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EFFECT OF MORTAR COATING ON CONCRETE CARBONATION

Wen-Hu Tsao^{1,3}, Ming-Te Liang², Jiang-Jhy Chang², and Nai-Ming Huang¹

Key words: carbonation, concrete, mortar coating, carbonation retard coefficient.

ABSTRACT

The mechanism of the effect of mortar coating on carbonation of concrete is investigated. Theoretical methods of Fick's first and second laws of linear diffusion are used to calculate the carbonation depth of concrete without and with mortar coating, respectively. Theoretical analyses are also done to obtain the carbonation retard coefficients of mortar coating on concrete with surface coatings. A great deal of well organized experimental tests are carried out to verify the values of calculation. The results of present study indicate that the suitable mortar coating on concrete can effectively delay carbonation of concrete. The carbonation depth is inversely proportional to the thickness of surface coating with mortar. The average values, measured from experiment and predicted from Fick's first and second laws of linear diffusion, of carbonation retard coefficient of mortar coating are 1.70 and 2.19, respectively.

I. INTRODUCTION

When the boom of concrete or reinforced concrete (RC) construction began in the 1930s, it was generally believed that concrete or RC structures, typically designed for a service life of 40 to 50 years, would actually last much longer with little or no maintenance. Chiefly owing to economic factors, the durability of concrete or RC is being taken much seriously now than before. It is more economical to extend the service life of an existing concrete or RC structure, with only minor maintenance expense, than to replace it with new construction. It seems that economic realities of today are partly responsible for a growing interest in building more durable structures with an intended service life of 100 years or more. The durability

of concrete or RC is obtained by the following methods (Mehta, 1997): (1) Use of fly ash or slag as a partial replacement for cement, (2) Precooling of the concrete mixture, (3) Use of silica fume and a superplasticizer, (4) Increase of concrete cover thickness with 15.24 mm (0.6 in), (5) Addition of corrosion-inhibiting admixture, (6) Epoxy-coating of reinforcing steel, (7) External coatings, and (8) Cathodic protection. The external coatings for concrete are studied in this paper.

Zhang (1989) used nine kinds of surface coating to study the influence on concrete carbonation and calculated the retarded coefficient to each surface coating material. His studied results indicate that the surface coating materials with compatibility and impermeability are very valid to delay the carbonation of concrete and are used to resist the carbonation of cover of concrete surface. Papadakis et al. (1992) applied a mathematical model developed from Fick's first law of diffusion to investigate the effect of composition, environmental factors, and cement-lime mortar coating on concrete carbonation. On the condition that its water/cement ratio is relatively low and its lime content high, a lime-cement mortar coating of the usual thickness (around 20 mm) is found to be an extremely effective means of postponing or even preventing carbonation-induced corrosion initiation. This means that it postpones the commence of concrete carbonation by the time required for carbonation to fully penetrate the coating, and it delays its further penetration into the concrete because atmosphere CO₂ has to travel farther to reach the carbonation front. Kazmierczak and Helene (1995) used accelerated carbonation tests to evaluate concrete coating resistance to CO₂ permeability. The coating materials are four types of resin such as acrylic emulsion or dispersion, methyl methacrylate dispersion, polyurethane and silane/siloxane plus acrylic dispersion. They found that the painting procedure leads to different coating thickness, which will result in different carbonation depths in the same specimen. Roy et al. (1996) carried out a study of the effect of plastering on the carbonation of a 19-year-old RC commercial building in a tropical environment. If the plaster (render) thickness was at least 30 mm thick then no carbonation of the concrete occurred in this building. Liu et al. (1987) developed a theoretical method from Fick's first law of diffusion to calculate carbonated depth of concrete with surface coatings. Analysis is also done in the present study to obtain the sensitiveness of carbonated delayed

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parameters of surface coatings. We conducted a number of well organized experimental tests to verify the calculation, the tested results indicate that suitable surface coating can effectively delay carbonation of concrete. Swamy et al. (1998) studied the performance of concrete slabs coated with an acrylic-based coating against atmospheric carbon dioxide attacks. During the period of field exposure, uncoated concrete specimens with water to cement ratio of 0.6 and 0.75 disclosed average carbonation depths of 3 and 7.5 mm, while the acrylic-based coating on concrete specimens decreased the average carbonation depths to 0.5 and 3 mm, respectively. Seneviratne et al. (2000) employed dynamic mechanical thermal analysis to investigate three elastomeric surface coatings. All three coating systems were applied to naturally carbonated concrete components obtained from buildings that were suffering from reinforcement corrosion. It was shown that the use of an elastomeric coating system can protect carbonated concrete from water ingress. It can thus extend the service life of a carbonated RC structure by controlling the rate of corrosion of embedded steel in cases where significant chloride contamination does not exist and where the only substantive route for moisture ingress is via the coating. Sanjuan and del Olmo (2001) investigated mortar coating on the surface of specimens. The resistance to carbon dioxide penetration into the concrete was enumerated by comparing the difference of carbonation depths between coated and uncoated surfaces. An industrial mortar coating was showed excellent performance as a carbon dioxide barrier when applied to plain concrete. Park (2008) constructed a diffusion-reaction carbonation model to predict the carbonation depth of concrete with coated surface. The diffusion coefficient of carbon dioxide was measured by a permeation-measuring apparatus employing a differential pressure method, and the protection performance of the coating materials tested was graded in the following order: acrylic, epoxy, polyurethane, polyvinyl chloride. Yodmalai et al. (2011) experimentally studied the carbonation resistance of concrete coated with crystalline coating material (CCM). Specimens with different water to binder ratios of 0.4, 0.5, and 0.6 and fly ash concretes of supplementary materials 0 and 30% fly ash for cements with and without CCM coating were tested under an accelerated carbonation environment. It was found that carbonation depths of coated specimens were smaller than those of the uncoated specimens of the same mix proportion. Huang et al. (2012) examined concrete carbonation of a 35-year-old educational RC building in a subtropical environment. A very notable reduction in carbonation was discovered for the columns and beams of building that was plastered (sand-cement render) and/or putted tile/coating. There was no carbonation of the concrete when the plaster (render) thickness surpassed 50 mm. The surface coating such as tile with high compacted and impermeable material may effectively delay the carbonation of concrete.

The principal aim of this paper is to study the effect of mortar coating on concrete carbonation. To do this project, the theoretical background of Fick's first and second laws of

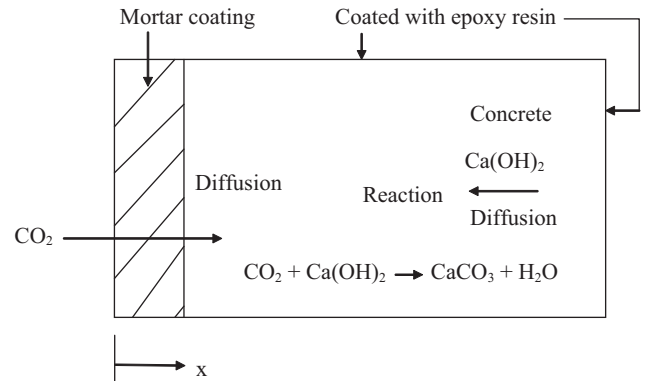


Fig. 1. Schematic illustration of concrete carbonation in the presence of a mortar coating.

linear diffusion is first introduced. Some concrete cylinders were plastered (in this case with a cement-sand mortar), the control set of concrete cylinders were not plastered, and their compressive strengths were also determined. In this way we were able to examine the relationships between carbonation depth, plaster thickness and the compressive strength of concrete. The concentration profiles of concrete carbonation obtained from both theory and experiment were compared. The studied results may be offered as a durability design of concrete structures with surface coating material.

II. MATHEMATICAL MODEL

1. Diffusion-Reaction Carbonation Model

The reaction between concrete and carbon dioxide that has diffused the mortar coating is depicted conceptually in Fig. 1. The carbon dioxide contacts the surface of mortar coating, dissolution occurs, and the carbon dioxide then diffused through the coating. Once the carbon dioxide reaches the concrete it generates calcium carbonate by carbonating calcium hydroxide, which is a cement hydration product. When calcium hydroxide is consumed by this reaction, the pH in the concrete diminishes, neutralization progresses, and eventually the reinforcing steel bars become corroded. In this study the depth of concrete carbonation was measured by use of a colorimetric method with phenolphthalein indicator.

2. Fick's First Law of Diffusion

Based on Fick's first law of diffusion, Kropp (1995) and Zhang and Jiang (1998) derived the following formula:

$$x(t) = \sqrt{\frac{2D(C_s - C_{cf})t}{a}} \quad (1)$$

where $x(t)$ is the depth of carbonation at time t (m), D is the diffusion coefficient for CO_2 through carbonated concrete (m^2/s), C_s is the surface concentration of CO_2 on concrete (g/m^3), C_{cf} is the concentration of CO_2 at the carbonation front

(g/m^3), t is the time (s), and a is an amount of CO_2 reacted with the alkaline compounds in unit volume of concrete (g/m^3).

Eq. (1) can be rewritten as (Huang et al., 2012; Liang et al., 2002)

$$x(t) = K_1 \sqrt{t}, K_1 = \sqrt{\frac{2D(C_s - C_{cf})}{a}} \quad (2)$$

where K_1 is the rate of carbonation ($\text{m}/\sqrt{\text{s}}$) and is the slope of the curve of relationship between $x(t)$ and \sqrt{t} .

Both Eqs. (1) and (2) are suitable to predict the carbonation depth of concrete without surface coating. However, if we want to calculate the carbonation depth of concrete with surface coating, then we need to modify Eqs. (1) and (2) as in the following formulas (Liu et al., 1987; Zhang, 1989).

$$x_c(t) = \sqrt{\frac{2D(C_s - C_{cf})}{a} \frac{t}{\beta}} \quad (3)$$

and

$$x_c(t) = K_1 \sqrt{\frac{t}{\beta}} = \frac{K_1}{\sqrt{\beta}} \sqrt{t}, K_1 = \sqrt{\frac{2D(C_s - C_{cf})}{a}} \quad (4)$$

where $x_c(t)$ is the depth of carbonation of concrete with surface coating at time t (m), $\beta = [x(t)/x_c(t)]^2$ is the carbonation retard coefficient, and $\frac{1}{\sqrt{\beta}} = \frac{x_c(t)}{x(t)}$ is the carbonation-velocity ratio.

It is worth to point out that Liu et al. (1987) used Fick's first law of linear diffusion, which the effective diffusivity of CO_2 was replaced by the regression formula of experimental data worked by Papadakis et al. (1991a), to predict the carbonation retard coefficient. Zhang (1989) used a previous carbonation depth formula, which consists of water/cement ratio, carbonation time, concrete quantity factor, environmental factor, and carbonation retard coefficient, to predict the carbonation retard coefficients of different surface coatings influenced on concrete carbonation.

3. Fick's Second Law of Diffusion

Fick's second law of linear diffusion for a semi-infinity medium with constant CO_2 exposure can be established as follows:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (5a)$$

$$C(x, 0) = 0 \quad (5b)$$

$$C(0, t) = C_s \quad (5c)$$

$$C(x \rightarrow \infty, t) = 0 \quad (5d)$$

where $C(x, t)$ is the CO_2 concentration at depth x at time t , C_s is the surface concentration of concrete, and D is the diffusion coefficient or diffusivity.

Applying the Laplace transformation (O'Neil, 2003) to Eq. (5), the analytical solution (Carslaw and Jaeger, 1959; Crank, 1975; Poulsen and Majlbrot, 2006) of Eq. (5) is obtained

$$C(x, t) = C_s \operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}}\right) \quad (6)$$

where erfc is the complementary error function.

Eq. (6) can be rewritten as (Huang et al., 2012; Liang et al., 1999; Liang et al., 2003)

$$x(t) = K_2 \sqrt{t}, K_2 = \sqrt{4D} \operatorname{erfc}^{-1}\left(\frac{C}{C_s}\right) \quad (7)$$

where $x(t)$ is the depth of carbonation of concrete without surface coating at time t (m) and K_2 is the rate of carbonation ($\text{m}/\sqrt{\text{s}}$) and is the slope of the curve of relationship between $x(t)$ and \sqrt{t} .

If we demand to predict the carbonation depth of concrete with surface coating, then we must make a virtue of necessity to modify Eq. (7) in terms of (Liu et al., 1987; Zhang, 1989)

$$x_c(t) = K_2 \sqrt{\frac{t}{\beta}} = \frac{K_2}{\sqrt{\beta}} \sqrt{t} \quad (8)$$

where $x_c(t)$ is the depth of carbonation of concrete with surface coating at time t (m), β is the carbonation retard coefficient, and $\frac{1}{\sqrt{\beta}}$ is the carbonation-velocity ratio.

III. EXPERIMENTAL WORK

1. Proportion of the Concrete Mix

ASTM Type I ordinary Portland cement (OPC) was used in the concrete mix for the test specimens. Table 1 indicates the chemical and physical properties of the OPC. The coarse aggregate used had a maximum size of 19 mm, a specific gravity of 2.65, and a fineness modulus of 6.13, and the water absorption was 0.2%. The fine aggregate (sand) used had a maximum size of 5 mm, a specific gravity of 2.62, and fineness modulus of 2.68, and the water absorption of 2.41%. Table 2 denotes the proportion of constituents in the mix and its compressive strength, for water-cement ratio of 0.68, 0.63

Table 1. Chemical and physical properties of cement.

Results of chemical analysis	Cement (%)	Requirements ASTM C150 Type 1 (%)
Silicon dioxide, SiO ₂	21.4	-
Aluminum oxide, Al ₂ O ₃	3.51	-
Ferric oxide, Fe ₂ O ₃	2.84	-
Sulfur trioxide, SO ₃	1.78	3.0 max.
Calcium oxide, CaO	68.02	-
Magnesium oxide, MgO	2.03	6.0 max
Titanium dioxide, TiO ₂	0.0	-
Potassium oxide, K ₂ O	0.53	-
Sodium oxide, Na ₂ O	0.19	-
Loss on ignition	1.55	3.0 max.
Physical tests		
Air content (%)	7.01	12 max.
Fineness (m ² /kg)	385	280 min.
Autoclave expansion (%)	-0.03	0.8 max.
Specific gravity	3.12	-
Compressive strength (kgf/cm ²)		
1-day	93.94	-
3-day	284.99	12.6 min.
7-day	379.75	19.3 min.
28-day	531.52	-

Table 2. Details of concrete mixes.

Designed Strength f_d (kgf/cm ²)	Water W (kg/m ³)	Cement C_m (kg/m ³)	Sand S (kg/m ³)	Gravel G (kg/m ³)	Mild Steel S_m (kg/m ³)	Compressive strength f'_c (kgf/cm ²)		
						Specimen		
						1	2	Ave.
210	170	250	630	1300	50	224	230	227
245	170	271	609	1300	50	251	259	255
280	170	290	588	1300	50	290	294	292

and 0.58 corresponding to 210, 245, and 280 kgf/cm², respectively.

2. Casting and Curing of Test Specimens

One hundred and forty-four cylinders (10 cm (diameter) \times 20 cm (height)) were cast for this test. Test specimens after casting were covered with plastic sheets and left in the casting room for 24 h at a temperature of about 23°C. The specimens were then demolded and put into a curing room at 23 \pm 1.5°C and 100% relative humidity (RH) until testing.

3. Accelerated Carbonation

After curing for 28 days, the one end and cylindrical surface of each cylinder were coated with epoxy resin to secure that carbon dioxide (CO₂) could diffuse merely into the specimens in a one-dimensional mode. The specimens were transferred to a sealed chamber and subjected to carbonation at 23°C in temperature, 70% RH, and a CO₂ concentration of 100% by volume for 91.98 and 131.4 h (see Fig. 2).

**Fig. 2. Accelerated carbonation equipment.**

4. Tensile Splitting and Carbonation Depth Tests

The test cylinders were taken out of the carbonation chamber at 91.98 and 131.4 h and splitted in a tensile splitting test (ASTM C496) (see Fig. 3). The tensile splitting strengths have been converted to compressive strengths as shown in



(a) splitting equipment



(b) splitting machine

Fig. 3. Accelerated carbonation equipment.

Tables 3-6. After splitting the concrete specimens, the freshly split surface was cleaned and sprayed uniformly with phenolphthalein pH-indicator, a solution of 1% phenolphthalein ($C_{20}H_{14}O_4$) in 70% ethyl alcohol C_2H_5OH (Al-Khaiat and Hague, 1997; Dhir et al., 1989; Huang et al., 2012; Loo et al., 1994; Papadakis et al., 1991b). This indicator turns purple (magenta) for pH' higher than about 9 (Parott, 1991) i.e., the uncarbonated concrete, but is colorless at lower pH's, i.e., for the carbonated concrete. The depth of carbonation was measured with a steel ruler to the nearest 1 mm (see Fig. 4). Several measurements were taken on a given specimen.

5. Thermogravimetric Analysis (TGA)

Split face of the concrete specimens was oven-dried before taking samples from the split surface in belt of 5 mm width consecutively away from the edge of the split specimen. Sample power was then obtained using a 0.3 mm sieve. Concerning regions of the split surface where samples were not taken yet, plastic film was used to avoid carbonation of the fresh surface from CO_2 in the ambient air. The power sample was put in a crucible designed for making use of thermogravimetric analysis (TGA) (Villain and Platret, 2006) instrument. The temperature was set to increase at a rate of $10^\circ C/min$ from room temperature to $1000^\circ C$. Temperature as a function of thermogram was recorded to supply qualitative and quantitative information. The TGA instrument used was a PERKIN-ELMER DS C-7 type which is controlled by the Thermal analysis and



(a) 50AX0



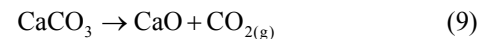
(b) 50BX0

Fig. 4. Cross-section of two split concrete cylinder specimens after carbonation.

Rheology software. The test results were analyzed by the Thermal solution analysis software.

The molar concentrations of $Ca(OH)_2$ and $CaCO_3$ were calculated and dependent on the thermogravimetric curve decided from the thermogravimetric analysis test for concrete specimens underwent miscellaneous periods of accelerated carbonation, and in addition from the rate of weight loss denoted by the thermogravimetric curve that contained the dehydration of $Ca(OH)_2$ and thermal decomposition of $CaCO_3$. Based on the facts mentioned above, changes in the amounts of $CaCO_3$ in concrete specimens under miscellaneous periods of carbonation could be analyzed (JCI Committee 984, 2000).

During the carbonated concrete in the temperature zone from $550^\circ C$ to $770^\circ C$, $CaCO_3$ will happen the following chemical dissolution:



The production of air phase CO_2 leads to the weight loss of concrete. Taking out the mortar of concrete in the zone of carbonated concrete is used to be accomplished the TGA test. Assume that the mix proportion of concrete is water: cement : sand : gravel i.e., $W : Cm : S : G$. The weight of per unit concrete volume included steel 50 kgf/m^3 is 2400 kgf/m^3 . If neglect the chemical variation of the other constituent materials in the temperature zone, then the content of $CaCO_3$ in the unit volume of carbonated concrete is (Jiang et al., 1996).

$$[\text{CaCO}_3] = 2400 \times \frac{W + C_m + S}{W + C_m + S + G} \times \frac{n}{44 \times 10^{-3}} \quad (10)$$

where $[\text{CaCO}_3]$ is the content of CaCO_3 in the unit volume of carbonated concrete (mole/m³), n is the weight loss of concrete (%), and 44×10^{-3} is the mole mass of CO_2 (kg/mole). The chemical equation of concrete carbonation divulged by Zhang and Jiang (1998) may be to prove that the CO_2 absorbed amount m of concrete in unit volume is equal to the CaCO_3 content of carbonated concrete in unit volume, i.e.,

$$m = [\text{CaCO}_3] \quad (11)$$

The precise meaning of Eq. (11) is needed to be described as follows: Based on Fick's first law of diffusion, the amount m of CO_2 diffusion into a concrete layer is defined as (Huang et al., 2012)

$$m = -DA \frac{C_s - C_{cf}}{x} dt \quad (12)$$

where A is the penetrated area (m²).

At the carbonation front the predicted CO_2 reacts with the alkaline compounds useful in a given concentration. For the carbonation of these alkaline compounds included in a unit volume of concrete an amount of CO_2 a (g/m³) is demanded, and

$$m = aAdx \quad (13)$$

represents the mass of CO_2 needed to increase the depth of carbonation by an increment dx (Huang et al., 2012). According to Eqs. (12) and (13) and taking integral, we may obtain Eq. (1).

Taking out the mortar fragments of specimen with carbonated layer and using earthen bowl to grind it to pieces, the thermal analyze system of PERKIN-ELMER DS C-7 Type is adopted to do TGA for testing $[\text{CaCO}_3]$ and then for checking the m value of theoretical calculation.

IV. RESULTS AND ANALYSES

Tables 3, 4, 5, and 6 indicate the carbonation depths and compressive strengths of specimen sets 35A, 35B, 50A, and 50B, respectively. Based on these Tables, it is obvious that the carbonation depths of specimen sets 35A and 50A are less than those of 35B and 50B, respectively. The reason is that the tightness of specimen sets 35A and 50A with cement-sand ratio 1/2 are better than those of 35B and 50B with cement-sand ratio 1/3, respectively. The carbonated samples with X, Y, and Z (X, Y, and Z represent concrete specimens with designed strengths 210, 245, and 280 kgf/cm², respectively.) of specimen sets 35A, 35B, 50A, and 50B were chosen one for doing TGA test. The mortars of these carbonated

Table 3. Carbonation depth and compressive strength of specimen set 35A.

Specimen set	Specimen Number	Carbonation depth (mm)		Compressive strength (kgf/cm ²)	
		(mm)	Ave. (mm)	(kgf/cm ²)	Ave. (kgf/cm ²)
35AX0 ⁺	1	10.5		95.8	
	2	12.5	11.5	99.6	97.9
	3	11.5		98.4	
35AX10	1	11.0		191.4	
	2	9.2	10.7	146.2	170.0
	3	11.9		172.3	
35AX15	1	11.0		146.7	
	2	9.3	10.4	139.9	149.6
	3	10.9		162.1	
35AX20	1	10.5		158.6	
	2	9.1	9.7	137.4	151.2
	3	9.6		157.5	
35AY0	1	21.0		186.5	
	2	20.5	21.0	155.5	164.8
	3	21.5		152.3	
35AY10	1	12.1		195.0	
	2	11.5	11.3	130.1	161.3
	3	10.3		158.8	
35AY15	1	10.6		186.1	
	2	10.3	10.2	149.8	168.2
	3	9.6		168.6	
35AY20	1	14.0		146.6	
	2	14.1	13.6	187.6	158.0
	3	12.6		139.7	
35AZ0	1	14.7		160.2	
	2	13.9	14.7	163.3	161.1
	3	15.5		159.9	
35AZ10	1	13.6		177.2	
	2	13.5	13.4	180.3	179.7
	3	13.2		181.7	
35AZ15	1	12.1		147.9	
	2	12.6	12.3	210.1	181.3
	3	12.2		185.0	
35AZ20	1	14.5		189.3	
	2	14.2	14.1	189.7	199.5
	3	13.6		219.4	

- ⁺: 1. "35" represents accelerated carbonation test for simulating 35 years. $\frac{C_{\text{CO}_2, \text{air}}}{C_{\text{CO}_2, 100\%}} = \frac{t}{35 \text{ years}}$, $t = 35 \text{ years} \frac{0.03\%}{100\%} = 0.0105$ years = 91.98h
2. "A" represents mortar coating with $\frac{\text{cement}}{\text{sand}} = \frac{1}{2}$.
3. "X, Y, and Z" represent concrete specimen with designed strength 210, 245, and 280 kgf/cm², respectively.
4. "0, 10, 15, and 20" represent coating thickness with 0, 10, 15, and 20 mm, respectively.

Table 4. Carbonation depth and compressive strength of specimen set 35B.

Specimen set	Specimen Number	Carbonation depth (mm)		Compressive strength (kgf/cm ²)	
			Ave. (mm)		Ave. (kgf/cm ²)
35BX0 ⁺⁺	1	25.0		157.1	
	2	24.7	24.9	157.0	157.8
	3	24.9		159.2	
35BX10	1	14.7		105.7	
	2	13.5	13.8	139.9	127.2
	3	13.3		136.0	
35BX15	1	12.9		150.2	
	2	13.0	13.5	133.1	136.4
	3	14.5		126.0	
35BX20	1	14.4		166.4	
	2	13.8	14.1	151.7	147.8
	3	14.2		125.3	
35BY0	1	20.9		154.2	
	2	21.0	21.5	187.0	172.4
	3	22.6		176.1	
35BY10	1	13.9		114.1	
	2	14.8	14.4	168.1	146.6
	3	14.4		157.6	
35BY15	1	11.2		123.8	
	2	12.3	12.1	151.4	144.3
	3	12.8		157.6	
35BY20	1	10.7		175.7	
	2	11.4	11.1	137.7	160.6
	3	11.1		168.4	
35BZ0	1	14.4		148.0	
	2	14.6	14.6	129.9	144.0
	3	14.7		154.0	
35BZ10	1	13.1		140.9	
	2	13.4	13.6	161.8	156.9
	3	14.2		167.9	
35BZ15	1	12.6		146.0	
	2	11.9	12.3	196.2	168.2
	3	12.4		162.3	
35BZ20	1	12.7		155.5	
	2	13.1	13.2	179.5	167.5
	3	13.8		167.5	

⁺⁺: 1. "35" represents accelerated carbonation test for simulating 35 years. $\frac{C_{CO_2,air}}{C_{CO_2,100\%}} = \frac{t}{35 \text{ years}}, t = 35 \text{ years} \frac{0.03\%}{100\%} = 0.0105$ years = 91.98h

2. "B" represents mortar coating with $\frac{cement}{sand} = \frac{1}{3}$.

3. "X, Y, and Z" represent concrete specimen with designed strength 210, 245, and 280 kgf/cm², respectively.

4. "0, 10, 15, and 20" represent coating thickness with 0, 10, 15, and 20 mm, respectively.

Table 5. Carbonation depth and compressive strength of specimen set 50A.

Specimen set	Specimen Number	Carbonation depth (mm)		Compressive strength (kgf/cm ²)	
			Ave. (mm)		Ave. (kgf/cm ²)
50AX0*	1	34.0		124.3	
	2	32.5	32.5	136.7	124.9
	3	31.0		113.8	
50AX10	1	22.6		67.5	
	2	23.5	23.5	67.3	67.7
	3	24.5		68.4	
50AX15	1	12.5		140.3	
	2	11.5	11.5	122.8	125.3
	3	10.5		112.8	
50AX20	1	12.6		143.7	
	2	12.6	12.9	118.5	141.6
	3	13.5		162.6	
50AY0	1	23.6		144.6	
	2	25.0	25.0	118.6	132.8
	3	26.4		135.3	
50AY10	1	22.7		135.8	
	2	21.5	22.6	162.4	151.2
	3	23.6		155.8	
50AY15	1	19.2		186.2	
	2	18.2	19.5	150.8	159.5
	3	21.1		141.4	
50AY20	1	22.1		139.3	
	2	20.6	22.1	174.7	160.8
	3	23.5		168.3	
50AZ0	1	22.6		145.5	
	2	24.5	24.5	141.7	142.2
	3	26.4		139.5	
50AZ10	1	21.6		138.5	
	2	22.6	21.4	193.3	155.3
	3	20.0		134.1	
50AZ15	1	19.4		155.1	
	2	18.7	18.9	170.3	162.7
	3	18.6		162.7	
50AZ20	1	20.7		151.4	
	2	20.1	20.4	189.8	171.5
	3	20.4		173.2	

*: 1. "50" represents accelerated carbonation test for simulating 50 years. $\frac{C_{CO_2,air}}{C_{CO_2,100\%}} = \frac{t}{50 \text{ years}}, t = 50 \text{ years} \frac{0.03\%}{100\%} = 0.015$ years = 131.4h

2. "A" represents mortar coating with $\frac{cement}{sand} = \frac{1}{2}$.

3. "X, Y, and Z" represent concrete specimen with designed strength 210, 245, and 280 kgf/cm², respectively.

4. "0, 10, 15, and 20" represent coating thickness with 0, 10, 15, and 20 mm, respectively.

Table 6. Carbonation depth and compressive strength of specimen set 50B.

Specimen set	Specimen Number	Carbonation depth (mm)		Compressive strength (kgf/cm ²)	
			Ave. (mm)		Ave. (kgf/cm ²)
50BX0**	1	32.1		149.7	
	2	32.5	33.5	136.2	143.0
	3	35.9		143.2	
50BX10	1	20.7		116.5	
	2	22.5	23.5	147.2	121.5
	3	27.3		100.8	
50BX15	1	21.4		113.4	
	2	20.5	21.5	78.7	97.9
	3	22.6		101.6	
50BX20	1	24.0		141.7	
	2	22.9	23.5	137.0	138.9
	3	23.5		137.9	
50BY0	1	28.0		167.2	
	2	25.0	26.5	163.3	145.8
	3	26.5		106.7	
50BY10	1	19.8		109.7	
	2	19.2	19.3	146.2	127.9
	3	18.8		127.7	
50BY15	1	16.4		132.8	
	2	15.5	16.3	141.3	134.2
	3	17.6		128.4	
50BY20	1	15.7		142.2	
	2	16.4	16.1	161.2	154.0
	3	16.1		158.6	
50BZ0	1	26.5		178.9	
	2	25.8	26.4	185.0	163.6
	3	26.9		127.0	
50BZ10	1	23.5		148.5	
	2	21.5	21.5	166.4	158.6
	3	19.5		161.0	
50BZ15	1	18.5		155.1	
	2	17.2	16.9	174.2	170.4
	3	15.0		181.9	
50BZ20	1	19.7		176.9	
	2	20.5	21.0	149.4	166.0
	3	22.8		171.7	

** : 1. “50” represents accelerated carbonation test for simulating 50 years. $\frac{C_{CO_2,air}}{C_{CO_2,100\%}} = \frac{t}{50 \text{ years}}$, $t = 50 \text{ years} \frac{0.03\%}{100\%} = 0.015 \text{ years} = 131.4h$

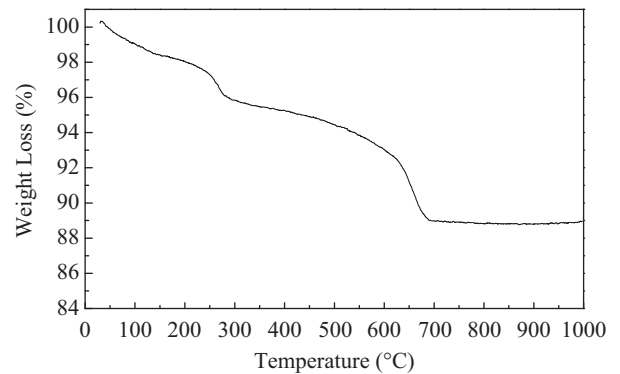
2. “B” represents mortar coating with $\frac{cement}{sand} = \frac{1}{3}$.

3. “X, Y, and Z” represent concrete specimen with designed strength 210, 245, and 280 kgf/cm², respectively.

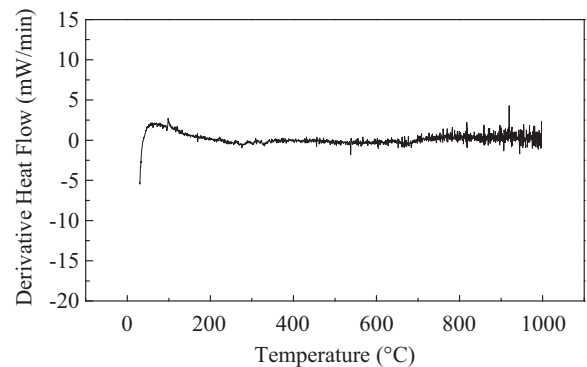
4. “0, 10, 15, and 20” represent coating thickness with 0, 10, 15, and 20 mm, respectively.

Table 7. Results of thermogravimetric analysis for specimen 35AY20.

Specimen 35AY20	Carbonation depth x(mm)					
	0	2.5	7.5	12.5	17.5	22.5
Weight loss n(%)	12.62	12.60	11.07	10.97	8.91	8.64
CO ₂ Absorbed amount m (mole/m ³)	3075.7	3070.8	2832.0	2697.9	2171.7	2105.7



(a) weight loss versus temperature



(b) derivative heat flow versus temperature.

Fig. 5. Dissociation of carbonated sample 35AY20 of crushed concrete mortar during TGA test.

samples taken out of crushed concrete at depths $x = 0, 2.5, 7.5, 12.5, 17.5$ and 22.5 mm were respectively done the TGA test. Fig. 5 shows the dissociation of carbonation sample 35AY20 at depth $x = 22.5$ mm of mortar taken out of crushed concrete during the TGA test. Fig. 5(a) demonstrates the weight loss versus temperature. The rate of weight loss from 222.37°C to 685.21°C is 8.64%. Fig. 5(b) displays that the crushed sample is heated from 50°C to 1000°C at a rate of 10°C per minute. The designed strength of specimen 35AY20 is 245 kgf/cm^2 . The mix proportion of per unit concrete volume is $W : C_m : S : G$ with $170:271:609:1300 \text{ kgf/m}^3$, respectively. Putting these values into Eq. (10), we obtain the value of $[\text{CaCO}_3]$ of the 35AY20 at $x = 22.5$ mm is 2105.69 mole/m^3 . Similarly, the other weight losses $n(\%)$ and CO_2 absorbed amount m (mole/m^3) were obtained and shown in Table 7.

Table 8. Values of diffusivity, rate of carbonation and carbonation retard coefficient for specimen sets 35A and 35B.

Specimen	Fick's first law			Fick's second law			Carbonation retard coefficient β
	Diffusivity $D_1(\text{m}^2/\text{s}) \times 10^{-12}$	Rate of Carbonation $K_1(\text{m}/\sqrt{\text{s}}) \times 10^{-7}$	Carbonation retard coefficient β_1	Diffusivity $D_2(\text{m}^2/\text{s}) \times 10^{-12}$	Rate of Carbonation $K_2(\text{m}/\sqrt{\text{s}}) \times 10^{-7}$	Carbonation retard coefficient β_2	
35AX0	0.88	0.75	1.00	2.13	0.75	1.00	1.00
35AX10	0.11	1.05	1.96	1.74	1.05	1.96	1.16
35AX15	0.34	1.20	2.56	8.48	1.20	2.56	1.22
35AX20	0.12	1.35	3.24	1.31	1.35	3.24	1.41
35AY0	0.13	0.75	1.00	4.56	0.75	1.00	1.00
35AY10	0.20	1.05	1.96	5.24	1.05	1.96	3.45
35AY15	0.46	1.20	2.56	3.10	1.20	2.56	4.24
35AY20	0.99	1.35	3.24	5.27	1.35	3.24	2.38
35AZ0	0.13	0.75	1.00	4.59	0.75	1.00	1.00
35AZ10	0.11	1.05	1.96	2.58	1.05	1.96	1.20
35AZ15	0.18	1.20	2.56	3.21	1.20	2.56	1.43
35AZ20	0.30	1.35	3.24	6.57	1.35	3.24	1.09
35BX0	0.19	0.75	1.00	12.4	0.75	1.00	1.00
35BX10	0.13	1.05	1.96	2.45	1.05	1.96	3.26
35BX15	0.59	1.20	2.56	1.73	1.20	2.56	3.40
35BX20	0.15	1.35	3.24	1.72	1.35	3.24	3.12
35BY0	0.26	0.75	1.00	17.8	0.75	1.00	1.00
35BY10	0.20	1.05	1.96	5.61	1.05	1.96	2.23
35BY15	0.50	1.20	2.56	2.12	1.20	2.56	3.16
35BY20	0.14	1.35	3.24	1.72	1.35	3.24	3.75
35BZ0	0.14	0.75	1.00	5.2	0.75	1.00	1.00
35BZ10	0.13	1.05	1.96	2.32	1.05	1.96	1.15
35BZ15	0.18	1.20	2.56	3.71	1.20	2.56	1.41
35BZ20	0.17	1.35	3.24	2.37	1.35	3.24	1.22
Average			2.19			2.19	1.70

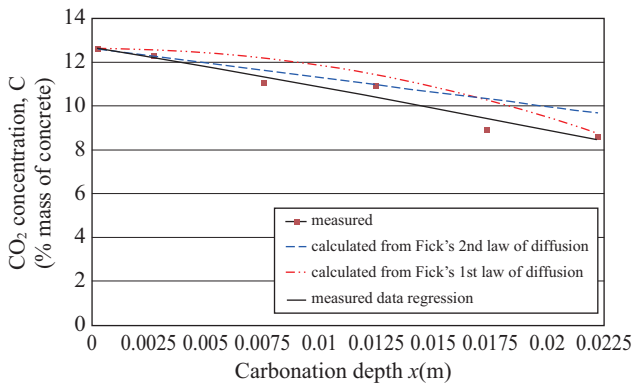


Fig. 6. Relationship between CO₂ concentration and carbonation depth for specimen 35AY20.

According to Table 7, we may plot the relationship between CO₂ concentration and carbonation depth (i.e., carbonation profile) as sketched in Fig. 6. It is noteworthy to point out that the regression line as shown in Fig. 6 is done by least square method. Based on Fig. 6, the CO₂ concentration on concrete surface C_s is 3075.67 mole/m³ = 135.33 kgf/m³ = 5.64% (mass of concrete). According to Eqs. (2), (4), (7), and (8) and using

the commercial software programmed “Mathematica” (1999), we may inversely calculate the diffusion coefficients of CO₂ for Fick’s first and second laws of linear diffusion, respectively (Buenfeld and Newman, 1987; Collepardi et al., 1972). Furthermore, we may also calculate the rate of carbonation and carbonation retard coefficient for the Fick’s first and second laws of linear diffusion, respectively. These values were shown in Tables 8 and 9. The average value of the carbonation retard coefficient of mortar coating predicted from Fick’s first and second laws of linear diffusion is 2.19. It is worthy to point out that both Fick’s first law and Fick’s second law of linear diffusion can be reduced to the same carbonation depth formula $x(t) = K\sqrt{t}$. Although Fick’s first laws of linear diffusion belongs to steady state, i.e., $\partial C/\partial t = 0$ while Fick’s second law of linear diffusion belongs to nonsteady state, i.e., $\partial C/\partial t \neq 0$, the value of K₁ (see Eq. (4)) is obviously not equal to that of K₂ (see Eq. (7)). However, Tables 8 and 9 show that K₁ = K₂ due to the carbonation depth x(t) measured at the same simulated time to each experimental data.

According to Tables 3, 4, 5 and 6, and using Eqs. (4) and (8), we may also calculate the values of carbonation retard coefficient obtained from experimental measure as listed in Tables 8

Table 9. Values of diffusivity, rate of carbonation and carbonation retard coefficient for specimen sets 50A and 50B.

Specimen	Fick's first law			Fick's second law			Carbonation retard coefficient β
	Diffusivity $D_1(\text{m}^2/\text{s}) \times 10^{-12}$	Rate of Carbonation $K_1(\text{m}/\sqrt{\text{s}}) \times 10^{-7}$	Carbonation retard coefficient β_1	Diffusivity $D_2(\text{m}^2/\text{s}) \times 10^{-12}$	Rate of Carbonation $K_2(\text{m}/\sqrt{\text{s}}) \times 10^{-7}$	Carbonation retard coefficient β_2	
50AX0	1.06	0.63	1.00	6.47	0.63	1.00	1.00
50AX10	0.80	0.88	1.96	1.18	0.88	1.96	1.91
50AX15	1.21	1.01	2.56	2.11	1.01	2.56	7.99
50AX20	3.22	1.13	3.24	5.94	1.13	3.24	6.35
50AY0	0.37	0.63	1.00	0.57	0.63	1.00	1.00
50AY10	0.52	0.88	1.96	0.63	0.88	1.96	1.22
50AY15	0.43	1.01	2.56	0.34	1.01	2.56	1.64
50AY20	0.72	1.13	3.24	0.67	1.13	3.24	1.28
50AZ0	0.13	0.63	1.00	2.25	0.63	1.00	1.00
50AZ10	0.39	0.88	1.96	0.33	0.88	1.96	1.31
50AZ15	0.76	1.01	2.56	0.96	1.01	2.56	1.68
50AZ20	0.68	1.13	3.24	0.59	1.13	3.24	1.44
50BX0	0.48	0.63	1.00	1.85	0.63	1.00	1.00
50BX10	0.35	0.88	1.96	0.30	0.88	1.96	2.03
50BX15	0.74	1.01	2.56	0.98	1.01	2.56	2.43
50BX20	0.87	1.13	3.24	0.99	1.13	3.24	2.03
50BY0	1.16	0.63	1.00	8.71	0.63	1.00	1.00
50BY10	0.72	0.88	1.96	0.98	0.88	1.96	1.89
50BY15	0.42	1.01	2.56	0.33	1.01	2.56	2.64
50BY20	0.84	1.13	3.24	0.93	1.13	3.24	2.71
50BZ0	1.34	0.63	1.00	10.81	0.63	1.00	1.00
50BZ10	0.61	0.88	1.96	0.81	0.88	1.96	1.51
50BZ15	1.78	1.01	2.56	4.81	1.01	2.56	2.44
50BZ20	0.48	1.13	3.24	0.39	1.13	3.24	1.58
Average			2.19			2.19	1.70

and 9. Based on Tables 8 and 9, the average value of carbonation retard coefficient, obtained from experimental measure, of mortar coating used in this study is 1.70. The results of the present study show that the carbonation depth of concretes is inversely proportional to the thickness of surface coating with mortar.

In the case of the carbonation retard coefficient, every surface coating material has its own resistance value and characteristic property. Accordingly, the average values of carbonation retard coefficient calculated and measured of mortar coating in Tables 8 and 9 are identical to 2.19 and 1.70, respectively. The upper and lower limits of carbonation retard coefficient calculated of mortar coating for 35A, 35B, 50A and 50B in Tables 8 and 9 are 3.24 and 1.96, respectively. The upper and lower limits of carbonation retard coefficient measured of mortar coating for 35A and 35B, and 50A and 50B in Tables 8 and 9 are 4.24 and 1.09, and 7.99 and 1.22, respectively. It is worth pointing out that the carbonation retard coefficient calculated by theoretical model is impossible equal to that value measured by experimental technique. The reason is the theoretical model that is usually considered a few variables and only an ideal approach. Thus, the theo-

retical model is not completely approached the true property of mortar.

V. CONCLUSIONS

Based on the investigated results mentioned before, some important and valuable conclusions may be made as in the following:

1. The specimens of 35BY10, 35BY15, and 35BY20 in Table 4 have carbonation depths of 14.4, 12.1, and 11.1 mm, respectively; the specimens of 50BY10, 50BY15, and 50BY20 in Table 6 have carbonation depths of 19.3, 16.3, and 16.1 mm, respectively. The results of the present study indicate that the carbonation depth of concrete is inversely proportional to the thickness of surface coating with mortar.
2. The surface coating can retard the carbonation of concrete. The average value, obtained from experimental measure, of carbonation retard coefficient of mortar coating is 1.70 while the average value, predicted from Fick's first and second laws of linear diffusion, of that is 2.19. The value of 2.19 is much better than that of 1.70.

3. The simple version of the theoretical model is extended herein to mortar coating-concrete systems, in which the mortar coating is applied to the concrete surface. The information required for the application of the simple form of the model is readily available to the designer of a concrete structure. It is composed of (i) the mix proportion of the mortar coating and the concrete; (ii) the (constant) RH and CO₂ concentration; and (iii) the thickness and time of any mortar coating.
4. The carbonation retard coefficient predicted by the theoretical model of Fick's first and second laws of linear diffusion is not equal to that value measured by experimental programme. The explanation is the theoretical model that is simply an ideal approach and is generally considered a small number of variables. If theoretical model is expectedly approached the true property of surface coating material then a suitable theoretical model should be formulated in-depth.

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