Chloride Transport in Concrete Structures Exposed to Marine Environments Considering Time Dependent Characteristics

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ABSTRACT

The present study surveyed published data on chloride transport in concrete structures exposed to a marine environment for the duration ranging from 1 to 49 years. In particular, time-dependent characteristics of the diffusion coefficient \( D \) and surface chloride concentration \( C_S \) were extensively investigated for the prediction of the ingress of chlorides. As a result, it was found that both \( D \) and \( C_S \) are time dependent; \( D \) decreases and \( C_S \) increases with time. A build-up of the \( C_S \) was considered to solve the Fick’s 2nd law and the time dependency of the \( D \) was applied to the solution for the chloride ingress, and then chloride profiles were comparably predicted, using both time dependent and time independent models. From the comparison, the chloride profiles calculated by the time dependent model are always higher than those by the time independent model. Consequently, the time dependent model predicts shorter service life which is the shorter time to corrosion initiation of rebar. It was found that decreased \( D \) with time is more influencing on the rate of chloride ingress than the increased \( C_S \). It was also found that the conventional model, utilizing constant values of \( D \) and \( C_S \) may underestimate the rate of chloride transport and thus predict less risk of chloride-induced corrosion.

KEYWORDS

Concrete structures, Marine environments, Corrosion, Diffusion coefficient, Surface chloride concentration

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1 INTRODUCTION

The assessment of chloride-induced corrosion of steel embedment in concretes exposed to marine environments has received increasing attention, because of its widespread occurrence and high cost of repair. Corrosion of steel in concrete reduces the service life of concrete structures, and thus the service life should be predicted by comparison between the amount of chloride concentration at cover depth by chloride transport and chloride threshold value [Song et al. 2006a]. In the majority of previous studies on the service life prediction, a conservative chloride threshold value for corrosion initiation such as 0.2 or 0.4% by weight of cement has been used to predict the service life [Ann & Song 2007]. For chloride transport, the Fick’s 2nd law is often used to predict chloride penetration in terms of diffusion [Collepardi et al. 1972], due to its convenient and easy calculation with constant values of the apparent diffusion coefficient ($D$) and surface chloride concentration ($C_S$), which are in fact dependent on concrete mix proportion and exposure condition to a salt environment (eg. submerged, tidal, splash and aerated zones in marine environments) [Song et al. 2007a]. The diffusivity decreasing with time due to development of the pore structure with time has been currently considered in assessing the rate of chloride transport [Thomas & Bentz 2000, Bamforth 1999]. Due to the hypothesis that chloride ions and surface concrete make a chemical equilibrium in the form of dielectric layer, the time dependency of the $C_S$ has been intuitively ignored in conventional chloride transport model, so that a constant value of the $C_S$ has been widely used in modeling chloride transport. Only when concrete structures are exposed to a marine atmospheric condition, a build-up of the $C_S$ has been taken into account [Kassir & Ghosn 2002]. It was, however, observed in a survey on in-situ that a build-up of the $C_S$ occurs, even when concretes are exposed to direct contact to seawater such as in tidal/splash zones [Uji et al. 1990].

The present study examined 6 concrete bridges located in the West Sea side of Korea exposed to tidal zone, where data on the $D$ and $C_S$ were obtained. These data were fitted as a function of time, and used in modelling to predict chloride profiles and the corrosion risk of concrete structures exposed to marine environments. The characteristic of a $C_S$ build-up was considered in solving the Fick’s 2nd law and the time dependency of the diffusivity was subsequently applied for the solution of the chloride ingress in concrete.

2 TIME DEPENDENCY OF CHLORIDE TRANSPORT

In this study, 6 concrete bridges exposed to marine environments were examined to assess the rate of chloride transport, depending on exposure duration. The bridges at ages ranging from 0.65 to 48.65 years were built in ordinary Portland cement (OPC) concrete as a binder. Concrete samples ground from surface concretes were obtained from a pier of the bridges in tidal zone at the time of tide down by drilling and grinding with 2 mm increments up to 50 mm. The chloride content of each sample was determined by acid soluble extraction in a nitric acid solution followed by potentiometric titration against silver nitrite. The chloride profiles at the time of sampling were also obtained. Then, the $D$, non-steady state diffusion in a semi-infinite medium, was determined for each specimen by fitting the error function solution to the Fick's second law, for.

Fig. 1 describes the $D$ and $C_S$ for target structures exposed to tidal zone. The best fit curves for the $D$ are expressed as a power function of time, and for the $C_S$ as a logarithm function of time. It is seen that the $D$ decreased with exposure duration, despite their high deviation at exposure conditions, including different degrees of wave, weathering and presumably segregation of concrete in mixing. The $D$ initially at 0.65 years ranged from $5.53 \times 10^{-12}$ to $7.89 \times 10^{-12}$ m$^2$/s and at 48.65 years from $4.47 \times 10^{-12}$ to $5.55 \times 10^{-12}$ m$^2$/s respectively. The $C_S$ were also much affected by the exposure duration. The $C_S$ ranged from 1.85 to 2.21% by weight of cement at 0.65 years and from 2.71 to 3.11% at 48.65 years respectively. These results were used to model chloride penetration considering its time dependency in terms of only diffusion in the present study.
3 MODELLING OF CHLORIDE TRANSPORT

3.1 Time independent transport

The Fick’s 2nd law is commonly used to describe chloride ion diffusion in concrete as given in Eq. 1, which is used for the time independent model. Theoretically, the $D$ can be calculated by measuring the concentration of the $C_S$ and the concentration of chloride ions $C(x, t)$ at the depth $x$ and the exposure duration $t$.

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

where, $erf$ is an error function.

3.2 Time dependent diffusion coefficient

The diffusivity often decreases with time, as cement hydration proceeds to refine the concrete pore structure, thereby letting connectivity of the pores significantly decrease [Thomas & Bentz 2000]. A package program [Thomas & Bentz 2000] for service life prediction uses a model in determining the $D$ in predicting a chloride profile as follows.

$$D(t) = D_R \left( \frac{t_R}{t} \right)^m \tag{2}$$

where, $D(t)$ is the diffusion coefficient at time $t$, $D_R$ is the diffusion coefficient at reference time $t_R$ (i.e. usually 28 days), and $m$ is an age factor. This model is known to fit well for marine environments, as a change in the pore structure imposes a development of cement hydration [Bamforth 1999]. However, a direct application of this model for predicting the rate of chloride transport has a defect, that the historic change of the $D$ for a given exposure duration is not considered, which may lead to an erroneous judgment on chloride ingresses and thus the risk of chloride-induced corrosion.

In this study, in order to remedy the defect by considering hysteresis of the $D$, the mean value of the $D$ for exposure duration to marine environments was used to predict a chloride profile. Thus, the mean $D$ was calculated by integrating the definite $D$ for a given exposure duration, and then by dividing the exposure duration, as given in Eq. 3.
where $D_m(t)$ is the mean diffusion coefficient for the exposure duration, $t$. In this study, the time dependency of the $D$ was expressed in the same power function as seen in Eq. 2. Thus the mean $D$ can be obtained by substituting Eq. 2 into Eq. 3:

$$D_m(t) = \frac{D_R}{1 - m} \left( \frac{t_R}{t} \right)^m$$

(4)

This equation is more useful to solve the Fick’s 2nd law for a chloride profile, rather than a constant $D$, since both the time dependency and the hysteresis of the diffusivity are encompassed [Song et al. 2006b].

### 3.3 Time dependent surface chloride

A build-up of the $C_S$ for concrete structures exposed to seawater was obviously observed in previous survey [Uji et al. 1990]. In this study, the time dependency of the $C_S$ as well as the $D$ is considered in solving the Fick’s 2nd law, based on the in-situ data (Fig. 1). The time dependency of the $C_S$ was observed as shown in Fig. 1. Hence, a build-up of the $C_S$ was taken into account in calculating a chloride profile using the best fit of a change in the $C_S$ with time [Song et al. 2006b] from the field data as Eq. 5.

$$C_S(t) = \alpha [\ln(\beta t + 1)] + k$$

(5)

Here, $t$ is the time of exposure in years and $\alpha$, $\beta$ and $k$ are constants obtained from in-situ environments as given in Fig. 1. The chloride content, $C(x, t)$, at a given time $t$ and a depth $x$, can be expressed with the time dependent $C_S$, by utilizing a heat conduction solution in solids [Carslaw & Jaeger 1959].

$$C(x,t) = \frac{2}{\sqrt{\pi}} \int_x^\infty C_S \left( t - \frac{x^2}{4D\omega^2} \right) \cdot e^{-\omega^2} d\omega$$

(6)

Eq. 6 was derived from the Fick’s law by considering $C_S$ variation with time while $D$ remains constant. Although consideration of the time dependent $D$ to solve the Fick’s 2nd law could provide a more accurate prediction on the ingress of chlorides, the calculation for the solution could be subject to an extreme complexity. Hence, the term $D$ in the solution Eq. 6 was substituted by the time-varying $D$ as Eq. 4, even it produce a marginal error. Thus, a final expression for the chloride transport can be written by the following equation.

$$C(x,t) = \frac{2}{\sqrt{\pi}} \int_x^\infty C_S \left( t - \frac{x^2}{4D_m(t)\omega^2} \right) \cdot e^{-\omega^2} d\omega$$

(7)

### 4 Results

#### 4.1 Chloride penetration

The chloride penetration by both the time-dependent model and time-independent model at 25, 50, and 100 mm of concrete covers is calculated in Fig. 2. The chloride content was calculated with 2.5 years of the time interval. It is seen that the penetrated chloride ions calculated from the time dependent model is always higher than the time independent model. At an early age within 5-10 years, the penetration of chloride ions seems not to be affected by time dependency of chloride transport; there is no particular difference between the time-dependent model and the time-independent model.
However, for chloride content penetrated through the depths of cover concrete, the time dependent model predicts higher chloride content than that by the time independent model. It can be seen that the influence of the increased $C_S$ is very dominant for chloride penetration due to higher concentration gradient of chloride ions on the concrete surface. However, as the cover depth increases, the difference of penetration of chlorides between two models decreases, since the increased $C_S$ is less influencing and only $D$ governs the rate of chloride ingress.

The influence of the time dependency of $C_S$ to chloride profiles is given in Fig. 3. The chloride profiles show up to the depth 100 mm of the concrete cover at 5, 20, and 100 years. The chloride ingresses by the time dependent model were always higher than those by the time independent model, and the chloride ingress increases much higher with time, presumably due to the higher $C_S$ by time-dependent build-up of $C_S$. The concentration gradient of chloride ions on the surface concrete significantly increases with time and thus the higher level of chloride ingress at all depths occurs.

![Figure 2. Penetration of chloride ions at different concrete cover depths](image)

![Figure 3. Chloride profiles with time](image)

4.2 Time to corrosion

The time to corrosion, i.e. corrosion initiation, is calculated as in Fig. 4 with different chloride threshold level, $C_{lim}$, of 0.4%, 0.6%, and 0.8% by weight of binder, respectively. The concrete cover depth of up to 100 mm in a tidal zone is considered. It was found that the time dependent model predicts earlier corrosion initiation due to greater build-up of the $C_S$ with time and relatively lower
decrease in the $D$. With 0.4% of $C_{lim}$, the difference in prediction of corrosion initiation by two models is negligible, whereas corrosion initiation predicted by time independent model is greater up to by about 50% than that by time dependent model for 0.8% of $C_{lim}$. It was also found that the difference by two models becomes large with an increase of $C_{lim}$.

![Graphs showing time to corrosion for different $C_{lim}$ values.](image)

**Figure 4.** Time to corrosion for a concrete structure exposed to marine environments (tidal zone)

### 5 DISCUSSION

#### 5.1 Chloride transport

The chloride transport via capillary pores is dependent on volume fraction and connectivity of the pores inside concrete, and it can be depending on the W/C ratio, cement content, cement type, and use of secondary cementitious materials. For example, low W/C, good curing and use of pozzolanic materials result in the capillary pores being blocked with gel and reduced permeability to water containing aggressive ions such as chlorides. The reduction of the rate of chloride transport is also ascribed to the development of cement hydration. Cement matrix usually completes 85-90% of the hydration within 28-56 days after casting. The rest of hydration takes place in a very long term, ranging from a couple of years to decades. When cement hydration proceeds, the hydration products expand twice of the volume and thus may occupy the capillary pore or block the interconnected network. Thus, the rate of chloride transport could significantly decrease with time. This effect was once modelled using a computational technique [Garboczi & Bentz 1992], but the results was less conclusive, since only the change of geometry in the capillary pore network (i.e. volume fraction) with time was taken into account. In fact, the rate of chloride transport is much affected by other factors including chemistry between chloride ions and cement matrix [Ann et al. 2007], and physical condition of the interfacial zone between cement paste and aggregate, which are also attributed to the chloride ions’ mobility. Hence, it seems to be necessary to further investigate the time dependency of the rate of chloride transport, considering the complexity of physical and chemical change in cement matrix.

A proportion of chloride ions present in concrete is chemically bound, primarily by tricalcium aluminate ($C_3A$) to form Friedel’s salt. Recent studies have modelled the influence of binding on the penetration of chloride [Glass & Buenfeld 2000]. Glass & Buenfeld [2000] found that with increased chloride binding capacity, total chloride contents increase nearer the surface of the concrete, but decrease deeper in the concrete. An increase in the $C_S$ is induced by the binding effect which allows the progressive build-up of higher total chloride content at increasing distances from the concrete surface. Chloride binding also reduces the content of free chloride within concrete and the concentration gradient at depth, because chloride binding removes chloride from the transport process [Song et al. 2007b]. It is notable that the content of bound chloride depends on the binding behaviour of cement matrix and the concentration of chloride source.
5.2 Corrosion of steel

A reduction of ionic diffusivity through concrete with time is beneficial in delaying the onset of chloride-induced corrosion and thus enhancing the corrosion free life of structures. However, a build-up of the $C_S$ may mitigate the benefit of decreased diffusivity. It can be seen from the analytical results between two models that the increased $C_S$ with time plays a more important role than the decreased $D$ does in penetration of chloride ion. Pulverised fly ash (PFA), ground granular blast furnace slag (GGBS) or silica fume (SF) in concrete is effective in enhancing the resistance to chloride diffusion as compared with concrete with plain Portland cement as binder. The decrease in $D$ for PFA, GGBS or SF concretes generally arises from (1) refinement of pore structure, and (2) increased binding capacity of GGBS [Luo et al. 2003]. These influences of concrete containing PFA and GGBS on the chloride diffusivity seem to continue for a long period of time. The $D$ reduces more dramatically in concrete mixtures containing pozzolans showing their long-term hydration properties rather than in the OPC concrete [Bamforth 1999]. Even the structures investigated in the present study were built in OPC as binder, and then a reduction of diffusivity in concrete with time did not affect significantly to the diffusion resistivity, it is possible to delay the corrosion initiation of the structures by using the pozzolanic admixtures, such as PFA and GGBS, when considering time dependent characteristics. The presence of moisture and oxygen are necessary for corrosion to proceed at a significant rate after initiation, so corrosion propagation is dependent on cathodic reaction in terms of oxygen and moisture, the estimates of corrosion rates may be given on the bases of oxygen permeability [Andrade et al. 1989]. Concrete permeability depends largely on diameter, shape, and connectivity of pores. Pore volume in PFA concrete and SF concrete is rapidly reduced with time, permeability of 50% PFA concrete is approximately 50% less than that of OPC concrete [Day et al. 1985]. Therefore, pozzolanic materials give low permeability of oxygen and moisture inside concrete, and it results in delaying time to repair and/or mitigate corrosion development.

6 CONCLUSION

The conclusion of this study is as follows.

(1) Diffusion coefficient ($D$) of chloride ions in concrete obtained from in-situ marine environments decreased with time, whereas surface chloride concentration ($C_S$) increased. The $D$ decreased dramatically for the first 20 years after exposure in marine environments and then still decreased but at a lower rate up to about 75% of the initial $D$, while the $C_S$ highly increased up to by about 70% compared to the initial $C_S$.

(2) The chloride profiles were calculated by both the time dependent and independent models. The time dependent model predicted higher chloride ingress than the time independent model did and the chloride ingress increased with time at a much higher rate, since the decreased $D$ with time is more influencing on the rate of chloride ingress than the increased $C_S$.

(3) Using the time dependent model, the time to corrosion initiation was predicted shorter than that by the time independent model, mainly due to a higher build-up of the $C_S$ and relatively a lower fall of the $D$. It was found that the time independent model for chloride transport, which has been used for the prediction of service life, may underestimate the risk of chloride-induced corrosion in concrete structures.

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REFERENCES


