



## STUDIES OF THE EFFECT OF DIFFUSION-INDUCED CHLORIDE BINDING ON CHLORINATION LIFE PREDICTIONS FOR EXISTING REINFORCED CONCRETE BRIDGES

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# STUDIES OF THE EFFECT OF DIFFUSION-INDUCED CHLORIDE BINDING ON CHLORINATION LIFE PREDICTIONS FOR EXISTING REINFORCED CONCRETE BRIDGES

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Key words: bridge, chloride binding, chlorinational life, Langmuir isotherm, Freundlich isotherm.

## ABSTRACT

The chloride ions diffusion is one of important factors of corrosion of reinforced concrete (RC) structures. The total chloride concentration penetrated into concrete can be expressed as the sum of bound and free chloride concentrations. The principal purpose of this paper is to study the chlorination life prediction of existing RC bridges due to chloride binding effect. The investigation method is that the no binding, linear binding, Langmuir and Freundlich adsorption isotherms are substituted into the analytical solutions of linear (diffusivity  $D = \text{constant}$ ) and non-linear ( $D \neq \text{constant}$ ) diffusion equations associated with initial and boundary conditions, respectively. The chlorination life can be calculated from the analytical solutions through the Mathematica software. These theoretical models are used to apply the existing Lin-bian and Dah-jin RC bridges in Taiwan. The results of the present study show that the Langmuir adsorption isotherms is suitable for bridge deck with small concrete cover while the linear binding is suitable for pier and abutment with large concrete cover. The studied results can be provided as a crucial reference for engineering decision-making for repair, strengthening or demolition of existing RC bridges.

## I. INTRODUCTION

Chloride-induced corrosion of reinforcing steel bars in concrete exposed to marine environments and de-icing salts used

in winter has become one of the principal causes of deterioration in many chief facilities made of reinforced concrete (RC) (e.g. bridge decks, piers, parking garages, off-shore platforms, etc.). The corrosion of the steel bars results in concrete fracture by way of cracking, delamination and spalling of the concrete cover, reduction of concrete and steel bars cross sections, loss of bond along the steel-concrete interface as well as reduction in strength and durability [2]. Accordingly, the safety and serviceability of RC structures are reduced.

Concrete is porous. The chloride ions in atmosphere from concrete surface through pore void into the interior concrete can be either physically and chemically bound to the cement hydrates and their surfaces (bound chlorides,  $C_b$ ), or dissolved in the pore solution (free chlorides,  $C_f$ ). Only the free chlorides dissolved in the pore solution are expected to account for initiating the process of corrosion [10], because it is in this condition that they continue to ingress through the concrete cover.

Sergi *et al.* [13] experimentally verified that the relationship between total chlorides ( $C_t$ ) and  $C_f$  and depth can be expressed by Fick's second law. They also verified that the Langmuir adsorption isotherm can be represented the relationship between  $C_b$  and  $C_f$ . Yu *et al.* [18] experimentally examined that the relationship between  $C_b$  and  $C_f$  expressed by the Langmuir adsorption isotherm may explain the effect of chloride binding on diffusion. They also verified that Fick's second law derived from Fick's first law and the principle of mass conservation may describe the diffusion characteristics of  $C_f$ . The magnitude of diffusivity of  $C_f$  in concrete not only can reflect the permeability of concrete but also can be used to predict the service life of concrete as the model is based on the corrosion of steel bar. Arya and Newman [1] studied the  $C_f$  content in concrete using extraction and analysis of pore fluid, leaching techniques, quantitative X-ray diffraction analysis, and empirical relationships. Tang and Nilsson [15] experimentally explored the chloride binding capacity by using cement paste and mortar specimen. They pointed out that the Freundlich adsorption isotherm expressed the relation of  $C_b$  and  $C_f$  at high  $C_f$  concentration (i.e.,  $> 0.01 \text{ mol/l}$ ) while the Langmuir adsorption isotherm expressed the relation of  $C_b$  and

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$C_f$  at low  $C_b$  concentration (i.e.,  $< 0.05$  mol/l). Martín-Pérez *et al.* [10] substituted four mathematical models, i.e., no binding, linear binding, Langmuir and Freundlich adsorption isotherms, into 1-D nonlinear Fick's second law and used the finite difference method to predict the service life of concrete specimen. Jheng [4] employed the Kirchhoff transformation associated with the Laplace transformation to obtain the analytical solution of the 1-D nonlinear Fick's second law with initial and boundary conditions. Using the same input data as Martín-Pérez *et al.*, the predicted results obtained from the analytical solution have difference from those of Martín-Pérez *et al.* calculated the approximate solution by the finite difference method. Lu *et al.* [10] obtained the relation  $C_t \cong 3C_f$  and  $D_t \cong 3D_f$ , in which  $D_t$  and  $D_f$  are the coefficients of diffusion of  $C_t$  and  $C_f$ , on the basis of the experiment of concrete specimen. Jeng [4] theoretically examined the exactly experimental results obtained by Lu *et al.* [9]. The literature mentioned above has not studied the effect of chloride binding on the service life prediction of existing RC bridges. This is a shortcoming. This article will conduct the effect of diffusion-induced chloride binding on chlorination life prediction for existing RC bridges.

The main aim of this paper is to use four mathematical models, i.e., no binding, linear binding, Langmuir and Freundlich adsorption isotherms substituting into the analytical solutions of linear (coefficient of diffusion  $D = \text{constant}$ ) and nonlinear ( $D \neq \text{constant}$ ) Fick's second law with initial and boundary conditions. In order to verify those feasible and reliable theoretical models, the existing Dah-jin and Lin-bian RC bridges in Taiwan are used as illustrative examples. For calculating the chlorination lives of bridge deck, pier and abutment of existing RC bridges, the commercial software "Mathematica" [17] is used as an algorithm tool. The results of present study may offer as an engineering reference of decision making for repair, strengthening or demolition for existing RC bridges.

## II. THEORETICAL MODEL

### 1. Linear Diffusion Equation

Provided that concrete is in a saturated state, chloride ions penetrate the concrete by ionic diffusion resulting from the existing concentration gradient between the exposed surface and the pore solution of the cement matrix. This process due to diffusion driving force is usually expressed by Fick's first law of diffusion [10]

$$J_c = -D_c w_e \frac{\partial C_f}{\partial x} = -\bar{D}_c \frac{\partial C_t}{\partial x} \quad (1)$$

where  $J_c$  is the flux of chloride ions due to diffusion,  $D_c$  is the effective diffusion coefficient when the concentration is represented in kilograms per cubic meter of concrete,  $\bar{D}_c$  is the effective diffusion coefficient when the concentration is expressed in kilograms per cubic meter of pore solution,  $w_e$  is the

evaporable water content ( $w_e = 0.8\%$  [10]), and  $C_f$  is the free chloride concentration at depth  $x$ .

Based on the concrete in a saturated situation, the mass conservation of chloride ions in concrete leads to

$$\frac{\partial C_t}{\partial t} = -\frac{\partial J_c}{\partial x} \quad (2)$$

where  $C_t$  is the total chloride concentration and  $t$  is the time.

The relationship among the total, bound, and free chloride concentrations in concrete can be expressed as

$$C_t = C_b + w_e C_f \quad (3)$$

where  $C_b$  is the concentration of bound chlorides.

Assume the effective diffusion coefficient,  $D_c$ , to be constant. Inserting Eqs. (1) and (3) into Eq. (2) and using chain rule, we obtain

$$\left(\frac{\partial C_b}{\partial C_f} + w_e\right) \frac{\partial C_f}{\partial t} = D_c w_e \frac{\partial^2 C_f}{\partial x^2} \quad (4)$$

where  $\partial C_b / \partial C_f$  is the binding capacity of the concrete binder [10]. Eq. (4) can be rewritten as

$$\frac{\partial C_f}{\partial t} = D_c^* \frac{\partial^2 C_f}{\partial x^2}, \quad D_c^* = \frac{D_c w_e}{\frac{\partial C_b}{\partial C_f} + w_e} = \frac{D_c}{1 + \frac{1}{w_e} \frac{\partial C_b}{\partial C_f}} \quad (5a)$$

where  $D_c^*$  is the apparent diffusion coefficient.

The associated with initial and boundary conditions of Eq. (5a) are

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

$$C_f(0, t) = C_0 \quad (5c)$$

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

where  $C_0$  is the chloride concentration on the concrete surface.

By applying the method of Laplace transform [12] to Eq. (5), the analytical solution of Eq. (5) [3] yields

$$C_f(x, t) = C_0 \operatorname{erfc}\left(\frac{x}{\sqrt{4D_c^* t}}\right) \quad (6)$$

where  $\operatorname{erfc}$  is the complementary error function.

### 2. Nonlinear Diffusion Equation

If the coefficient of diffusion,  $D_c$ , is not constant, then the substitution of Eq. (1) into Eq. (2) yields

$$\frac{\partial C_t}{\partial t} = \frac{\partial}{\partial x} (D_c w_e \frac{\partial C_f}{\partial x}) \quad (7)$$

Inserting Eq. (3) into Eq. (7), we have

$$\frac{\partial C_f}{\partial t} = \frac{\partial}{\partial x} (D_c^* \frac{\partial C_f}{\partial x}) \tag{8a}$$

where

$$D_c^* = \frac{D_c}{1 + \frac{1}{w_e} \frac{\partial C_b}{\partial C_f}} \tag{8b}$$

associated with initial and boundary conditions

$$C_f(x, 0) = 0 \tag{8c}$$

$$C_f(0, t) = C_0 \tag{8d}$$

$$C_f(x \rightarrow \infty, t) = 0 \tag{8e}$$

Using the Kirchoff transformation in conjunction with the Laplace transformation [14], the analytical solution of Eq. (8) can be obtained

$$\int_{C_R}^{C_f} D_c^*(C_f) dC_f = \int_{C_R}^0 D_c^*(C_f) dC_f + [\int_{C_R}^{C_0} D_c^*(C_f) dC_f - \int_{C_R}^0 D_c^*(C_f) dC_f] \operatorname{erfc}\left(\frac{x}{\sqrt{4D_c^*t}}\right) \tag{9}$$

where  $C_R$  is the any reference value of chloride concentration. For convenience, we may take  $C_R = 0$ . Thus, Eq. (9) can be rewritten as

$$\frac{\int_0^{C_f} D_c^*(C_f) dC_f}{\int_0^{C_0} D_c^*(C_f) dC_f} = \operatorname{erfc}\left(\frac{x}{\sqrt{4D_c^*t}}\right) \tag{10}$$

Eq. (10) provides the relationship among apparent diffusion coefficient  $D_c^*$ , free chloride concentration  $C_f$ , penetration depth  $x$ , and time  $t$ . The left side of Eq. (10) purely represents the area ratio between areas under the  $D_c^* - C_f$  curve from  $C_R = 0$  to  $C_f$  and  $C_R = 0$  to  $C_0$ , respectively.

**3. Chloride Binding Isotherm**

The chloride binding isotherm is defined as the described relationship between the bound and free chloride concentrations in concrete under a given temperature condition. Now a brief description is introduced in the following [10]:

- No binding

$$C_b = 0, \frac{\partial C_b}{\partial C_f} = 0, D_c^* = D_c \tag{11}$$

- Linear binding

$$C_b = \alpha C_f, \frac{\partial C_b}{\partial C_f} = \alpha, D_c^* = \frac{D_c}{1 + \frac{\alpha}{w_e}} \tag{12}$$

where  $\alpha$  is the binding capacity.

- Langmuir isotherm

$$C_b = \frac{\alpha C_f}{1 + \beta C_f}, \frac{\partial C_b}{\partial C_f} = \frac{\alpha}{(1 + \beta C_f)^2}, D_c^* = \frac{D_c}{1 + \frac{\alpha}{w_e(1 + \beta C_f)^2}} \tag{13}$$

where  $\alpha$  and  $\beta$  are the binding constants.

- Freundlich isotherm

$$C_b = \alpha C_f^\beta, \frac{\partial C_b}{\partial C_f} = \alpha \beta C_f^{\beta-1}, D_c^* = \frac{D_c}{1 + \frac{\alpha \beta}{w_e} C_f^{\beta-1}} \tag{14}$$

where  $\alpha$  and  $\beta$  are the binding constants.

Substituting the values of  $C_0$  and  $D_c^*$  represented by Eqs. (11)-(14) into Eqs. (6) and (10), we can obtain the free chloride concentrations at depth  $x$  and time  $t$  of the analytic solutions of linear and nonlinear diffusion equations, respectively.

**4. Fick's Second Diffusion Law**

First, Fick's second law of linear diffusion equation in a semi-infinite quasi homogeneous and isotropic concrete is used to state the free chloride concentration profile. This equation with initial boundary conditions can be expressed as [12]

$$\frac{\partial C_f}{\partial t} = D_f \frac{\partial^2 C_f}{\partial x^2}, D_f = \text{constant} \tag{15a}$$

$$C_f(x, 0) = 0 \tag{15b}$$

$$C_f(0, t) = C_{0f} \tag{15c}$$

$$C_f(x \rightarrow \infty, t) = 0 \tag{15d}$$

where  $C_{0f}$  is the free chloride concentration on the concrete surface.

Using the method of Laplace transform [12], the analytic solution [3] of Eq. (15) can be obtained

$$C_f(x, t) = C_{0f} \left[ 1 - \operatorname{erf}\left(\frac{x}{\sqrt{4D_f t}}\right) \right] = C_{0f} \operatorname{erfc}\left(\frac{x}{\sqrt{4D_f t}}\right) \tag{16}$$

where erf is the error function and erfc is the complementary error function.

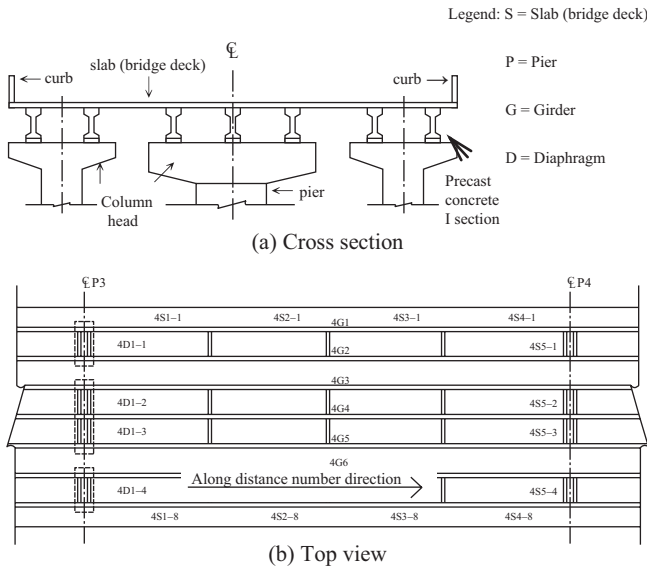


Fig. 1. Schematic diagram of component number system of the Lin-bian bridge.

Finally, Fick's second law of linear diffusion equation in a semi-infinite quasi-homogeneous and isotropic concrete is employed to describe the total chloride concentration profile. This equation with initial and boundary conditions can be put forward as

$$\frac{\partial C_t}{\partial t} = D_t \frac{\partial^2 C_t}{\partial x^2}, D_t = \text{constant} \quad (17a)$$

$$C_t(x, 0) = 0 \quad (17b)$$

$$C_t(0, t) = C_{0t} \quad (17c)$$

$$C_t(x \rightarrow \infty, t) = 0 \quad (17d)$$

In a similar way, the analytic solution of Eq. (17) can be stated as

$$C_t(x, t) = C_{0t} \left[ 1 - \operatorname{erf} \left( \frac{x}{\sqrt{4D_t t}} \right) \right] = C_{0t} \operatorname{erfc} \left( \frac{x}{\sqrt{4D_t t}} \right) \quad (18)$$

### III. ILLUSTRATIVE EXAMPLES

In order to verify the feasibility and reliability of the theories mentioned above, both the Lin-bian [5] and Dah-jin [6] bridges in Taiwan are used to do illustrative examples. Figs. 1 and 2 demonstrate the schematic diagram of component number system of both bridges. The results predicted from the analytic solution of Eqs. (6), (10), (16), and (18) can be calculated by the Mathematica software [17]. Tables 1 and 2 show the basic data of the Lin-bian and Dah-jin bridges, respectively. Inserting the relative parameters obtained from

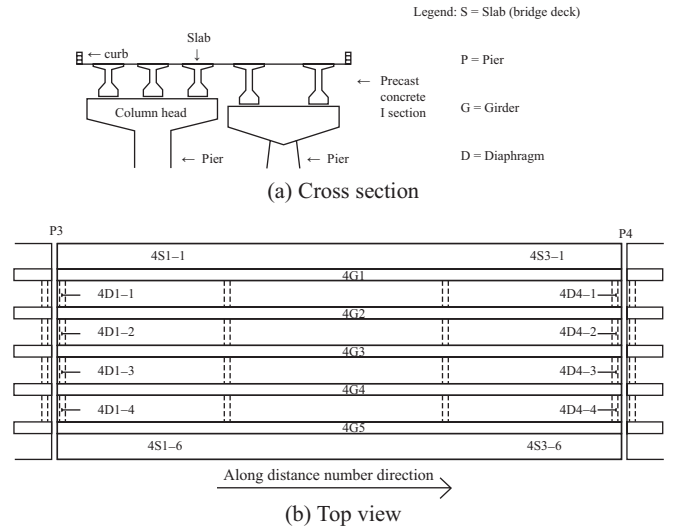


Fig. 2. Schematic diagram of Component number system of the Dah-jin bridge.

field measure of the two bridges into the analytical solutions of Eqs. (6), (10), (16) and (18), the service lives of the two bridges can be predicted by the Mathematica software.

Cored cylindrical specimens from abutment, pier, and bridge deck components of the existing Lin-bian and Dah-jin bridges in Taiwan and used acid-soluble method for determining chloride content, the concentration measured from the method is total chloride concentration. Lu *et al.* [9] pointed out that total chloride concentration is about 2.2~3.2 times free chloride concentration. In present study, the total chloride concentration is taken as 2.5 times the free chloride concentration. As to the effective coefficient of diffusion, Lu *et al.* [9] also pointed out that the total diffusivity of chloride concentration is 2.8 times the diffusivity of free chloride concentration. Arya and Newman [1] pointed out that both the surface chloride concentration and coefficient of diffusion can be predicted from the relation of chloride concentration versus chlorination depth under given service life. Since the relationship between chloride concentration and chlorination depth has not carried out by the Join Engineering Consultant Company [5, 6],  $C_f$  concentration, surface concentration ( $C_0$ ), effective coefficient of diffusion ( $D_c$ ),  $\alpha$  and  $\beta$  values used for four mathematical models are cited from Marín-Pérez *et al.* [10]. When  $D_c \neq$  constant, numerical simulation was adopted. That is, substituting the service life  $t$  obtained from Eq. (6) into Eq. (10), the relation of inconstant coefficient of diffusion, time and depth can be drawn after putting relative parameters into Eq. (10). As a result, the surface chloride concentrations and true diffusivity of the components such as bridge deck, pier and abutment of existing RC bridges can be obtained.

Tables 3 and 4 show the total and surface  $Cl^-$  concentrations and cover thickness of the existing Lin-bian and Dah-jin bridges, respectively. It is worthwhile to point out that the total  $Cl^-$  concentration are directly measured from concrete specimen cored from field. The  $C_f$  concentrations are

**Table 1. Overall structural condition of the Lin-bian bridge.**

Item	Description
Bridge site	This bridge is located between 274K+387.54 and 274K+846.54 of the 17 <sup>th</sup> line of provincial road in Taiwan, strides over the Lin-bian river, and connects the Lin-bian and Jia-dong countries.
Date of completed construction	This bridge was completed in April, 1976. The expanded engineering of single side was performed in October 1982.
Material strength	1. Plain concrete: 1:3:6 concrete 2. Reinforced concrete (RC): $fc' = 210 \text{ kgf/cm}^2$ 3. Prestressed concrete beam: $fc' = 350 \text{ kgf/cm}^2$ 4. Deformed steel : $f_y = 2800 \text{ kgf/cm}^2$ 5. Pre-stressed tendon: 12-7 mm $\Phi$ HTW (Girder used), 17-5 mm $\Phi$ HTW (Transverse diaphragm used), $f_y = 14500 \text{ kgf/cm}^2$ , $fs' = 16500 \text{ kgf/cm}^2$ (7 mm $\Phi$ ) $f_y = 15500 \text{ kgf/cm}^2$ , $fs' = 17500 \text{ kgf/cm}^2$ (5 mm $\Phi$ )
Concrete cover	1. Bridge deck: 2.9 cm 2. Balustrade: 2.0 cm 3. Beam and diaphragm: 3.3 cm 4. Pier: 7.5 cm 5. Abutment: 7.0 cm
Simply structural introduction	1. The superstructure is constructed by the inverse T-type beams of RC and is divided into 15 spans with total 459 m. The allocation of stridden length is 15@30.6 m. The width is 20 m after the expanded engineering. The thickness of bridge deck is 17 cm and is of 5 cm design friction layer. 2. The substructure is constructed by the single column RC pier and abutment with pile foundations.
Geological condition	Silty sand and clay.

**Table 2. Overall structural conditions of the Dah-jin bridge.**

Item	Description
Bridge site	This bridge is located at 25K+015 of the 27 <sup>th</sup> line of provincial road in Taiwan, strides over the Jwo-koon river and connects the Maw-lin and Kuo-shuh districts.
Date of completed Construction	This bridge was completed in June, 1981. The expanded engineering of single side was carried out in December, 1990.
Material strength	1. Reinforced concrete (RC) (abutment, pier, bridge deck, RC beam, retaining wall, balustrade, and diaphragm) $fc' = 210 \text{ kgf/cm}^2$ 2. Cassion: $fc' = 280 \text{ kgf/cm}^2$ 3. Deformed steel: $f_y = 2800 \text{ kgf/cm}^2$
Concrete cover	Bridge deck, balustrade, and breast wall of abutment: 2.5 cm Superstructure: 5.0 cm Substructure: 7.5 cm
Simply structural introduction	1. The superstructure is constructed by the inverse T-type beams of RC, divided into 10 spans with total length 248.89 m. The allocation of stridden length is 10@24.989 m (average). The original width of this bridge is 4.6 m while the width is 12.6 m after the expanded engineering. The thickness of bridge deck is 18 cm and is of 5 cm design friction layer. 2. The substructure is constructed by the cassion. The depths of P1-P4 and P6-P9 are 10 m where as the depth of P5 is 4.1 m.
Geological condition	Boulder and shale.

**Table 3. Cl<sup>-</sup> concentration and cover thickness of the Lin-bian bridge.**

Bridge member	Tested Points	Total Cl <sup>-</sup> concentration (% mass of concrete)	*Free Cl <sup>-</sup> Concentration (% mass of concrete)	Cover thickness c (mm)
Abutment	A1-1	0.0084	0.0034	70
	A2-1	0.0082	0.0033	70
	A2-2	0.0086	0.0034	70
Slab	1S4-8	0.0195	0.0078	29
	2S1-8	0.0168	0.0067	29
	S3	0.0070	0.0028	29
	S4	0.0096	0.0038	29
	S5	0.0082	0.0033	29
	S6	0.0071	0.0028	29
	S7	0.0052	0.0021	29
	S8	0.0073	0.0029	29
	S9	0.0074	0.0030	29
	S10	0.0047	0.0019	29
Pier	P1-1	0.0066	0.0026	75
	P1-2	0.0066	0.0026	75
	P1-3	0.0062	0.0025	75
	P2-1	0.0068	0.0027	75
	P2-2	0.0068	0.0027	75
	P2-3	0.0075	0.0030	75
	P12-1	0.0093	0.0037	75
	P12-2	0.0147	0.0059	75
	P12-3	0.0065	0.0026	75
	P12-3 Cap beam	0.0074	0.0030	75
	P13-1	0.0104	0.0042	75
	P13-2	0.0070	0.0028	75
	P13-2 Cap beam	0.0063	0.0025	75
	P13-3	0.0097	0.0039	75
	P14-1 Column	0.0067	0.0027	75
	P14-2 Column	0.0060	0.0024	75
	P14-3 Column	0.0062	0.0025	75
	P14-3 Cap beam	0.0070	0.0028	75

\* Free Cl<sup>-</sup> concentrations calculated from the relationship between the total and free Cl<sup>-</sup> concentrations suggested by Lu *et al.* [9].

**Table 4. Cl<sup>-</sup> concentration and cover thickness of the Dah-jin bridge.**

Bridge member	Tested Points	Total Cl <sup>-</sup> concentration (% mass of concrete)	*Free Cl <sup>-</sup> concentration (% mass of concrete)	Cover thickness c (mm)
Slab	5S3-2	0.0026	0.0010	25
	5S3-5	0.0018	0.0007	25
	6S1-5	0.0030	0.0012	25
Pier	P2-1 Column (1)	0.0033	0.0013	50
	P2-1 Column (2)	0.0033	0.0013	50
	P2-2 Column (1)	0.0093	0.0037	50
	P2-2 Column (2)	0.0063	0.0025	50
	P3-1 Column	0.0023	0.0009	50
	P3-1 Cap beam (1)	0.0023	0.0009	50
	P3-1 Cap beam (2)	0.0043	0.0017	50
	P3-2 Column	0.0103	0.0041	50
	P3-2 Cap beam (1)	0.0043	0.0017	50
	P3-2 Cap beam (2)	0.0033	0.0013	50
	P4-1 Column	0.0033	0.0013	50
	P4-1 Cap beam (1)	0.0033	0.0013	50
	P4-1 Cap beam (2)	0.0023	0.0009	50
	P4-2 Column	0.0083	0.0033	50
	P4-2 Cap beam (1)	0.0033	0.0013	50
	P4-2 Cap beam (2)	0.0033	0.0013	50
	P5-1 Cap beam (1)	0.0053	0.0021	50
	P5-1 Cap beam (2)	0.0033	0.0013	50
	P5-2 Cap beam (1)	0.0033	0.0013	50
	P5-2 Cap beam (2)	0.0023	0.0009	50
	P6-1 Cap beam (1)	0.0033	0.0013	50
	P6-1 Cap beam (2)	0.0033	0.0013	50
	P6-2 Column	0.0033	0.0013	50
	P6-2 Cap beam (1)	0.0043	0.0017	50
	P6-2 Cap beam (2)	0.0033	0.0013	50

\* Free Cl<sup>-</sup> concentrations calculated from the relationship between the total and free Cl<sup>-</sup> concentrations suggested by Lu *et al.* [9].



**Table 5. The requirement substitution parameters of calculation chlorination life for the Lin-bian bridge under total chloride with constant diffusivity.**

Bridge member	Mathematical model	Total chloride					
		Surface Cl concentration $C_0$ (% mass of concrete)	Total Cl concentration $C_t^*$ (% mass of concrete)	True diffusivity $D_{ct}$ (mm <sup>2</sup> /year)	Cover thickness $c$ (mm)	$\alpha$	$\beta$
Abutment	Fick's 2nd diffusion law	0.05763	0.00842	88.3008	70	-----	-----
	No binding	0.05763	0.00842	88.3008	70	-----	-----
	Linear binding	0.05763	0.00842	88.3008	70	0.2177	-----
	Langmuir isotherm	0.05763	0.00842	88.3008	70	1.1160	0.3407
	Freundlich isotherm	0.05763	0.00842	88.3008	70	1.0254	0.36
Slab	Fick's 2nd diffusion law	0.05763	0.00929	88.3008	29	-----	-----
	No binding	0.05763	0.00929	88.3008	29	-----	-----
	Linear binding	0.05763	0.00929	88.3008	29	0.2177	-----
	Langmuir isotherm	0.05763	0.00929	88.3008	29	1.1160	0.3407
	Freundlich isotherm	0.05763	0.00929	88.3008	29	1.0254	0.36
Pier	Fick's 2nd diffusion law	0.05763	0.00767	88.3008	75	-----	-----
	No binding	0.05763	0.00767	88.3008	75	-----	-----
	Linear binding	0.05763	0.00767	88.3008	75	0.2177	-----
	Langmuir isotherm	0.05763	0.00767	88.3008	75	1.1160	0.3407
	Freundlich isotherm	0.05763	0.00767	88.3008	75	1.0254	0.36

\* The value of  $C_t$  (% mass of concrete) of each member is the average of  $C_t$  (% mass of concrete) listed in Table 3.

**Table 6. The requirement substitution parameters of calculation chlorination life for the Lin-bian bridge under free chloride with constant diffusivity.**

Bridge member	Mathematical model	Free chloride					
		Surface Cl concentration $C_0$ (% mass of concrete)	Free Cl concentration $C_f^*$ (% mass of concrete)	True diffusivity $D_{cf}$ (mm <sup>2</sup> /year)	Cover thickness $c$ (mm)	$\alpha$	$\beta$
Abutment	Fick's 2nd diffusion law	0.05763	0.00337	31.536	70	-----	-----
	No binding	-----	-----	-----	-----	-----	-----
	Linear binding	0.05763	0.00337	31.536	70	0.2177	-----
	Langmuir isotherm	0.05763	0.00337	31.536	70	1.1160	0.3407
	Freundlich isotherm	0.05763	0.00337	31.536	70	1.0254	0.36
Slab	Fick's 2nd diffusion law	0.05763	0.00372	31.536	29	-----	-----
	No binding	-----	-----	-----	-----	-----	-----
	Linear binding	0.05763	0.00372	31.536	29	0.2177	-----
	Langmuir isotherm	0.05763	0.00372	31.536	29	1.1160	0.3407
	Freundlich isotherm	0.05763	0.00372	31.536	29	1.0254	0.36
Pier	Fick's 2nd diffusion law	0.05763	0.00307	31.536	75	-----	-----
	No binding	-----	-----	-----	-----	-----	-----
	Linear binding	0.05763	0.00307	31.536	75	0.2177	-----
	Langmuir isotherm	0.05763	0.00307	31.536	75	1.1160	0.3407
	Freundlich isotherm	0.05763	0.00307	31.536	75	1.0254	0.36

\* The value of  $C_f$  (% mass of concrete) of each member is the average of  $C_f$  (% mass of concrete) listed in Table 3.

calculated by using of the multiple relation formula of  $C_f$  and  $C_t$  suggested by Lu *et al.* [9].

In the case of Eq. (6), the value of  $D_{cf} = 1.0 \times 10^{-12}$  m<sup>2</sup>/s is cited from Mart'in- Pérez *et al.* [10]. Mart'in-Pérez *et al.* [10] obtained the value of  $D_{cf}$  in concrete samples by chloride binding mechanism. While the value of  $D_{ct} = 2.8 \times 10^{-12}$  m<sup>2</sup>/s is obtained from the relation formula of  $D_{ct} = 2.8 D_{cf}$  which was established by Lu *et al.* [9] through the test results of

concrete samples using an electrochemical method. Thus, the requirement substitution parameters of calculation chlorination life for the Lin-bian bridge under total and free chloride with constant diffusivity were obtained and listed in Tables 5 and 6, respectively. In the same way, we gained the requirement substitution parameters of calculation chlorination life for the Dah-jin bridge under total and free chloride with constant diffusivity and listed in Tables 7 and 8, respectively.

**Table 7. The requirement substitution parameters of calculation chlorination life for the Dah-jin bridge under total chloride with constant diffusivity.**

Bridge member	Mathematical model	Total chloride					
		Surface Cl <sup>-</sup> concentration C <sub>0</sub> (% mass of concrete)	Total Cl <sup>-</sup> concentration C <sub>t</sub> * (% mass of concrete)	True diffusivity D <sub>cl</sub> (mm <sup>2</sup> /year)	Cover thickness c (mm)	α	β
Slab	Fick's 2nd diffusion law	0.01130	0.00244	88.3008	25	----	----
	No binding	0.01130	0.00244	88.3008	25	----	----
	Linear binding	0.01130	0.00244	88.3008	25	0.2195	----
	Langmuir isotherm	0.01130	0.00244	88.3008	25	1.1252	0.3442
	Freundlich isotherm	0.01130	0.00244	88.3008	25	1.0251	0.36
Pier	Fick's 2nd diffusion law	0.01130	0.00421	88.3008	50	----	----
	No binding	0.01130	0.00421	88.3008	50	----	----
	Linear binding	0.01130	0.00421	88.3008	50	0.2195	----
	Langmuir isotherm	0.01130	0.00421	88.3008	50	1.1252	0.3442
	Freundlich isotherm	0.01130	0.00421	88.3008	50	1.0251	0.36

\* The value of C<sub>t</sub> (% mass of concrete) of each member is the average of C<sub>t</sub> (% mass of concrete) listed in Table 4.

**Table 8. The requirement substitution parameters of calculation chlorination life for the Dah-jin bridge under free chloride with constant diffusivity.**

Bridge member	Mathematical model	Free chloride					
		Surface Cl <sup>-</sup> concentration C <sub>0</sub> (% mass of concrete)	Free Cl <sup>-</sup> concentration C <sub>f</sub> * (% mass of concrete)	True diffusivity D <sub>cl</sub> (mm <sup>2</sup> /year)	Cover thickness c (mm)	α	β
Slab	Fick's 2nd diffusion law	0.01130	0.00097	31.536	25	----	----
	No binding	----	----	----	----	----	----
	Linear binding	0.01130	0.00097	31.536	25	0.2195	----
	Langmuir isotherm	0.01130	0.00097	31.536	25	1.1252	0.3442
	Freundlich isotherm	0.01130	0.00097	31.536	25	1.0251	0.36
Pier	Fick's 2nd diffusion law	0.01130	0.00097	31.536	50	----	----
	No binding	----	----	----	----	----	----
	Linear binding	0.01130	0.00097	31.536	50	0.2195	----
	Langmuir isotherm	0.01130	0.00097	31.536	50	1.1252	0.3442
	Freundlich isotherm	0.01130	0.00097	31.536	50	1.0251	0.36

\* The value of C<sub>f</sub> (% mass of concrete) of each member is the average of C<sub>f</sub> (% mass of concrete) listed in Table 4.

**Table 9. The requirement substitution parameters of calculation chlorination life for the Lin-bian bridge under total chloride with inconstant diffusivity.**

Bridge member	Mathematical model	Total chloride					
		Surface Cl <sup>-</sup> concentration C <sub>0</sub> (% mass of concrete)	Total Cl <sup>-</sup> concentration C <sub>t</sub> (% mass of concrete)	True diffusivity D <sub>c</sub> (mm <sup>2</sup> /year)	Cover thickness c (mm)	α	β
Abutment	Fick's 2nd diffusion law	----	----	----	----	----	----
	No binding	0.05763	0.0085603	88.32429	70	----	----
	Linear binding	0.05763	0.0085356	88.32612	70	0.2177	----
	Langmuir isotherm	0.05763	0.0085169	99.41740	70	1.1160	0.3407
	Freundlich isotherm	0.05763	0.0093304	632.63408	70	1.0254	0.36
Slab	Fick's 2nd diffusion law	----	----	----	----	----	----
	No binding	0.05763	0.0093347	88.30216	29	----	----
	Linear binding	0.05763	0.0093247	88.25759	29	0.2177	----
	Langmuir isotherm	0.05763	0.0093238	100.55114	29	1.1160	0.3407
	Freundlich isotherm	0.05763	0.0094925	630.03178	29	1.0254	0.36
Pier	Fick's 2nd diffusion law	----	----	----	----	----	----
	No binding	0.05763	0.0078492	88.32579	75	----	----
	Linear binding	0.05763	0.0077893	88.32662	75	0.2177	----
	Langmuir isotherm	0.05763	0.0077717	98.41307	75	1.1160	0.3407
	Freundlich isotherm	0.05763	0.0089234	634.91610	75	1.0254	0.36

**Table 10. The requirement substitution parameters of calculation chlorination life for the Lin-bian bridge under free chloride with inconstant diffusivity.**

Bridge member	Mathematical model	Free chloride					
		Surface Cl <sup>-</sup> concentration C <sub>0</sub> (% mass of concrete)	Free Cl <sup>-</sup> concentration C <sub>f</sub> (% mass of concrete)	True diffusivity D <sub>cf</sub> (mm <sup>2</sup> /year)	Cover thickness c (mm)	$\alpha$	$\beta$
Abutment	Fick's 2nd diffusion law	----	----	----	----	----	----
	No binding	----	----	----	----	----	----
	Linear binding	0.05763	0.0033986	31.55062	70	0.2177	----
	Langmuir isotherm	0.05763	0.0033982	33.11662	70	1.1160	0.3407
	Freundlich isotherm	0.05763	0.0117489	232.33051	70	1.0254	0.36
Slab	Fick's 2nd diffusion law	----	----	----	----	----	----
	No binding	----	----	----	----	----	----
	Linear binding	0.05763	0.0037391	31.55027	29	0.2177	----
	Langmuir isotherm	0.05763	0.0037377	33.28019	29	1.1160	0.3407
	Freundlich isotherm	0.05763	0.010942	231.79375	29	1.0254	0.36
Pier	Fick's 2nd diffusion law	----	----	----	----	----	----
	No binding	----	----	----	----	----	----
	Linear binding	0.05763	0.0030977	31.55116	75	0.2177	----
	Langmuir isotherm	0.05763	0.0030974	32.97695	75	1.1160	0.3407
	Freundlich isotherm	0.05763	0.0124603	232.80677	75	1.0254	0.36

**Table 11. The requirement substitution parameters of calculation chlorination life for the Dah-jin bridge under total chloride with inconstant diffusivity.**

Bridge member	Mathematical model	Total chloride					
		Surface Cl <sup>-</sup> concentration C <sub>0</sub> (% mass of concrete)	Free Cl <sup>-</sup> concentration C <sub>f</sub> (% mass of concrete)	True diffusivity D <sub>ct</sub> (mm <sup>2</sup> /year)	Cover thickness c (mm)	$\alpha$	$\beta$
Slab	Fick's 2nd diffusion law	----	----	----	----	----	----
	No binding	0.01130	0.0024501	88.44942	25	----	----
	Linear binding	0.01130	0.0024502	88.43674	25	0.2195	----
	Langmuir isotherm	0.01130	0.0024491	91.64305	25	1.1252	0.3442
	Freundlich isotherm	0.01130	0.0024721	655.36454	25	1.0251	0.36
Pier	Fick's 2nd diffusion law	----	----	----	----	----	----
	No binding	0.01130	0.0042661	88.32368	50	----	----
	Linear binding	0.01130	0.0042396	88.32613	50	0.2195	----
	Langmuir isotherm	0.01130	0.0042388	93.87821	50	1.1252	0.3442
	Freundlich isotherm	0.01130	0.0042606	647.17176	50	1.0251	0.36

Inserting the values of  $D_c$ ,  $C_f$ ,  $w_e$ ,  $\alpha$  and  $\beta$  as listed in Tables 5-8 into Eqs. (11)-(14), we can calculate  $D_c^*$ . Putting the values of  $C_0$ ,  $C_f$ ,  $D_c^*$  and  $x = c$  ( $c =$  cover thickness), the chlorination lives of components of existing RC bridges under  $D_c =$  constant can be found.

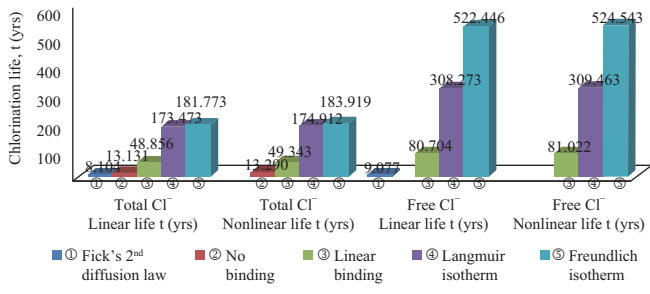
When the values of  $D_c$  is inconstant, the numerical simulation technique should be adopted and has been mentioned above. Tables 9 and 10 indicate the requirement substitution parameters of calculation chlorination life for the Lin-bian bridge under total and free chloride with inconstant diffusivity, respectively. Tables 11 and 12 depict the requirement substitution parameters of calculation chlorination life for the Dah-jin bridge under total and free chloride with inconstant diffusivity, respectively. Substituting the values of  $D_c$ ,  $C_f$ ,  $w_e$ ,  $\alpha$  and  $\beta$  as listed in Tables 9-12 into Eqs. (11)-(14), we may

find  $D_c^*$ . Inserting the values of  $C_0$ ,  $C_f$ ,  $D_c^*$  and  $x = c$  into Eq. (10), the chlorination lives of components of existing RC bridges under  $D_c \neq$  constant can be found.

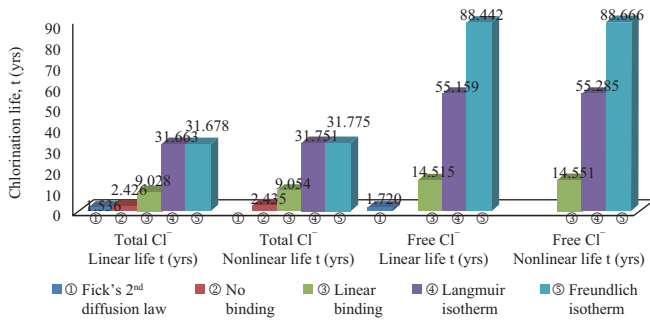
Using the four mathematical models of chloride binding isotherm and employing Eqs. (6), (10), (16) and (18), the chlorination lives of the components of the existing Lin-bian and Dah-jin bridges were predicted as shown in Figs. 3 and 4, respectively. In such measure as free chloride, the abutment and pier of the Lin-bian bridge have chlorination lives 80 and 88 years predicted by the linear binding while the bridge deck of the Lin-bian bridge has chlorination life 55 years predicted by the Langmuir isotherm as shown in Fig. 3. The pier of the Dah-jin bridge has 71 years calculated by the linear binding whereas the bridge deck of the Dah-jin bridge has 50 years calculated by the Langmuir isotherm as sketched in Fig. 4.

**Table 12. The requirement substitution parameters of calculation chlorination life for the Dah-jin bridge under free chloride with inconstant diffusivity.**

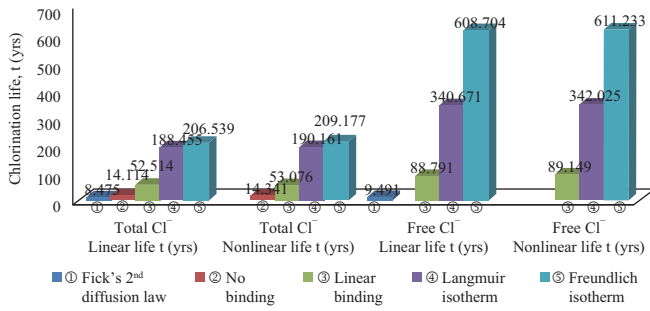
Bridge member	Mathematical model	Free chloride					
		Surface Cl <sup>-</sup> concentration C <sub>0</sub> (% mass of concrete)	Free Cl <sup>-</sup> concentration C <sub>f</sub> (% mass of concrete)	True diffusivity D <sub>ef</sub> (mm <sup>2</sup> /year)	Cover thickness c(mm)	α	β
Slab	Fick's 2nd diffusion law	----	----	----	----	----	----
	No binding	----	----	----	----	----	----
	Linear binding	0.01130	0.0009741	31.45935	25	0.2195	----
	Langmuir isotherm	0.01130	0.0009738	31.91282	25	1.1252	0.3442
	Freundlich isotherm	0.01130	0.0017859	237.13848	25	1.0251	0.36
Pier	Fick's 2nd diffusion law	----	----	----	----	----	----
	No binding	----	----	----	----	----	----
	Linear binding	0.01130	0.0016916	31.48521	50	0.2195	----
	Langmuir isotherm	0.01130	0.0016914	32.27226	50	1.1252	0.3442
	Freundlich isotherm	0.01130	0.0017630	235.35112	50	1.0251	0.36



(a) Abutment

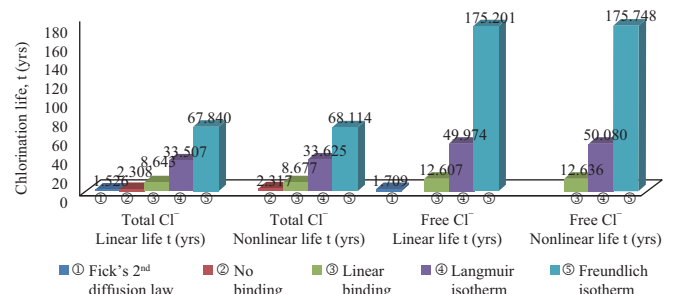


(b) Slab

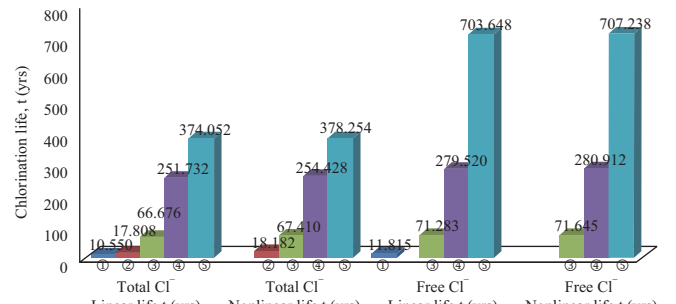


(c) Pier

**Fig. 3. Chlorination life predictions for the different binding isotherms and different Cl<sup>-</sup> concentrations and considering two different diffusivities D<sub>e</sub><sup>\*</sup> = Constant and D<sub>e</sub><sup>\*</sup> ≠ constant for the Lin-bian bridge exposed to the environmental condition with 0.05763 (% mass of concrete) of Cl<sup>-</sup>.**



(a) Slab



(b) Pier

**Fig. 4. Chlorination life predictions for the different binding isotherms and different Cl<sup>-</sup> concentrations and considering two different diffusivities D<sub>e</sub><sup>\*</sup> = constant and D<sub>e</sub><sup>\*</sup> ≠ constant for the Dah-jin bridge exposed to the environmental condition with 0.01130 (% mass of concrete) of Cl<sup>-</sup>.**

## IV. DISCUSSION

### 1. Definition of Total Service Life and Degree of Deterioration

The deterioration process of RC structures subjected to corrosion media attack is depicted in Fig. 5 [7, 8, 16]. The corrosion process in Fig. 5 is considered as three stages,

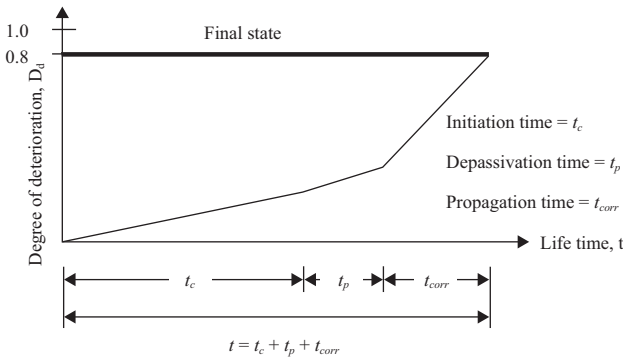


Fig. 5. Deterioration process of reinforced concrete structures due to corrosion.

initiation time ( $t_i = t_c$ ), depassivation time ( $t_p$ ), and corrosion (or propagation) time ( $t_{corr}$ ). The initiation time is defined as the time for chloride ions to penetrate from the concrete surface to the surface of the passive film. The depassivation time is defined as depassivation normally provided to the steel bars by the alkaline hydrated cement matrix is destroyed locally leading to pitting corrosion. The corrosion time extends to from the time when corrosion products form to the stage where they generate sufficient stress to disrupt the concrete cover by cracking or spalling, or when local attack on the reinforcement becomes sufficiently severe to impair its load-carrying capacity. Thus, the total service life of RC structure can be represented as [7]

$$t = t_c + t_p + t_{corr} \tag{19}$$

It is worthy to point out that the corrosion time ( $t_{corr}$ ) is defined up to degree of deterioration  $D_d = 0.8$  (see Fig. 5). This value of  $D_d$  is chosen just for the conservation to structural safety. The  $D_d$  can be defined as

$$D_d = 1 - \frac{I}{100} \tag{20}$$

where  $I$  stands for the integrity of RC structures. For instance, if RC structure is very integrated, i.e.,  $I = 100$ , then  $D_d = 0$ . If RC structure is collapsed, i.e.,  $I = 0$ , then  $D_d = 1$ . As  $t_{corr} = \frac{1}{4} t_c$  and  $t_p = 10$  years [8], Eq. (15) may be predicted the total chlorination lives for the existing RC bridges.

**2. Linear Diffusion Equation**

In the case of linear binding, the Lin-bian bridge has  $t_{max} = 121$  years and  $t_{min} = 29$  years predicted from Eq. (6). In sofar as linear binding, the Dah-jin bridge has  $t_{max} = 100$  years and  $t_{min} = 26$  years calculated from Eq. (6).

Because the coefficient of diffusion in concrete actually varies with depth and time due to hydration, service life of bridge predicted by  $D_c \neq \text{constant}$  is better than that of  $D_c = \text{constant}$ . than that of  $D_c = \text{constant}$ . Accordingly, assume that

the nonlinear life is correct. As to the larger chlorination life, the reason is caused that the  $t_c$  time may be increased due to abutment and pier with more thickness of concrete cover. Table 13 summarizes percentage errors of chlorination lives predicted by linear and nonlinear diffusion equations for the Lin-bian and Dah-jin bridges. It is worthwhile to notice that the percentage error ranking from small to large describes as follows: Langmuir isotherm, linear binding, Freundlich isotherm and no binding under total and free chlorides conditions. It is also noted from Table 13 that the percentage errors predicted by total chlorides are larger than those of free chlorides. Only the free chlorides are dissolved in the pore solution of concrete and continued to penetrate through the concrete cover. Consequently, it is reasonable that the chlorination life prediction may be used by the free chlorides.

**3. Nonlinear Diffusion Equation**

In the case of Langmuir isotherm, the Lin-bian bridge has  $t_{max} = 438$  years and  $t_{min} = 79$  years predicted from Eq. (10). In sofar as Langmuir isotherm, the Dah-jin bridge has  $t_{max} = 361$  years and  $t_{min} = 73$  years calculated from Eq. (10). Table 13 and Figs. 3 and 4 show that the Langmuir isotherm is very suitable for predicting the bridge deck with small concrete cover by the nonlinear diffusion model (see Eq. (10)) due to free chlorides diffusion. As to abutment and pier with larger concrete cover, the mathematical model of linear binding is a suitable prediction method.

Moreover, Eq. (12) is very proper for calculating the coefficient of diffusion in the more thicker concrete cover. However, the Freundlich isotherm is not fitting for calculating the coefficient of diffusion in the concrete cover with larger thickness. This reason may be that the effective coefficient of diffusion predicted by Eq. (14) may be reduced and the chlorination life prediction may be increased. From Table 13 and Figs. 3 and 4, we know that the mathematical model of no binding is the worst one due to only posing total chloride diffusion.

**4. Other Factors**

It was worthwhile to notice that some piers among the 12th and 20th of the Dah-jin bridge subjected to debris flow occurred from the typhoon Morakot on August 8, 2009 in Taiwan had been collapsed. However, they will be soon rehabilitated for keeping transportation flow.

**V. CONCLUSIONS**

In this paper, four mathematical models of chloride binding isotherm substituting into the analytical solutions of linear and nonlinear diffusion equations associated with initial and boundary conditions have been described. These theories also have been applied to predicting the chlorination lives of the components of the existing Lin-bian and Dah-jin bridges in Taiwan. After this investigation, some important conclusions may be drawn as follows:

**Table 13. Percentage errors of chlorination life predicted by linear to nonlinear diffusion equations for the Lin-bian and Dah-jin bridges.**

Bridge member	Mathematical model	Lin-bian bridge		Dah-jin bridge	
		*Percentage error (%)		Percentage error (%)	
		Total chloride	Free chloride	Total chloride	Free chloride
Abutment	No binding	1.214	-----	-----	-----
	Linear binding	0.997	0.394	-----	-----
	Langmuir isotherm	0.830	0.386	-----	-----
	Freundlich isotherm	1.181	0.401	-----	-----
Slab	No binding	0.387	-----	0.407	-----
	Linear binding	0.285	0.245	0.396	0.232
	Langmuir isotherm	0.277	0.229	0.351	0.212
	Freundlich isotherm	0.306	0.253	0.404	0.312
Pier	No binding	1.605	-----	2.100	-----
	Linear binding	1.070	0.403	1.101	0.508
	Langmuir isotherm	0.905	0.397	1.071	0.498
	Freundlich isotherm	1.277	0.415	1.123	0.510

$$* \text{ Percentage error (\%)} = \frac{\text{linear life} - \text{nonlinear life}}{\text{nonlinear life}} \times 100.$$

1. The difference of chlorination lives predicted by the linear and nonlinear diffusion models for the existing RC bridges is very small. The percentage errors of chlorination lives predicted by the linear and nonlinear diffusion models used free chlorides for the existing RC bridges are less than those of total chlorides. The chlorination life predicted by free chlorides is more suitable than that of total chlorides.
2. The chlorination life forecasted by the nonlinear diffusion model is better than that of linear diffusion model. Generally speaking, the constant value of coefficient of diffusion used is just for convenient. In fact, the coefficient of diffusion is dependent on time and space.
3. The ranking from small to large of percentage error of linear to nonlinear diffusion model is Langmuir isotherm, linear binding, Freundlich isotherm and no binding.
4. The chlorination lives of abutment and pier with larger concrete cover of existing RC bridges are suitably predicted by the mathematical model of linear binding while the chlorination life of bridge deck with small concrete cover of existing RC bridge is properly predicted by the mathematical model of Langmuir isotherm.
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