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# CARBONATION RESISTANCE OF CONCRETE WITH MORTAR COATING

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Key words: carbonation, composite medium, concrete, mortar coating.

## ABSTRACT

The principal purpose of this paper was theoretically to study the carbonation resistance of a semi-infinite medium which concrete has a mortar coating having diffusion properties different from those of the rest of the medium. The analytical solution of a semi-infinite composite medium was used to predict the time required for subsidence due to concrete with mortar coating. The inaccurate analytical solution was published in previous books. Thus, the analytical solution of a semi-infinite composite medium is re-derived in this article. The governing equations without initial and boundary conditions in the previous books are also pointed out. In order to verify the feasibility and applicability for this analytical solution, the previously experimental data were cited as input parameters. The investigated results show that the calculated time required for subsidence of concrete subjected to mortar coating is in good agreement with that the measured time required for retard the carbonation of concrete with surface mortar coating. The present studied results may be offered as a crucial reference for durability design of newly building concrete or reinforced concrete (RC) structures.

## I. INTRODUCTION

Concrete is one of the most generally employed construction materials. Owing to its composition and porous nature, it is frequently susceptible to crack, damage and deterioration in consequence of physical and chemical processes. Carbon dioxide ( $CO_2$ ) is one of the chemical materials which can generate deterioration of reinforced concrete (RC) structures. Deterioration of RC structures caused by carbon dioxide is commonly called carbonation. Concrete carbonation can lead to dangerous

corrosion of reinforcing bars (rebars) and substantially diminish the service life of RC structures. RC structures placed in the plenty of carbon dioxide environments should accordingly be completely enhanced the designed strength and the defended manipulation such as surface coating. In point of this issue, coating materials may be employed to protect both newly built and existing structures from carbonation.

Numerous important investigations on the performance of coated concrete have been narrated. Papadakis et al. (1992) employed a mathematical model derived from Fick's first law of diffusion to study the influence of composition, environmental factors, and cement-lime mortar costing on concrete carbonation. If its water/cement ratio is very low and its lime content higher than a lime-cement mortar coating of the usual thickness (around 20 mm) is found to be an extremely effective means of delaying or even preventing carbonation-induced corrosion initiation. This means that it delays the start of concrete carbonation by the time required for carbonation to fully penetrate the coating, and it postpones its further penetration into the concrete because atmosphere  $CO_2$  has to travel farther to reach the carbonation front. Kazmierczak and Helene (1995) used accelerated carbonation tests to estimate concrete coating resistance to  $CO_2$  permeability. The coating materials are four types resin such as acrylic emulsion or dispersion, methyl methacrylate dispersion, polyurethane and silane/siloxane plus acrylic dispersion. They found that the painting procedure results in different coating thickness, which will lead to different carbonation depths in the same specimen. Roy et al. (1996) performed the effect of plastering on the carbonation of a 19-year-old RC commercial building that was located 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. Swamy et al. (1998) investigated the performance of concrete slabs coated with an acrylic-based coating against atmospheric carbon dioxide attacks. Throughout the period of field exposure, uncoated concrete specimens with water to cement ratios of 0.6 and 0.75 disclosed average carbonation depths of 3 and 7.5 mm, while the acrylic-based coating decreased the average carbonation depths to 0.5 and 3 mm, respectively. Seneviratne et al. (2000) used dynamically mechanical thermal analysis to study three elastometric surface coatings. All these coating systems were applied to naturally carbonated concrete components obtained from buildings that

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were suffering from reinforcement corrosion. It was indicated that the use of an elastometric 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 pierce through the concrete was enumerated by comparing the difference of carbonation depths between coated and uncoated surface coatings. An industrial mortar coating was showed excellent performance as a carbon dioxide barrier when applied to plain concrete. 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 contents of 0 and 30% with and without CCM coating were tested under an accelerated carbonation environment. It was found that carbonation depths of coated specimens were lower than those of the uncoated specimens of the same mix proportion. Huang et al. (2012) inspected carefully concrete carbonation of a 35-year-old educational RC building that was located in a subtropical environment. A very important reduction in carbonation was detected for the column and beams of building that was plastered (sand-cement render) and/or putted tile/coating. No concrete carbonation was found when the plaster (render) thickness surpassed 50 mm. The surface coating such as tile with high compacted and impermeable material may evidently postpone the carbonation of concrete. To date, however, no studies have attempted to predict the time required for subsidence of the carbonation of concrete with mortar coating. This is a notable shortcoming, because the use of analytical solution of a semi-infinite composite medium in previous studies may have resulted in wrong results.

The primary purpose of this paper is to study the carbonation resistance of concrete with mortar coating. To do this scheme, the analytical solution of the semi-infinite composite medium is first re-derived. The previously experimental data (Huang, 2013) were cited as input parameters. The time required for subsidence due to the thickness of coating material will be predicted. The results of the present study may be provided as an important reference for durability design of newly building concrete or RC structures.

## II. THE SEMI-INFINITE COMPOSITE MEDIUM

In order to establish the theory for modeling the carbonation resistance of concrete with mortar coating, we assume the concrete with mortar coating to be a semi-infinite composite medium (Carslaw and Jaeger, 1959; Crank, 1975; Poulsen and Mejlbro, 2006) as shown in Fig. 1. A semi-infinite medium has a mortar coating which is of diffusion properties different from those of the concrete. In this way, suppose in the semi-infinite region  $-d < x < \infty$ , the diffusion coefficient

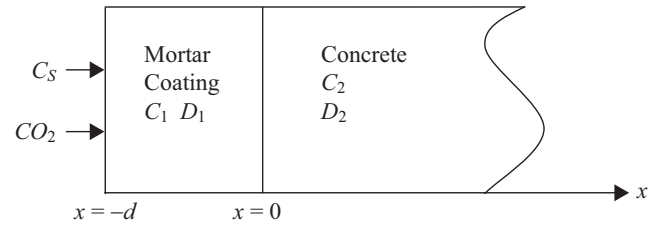


Fig. 1. Schematic diagram of concrete carbonation in the sight of a mortar coating.

(diffusivity) is  $D_1$  in the region  $-d < x < 0$ , and that the concentration of  $CO_2$  is denoted by  $C_1$  there, whereas the corresponding quantities in  $x > 0$  are  $D_2$  and  $C_2$ . The two linear partial differential equations (PDE, see Eqs. (1) and (2)) (Carslaw and Jaeger, 1959) with initial condition (see Eq. (3)), the discontinuous conditions at the interface between the two media (i.e. at  $x = 0$ , see Eqs. (4) and (5)) (Carslaw and Jaeger, 1959; Crank, 1975; Poulsen and Mejlbro, 2006), and boundary conditions (see Eqs. (6) and (7)) to be solved are

$$PDE : \frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2}, \quad -d < x < 0, t > 0 \quad (1)$$

$$PDE : \frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2}, \quad x > 0, t > 0 \quad (2)$$

$$IC : C_1(x, 0) = C_2(x, 0) = 0, \quad x = -d, t = 0 \quad (3)$$

$$DC : \lim_{x \rightarrow 0^-} D_1 \frac{\partial C_1(x, t)}{\partial x} = \lim_{x \rightarrow 0^+} D_2 \frac{\partial C_2(x, t)}{\partial x}, \quad x \rightarrow 0, t > 0 \quad (4)$$

$$DC : \lim_{x \rightarrow 0^-} C_1(x, t) = \lim_{x \rightarrow 0^+} C_2(x, t), \quad x \rightarrow 0, t > 0 \quad (5)$$

$$BC : C_1(x, t) = C_s, \quad x = -d, t > 0 \quad (6)$$

$$BC : C_2(x, t) = 0, \quad x \rightarrow \infty, t > 0 \quad (7)$$

where  $x$  is the distance,  $t$  is the time,  $d$  is the thickness of mortar coating, and  $C_s$  is the surface concentration of  $CO_2$  on mortar coating.

Taking Laplace transformation (O'Neil, 2003) with respect to  $t$  to Eqs. (1), (2), (4), (5), (6) and (7) and using Eq. (3), we obtain

$$\frac{\partial^2 \overline{C_1}}{\partial x^2} - q_1^2 \overline{C_1} = 0, \quad -d < x < 0, p > 0 \quad (8)$$

$$\frac{\partial^2 \overline{C_2}}{\partial x^2} - q_2^2 \overline{C_2} = 0, \quad x > 0, p > 0 \quad (9)$$

$$D_1 \frac{d\bar{C}_1(x, p)}{dx} = D_2 \frac{d\bar{C}_2(x, p)}{dx}, x = 0, p > 0 \quad (10)$$

$$\bar{C}_1(0, p) = \bar{C}_2(0, p), x = 0, p > 0 \quad (11)$$

$$\bar{C}_1(-d, p) = \frac{C_s}{p}, x = -d, p > 0 \quad (12)$$

$$\bar{C}_2(x \rightarrow \infty, p) = 0, x \rightarrow \infty, p > 0 \quad (13)$$

where  $q_1 = \left(\frac{p}{D_1}\right)^{\frac{1}{2}}$ ,  $q_2 = \left(\frac{p}{D_2}\right)^{\frac{1}{2}}$ , and  $p$  is a number whose real part is positive and large enough to make the Laplace's integral transformation convergent.

A solution of Eq. (8) which satisfies Eq. (12) is

$$\bar{C}_1(x, p) = \frac{C_s}{p} \cosh q_1(d+x) + A \sinh q_1(d+x) \quad (14)$$

where  $A$  is an unknown constant.

A solution of Eq. (9) which satisfies Eq. (13) is

$$\bar{C}_2(x, p) = B e^{-q_2 x} \quad (15)$$

where  $B$  is an unknown constant.

Inserting Eqs. (14) and (15) into Eq.(11), we have

$$B = \frac{C_s}{p} \cosh q_1 d + A \sinh q_1 d \quad (16)$$

Using Eqs. (10), (14), (15), and (16) and applying the following formulae (Beyer, 1981)

$$\frac{d}{dx} \sinh u = \cosh u \frac{du}{dx}, \frac{d}{dx} \cosh u = \sinh u \frac{du}{dx} \quad (17)$$

we obtain the unknown constant

$$A = -\frac{C_s (q_1 D_1 \sinh q_1 d + q_2 D_2 \cosh q_1 d)}{p (q_1 D_1 \cosh q_1 d + q_2 D_2 \sinh q_1 d)} \quad (18)$$

Putting Eq. (18) into Eq. (16) and using the following formulae (Beyer, 1981)

$$\sinh^2 u = \frac{1}{2}(\cosh 2u - 1), \cosh^2 u = \frac{1}{2}(\cosh 2u + 1) \quad (19)$$

we obtain the unknown constant

$$B = \frac{C_s q_1 D_1}{p (q_1 D_1 \cosh q_1 d + q_2 D_2 \sinh q_1 d)} \quad (20)$$

For convenience' sake, we set the following notations

$$k = \left(\frac{D_1}{D_2}\right)^{\frac{1}{2}}, \sigma = \frac{D_2 k}{D_1}, \alpha = \frac{\sigma - 1}{\sigma + 1} \quad (21)$$

Substituting Eq. (18) into Eq. (14) and using Eq. (21) and the following formulae (Beyer, 1981)

$$\sinh u \sinh v = \frac{1}{2} \cosh(u+v) - \frac{1}{2} \cosh(u-v) \quad (22a)$$

$$\sinh u \cosh v = \frac{1}{2} \sinh(u+v) + \frac{1}{2} \sinh(u-v) \quad (22b)$$

$$\cosh u \sinh v = \frac{1}{2} \sinh(u+v) - \frac{1}{2} \sinh(u-v) \quad (22c)$$

$$\cosh u \cosh v = \frac{1}{2} \cosh(u+v) + \frac{1}{2} \cosh(u-v) \quad (22d)$$

we obtain

$$\bar{C}_1(x, p) = \frac{C_s (\cosh q_1 x - \sigma \sinh q_1 x)}{p (\cosh q_1 d + \sigma \sinh q_1 d)} \quad (23)$$

Inserting Eq. (20) into Eq. (15) and using Eq. (21), we obtain

$$\bar{C}_2(x, p) = \frac{C_s}{p (\cosh h q_1 d + \sigma \sinh q_1 d)} e^{-q_2 x} \quad (24)$$

We express the hyperbolic functions (Beyer, 1981)

$$\sinh z = \frac{e^z - e^{-z}}{2}, \cosh z = \frac{e^z + e^{-z}}{2}, z = x + iy, i = \sqrt{-1} \quad (25)$$

in Eq. (24) in terms of negative exponentials, and expand in a series by the geometric series

$$\frac{1}{1 - \alpha e^{-2q_1 d}} = \sum_{n=0}^{\infty} \alpha^n e^{-2nq_1 d} \quad (26)$$

Further, using Eq. (21) and

$$L^{-1} \left( \frac{e^{-qx}}{p} \right) = \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right) \quad (27)$$

where *erfc* is the complementary error function and taking inverse Laplace transformation (O’Neil, 2003) to Eq. (24), we have

$$C_2(x, t) = \frac{2C_s}{1 + \sigma} \sum_{n=0}^{\infty} \alpha^n \operatorname{erfc} \left( \frac{(2n+1)d + kx}{2\sqrt{D_1 t}} \right), 0 < x < \infty, t > 0 \tag{28}$$

Similarly as above, we have

$$C_1(x, t) = C_s \sum_{n=0}^{\infty} \alpha^n \left\{ \operatorname{erfc} \left( \frac{(2n+1)d + x}{2\sqrt{D_1 t}} \right) - \alpha \operatorname{erfc} \left( \frac{(2n+1)d - x}{2\sqrt{D_1 t}} \right) \right\}, -d < x < 0, t > 0 \tag{29}$$

Taking the differentiation with respect to *x* at *x* = -*d* (Carslaw and Jaeger, 1959) and using Leibniz’s rule (Hildebrand, 1974), we obtain

$$\left( \frac{\partial C_1(x, t)}{\partial x} \right)_{x=-d} = -\frac{C_s}{\sqrt{\pi D_1 t}} \left\{ 1 + 2 \sum_{n=1}^{\infty} \alpha^n e^{-\frac{n^2 d^2}{D_1 t}} \right\} \tag{30}$$

For very large values of the time, the exponentials in Eq. (30) may all be replaced by unity (Carslaw and Jaeger, 1959).

Furthermore,  $\sum_{n=1}^{\infty} \alpha^n = \frac{\alpha}{1 - \alpha}$  and using Eq. (21), we have

$$\begin{aligned} \left( \frac{\partial C_1(x, t)}{\partial x} \right)_{x=-d} &= -\frac{C_s}{\sqrt{\pi D_1 t}} \left\{ 1 + 2 \sum_{n=1}^{\infty} \alpha^n \right\} \\ &= -\frac{C_s}{\sqrt{\pi D_1 t}} \left\{ 1 + \frac{2\alpha}{1 - \alpha} \right\} = -\frac{C_s}{\sqrt{\pi D_1 t}} \left( \frac{D_2}{D_1} \right)^{\frac{1}{2}} \end{aligned} \tag{31}$$

When the concrete surface is kept at zero and the initial CO<sub>2</sub> concentration of the whole concrete is C<sub>s</sub>, it is very clear that the concentration gradient at *x* = -*d* will be minus the above. Based on Eq. (31), it is known that the concrete structure contains very different physical and chemical properties from the outer coating material : on this assumption the time required for subsidence to the present concentration gradient is (D<sub>2</sub>/D<sub>1</sub>)<sup>1/2</sup> times -C<sub>s</sub>/√(πD<sub>1</sub>t) .

Following Crank (1975), the total quantity penetrating the medium CO<sub>2</sub> through unit area of the coating surface *x* = -*d* in time *t* is *M<sub>t</sub>* = - (∂C(*x*, *t*)/∂*x*)<sub>*x*=-*d*</sub> D<sub>1</sub> t . Based on this concept, Eq. (31) may be written as

$$\frac{M_t}{C_s d} = \left( \frac{D_1 t}{\pi d^2} \right)^{\frac{1}{2}} \left\{ 1 + \frac{2\alpha}{1 - \alpha} \right\}, \alpha^2 < 1 \tag{32}$$

Eq. (32) means that  $\frac{M_t}{C_s d}$  is a function of  $\left( \frac{D_1 t}{d^2} \right)^{\frac{1}{2}}$ .

### APPLICATION

In order to verify the applicability and feasibility of the present theory mentioned above, the experimental data previously obtained by Huang (2013) were cited for predicting the results of analytical solution stated above. He casted cylinders (10 cm (diameter) × 20 cm (height)) covered with different thickness of mortar coating. After curing for 28 days, the surface and one end of each cylinder were coated with epoxy resin to secure that carbon dioxide could diffuse only into the specimens in a one-dimensional mode. The specimens were transferred to a sealed chamber and subjected to accelerated carbonation at 23°C in temperature, 70% RH, and a CO<sub>2</sub> concentration of 100% by volume for 91.98 and 131.4 hr.

According to the previously experimental data (C<sub>s</sub> = 11.53% by mass of concrete, C<sub>1</sub> = 11.51% by mass of concrete, C<sub>2</sub> = 10.16% by mass of concrete, *t* = 35 yrs, *d* = 0.01 m, *x*<sub>1</sub> = -0.0075 m, *x*<sub>2</sub> = 0.0025 m (Huang, 2013), *n* = 2) and using Eqs. (21), (28) and (29), the values of D<sub>1</sub> = 1.74 × 10<sup>-12</sup> m<sup>2</sup>/s and D<sub>2</sub> = 0.40 × 10<sup>-12</sup> m<sup>2</sup>/s for the concrete specimen 35AX10 can be calculated by the Mathcad software (2007) and listed in Table 1. The values of D<sub>1</sub> and D<sub>2</sub> of the other concrete specimens can be calculated by the same way and listed in Tables 1 and 2. Based on Tables 1 and 2, the compressive strengths of all specimens are much less than the designed strengths after the accelerated carbonation test for simulating 35 and 50 years, respectively. In accordance with the previously experimental data (Huang, 2013) and using Eq. (31), the values of C<sub>s</sub>/√(πD<sub>1</sub>t)<sup>1/2</sup>, (D<sub>2</sub>/D<sub>1</sub>)<sup>1/2</sup> and [C<sub>s</sub>/√(πD<sub>1</sub>t)<sup>1/2</sup> · (D<sub>2</sub>/D<sub>1</sub>)<sup>1/2</sup> of concrete specimens were calculated and listed in Tables 1 and 2. It is obvious from Tables 1 and 2 that the carbonation depths of 35A and 50A specimen sets are smaller than those of 35B and 50B, respectively. This can be explained as the tightness of A with the ratio of cement to sand of 1/2 is better than B with that of 1/3 . It is clear from Tables 1 and 2 that the compressive strengths of concrete specimens 35A and 35B with X, Y and Z with 10, 15 and 20 mm are larger than those of 50A and 50B with X, Y and Z with 10, 15, and 20 mm, while the values of D<sub>1</sub> and D<sub>2</sub> of concrete specimens 35A and 35B with X, Y and Z with 10, 15, and 20 mm are smaller than those of 50A and 50B with X, Y and Z with 10, 15, and 20 mm, respectively. This may be interpreted as the carbonation depths of 35 years are less than those of 50 years. The time required for subsidence due to mortar coating were predicted by Eq. (31) and listed in Tables 1 and 2. Roughly speaking, the effect of compressive strength on predicting the time required for subsidence subjected to mortar coating on concrete specimen is increased if the designed strength increases. In the case of the thickness of mortar

**Table 1. Carbonation depth, compressive strength, diffusivity, and concentration gradient of 35A and 35B specimen sets.**

Specimen set	Carbonation depth <sup>a</sup> (mm)	Compressive strength <sup>b</sup> (kgf/cm <sup>2</sup> )	Diffusivity		Concentration gradient (Eq.(31))		
			Coating Material $D_1$ (m <sup>2</sup> /s 10 <sup>-12</sup> )	Concrete $D_2$ (m <sup>2</sup> /s 10 <sup>-12</sup> )	$\frac{C_s}{\sqrt{\pi D_1 t}}$	$\left(\frac{D_2}{D_1}\right)^{\frac{1}{2}}$	$\left(\frac{D_2}{D_1}\right)^{\frac{1}{2}} \frac{C_s}{\sqrt{\pi D_1 t}}$
35AX10+	10.7	170.0	1.74	0.40	1.48	2.09	3.09
35AX15	10.4	149.6	2.66	0.18	1.16	3.84	4.46
35AX20	9.7	151.2	7.07	0.14	0.70	7.24	5.07
35AY10	10.3	161.3	6.91	1.25	0.70	2.35	1.64
35AY15	10.2	168.2	2.66	0.18	1.14	3.86	4.41
35AY20	13.6	158.0	6.14	0.02	0.89	16.28	14.46
35AZ10	13.4	179.7	4.16	0.34	0.77	3.48	2.66
35AZ15	12.3	180.3	4.51	0.27	0.72	4.09	2.94
35AZ20	14.4	199.5	3.72	1.85	0.71	4.49	3.18
35BX10	13.8	127.2	5.87	0.44	0.74	3.65	2.69
35BX15	13.5	136.4	5.77	0.30	0.75	4.40	3.32
35BX20	14.1	147.8	8.86	0.36	0.73	4.97	3.61
35BY10	14.4	146.6	3.24	5.79	0.71	0.75	0.53
35BY15	12.1	144.3	5.71	0.19	0.58	5.54	3.21
35BY20	11.1	160.6	6.90	0.09	0.50	8.58	4.30
35BZ10	13.6	151.9	4.70	0.62	0.62	2.76	1.72
35BZ15	12.3	168.2	1.91	0.07	0.91	5.11	4.63
35BZ20	13.2	167.5	4.35	0.05	0.59	9.16	5.41

<sup>a, b</sup> Experimental results were cited from Huang [6].

<sup>+</sup> 1. “50” represents accelerated carbonation test for simulating 50 years.

$$\frac{C_{CO_2,air}}{C_{CO_2,100\%}} = \frac{t}{35 \text{ yrs}}, t = 35 \text{ yrs} \frac{0.03\%}{100\%} = 0.0105 \text{ years} = 91.98 \text{ hr}$$

2. “A” and “B” represent mortar coating with  $\frac{\text{cement}}{\text{sand}} = \frac{1}{2}$  and  $\frac{1}{3}$ , respectively.

3. “X, Y, and Z” represent concrete specimen with designed strength 210, 245, and 280 kgf/cm<sup>2</sup>, respectively.

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

coating, the rank of the time required for subsidence is : (1) 20 mm, (2) 15 mm, and (3) 10 mm. Moreover, using Eq. (32) and taking the 35AX10 as the semi-infinite to composite medium,

the relationship between  $\frac{M_t}{C_s d}$  and  $\left(\frac{D_1 t}{d^2}\right)^{\frac{1}{2}}$  is shown in the

Fig. 2. This is true that the concrete specimen 35AX10 at large times has some sorption curves with different values of  $D_1/D_2$ . The purposed of sorption curve in Fig. 2 can be expressed as relationship between the total quantity penetrating the medium  $CO_2$  through unit area of the coating surface  $x = -d$  in time  $t$  and the cross-section-area of mortar coating in non-dimensional form. The physical meaning of sorption

curve in Fig. 2 is that the relationship between  $\frac{M_t}{C_s d}$  and

$\left(\frac{D_1 t}{d^2}\right)^{\frac{1}{2}}$  is varied directly as the increases of values of  $D_1/D_2$

due to the formation of  $CaCO_3$  in the pore solution.

#### IV. DISCUSSION

In the case of the theory mentioned above, some important concepts are needed to be pointed out. As we know, the exact analytical solutions, Eqs. (28) and (29), are obtained from the governing PDE Eqs. (1) and (2) associated with initial condition Eq. (3), discontinuous conditions Eqs. (4) and (5), and boundary conditions Eqs. (6) and (7). However, Carslaw and Jaeger (1959) and Poulsen and Majlbro (2006) did not write out Eqs. (3), (6) and (7). Crank (1975) did not put down Eq. (7). Without Eqs. (3), (6) and (7), we cannot obtain the exact analytical solutions (see Eqs. (28) and (29)). Crank (1975) and Poulsen and Majlbro (2006) wrote out

$$C_2(x, t) = \frac{2kC_s}{k+1} \sum_{n=0}^{\infty} \alpha^n \text{erfc} \left( \frac{(2n+1)d + kx}{2\sqrt{D_1 t}} \right) \quad (33)$$

which was changed from Carslaw and Jaeger (1959).

If we use Leibniz’s rule (Hildebrand, 1974)

**Table 2. Carbonation depth, compressive strength, diffusivity, and concentration gradient of 50A and 50B specimen sets.**

Specimen set	Carbonation depth <sup>a</sup> (mm)	Compressive strength <sup>b</sup> (kgf/cm <sup>2</sup> )	Diffusivity		Concentration gradient (Eq. (31))		
			Coating material $D_1$ (m <sup>2</sup> /s 10 <sup>-12</sup> )	Concrete $D_2$ (m <sup>2</sup> /s 10 <sup>-12</sup> )	$\frac{C_s}{\sqrt{\pi D_1 t}}$	$\left(\frac{D_2}{D_1}\right)^{\frac{1}{2}}$	$\left(\frac{D_2}{D_1}\right)^{\frac{1}{2}} \frac{C_s}{\sqrt{\pi D_1 t}}$
50AX10+	23.5	67.7	6.49	0.75	0.67	2.95	1.98
50AX15	11.5	125.3	4.18	0.51	0.83	2.87	2.38
50AX20	12.9	141.6	7.37	1.25	0.57	2.43	1.39
50AY10	22.6	151.2	1.52	0.06	0.85	4.85	0.80
50AY15	19.5	159.5	2.73	0.02	0.57	11.08	6.32
50AY20	22.1	160.8	3.02	0.03	0.60	10.01	5.96
50AZ10	21.4	155.3	4.41	2.76	0.61	1.26	0.77
50AZ15	18.9	162.7	1.71	0.04	0.99	6.45	6.42
50AZ20	20.4	171.5	4.40	0.04	0.68	10.56	7.13
50BX10	23.5	121.5	2.04	0.07	1.10	5.62	6.18
50BX15	21.5	97.9	1.43	0.02	1.24	8.37	10.37
50BX20	23.5	138.9	3.14	0.02	0.76	11.80	9.00
50BY10	19.3	127.9	6.01	0.62	0.52	3.11	1.62
50BY15	16.3	134.2	2.74	0.02	0.55	11.06	6.04
50BY20	16.1	154.0	2.68	0.02	0.71	10.46	7.39
50BZ10	21.5	158.6	1.68	0.11	0.89	3.87	3.46
50BZ15	16.9	170.4	2.04	0.14	0.92	3.76	3.47
50BZ20	21.0	166.0	5.49	0.01	1.21	26.50	31.97

<sup>a, b</sup> Experimental results were cited from Huang [6].

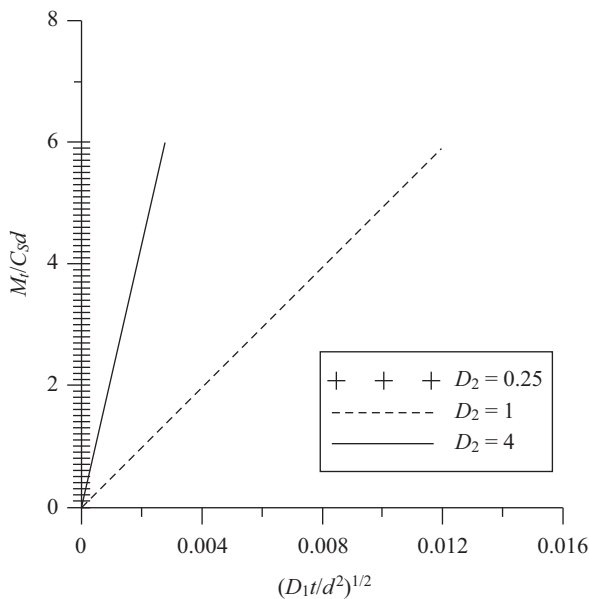
<sup>†</sup>: 1. “50” represents accelerated carbonation test for simulating 50 years.

$$\frac{C_{CO_2,air}}{C_{CO_2,100\%}} = \frac{t}{50yrs}, t = 50 yrs \frac{0.03\%}{100\%} = 0.0105 years = 131.4 hr$$

2. “A” and “B” represent mortar coating with  $\frac{cement}{sand} = \frac{1}{2}$  and  $\frac{1}{3}$ , respectively.

3. “X, Y, and Z” represent concrete specimen with designed strength 210, 245, and 280 kgf/cm<sup>2</sup>, respectively.

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



**Fig. 2. Sorption curves for a semi-infinite composite medium of 35AX10. Numbers on curves are values of  $D_1/D_2$ .**

$$\frac{d}{dx} \int_{\psi(x)}^{\phi(x)} f(t) dt = \int_{\psi(x)}^{\phi(x)} \frac{d}{dx} f(t) dt + f(\phi(x)) \frac{d\phi(x)}{dx} - f(\psi(x)) \frac{d\psi(x)}{dx} \quad (34)$$

and Eqs. (29) and (33) to be substituted into Eqs. (1)-(7) for checking the analytical solutions. It is actually failed. Obviously, Eq. (33) is really mistook. Further, Poulsen and Mejlbro (2006) wrote the governing PDE as

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D(x) \frac{\partial C}{\partial x} \right), \quad -d < x < 0, t > 0 \quad (35)$$

which is a non-linear PDE (Huang et al., 2012; Huang, 2013; Yodmalai et al., 2011) Nevertheless, Eqs. (1) and (2) are actually linear PDE.

Herein, it is also needed to be pointed out that Eqs. (3.57) and (3.58) in Crank (1975) are really not correct. They should be revised as

$$\frac{M_t}{C_s d} = \left( \frac{D_1 t}{\pi d^2} \right)^{\frac{1}{2}} \left\{ 1 + 2 \sum_{n=1}^{\infty} \alpha^n e^{-\frac{n^2 d^2}{D_1 t}} \right\} \quad (36)$$

and Eq. (32), respectively.

Eq. (31) denotes that concentration gradient shows the time required for subsidence due to the thickness of mortar coating

on the concrete specimen. The values of  $\left( \frac{D_2}{D_1} \right)^{\frac{1}{2}} \frac{C_s}{\sqrt{\pi D_1 t}}$  in

the Table 1 can strongly verify that the experimental data well present the verification of analytical solution while the values

of  $\left( \frac{D_2}{D_1} \right)^{\frac{1}{2}} \frac{C_s}{\sqrt{\pi D_1 t}}$  in the Table 2 cannot do. This reason may

be caused that the experimental data of Table 2 have an experimental deviation due to not good concrete specimen. It is needed to point out that the present theory is actually correct. In order to improve the defected trend occurred in Table 2, the potential way is more experimental programmes to be done.

Moreover, Fick's second law associated with initial and boundary conditions can be expressed as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad D = \text{constant} \quad (37a)$$

$$C(x, 0) = 0 \quad (37b)$$

$$C(0, t) = C_s \quad (37c)$$

$$C(x \rightarrow \infty, t) = 0 \quad (37d)$$

where  $C(x, t)$  is the  $CO_2$  concentration at depth  $x$  and time  $t$  and  $C_s$  is the  $CO_2$  concentration on the surface of concrete.

The solution of Eq. (37) for semi-infinite concrete (Crank, 1975) is

$$C(x, t) = C_s \left[ 1 - \text{erf} \left( \frac{x}{\sqrt{4Dt}} \right) \right] = C_s \text{erfc} \left( \frac{x}{\sqrt{4Dt}} \right) \quad (38)$$

where  $\text{erf}$  is the error function.

In general, Fick's second law is a good approximate of the  $CO_2$  penetration into concrete. Eq. (38) is suitable for predicting  $CO_2$  concentration profiles (i.e.,  $CO_2$  concentration as a function of concrete depth). This reason is due to the value of diffusivity ( $D$ ) of  $CO_2$  with a range from  $10^{-10}$  to  $10^{-14}$   $m^2/s$ . It is obvious that the value of diffusivity is very small. Alternatively, the rate of  $CO_2$  penetration into concrete is very slow. This means that  $CO_2$  concentration must vanish as  $x$  tends to infinity. As a result, we may use Eq. (38) to predict  $CO_2$  concentration profile with respect to concrete specimen with finite length. This notion can be extended for the semi-infinite composite medium stated as Eqs. (1), (2), and (3).

## V. CONCLUSIONS

Based on the theoretical investigation presented in this paper, the following conclusions may be made as follows:

1. The correct analytical solutions (see Eqs. (28) and (29)) of the two PDEs (Carslaw and Jaeger, 1959) (see Eqs. (1) and (2)) with initial condition (see Eq. (3)), discontinuous (interface) conditions (Carslaw and Jaeger, 1959; Crank, 1975; Poulsen and Mejlbro, 2006) (see Eqs. (4) and (5)), and boundary conditions (see Eqs. (6) and (7)) for a semi-infinite composite medium have been re-derived in this paper. The correct analytical solution of Eq. (28) to replace the Eq. (3.55) in Crank's book (1975) have also been pointed out in this article.
2. This paper has proposed the correct analytical solutions of Eqs. (36) and (32) to replace the Eq. of (3.57) and (3.58) and (7.44) and (7.45) in Crank's (1975) and Poulsen and Mejlbro's (2006) books, respectively. Eq. (36) for very large times is equivalent to Eq. (32). Based on Eq. (32), the

relationship between  $\frac{M_t}{C_s d}$  and  $\left( \frac{D_1 t}{d^2} \right)^{\frac{1}{2}}$  is called sorption

curve as shown in Fig. 2. The purpose of sorption curve can be expressed as relationship between the total quantity penetrating the medium  $CO_2$  through unit area of the coating surface  $x = -d$  in time  $t$  and the cross-section-area of mortar coating in non-dimensional form. The physical meaning of sorption curve is that the relationship between

$\frac{M_t}{C_s d}$  and  $\left( \frac{D_1 t}{d^2} \right)^{\frac{1}{2}}$  is varied directly as the increase of values of  $\frac{D_1}{D_2}$  due to the formation of  $CaCO_3$  in the pore solution. When  $k = 1$  and  $\alpha = 0$ , Eq. (3.58) in Crank's book

(1975) reduces to  $\frac{M_t}{C_s d} = 2 \left( \frac{D_1 t}{d^2} \right)^{\frac{1}{2}}$  while Eq. (32) of this

paper reduces to  $\frac{M_t}{C_s d} = \left( \frac{D_1 t}{d^2} \right)^{\frac{1}{2}}$ . When  $D_1 = 0$ , the coordinate of Fig. (3.8) in Crank's book (1975) is

$\left( \frac{M_t}{C_s d}, \left( \frac{D_1 t}{d^2} \right)^{\frac{1}{2}} \right) = \left( 0, -\frac{4\alpha}{1-\alpha^2} \right)$  whereas the coordinate of

Fig. 2 of this paper is  $\left( \frac{M_t}{C_s d}, \left( \frac{D_1 t}{d^2} \right)^{\frac{1}{2}} \right) = (0, 0)$ . It is particularly worth pointing out that the sorption curves of Fig. (3.8) in Crank's book (1975) are nonsensical when the values of  $D_2$  are equal to zero and infinite. Since Eq. (3.58) in Crank's book (1975) is wrong, the sorption curve as displayed in Fig. 3.8 in Crank's book (1975) is thus quite different from that of Fig. 2. Accordingly, the sorption



curve predicted by Eq. (3.58) in Crank's book (1975) is certainly of wrong consequence while the sorption curve predicted by Eq. (32) is actually of correct consequence.

3. Eq. (31) indicates that concentration gradient presents the time required for subsidence subjected to the thickness of mortar coating on the concrete specimen. The values of

$$\left(\frac{D_2}{D_1}\right)^{\frac{1}{2}} \frac{C_s}{\sqrt{\pi D_1 t}}$$

the experimental data well show the verification of ana-

lytical solution while the values of  $\left(\frac{D_2}{D_1}\right)^{\frac{1}{2}} \frac{C_s}{\sqrt{\pi D_1 t}}$  in the

Table 2 cannot do. This reason may be occurred that the experimental data of Table 2 have an experimental deviation due to not good concrete specimen. It is needed to point out that the present theory is certainly correct. In order to improve the defected trend occurred in Table 2, the potential method is more experimental works to be done.

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