# Prediction of Chloride Profile considering Binding of Chlorides in Cement Matrix

**Ha-Won Song[†], Chang-Hong Lee, and Ki Yong Ann**

*School of Civil and Environmental Engineering, Yonsei University, Seoul 120-749, Republic of Korea*

Chloride induced corrosion of steel reinforcement inside concrete is a major concern for concrete structures exposed to a marine environment. It is well known that transport of chloride ions in concrete occurs mainly through ionic/molecular diffusion, as a gradient of chloride concentration in the concrete pore solution is set. In the process of chloride transport, a portion of chlorides are bound in cement matrix then to be removed in the pore solution, and thus only the rest of chlorides which are not bound (i.e. free chlorides) leads the ingress of chlorides. However, since the measurement of free/bound chloride content is much susceptible to environmental conditions, chloride profiles expressed in total chlorides are evaluated to use in many studies In this study, the capacity of chloride binding in cement matrix was monitored for 150 days and then quantified using the Langmuir isotherm to determine the portions of free chlorides and bound chlorides at given total chlorides and the redistribution of free chlorides. Then, the diffusion of chloride ion in concrete was modeled by considering the binding capacity for the prediction of chloride profiles with the redistribution. The predicted chloride profiles were compared to those obtained from conventional model. It was found that the prediction of chloride profiles obtained by the model has shown slower diffusion than those by the conventional ones. This reflects that the prediction by total chloride may overestimate the ingress of chlorides by neglecting the redistribution of free chlorides caused by the binding capacity of cement matrix. From the evaluation, it is also shown that the service life prediction using the free chloride redistribution model needs different expression for the chloride threshold level which is expressed by the total chlorides in the conventional diffusion model.

*Keywords : concrete structures; corrosion; chloride profile; binding capacity; service life prediction*

## 1. Introduction

Chloride attack is a major cause of corrosion of steel in concrete. Chloride ions may penetrate the concrete cover from external environment such as seawater or deicing salts or be present in the original mix materials including admixtures ($CaCl_2$; accelerator), and contaminated aggregates.[1)-2)] In addition, an important process in the initiation of corrosion is the transport of chloride. The chloride transport process includes the chloride binding mechanism which contains both bound chloride ion and free chloride ion.[3)-5)]

The degree of chloride binding is influenced by the elements of the concrete, the composition of the pore solution, and the external environment. The most important factor is considered to be the quantity of the tricalcium aluminate ($C_3A$) phase in the cementitious binder.[5)] However, a number of recent advanced studies in modeling the transport

of chloride ions have resulted from a theoretical treatment of the effects of chloride binding.[6)-7)] It is evident that chloride binding depends on various environmental conditions or chemical reactions in concrete, which means that quantification of chloride profile is very difficult work. Thus, it is simple to use free chloride profile for evaluation of chloride profile.

Nowadays, Glass and Buenfeld[8)] attempt a prediction of chloride profile using three levels of $C_3A$ content. In their research, chloride profile was described as total, free, bound chloride using Langmuir isotherm. However, their research suggests only one diffusion coefficient, by assuming that the relation of $C_3A$ content and diffusion coefficient in the pore structures was independent each other. However, the variation of $C_3A$ has a different pore structure in the cement matrix, then in fact, it is related to different diffusion coefficient. Meanwhile, Perez et al.[9)] also attempt a prediction of free chloride profile using linear isotherm, no binding isotherm and Freundlich binding isotherm, respectively. However, in their research, it is ig-

nored that the $C_3A$ content in chemical compositions, the isotherm effect according to curing age was not considered either. In addition, they attempt to predict corrosion initiation time without using the binding isotherm and using linear binding isotherm with non-realistic values. Moreover, chloride threshold value (CTL) was assumed that 0.09% (by weight of binder) (5.0 kg/m$^3$), which is non-comprehensible value.

In this study, chloride binding dissolution is represented by the redistribution of free chloride concentration. Moreover, in order to quantify the effects of the binding capacity of cement matrix on prediction of chloride profile, redistribution of free chlorides has been modeled using experimental data on the binding capacity. Then, the chloride binding capacity was examined, using ordinary Portland cement (OPC) paste, by measuring the binding capacity at total chlorides ranging from 0.1 to 3.0% at 7, 28, 60 and 150 days, respectively. Finally, a model utilizing the redistribution of free chloride is proposed and discussed.

## 2. Chloride binding isotherm

### 2.1 Experiments

In this study, experiment was executed by the binding behavior with curing age. Specimen was used only cement paste using ordinary Portland cement, was cast in the cube moulds (100×100×200 mm) at 0.4 of a free W/C. Cement composition is described in Table 1. To make specimen, age variables were set to 7, 28, 60, 150 days, to minimize the experimental error, made a three same sample. Moreover, set the nine levels of chloride (0.1, 0.2, 0.3, 0.5, 1.0. 1.5, 2.0, 2.5, 3.0 % of cement weight), measuring the free chloride concentration purpose of binding capacity measurement.

After 1 day curing, demoulding was conducted. Then, to prevent water-evaporation, wrapping was accomplished using polythene film. The next step was specimen curing at 20±1 °C condition, to avoid a leaching out of chloride and hydroxyl ions from cement matrix, which may take place in an open-wet curing. The specimens were dried in oven at 100 °C for 24 h to avoid a loss of the residues of alkalis and chlorides in powder-sampling. Then, crushed and ground to obtain dust samples, which was then sieved

into the 300 μm sieve in fineness. Collected dust sample was stirred for 5 min in distilled water at 50 °C to extract "water-soluble chloride (i.e. free chloride)," and stood for 30 min. Then, the sample was filtered through a filtering paper, then to measure the concentration of free chloride ions, using the potentiometric titration against silver nitrate. Finally, total chloride contents was already known, thus it is easy to calculate the bound chloride content using subtraction.

### 2.2 Chloride binding isotherm

The concentration of chloride ion measured in ppm from extraction water was converted into a percentage to the weight of binder. The subtraction of the concentration of water soluble (free) chloride ion from total chloride was taken as the content of bound chloride. Fig. 1 shows the chloride binding isotherms of OPC pastes at 7, 28, 60 and 150 days respectively. The fitted lines describe the relation between free and bound chloride using the Langmuir isotherm as given in Eqn. (1).

$$C_b = \frac{\alpha C_f}{1 + \beta C_f} \tag{1}$$

where, $C_b$ is the content of bound chloride, $C_f$ is the content of free chloride, $\alpha$ and $\beta$ are constants.

It is shown that chloride binding of pastes increases as the curing age increased from 7 to 150 days. At 7 days, the binding capacity was very marginal, accounting for about 0.5-0.6% to 3.0% of total chlorides. While, at 7, 28 and 60days, isotherm were largely different with that at 150days. i.e., early age binding capacity (bound chloride/total chloride) was calculated by just 22%, however, 150days binding capacity was by 64%. Therefore, it is noted that the binding behavior was much stabled after 150 days curing.

## 3. Model for chloride transport

### 3.1 Diffusion process and model

When concrete is in saturated state, chloride ions enter the concrete by ionic diffusion due to the existing concentration gradient between the exposed surface and the pore solution of the cement matrix (diffusion driving force).

**Table 1. Oxide composition of binders**

|  | CaO | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | MgO | Na$_2$O | K$_2$O | Mn$_2$O$_3$ | TiO$_3$ | SO$_3$ | Ign.* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| OPC | 64.7 | 20.7 | 4.6 | 3.0 | 1.0 | 0.13 | 0.65 | - | - | 3.0 | 1.30 |

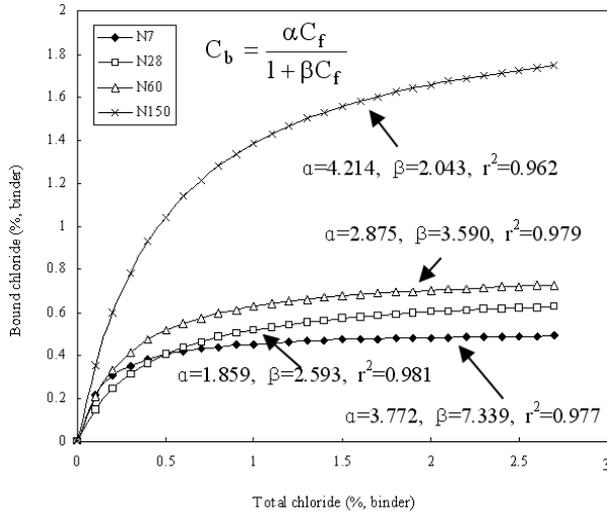*: Ignition loss

$$C_b = \frac{\alpha C_f}{1 + \beta C_f}$$

**Fig. 1.** Chloride binding capacity of OPC at different curing age

This process is often described by Fick's $2^{nd}$ law of diffusion. The Fick's $2^{nd}$ law is usually expressed as Eqn. (2), which is used for a solution of the diffusion with no binding often encountered for chloride transport in concrete.

$$C(x,t) = C_S[1 - erf\frac{x}{2\sqrt{Dt}}] \qquad (2)$$

Where
D = Diffusion coefficient
t = Time of exposure
C(x,t) = Chloride concentration at depth $x$ after time $t$
$C_S$ = Surface chloride concentration
erf = Error function

The characteristic material property D describes the ability of transfer at a given substance. If concrete is homogeneous, D and $C_S$ are constant with time, and the chlorides do not react with cement matrix so that the ratio of chloride binding is constant. The model using the Eqn. (2) is commonly used in determining the chloride transport in concrete.

In many cases, the transfer of mass is superimposed by mechanisms other than random motion of molecules such as surface flow of condensed gas along pore walls or saturated capillary flow due to surface forces. In porous solids, for example, moisture may flow as the diffusion of water vapor, at the same time non-saturated or even saturated capillary flow may occur in finer pores. Although additional transport mechanisms are acting as explained, the Fick's law of diffusion may also be applied to quantify

the multiple transport phenomena. The diffusion is the primary mechanism of chloride transport in concrete where there is no applied electric field and where the moisture condition of the concrete pore structure is stable. A concentration gradient is then considered as the common driving force. The diffusion coefficient D, however, may depend strongly on the local concentration of free ions or molecules. In inhomogeneous solids, the coefficient D may depend on location of the ions or molecules. Therefore the diffusion is the process by which ions or molecules move from place of higher concentration to that of lower concentrations.

With the Fick's $2^{nd}$ law on the governing equation, our main concern is the prediction of service life or remaining life concrete structures, then it is true that one of judgments for the service life prediction is a corrosion initiation. It is the fact that the initiation of steel corrosion depends on free chlorides on pore solution in cement matrix, then the free chloride affects a corrosion mechanism and chloride ion transport. However, it is true that previous chloride prediction models[10)-14)] just use total chlorides and their profiles, even it is known that the steel corrosion is only affected by free chloride.

Eqn. (2) would perfectly describe the diffusion of chlorides in a completely saturated homogenous material having a constant diffusion coefficient and when no other chemical reactions with chloride ions would occur. This is not the case for chloride penetration in concrete structures. In order to evaluate service life prediction with the free chloride profile, we have to evaluate the binding capacity of cement matrix from experiments, which are not trivial. This means that, in the case of experiments, the first step is coring from structure, but the core has limitation. In the process of chloride extraction, if thickness of the slice was too small, they are affected by carbonation and water content of concrete. On the other hand, if a core specimen is obtained from cutting with big size, they are not practical. Generally, the pore press method is accurate to extract free chloride ion from large specimens, Thus, the prediction of free chloride profile using pore press method was not practical in real RC structures.

In this study, we evaluate the prediction of chloride profile using the 7, 28, 60, 150 days curing isotherm of the OPC pastes. Each isotherm data is divided from a total chloride into free chloride and bound chloride. Then, we would like to find a way to predict the service life based on the free chlorides.

### 3.2 Free chloride redistribution model

This proposed model is based on binding theory with an assumption that only free chloride affects steel corro-

sion overcomes the limitation of the aforementioned deterministic model (Eqn. (2)). We propose a model so called redistribution free chloride diffusion model. For the model, the prediction of the actual distribution of chloride concentration at any given depth or time utilizes Langmuir isotherm Eqn. (1) and the Fick's law, Eqn. (2),

$$(C_f + C_b) = C_S[1 - \text{erf}\frac{x}{2\sqrt{Dt}}] \qquad (4)$$

where $C_f$, $C_b$, $C_s$, erf, t and D mean the free chloride concentration, bound chloride concentration, surface chloride concentration (as total chloride content), error function, time of exposure, diffusion coefficient, respectively.

Since $C_b$ can be rewritten only with $C_f$ term, Eqn. (4) becomes Eqn. (5) as with the Langmuir isotherm, Eqn. (1).

$$(C_f + \frac{\alpha C_f}{1 + \beta C_f}) = C_S[1 - \text{erf}\frac{x}{2\sqrt{Dt}}] \qquad (5)$$

where $\alpha$, $\beta$ are experimental coefficients from the Langmuir isotherm. According to Eqn. (5), $C_f$ can be obtained as a function,

$$C_f = Z[C_S[1 - \text{erf}\frac{x}{2\sqrt{Dt}}]] \qquad (6)$$

where Z is transposition function contain simultaneous equations.

Eqn. (6) can be rewritten with the information on the redistribution of free chlorides, where, $C_{f'}$ is redistributed free chlorides and $C_{fb}$ is redistributed bound chlorides and $C_{sf}$ is free chloride of Cs. For example, in order to calculate the initial $C_{sf}$ value, the $C_{sf}$ was calculated using 0.1 mm cover depth.

$$C_f = (C_{f'} + C_{fb}) = Z[C_{sf}[1 - \text{erf}\frac{x}{2\sqrt{Dt}}]] \qquad (7)$$

By applying the Langmuir isotherm again, we obtain the Eqn. (8) and Eqn. (9).

$$C_f = (C_{f'} + \frac{\alpha' C_{f'}}{1 + \beta' C_{f'}}) = Z[C_{sf}[1 - \text{erf}\frac{x}{2\sqrt{Dt}}]] \qquad (8)$$

$$C_{f'} = \gamma[C_{Sf}[1 - \text{erf}\frac{x}{2\sqrt{Dt}}]] \qquad (9)$$

It is shown that the Eqn. (9) is only redistribution using

the transposition equation, where, $\gamma$ is a re-transposition function containing simultaneous equations.

In order to consider the inherent physical uncertainty of parameters in Eqn. (9), we consider variables on Cs, D and t, respectively. It is worthwhile to note that, for the free chloride model, Perez et al.[9] and Glass and Buenfeld.[8] attempt prediction using free chloride profile, however, we go further to consider redistribution of free chloride.

## 4. Results and discussion

Table 2 shows the explanation of case for the analysis such as the N-①-②-③ which used for the analytical cases. Fig. 2(a) describes the relation between free and total chloride contents. The surface chloride, service life, apparent diffusion coefficient are assumed to be 2.5%/m³, 10year, 2.0*10⁻¹² m²/s, (i.e. Cs=2.5%/m³, t=10year and D=2.0*10⁻¹² m²/s), Note that Fig. 1 showed an OPC binding capacity at 7, 28, 60 and 150 days, respectively.

The chloride penetration to cover concrete is presented separately by free and bound chlorides. The binding capacity increases with chloride penetration through a concrete cover. Thus, if the free chlorides mainly drive chloride transport, the bounding capacity depends on the time to ingress of the chlorides.

Fig. 2(b) describes the free chloride profile according to different ionic diffusivity, D=2.0*10⁻¹¹ m²/s, 2.0*10⁻¹² m²/s and 2.0*10⁻¹³ m²/s, Cs=2.5%/m³, t=10year, as a result, with an increase of diffusion coefficient, the chloride ingress by the free chlorides was also increased. Fig. 2(c) shows exposure effect of chloride profile. By an increase of exposure time, their chloride ingress was also increased. Fig. 2(d) shows the Cs effect of chloride profiles. Fig. (2) show that the free chloride profiles is almost same shape of the total chloride profiles.

Fig. 3 shows chloride profiles obtained from the free chloride redistribution model in this study. Fig. (3) shows that chloride ingress is slow if we consider the redistribution of free chlorides.

Fig. 4 shows free chloride profiles and their redistribution profiles with curing ages. It is noted that, as increase of curing age, binding capacity is also increased. Thus, free chloride contents by the redistribution can be decreased so that the corrosion risk is also decreased, so that the service life of concrete structures is increased.

Fig. 5 shows the chloride profiles after 30years as a total, free and redistribution free chlorides after 30years, when surface chloride and apparent diffusion coefficient are assumed to 2.5%/m³ and 2.0*10⁻¹² m²/s, (i.e. Cs= 2.5%/m³ and D=2.0*10⁻¹² m²/s). Each chloride concen-

**Table 2. Explanation of abbreviated symbols**

| Contents | Explanation | | Abbreviation |
|---|---|---|---|
| Binder | OPC | | N |
| Curing age | 7 days curing isotherm | ① | 7 days |
| | 28 days curing isotherm | | 28 days |
| | 60 days curing isotherm | | 60 days |
| | 150 days curing isotherm | | 150 days |
| Chloride type | Total chloride profile | ② | Total |
| | Free chloride profile | | Free |
| | Bound chloride profile | | Bound |
| | Redistribution free chloride profile | | Redistribution |
| Analytical variable | Time (year) | ③ | 1 year |
| | | | 10 year |
| | | | 100 year |
| | Diffusion coefficient(m$^2$/s) ($2.0*10^{-11}$ to $2.0*10^{-13}$) | | D11 |
| | | | D12 |
| | | | D13 |
| | Surface chloride ion(%/m$^3$) (1.5 to 3.5) | | S1.5 |
| | | | S2.5 |
| | | | S3.5 |



(a)

(b)

(c)

(d)
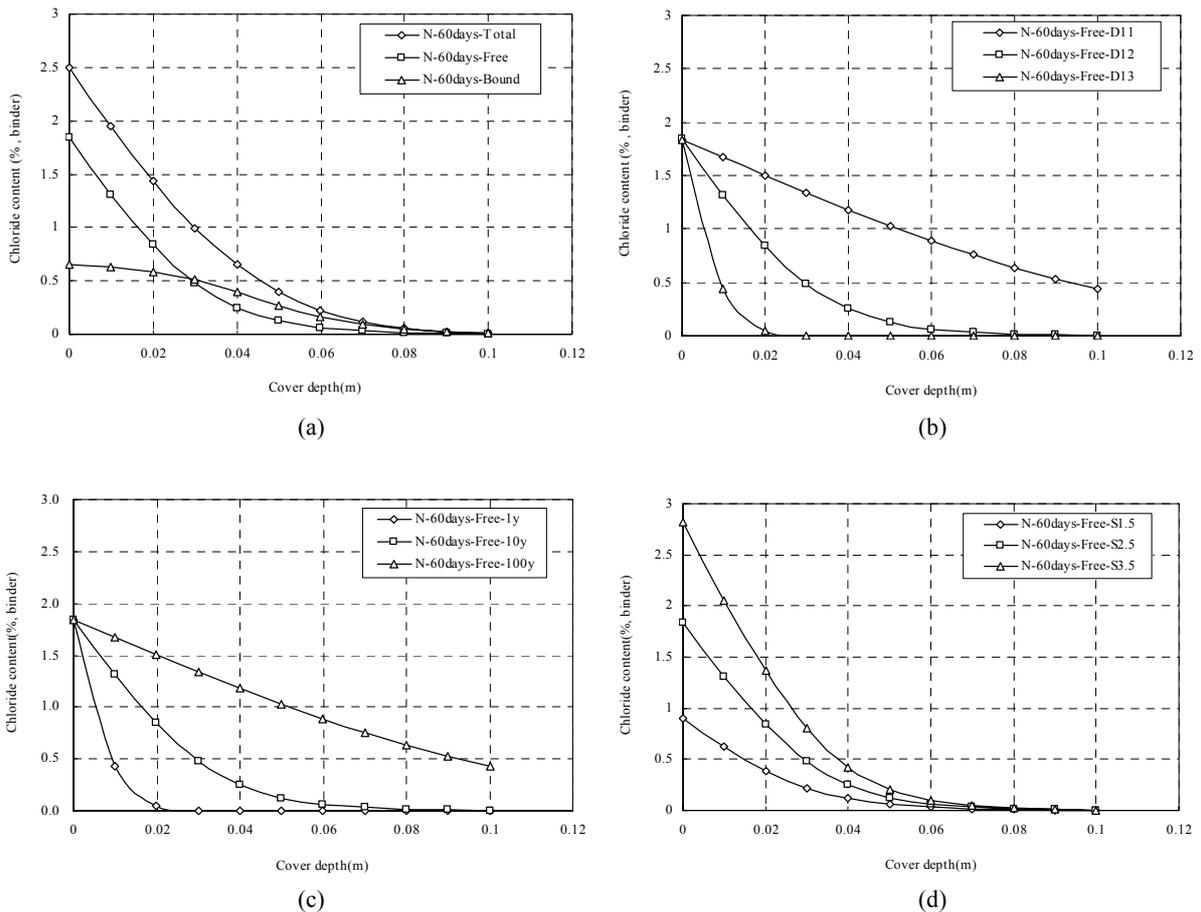
**Fig. 2.** Chloride profiles in OPC according to different D, t and Cs.
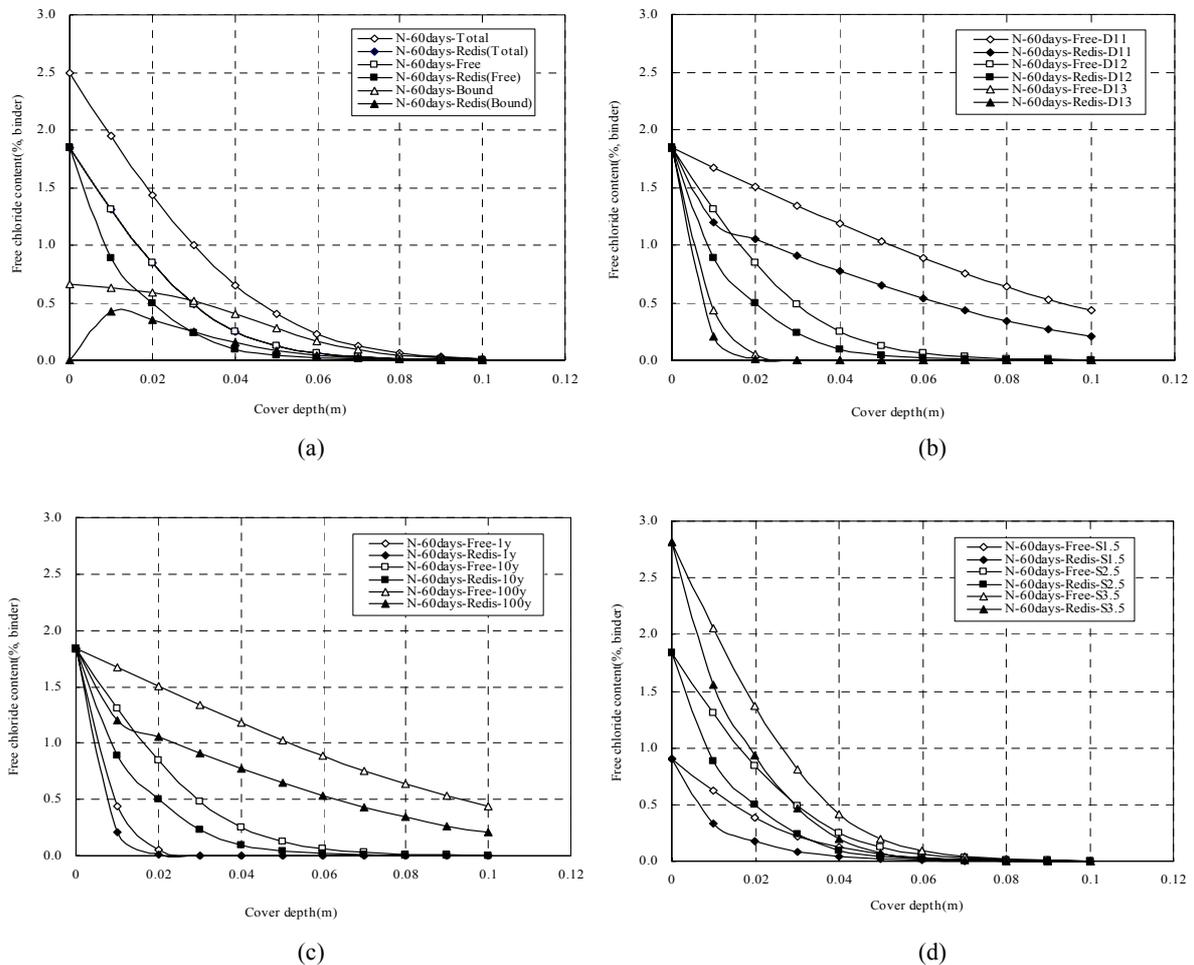
**Fig. 3.** Redistribution chloride profiles in OPC with redistribution of free chlorides.

trations (i.e. total, free and redistribution free chlorides) are calculated by 1.29, 0.721 and 0.4, at 40 mm cover depth. Thus, conversion rate of each concentration was calculated by 3.225 : 1.803 : 1. (i.e. total chloride concentration: free chloride concentration : redistribution free chloride concentration) Moreover, both total and free chlorides conversion rates is calculated by 1.789 : 1. The difference in the rates shows that the CTL by the total chloride content, which is 0.4 (% of cement weight) of BS 8110,[15] should be set differently for that by free chloride ions and the redistribution.

Fig. 6 shows corrosion initiation profiles at 6.4years of chloride penetration when total chlorides reach 0.4% of cement weight at rebar surface at 40 mm cover depth. It is also shown that the CTL which is located with about 40mm cover depth for free chloride without and with redistribution are not the 0.4, but 0.125 and 0.039, respectively for same chloride exposure. Thus, the CTL should be set with different values when we use the free

chloride profiles for the service life prediction.

## 5. Conclusions

This study evaluates binding capacity of ordinary Portland cement concrete and proposes a model to consider redistribution of free chlorides utilizing chloride binding capacity. The conclusions of this study are as follows:

1) This study obtained binding isotherms, from experiments at 7, 28, 60 and 150 days, which applied to the prediction of chloride profile. By increase of curing age, binding capacity is increased and redistribution of free chloride profile occurs. Then, a chloride prediction model is proposed to consider free chloride and the redistribution of free chloride.

2) Prediction by total and free chlorides showed that chloride ingresses also increased with increase of the surface chloride concentration, diffusion coefficient and time of exposure. It is noted that the binding capacity is also
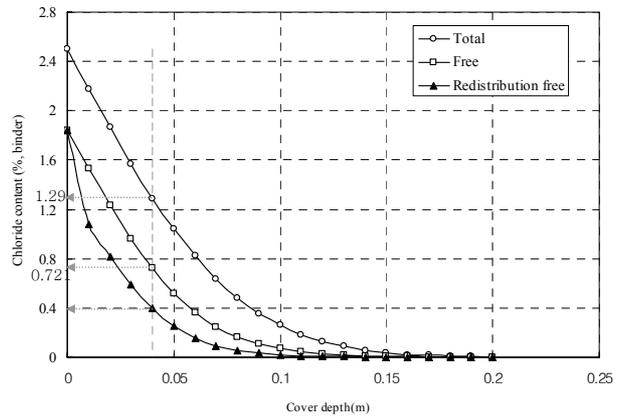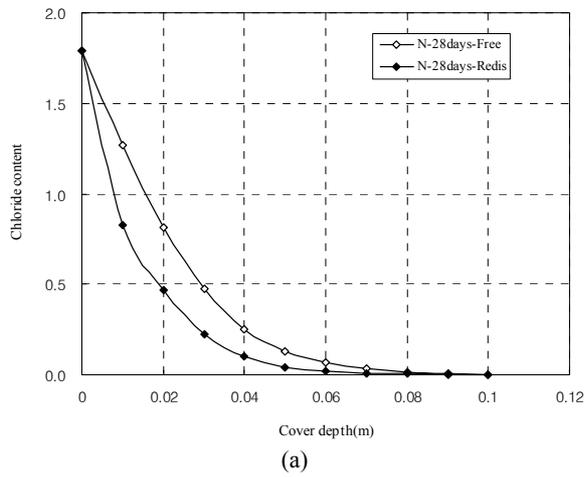
(a)



(b)



(c)

**Fig. 4.** Chloride profiles in OPC paste with different age



**Fig. 5.** Comparison of chloride profiles after 30years as a total, free and redistribution free chlorides
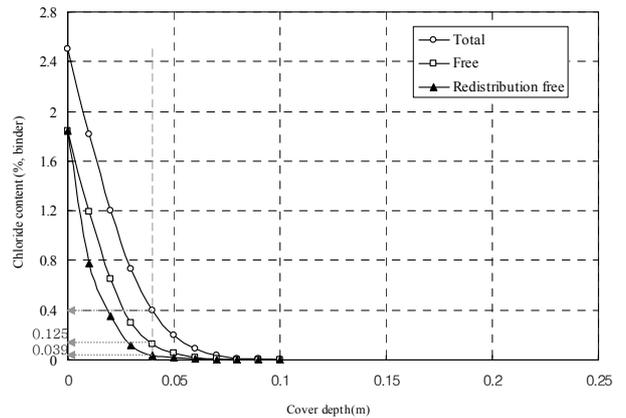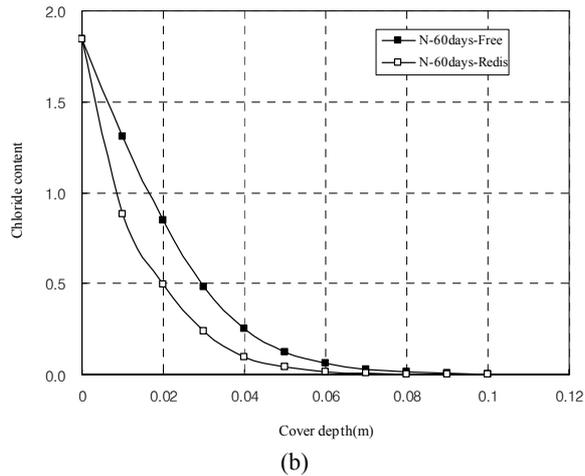


**Fig. 6.** Chloride profiles for corrosion initiation
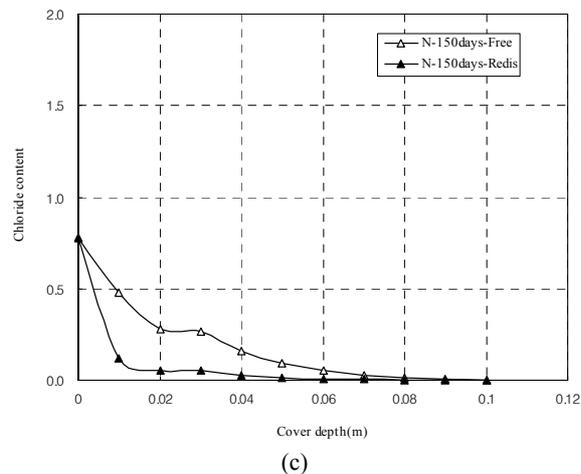
ing the profiles with a CTL value specified in concrete standards. It is shown that the corrosion prediction by the free chloride redistribution model should use different chloride threshold value than that by the total chlorides for the service life prediction.

## Acknowledgments

increased with curing. Therefore, with increased curing age, the free chlorides contents to ingress are decreased so that the corrosion risk is decreased.

3) This study evaluates the time to corrosion by comparing

## References

1. J. Tritthard, *Cem Concr Res*, **19**, 586 (1989).
2. M. Castellote, C. Andrade, and C. Alonso, *Cem Concr Res*, **29**, 1799 (1999).
3. S. E. Hussain, Rasheeduzzafar, A. S. Al-Gahtani, *Cem Concr Res*, **24**, 8 (1994).

4. O. Amiri, H. Friedmann, A. Ait-Mokhtar, *Mag Concr Res*, **58**, 93 (2006).
5. M. Jirickova and R. Cerny, *J. Build Physics*, **29**, 189 (2006).
6. P. Arora, B. N. Popov, B. Haran, M. Ramasubramanian, S. Popova, R. E. White, *Corr Sci*, **39**, 739 (1997).
7. M. D. A. Thomas and P. B. Bamforth, *Cem Concr Res*, **29**, 487 (1999).
8. G. K. Glass and N. R. Buenfeld, *Corr Sci*, **42**, 329 (2000).
9. B. Martin-Perez, H. Zibara, R. D. Hooton, and M. D. A. Thomas, *Cem Concr Res*, **30**, 1215 (2000).
10. S. Engelund and J. D. Sorensen, *Structural Safety*, **20**, 69 (1998).
11. R. B. Polder and W. H. A. Peelen, *Cem Concr Comp* **24**, 427 (2002).
12. M. K. Kassir and M. Ghosen, *Cem Concr Res*, **32**, 139 (2002).
13. P. Arora, B. N. Popov, B. Haran, M. Ramasubramanian, S. Popova, R. E. White, *Corr Sci*, **39**, 739 (1997).
14. S. Erdogud, I. L. Kondratova, and T. W. Bremner, *Cem Concr Res*, **34**, 603 (2004).
15. British Standard 8110: part 1, Structural use of concrete-code of practice for design and construction, *British Standard Institute*, London UK. (1985).