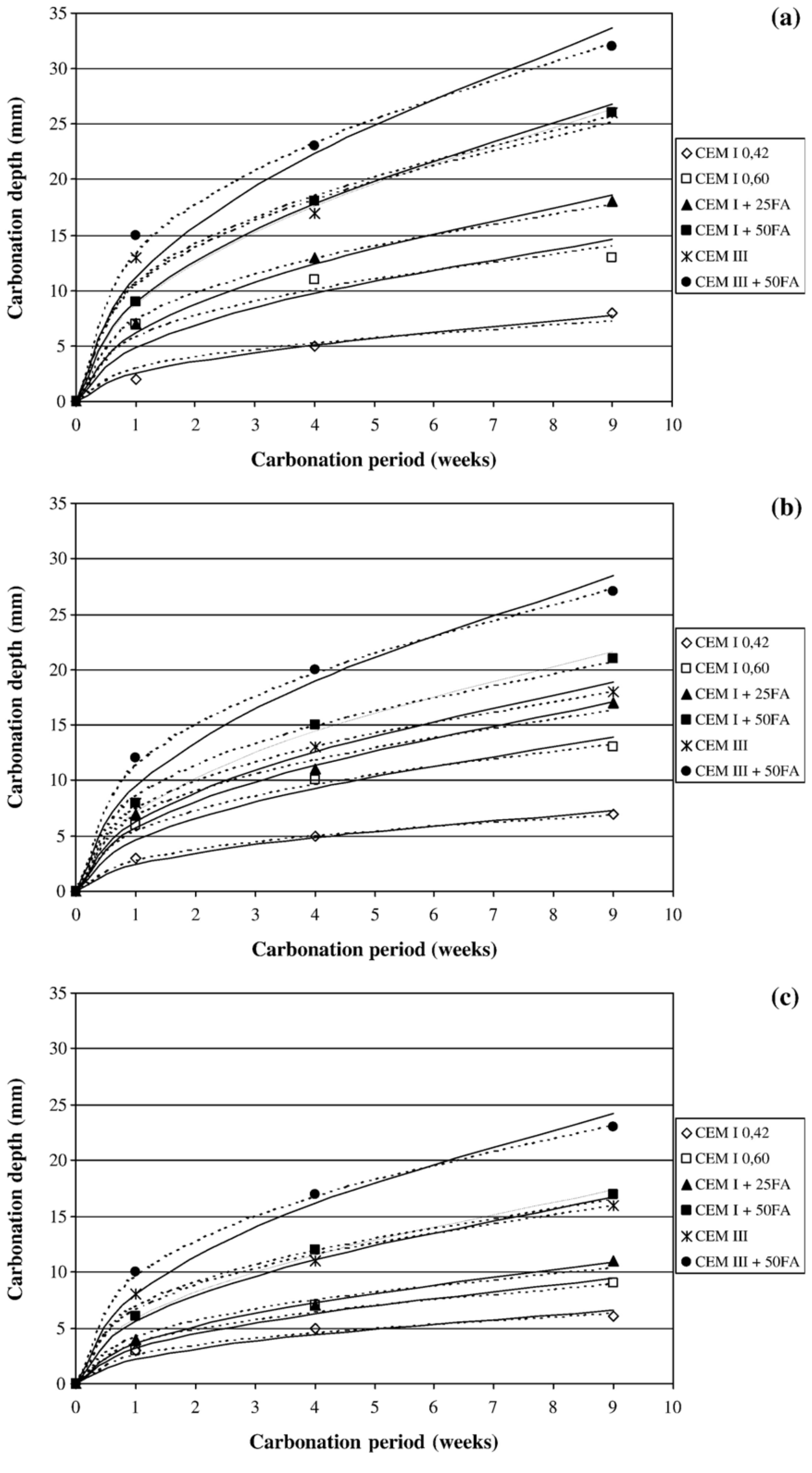

Fig. 1. (a–c) Relationship between the best fit of carbonation depth and linear exposure time in accelerated tests of concrete samples: (dots) *experiments*, (solid line) $t^{0.5}$, (dashed line) $t^{0.4}$; (a) 3-day curing, (b) 7-day curing, (c) 28-day curing.

Consider the amount of gaseous CO_2 diffusing into the concrete in the unit of mass, the mass of CO_2 can be written in the following function:

$$dm = -DA\frac{c_2 - c_1}{x}dt \tag{3}$$

where m is a mass of CO_2 penetrated into the concrete, c_1 is a CO_2 concentration in the environment, c_2 is a CO_2 concentration at a considering carbonation front inside the sample, A is a surface area, and x is the considered depth of carbonation.

The mass of CO_2 penetrated into the concrete can also be written in another form. As shown in the following equation, C_0

represents an amount of CO_2 (g/m^3) required to react with alkali phases contained in a unit volume of a sample

$$dm = C_0 A dx. \tag{4}$$

Therefore,

$$C_0 A dx = DA \frac{c_1 - c_2}{x} dt. \tag{5}$$

Integration of the above equation, finally yields

$$x = \sqrt{\frac{2D}{C_0}(c_1 - c_2)}\sqrt{t}. \tag{6}$$

Comparing the above equation to the assumption, $x = k\sqrt{t}$, mentioned previously, if the term $\sqrt{\frac{2D}{C_0}(c_1 - c_2)}$ in the equation is assumed to be a constant, then $k = \sqrt{\frac{2D}{C_0}(c_1 - c_2)}$.

However, the CO_2 concentration in concrete at carbonation front, c_2, is normally much lower than those in the environment (c_1). Thus, the value c_2 can be neglected, and finally yields the carbonation coefficient as $k = \sqrt{\frac{2D \cdot c_1}{C_0}}$.

The concentration of CO_2 in the exposed environment, c_1, is normally equal to 0.03–0.04% in the natural exposure. In accelerated carbonation test, the significantly increasing of the value induces the higher carbonation coefficient (k), which shortens the duration of the testing.

From Fick's law of diffusion, the relation, $x = k \cdot t^{0.5}$, is set up to be based on the steady-state condition, so that each sample has a constant carbonation coefficient. However, in reality, the carbonation reaction itself also influences the pore structure, especially the pore volume reduction. The calcium carbonate which is a main product of carbonation blocks the air pore in concrete, and causes the reduction in gas diffusivity (D). If the reduction of the diffusivity or carbonation coefficient is considered as a parameter, the carbonation coefficient (k) should decrease as a function of time. Simplifying the relation by still keeping k as a constant (time independence), the relation of carbonation rate with respect to time, taking into account the effect of pore reduction, can be written in a function, $x = k \cdot t^n$: where n is the exponent value which is less than 0.5. From the experimental results in this study and also from various literature publications [9–13], the empirical exponent value, n of 0.4 was chosen here.

In particular, the application of exponent value of 0.4 has a significance in the case of high carbonation risk concrete with a high w/b ratio or with a high amount of pozzolanic replacement. The high porosity in the samples play an important role on the gas diffusivity, therefore the pore reduction subjected to the carbonation reaction is essentially taken into account. The comparison between the classical square root theory of carbonation and the modified equation taking into account the effect of porosity reduction is shown in Fig. 1(a–c).

4. Estimation of carbonation rate in real environment

The accelerated carbonation is an essential test in the carbonation study. The method shortens the period of carbonation from ten years under normal condition to only a few weeks in the accelerated test conditions. However, in practice, the depths of carbonation at normal conditions are the more important information, particularly in view of reinforced concrete structure design. Knowing the depth of carbonation under real conditions is an important pre-condition for the design of the concrete cover thickness and the service life calculation of reinforced concrete structure. The depth of carbonation under real environmental conditions can be approximated from the results of the depth in the accelerated tests.

Table 2

Correlation between the ratios of carbonation rate and the theoretical values

References	$C_{1,\mathrm{acc}}$ (%)	Long term exposure conditions	$\left(\frac{k_{\mathrm{acc}}}{k_{\mathrm{envi}}}\right)_{\mathrm{measured}}$	$\left(\frac{k_{\mathrm{acc}}}{k_{\mathrm{envi}}}\right)_{\mathrm{theoretical}}$
Dhir [9]	4.0	Outdoor/sheltered	8.06	10.69
Khunthongkaew [14]	4.0	City/sheltered	8.96	10.69
	4.0	City/non-sheltered	10.25	10.69
Ohga [15]	7.0	Indoor	13.62	14.14
Chin [16]	7.0	Outdoor/sheltered	14.37	14.14
	12.0	Outdoor/sheltered	19.44	18.51
	18.0	Outdoor/sheltered	20.46	22.68

To reflect the results from the accelerated carbonation to predict the carbonation depth under field conditions, the relation of both conditions were derived by Fick's law of diffusion. The ratio of carbonation coefficient in the accelerated test and under field conditions can be written as shown below.

$$\frac{k_{\mathrm{acc}}}{k_{\mathrm{env}}} = \frac{\sqrt{\frac{2D \cdot c_{1,\mathrm{acc}}}{C_0}}}{\sqrt{\frac{2D \cdot c_{1,\mathrm{env}}}{C_0}}} \tag{7}$$

where the subscripts acc and env represent the conditions of accelerated test and environmental conditions, respectively.

Considering the value of gas diffusivity, D, and carbon dioxide capacity, C_0, as sample properties constants for each concrete, the relation of the carbonation coefficients can be expressed in terms of carbon dioxide concentration in the atmosphere alone as shown in the following:

$$\frac{k_{\mathrm{acc}}}{k_{\mathrm{envi}}} = \frac{\sqrt{c_{1,\mathrm{acc}}}}{\sqrt{c_{1,\mathrm{env}}}} \approx \frac{\sqrt{3.00\%}}{\sqrt{0.03\%}} = 10. \tag{8}$$

The carbon dioxide concentration contained in the conventional environment is normally about 0.03%, whereas the concentration of 3% was performed in the accelerated test. Hence, the ratio of carbonation coefficient of the two cases is equal to 10, or it means that the carbonation rate under conventional conditions is approximately ten times slower than of the accelerated carbonation test (3% CO_2) carried out in this study. The estimation is based on the conditions of 65% RH and 20 °C constantly, which does not take into account the variations in the real environment.

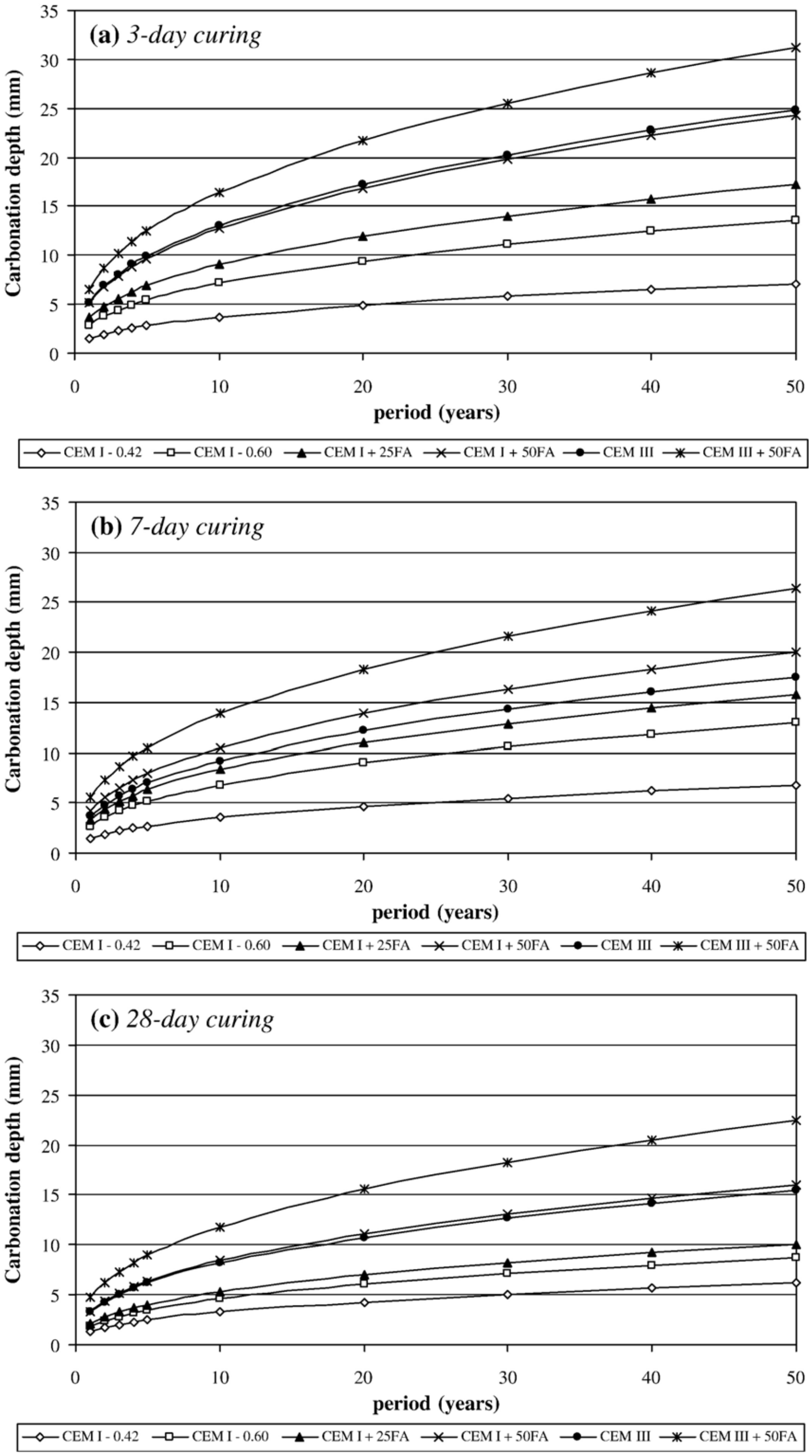

Fig. 2. (a–c) The predicted carbonation depth subjected to the conventional environment.

To confirm the robustness of the assumption, the carbonation rate ratio $\left(\frac{k_{\mathrm{acc}}}{k_{\mathrm{envi}}}\right)$ obtained from various literatures was compared to the theoretical values as shown in Table 2.

According to the assumption mentioned above, the estimations of carbonation propagation in concrete are expressed in chart form as shown in Fig. 2(a–c).

Table 3 shows the time taken to reach the specified carbonation depth exposed under natural conditions. Comparisons of the results reveal that the induction period for carbonation of pozzolanic mixtures, particularly in the case of CEM III series, is considerably shorter than of CEM I concretes with the same curing. Considering the period of 50 years as a structure service life, it can also be seen from the table that the time required to have a carbonation depth of 15 mm is longer than 50 years for both CEM I mixtures. Therefore, in the case of CEM I mixture, the cover thickness of 20 mm is enough to ensure the steel rebar

Table 3
Time taken to reach the specified carbonation depth [years]

Carbonation depth	Mixture	3-day curing	7-day curing	28-day curing
10 mm	CEM I 0.42	>50	>50	>50
	CEM I 0.60	23	26	>50
	CEM I+25FA	13	16	49
	CEM I+50FA	5	9	15
	CEM III	5	8	16
	CEM III+50FA	3	4	6
15 mm	CEM I 0.42	>50	>50	>50
	CEM I 0.60	>50	>50	>50
	CEM I+25FA	35	43	>50
	CEM I+50FA	15	24	42
	CEM III	14	34	46
	CEM III+50FA	8	12	18
20 mm	CEM I 0.42	>50	>50	>50
	CEM I 0.60	>50	>50	>50
	CEM I+25FA	>50	>50	>50
	CEM I+50FA	30	50	>50
	CEM III	29	>50	>50
	CEM III+50FA	16	25	37
25 mm	CEM I 0.42	>50	>50	>50
	CEM I 0.60	>50	>50	>50
	CEM I+25FA	>50	>50	>50
	CEM I+50FA	>50	>50	>50
	CEM III	50	>50	>50
	CEM III+50FA	28	43	>50
30 mm	CEM I 0.42	>50	>50	>50
	CEM I 0.60	>50	>50	>50
	CEM I+25FA	>50	>50	>50
	CEM I+50FA	>50	>50	>50
	CEM III	>50	>50	>50
	CEM III+50FA	45	>50	>50

protection from carbonation attack when the curing period is not less than 3 days. However, these results should be treated with caution as carbonation rate in practice are strongly influenced by the exposure conditions in the natural environment.

The pozzolanic mixtures studied have a lower carbonation resistance, therefore have also shorter induction period for carbonation. It can be seen in the table that the minimum cover depth of 25 mm is required in the case of CEM I with fly ash replacement mixtures. Hence, for the CEM I mixtures with up to 50% fly ash replacement, the cover thickness of 30 mm is sufficient to guarantee the passivity condition of the steel rebar in 50 years service life. From these experiments, a cover thickness of 35 to 40 mm is considered necessary for reinforced concrete made of CEM III or CEM III with fly ash replacement up to 50%.

To protect the steel rebar embedded in the pozzolanic concrete from corrosion, either the greater concrete cover depth or extending of curing period would be necessary. For pure CEM I concrete without fly ash replacement, the depths of carbonation required are less than 15 mm for all curing periods. Therefore, the minimum cover depth of 20 mm which is conventionally performed in practice for the structure in dry environment with up to 12 mm diameter rebar [17] is sufficient to protect the reinforcement from carbonation attack. The results also reveal an increased rate of carbonation corresponding to the increasing of fly ash replacement in concrete mixtures. In the case of 3-day curing period, the depths of carbonation are about 16 and 24 mm for the mixtures of 25FA and 50FA replacement, respectively. Hence, the cover thickness of about 25 and 30 mm are required to obtain the same level of safety for the CEM I+25FA and CEM I+50FA, respectively. On the other hand, the other alternative for improving the carbonation resistance can be performed by extending the submerged curing period. For CEM I+50FA concrete, if the curing period is extended from 3 days to 28 days, the carbonation depth would be comparable to those of pure CEM I cured 3 days under water. Hence, the cover of 20 mm is also sufficient for the case. In the case of CEM III-B concrete with fly ash, if the structures are designed for a 3 curing day period, the cover depth of 30 and 35 mm are recommended in the case of CEM III and CEM III+50FA, respectively. However, the results also show the significance of 7 days curing period on carbonation resistance of the mixtures. The depths of carbonation of CEM III series are dramatically reduced by extending the curing period from 3 days to 7 days.

5. Conclusion

Generally, the increase of carbonation depth in concrete with respect to time is considered to follow the square root theory, $x=k\cdot t^{0.5}$; where k is a carbonation rate which is a concrete constant. However, particularly in case of high carbonation attack, it was found that the rate of carbonation (k) declines with age and carbonation period. The value of k is reduced with time dependence. To simplify the relation by keeping k as a time independent constant, the new relationship, $x=k\cdot t^{0.4}$, was chosen. In this study, the depth of carbonation in real environment was estimated based on the results obtained from the accelerated carbonation test. According to Fick's law of diffusion, the relation of the carbonation rates between both cases can be written in the relation, $\frac{k_{\mathrm{acc}}}{k_{\mathrm{env}}}=\sqrt{\frac{c_{1,\mathrm{acc}}}{c_{1,\mathrm{env}}}}$; where $c_{1,\mathrm{acc}}$ and $c_{1,\mathrm{env}}$ are the concentrations of carbon dioxide in the test chamber and the environment, respectively. Therefore, according to the proposed equation when using an accelerating CO_2 concentration of 3%, the difference in the rate of carbonation is about a factor of 10, which means that the carbonation rate in natural exposure is estimated to be approximately 10 times slower than the accelerated tests performed in this study. The influence of pozzolanic additives such as blast-furnace slag and fly ash and of the curing period on the carbonation rate and the cove thickness necessary were analyzed. The results of this investigation allowed a tentative carbonation model to be proposed.

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