

Cement & Concrete Composites 30 (2008) 113-121

Cement & Concrete Composites

www.elsevier.com/locate/cemconcomp

Factors influencing chloride transport in concrete structures exposed to marine environments

Ha-Won Song *, Chang-Hong Lee, Ki Yong Ann

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

Received 4 May 2006; received in revised form 30 August 2007; accepted 18 September 2007

Available online 25 September 2007

Abstract

The present study concerns a literature review regarding chloride transport in terms of the diffusion coefficient (D) and surface chloride content (C_S) in concrete structures exposed to a marine environment. In addition, a refined model is proposed for D and C_S for time-dependent chloride transport. It is found that both D and C_S are time-dependent: D decreases and C_S increases with time, due to further cement hydration development. D and C_S are significantly influenced by concrete mix proportion, air void content in concrete, curing methods, degree of exposure to seawater and climate. Blended cement concretes are beneficial in decreasing D, but increase C_S , presumably due to a refinement of the concrete pore structures and chloride binding. An increase in the air void content in concrete increases D, but decreases C_S . The C_S depends on curing methods such as water, membrane and aeration. The degree of exposure to seawater does not have a clear relationship with C_S : higher exposure levels did not result in a higher level of C_S . Exposure in tropical areas results in higher C_S in concrete jetty structures with a similar level of D, mainly due to an increased temperature and concentration of salinity. Based on these findings, a refined model for C_S was proposed to provide more realistic prediction of the build-up of chlorides by chloride transport in concrete structures exposed to marine environments.

Keywords: Chloride transport; Diffusion coefficient; Surface chloride; Concrete structures; Marine environment

1. Introduction

Reinforced concrete is usually durable and cost effective, which has resulted in its widespread use for the construction of semi-permanent structures. However, it has become increasingly apparent that attack by aggressive agents such as chloride ions, leading to corrosion of embedded steel, may cause a structure to deteriorate. Thus, the corrosion of reinforcing steel in concrete due to chloride transport in concrete structures in a marine environment has received increasing attention in recent years because of its widespread occurrence and the high cost of repair [1,2].

E-mail address: song@yonsei.ac.kr (H.-W. Song).

The steel in concrete is protected by an oxide passive film generated in a highly alkaline environment [3], although the corrosion cell is fully composed: cathodic molecules such as moisture and oxygen, anode, electrolyte and electric circuit. However, a build-up of chloride at the depth of the steel accompanied by a local fall in the pH of the pore solution depassivates the protective film prior to steel corrosion [4]. To prevent the chloride permeation into concrete, the use of finely grained materials [5–7] and resin-based treatment on the cover concrete [8] have been investigated and achieved some success.

Simultaneously, investigation on predicting the chloride profile in concrete exposed to a marine environment has been performed using the Fick's second law. Many authors have used this model to predict the time to chloride-induced corrosion with a given diffusion coefficient (D) and surface chloride content (C_S) , assuming that cement

^{*} Corresponding author. Tel.: +82 (0)2 2123 2806; fax: +82 (0)2 364

matrix in concrete is chemically inert and evenly porous [9–12]. However, this hypothesis and models have been challenged, since Bamforth and Price [13] addressed the time-dependent characteristic of chloride transport in terms of D and C_S , and Bentz et al. [14] showed a change of D with time.

The present study surveys published data on chloride transport of concrete specimens or structures exposed to a marine environment (i.e. aerated, splash and tidal zones) for the duration from 1 to 64 years. Time-dependent characteristics of D were extensively investigated altogether with other factors influencing chloride transport such as concrete mix proportion, curing method, degree of exposure to seawater and climate, while a change in C_S has been rarely dealt with. The present study suggests a refined model for chloride transport considering time-dependency of the C_S along with extensive investigation on C_S .

2. Chloride transport model

2.1. Diffusion model

There are a number of mechanisms by which chloride transport can take place in concrete. These include diffusion under the influence of a concentration gradient, absorption due to a capillary action, migration in an electrical field, a pressure-induced flow and wick action when water absorption and water vapor diffusion are combined [15].

Diffusion is the process by which ions or molecules move from an area of higher concentrations to lower concentrations. Diffusion is the primary mechanism of chloride transport in concrete where there is no applied electric field and the moisture condition of the concrete pore structure is stable. For one dimensional into a semi-infinite medium, an error function solution to the Fick's second law [16] is usually used as follows:

$$C(x,t) = C_{\rm S} \left[1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}} \right],\tag{1}$$

where D = diffusion coefficient (m²/s); t = time of exposure (s); C(x,t) = chloride concentration at depth x after time t (%/m³); $C_s =$ surface chloride concentration (%/m³); and erf is the error function. A true D can be achieved using Eq. (1), if concrete is homogeneous as being an ideal media, D and C_s are constant with time, and the chlorides either do not react with cement matrix or if the ratio of chloride binding is constant. This model is commonly used in determining chloride transport in concrete [17].

2.2. Measurement

Measurements of a chloride profile to calculate D and $C_{\rm S}$ usually follow the following procedures. The chloride profile is obtained from samples collected by grinding the concrete in a certain increment of depth from concrete surface to the steel. The chloride content of each sample can be usually determined in total chloride content for

the convenience by acid soluble extraction in a nitric acid solution followed by potentiometric titration against silver nitrite. The chloride concentration of each solution sample is often given in ppm, which is then converted to the percentage by weight of concrete and finally the percentage of chloride by weight of cement, assuming a uniform distribution of cement through the cover concrete. This gives the chloride profile at the time when the specimens are removed from concrete structures in seawater or saline environment.

The D can be determined by fitting the error function solution to Fick's second law, for non-steady state diffusion in a semi-infinite medium, given by Eq. (1). In the analysis of the chloride profile, the sum of the squared differences between the fitted (theoretical) and the actual data for the chloride content of each sample must be minimised by adjusting the regressor variable. Once a best fit is achieved, the D can be calculated. The initial chloride content (i.e. from the mix ingredients) is usually very low and thus is neglected in analyzing the chloride profiles.

D can be calculated from a measurement of the chloride concentrations at each depth of concrete, whereas a direct measurement of the $C_{\rm S}$ is unreliable, because the $C_{\rm S}$ is the chloride content at the exposed surface of concrete. The approach to obtain the $C_{\rm S}$ is to fit a curve to the chloride profile with the $C_{\rm S}$ and the D as independent variables.

The difficulty in determining the $C_{\rm S}$ usually arises from the reduction of chloride content at the concrete surface of cover concrete as shown in Fig. 1. The chloride content within millimeters inside the outer surface of cover concrete is decreased, because the concrete skin has a different composition, compared to the internal concrete, due to phenomena such as a contact with the moulds, segregation of aggregates or dielectric reaction between the concrete surface and chloride environment [18]. Moreover, chlorides at the surface of cover concrete can often be washed out in preparation of sampling and thus lowers the $C_{\rm S}$.

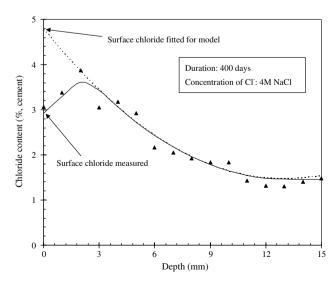


Fig. 1. An example of the chloride profile with fitted curves for surface chloride content.

3. Reported values of D and C_S

A summary of D and $C_{\rm S}$ reported from published data is given in Table 1, which includes information on the type of sample and its exposure condition from which the data was obtained. The information includes reinforced structures, laboratory concrete specimens exposed to an outdoor environment and concrete specimens exposed in a controlled laboratory environment. In this study, total chloride content is expressed as a percentage by weight of cement/binder. For the cases that the chloride content is only reported as a percentage by weight of concrete specimen/structure but its mix design is not reported, a cement content of 350 kg/m³ and a concrete density of 2300 kg/m³ have been assumed. If D and $C_{\rm S}$ were not provided, D in all the works have been estimated using the Fick's second law and $C_{\rm S}$ was obtained by fitting the curve to the chloride profile.

The degree of contact with chlorides in an environment is a key factor for each different level of the surface chloride content. The $C_{\rm S}$ for a concrete exposed to seawater may not be changed with time due to the chemical equilibrium, but at the tidal zone the chloride content on concrete surface can be increased by a number of wet and dry cycles. Also it is seen that degree of contact to seawater much influences $C_{\rm S}$. For example, $C_{\rm S}$ obtained from submerged condition in seawater was higher than that for tidal/splash, and specimens/structures exposed to airborne chlorides produces the lowest level of $C_{\rm S}$. However, D or $C_{\rm S}$ from

published data does not provide clear relationship with the time of exposure, due to other various factors to chloride transport including binder type, free water/binder ratio (W/B), curing condition, location of sampling in structure and weathering.

4. Influencing factors to chloride transport

For chloride transport, aggregates usually have very low permeability and therefore have little impact on the permeation of chloride. Although the interface between coarse aggregate and cement paste often provides an easier path for chloride ions to move through concrete so that the size of aggregate affects D [27], the rate of transport in a concrete is largely dependant on the characteristics of cement paste. In this study, concrete mix proportion, curing condition, exposure to seawater and other physical properties of concrete are mainly taken as influencing factors to chloride transport.

4.1. Concrete mix

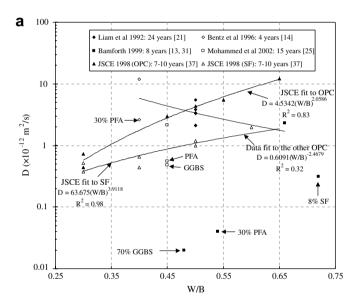
It is well known that binder type and W/B significantly affects chloride transport because formation of pore structure is different, depending on concrete mix proportion. For example, pulverized fuel ash (PFA) or ground granulated blast-furnace slag (GGBS) in concrete produces a dense cement matrix with fewer capillary pores due to the

Table 1 Reported values of the diffusion coefficients D and surface chloride contents C_S of concrete structures and specimens exposed to marine environments

C _S (%, cem.)	$D (\times 10^{-12} \text{ m}^2/\text{s})$	Time (years)	Exposure	Concrete mix		References
				Binder	W/B	
4.08 2.55 1.33	Unknown	2	Laboratory (submerged)	OPC	0.4 0.5 0.6	Gjørv and Vennesland [19]
3.74–5.54 0.43–2.22 0.83–5.23 2.39–6.41	3.52–4.66 Unknown	16 23–58	Structure (tidal/splash) Structure (aerated) Structure (splash) Structure (tidal)	OPC OPC	Unknown Unknown	Funahashi [10] Uji et al. [20]
1.50–3.10 1.97 0.20–2.43 0.016–0.143 2.93, 4.72 2.10, 4.80	2.13–3.39 3.50 Unknown 4.41–4.91 12, 20 1.3, 5.0	24 20 30 1 1, 4	Structure (splash/tidal) Structure (splash/tidal) Structure (aerated) Specimen (aerated) Specimen (submerged)	OPC OPC OPC OPC OPC 30% PFA	0.5 Unknown Unknown 0.5 0.4	Liam et al. [21] Kudoh et al. [22] Morinaga [23] Mustafa and Yusof [24] Bentz et al. [14]
0.48, 3.05 0.63, 4.54 0.64, 3.25 0.69, 3.66	6.53, 7.85 0.89, 0.78 0.76, 0.56 3.98, 3.25	3, 8	Specimen (tidal)	OPC 30% PFA 70% GGBS 8% SF	0.66 0.54 0.48 0.72	Bamforth and Price [13,31]
3.53 4.12 5.80	2.142 0.486 0.552	15	Specimen (submerged)	OPC GGBS PFA	0.45	Mohammed et al. [25]
10.51 10.51 9.26 11.96	0.042 0.648 0.027 0.136	33 38 60 64	Structure (splash/tidal)	OPC	0.44-0.6	Troconis de Rincón et al. [26]

pozzolanic reaction [28]. Moreover, the particle size distribution in the finest range, which accounts for 100–1000 Å, along with filler effect is more likely to reduce a chloride transport [29].

This study collected published data on D and C_S of concrete containing OPC, PFA, GGBS and silica fume (SF) exposed to a marine environment. Fig. 2 shows the relationship between D and W/B, and C_S and W/B. A curve was fitted to the values of D for OPC concretes, in the form of $D = ae^{b(W/B)}$, indicating an increase in D, by an increase in W/B by neglecting exposure durations. In contrast, the curves by recent data from JSCE [30] were fitted in the form of $D = a(W/B)^b$ to the values for OPC and SF concretes. It is seen that an increase in W/B results in an increase in D for both OPC and SF concrete, and D for SF concrete was lower than that for OPC concrete. PFA, GGBS or SF in concrete was, as expected, effective in enhancing the resistance to chloride transport. Decrease



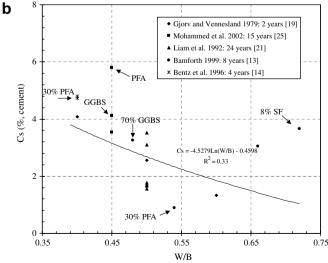


Fig. 2. Apparent diffusion coefficients (a) and surface chloride content (b) of concrete structures and specimens exposed to a marine environment.

in *D* for PFA, GGBS or SF concretes occurs due to mainly a refinement of pore structure [29], and the increased binding capacity of GGBS [31,32].

The comparison of the results by Bentz et al. [14] and Bamforth [33] shows that the D for the concrete with W/B = 0.4 was about one order greater than the D with W/B = 0.66, even with similar exposure duration and external environment, which may be explained by the effect of binder content. Buenfeld and Okundi [34] also showed, from chloride solution-exposure testing, that the higher binder content, at a given W/B, could increase chloride ion ingress in concrete.

A reduction of C_S with higher W/B was reported as shown in Fig. 2b. In Fig. 2b, a single study with same conditions from Gjørv and Vennesland [19] showed that the C_S at a given cement content was reduced by an increase in W/B for a two-year submerge in chloride solution. This can be explained by the skin effect that reduces C_S by a formation of cement paste layer on the outer surface of cover concrete of the specimen. Higher W/B is more likely to form a thicker cement paste layer on the concrete surface (i.e. concrete skin), so that the layer would enhance the dielectric activity between hydroxyl ions in the concrete skin and chloride ions in solution, and thus the increased repulsive force removes chloride ions from the surface of concrete. The $C_{\rm S}$ was also much influenced by binder type as shown in Fig. 2b. Irrespective of exposure condition and duration, $C_{\rm S}$ for blended cement concretes was greater than that for OPC concrete, presumably due to the higher level of chloride binding and sorptivity. With increased chloride binding capacity, total chloride contents increase nearer the surface of the concrete, but decrease deeper in the concrete [35]. The increase in the $C_{\rm S}$ can be induced by the binding effect which allows the progressive build-up of higher total chloride content on the surface of cover concrete.

4.2. Curing

Curing methods and duration can control the concrete quality including mainly strength and durability of concrete. Bamforth [33], and Bamforth and Price [13] addressed the influence of curing methods on chloride transport reporting that D for OPC, 30% PFA, 70% GGBS and 8% SF concretes was not significantly affected by the curing method, while the $C_{\rm S}$ was varied with curing. Fig. 3 shows the various levels of C_S for different curing methods (water, membrane and aeration), when the concrete specimens were submerged in seawater for 3 and 8 years, respectively. It is seen again that the C_S was increased with time, ranging from 0.44% to 0.69% by weight of cement for the 3 year exposure, while the $C_{\rm S}$ increased up to 1.66-6.45% after the 8 year exposure. The C_S shows a marginal change for the first 3 years with curing methods, whereas the C_S for the 8 years exposure was varied much with each curing method. For OPC and 8% SF concretes, aerated curing is beneficial in reducing $C_{\rm S}$, compared to water curing. For 30% PFA concretes,

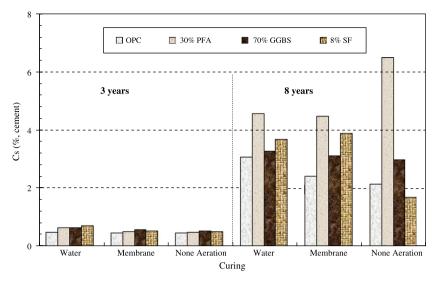
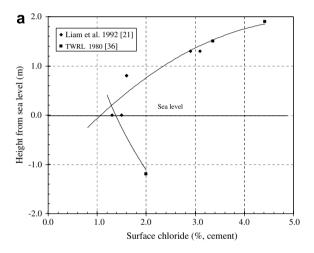


Fig. 3. Time and curing-dependence of surface chloride from [13,32].

 $C_{\rm S}$ is much less with either water curing or membrane, compared with aerated curing. Hence, curing method should be carefully chosen, depending on binder type, in order to minimise $C_{\rm S}$ and thus the chloride transport in concrete.

4.3. Exposure condition

The value of D and C_S may vary to a large degree by the location of the structure in a marine environment, i.e., the degree of exposure to chloride environment and weathering condition with regard to prevailing winds and rainfall. For marine concrete structures, the vicinity to seawater could mainly govern the chloride transport behaviour. However, there has been little study concerning the effect of location from sea level, except several limited data [21,36], which are shown in Fig. 4 for D and C_S for jetty structures exposed to tidal/splash zones for 24 years. The height from sea level was limited within 2 m higher or about 1 m lower from sea level. It seems that splash zone near sea level is the easiest for chlorides to accumulate on the surface of concrete, while a build-up of C_S took place the least at the sea level. This may be due to the wet/dry cycles, resulting in a successive supply of chlorides by wetting with seawater, and evaporation and salt crystallization by drying. Water absorption may lead to very rapid penetration of chloride ions dissolved in seawater. It is, for example, well known that concrete in the tidal zone of an offshore structure or bridge decks subjected to regular applications of deicing salts, may suffer from rapid chloride ion ingress due to the water absorption. However, Uji et al. [20] showed from a long term monitoring from 23 to 58 years that the order of $C_{\rm S}$ with regard to the level from seawater is tidal > splash > atmospheric zone. The difference of C_S build-up between these data is not clearly known, but presumably different weathering and concrete mix may have affected to the process of chloride transport.



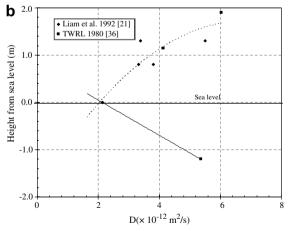


Fig. 4. (a) Apparent diffusion coefficient and (b) surface chloride content of a jetty concrete structure exposed to splash/tidal conditions for the 24 years.

Fig. 5 shows two sets of the $C_{\rm S}$ build-up measured from specimens and structures exposed to a chloride aerated environment (i.e. coastal area) for 1 and 30 years,

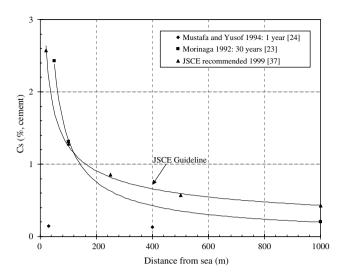
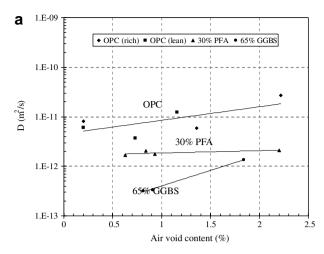


Fig. 5. Surface chloride content in aerated conditions with the distances from sea for 1 and 30 years exposures.

respectively [23,24], along with a Japanese Standard Specification for airborne chloride build-up [37]. The C_S from Mustafa and Yusof [24] was marginally changed with the distance from sea, because of a relatively short-term exposure to the chloride atmospheric condition. Moreover, the values of $C_{\rm S}$ were too small to set a high level of chloride concentration gradient in concrete for corroding the embedded steel. For a 30-year exposure period, it is clearly seen that the distance from the sea strongly influences a build-up of $C_{\rm S}$, ranging from 0.20% to 2.43% by weight of cement, for the distance 50-1000 m away from sea. It is notable that the values of C_S specified by the Japanese Standard [37] nearly equate to the C_S after a 30 years exposure to airborne conditions. It suggests that aerated chlorides also may impose a risk of corrosion of steel, when structures are located in the coast close to sea and the exposure duration is long enough for C_S to accumulate. However, structures about 1 km away from coast may be free from a chloride-induced corrosion deterioration, because it would take extremely long for chloride ions, with a lower level of $C_{\rm S}$, to reach the chloride threshold level [39] for steel corrosion at the depth of the steel. Miera et al. [44] provide additional information on chloride accumulation in concrete due to natural exposure to marine aerosols.

4.4. Other factors

The importance of air void content in concrete has been emphasized due to its influence on concrete strength as well as corrosion initiation [38]. However, to date, the influence of air void on chloride transport has rarely been addressed. Ann and Song [39] indicated an increase in D and a decrease in C_S , resulting from an increase in air void content. Fig. 6 shows D and C_S with the air void content for OPC, 30% PFA and 65% GGBS concretes. As expected, 65% GGBS and 30% PFA concrete indicated lower levels of D, compared to D for OPC concrete. For each mix, D



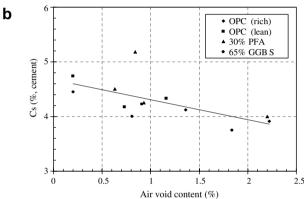


Fig. 6. Apparent diffusion coefficient (a) and surface chloride content (b) of concrete specimens exposed to 4 M NaCl solution [43].

slightly increased as the air voids increased, except for the 30% PFA concrete where D was relatively constant. It seems likely that larger air void content, which may be induced by various sources (e.g., poor compaction in the casting of the concrete) results in the formation of pore structures that favor the transport of chloride ions. It is, however, notable that an increase in the air void content resulted in a decrease in $C_{\rm S}$, irrespective of binder as shown in Fig. 6b.

Fig. 7 shows an influence of climate on chloride transport in terms of C_S . Three different series of C_S were measured in the UK, Japan and Venezuela, where the latitudes of sampling places are different. The exposed duration was 8, 7–58 and 7–64 years from the UK, Japan and Venezuela, respectively. The specimens from the UK were only submerged in seawater and the others were exposed in the tidal/splash zones. The C_S from the UK (i.e. the highest in the latitude) were the lowest, probably because of the short duration of exposure as well as the submerged condition, compared to the $C_{\rm S}$ from Japan and Venezuela, which were measured after the even longer durations of exposure. However, the C_S from Venezuela was much higher than that from Japan, despite a similar exposure condition and duration. This difference may be due to different climates, since the tropical climate fosters chloride ion movement

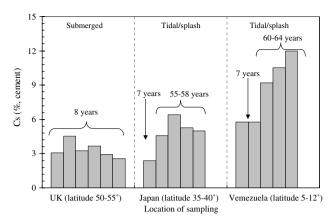


Fig. 7. Surface chloride contents of concrete structures measured in the UK, Japan and Venezuela [20,26,32].

into concrete due to the high levels of relative humidity, temperature and chloride concentration. High temperature and high humidity will help chloride ions to transport in concrete via absorption altogether with diffusion. Moreover, higher concentration of chloride ions in seawater will increase the chloride ingress, which is responsible for the high $C_{\rm S}$.

5. Refinement of basic model

The fixed value of D and C_S have been extensively used in predicting the chloride ingress using the Fick's second law, when structures are exposed to a marine environment [17]. However, the D decreases with time, because development of cement hydration reduces the pore distribution in the fine size, and hydration products react with chloride ions to form Friedel's salt and/or to adsorb the chlorides physically, which delays chloride transport in concrete. Also, the $C_{\rm S}$ has been intuitively hypothesized to be independent of time, when concrete structures are exposed to a tidal/splash environment, whereas in salt aerated condition, chlorides have been considered to be accumulated on the surface of concrete with time [40,44]. A literature review showed that both D and C_S are time-dependent and moreover the values are influenced by binder type, W/B, exposure condition and even weathering. To predict the service life of concrete structures subjected to chlorideinduced corrosion, the complexity of chemical, physical reactions between the cement hydration species and chloride ions must be taken into account for the analysis of chloride transport. However, it would be very difficult to consider all these factors in the analysis of chloride transport. Thus, the present study suggests a refined model, considering the time-dependent characteristics of D and $C_{\rm S}$. A number of works used for the model for time-dependent D in predicting the chloride profile [30,36]. Timedependency of D and C_S may be mainly associated with hydration of the cement matrix. Capillary pore volume and its connectivity are important in assessing chloride transport, and the capillary pores reduce and are partially blocked as the cement matrix hydrates [41,42], which implies a loss of paths for chloride ions. Thus, D can be decreased by time (i.e. degree of hydration) and C_S can be increased by the increase in chloride binding and the build-up of chlorides.

The so-called time-dependent model of D in the most cases was empirically obtained as follows:

$$D(t) = D_0 \left(\frac{t_0}{t}\right)^m,\tag{2}$$

where D(t) = diffusion coefficient at time t (m²/s); $D_0 =$ diffusion coefficient at t_0 (m²/s); $t_0 =$ standard time (1 year or 28 days) (s); t = time (s); and m = constant value. For C_S , a refined model was previously suggested [17,40] and is being used commercially (eg. LIFE 365). For a linear build-up of C_S over time, the chloride ingress with regard to the concrete cover depth and time can be obtained from Eq. (3), and for a square root build-up of C_S over time, Eq. (4) can be used to determine the chloride ingress,

$$C_{\mathbf{S}}(t) = k_1 t,\tag{3}$$

$$C_{\rm S}(t) = k_2 \sqrt{t},\tag{4}$$

where $C_{\rm S}(t) = {\rm surface}$ chloride concentration at time $t (\%/m^3)$; and k_1, k_2 are constant values. However, these models do not consider an initial build-up of chlorides on the surface of cover concrete, at an early age concrete exposed to a salt environment. For example, the C_S would be negligibly small for a 1-year exposure, accounting for 0.10% and 0.77% by weight of cement from Eqs. (3) and (4), respectively, whereas a measured C_S accounts for 2.1–2.5% for only a 28-day exposure. For 60 years of exposure, Eqs. (3) and (4) overestimate C_S build-up as 7.6–8.2%, compared to 6% obtained from exposure test data [14]. Moreover, these models for C_S do not consider the chloride build-up for the different conditions of tidal/splash, submerged zone and aerated zone. Hence, the models may not apply for predicting chloride transport of concrete structures exposed to a marine environment both for different very short-term and long-term exposure and chloride content at an early stage of exposure in a chloride environment is nullified.

Hence, it is required to refine a model for the time-dependent C_S , considering the initial build-up of chlorides on the surface of concrete. The following model empirically derived from published data on C_S is proposed to consider the initial build-up of chlorides:

$$C_{\mathcal{S}}(t) = C_0 + \alpha \ln(t),\tag{5}$$

where C_0 = surface chloride at the standard time (1 year or 28 days) (%/m³) and α = a constant value.

Fig. 8 shows an increase of C_S with time, based on Eqs. (3)–(5). For the best fit, k_1 , k_2 , and α were determined as 0.137%/yr, 1.001%/yr^{0.5} and 0.977%/exp(yr), respectively. For Eq. (5), C_0 was taken as the C_S for a 28 days exposure from Bentz et al. [14]. It is seen that the C_S values from models of linear and square root build-up (Eqs. (3) and (4), respectively) are unrealistically low at an early age, while the refined model in this study indicated the C_S above

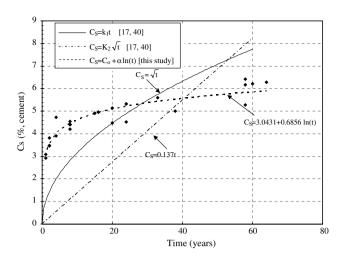


Fig. 8. Surface chloride content with time from a linear and square root build-up models, and the proposed model in this study.

2.0%. After 60 years, the rate of $C_{\rm S}$ increase for the proposed model is the lowest and reaching a plateau, whereas the $C_{\rm S}$ for linear and square root build-up models are increasing more rapidly.

6. Conclusion

This paper studied the change of the apparent diffusion coefficient D and surface chloride content C_S with time from structures/specimens exposed to marine environments, as reported from published data. It was found that D for a concrete structure decreases with time due to a subsequent hydration of cement matrix, which makes the concrete pore structure denser, or removes chloride ions by binding. C_S is also time-dependent, when exposed to tidal and splash zones or even submerged in seawater. Altogether with the time-dependent characteristics, there are a number of influencing factors in chloride transport in terms of D and C_S : concrete mix proportion (i.e. free water/binder ratio (W/B) and binder type), curing methods, the proximity to seawater, air void content in concrete and external environments. This study provides the following conclusions.

- (1) It was found that, from a single series of data, an increase in W/B resulted in an increase in D, due to formation of increased pore structure, and C_S was decreased by an increase in W/B, which seems due to the concrete skin effect. Blended cement concrete containing PFA, GGBS or SF decreases D and increases C_S , due to a refinement of the concrete pore structure and an increased chloride binding capacity, respectively.
- (2) It was seen that chloride transport depends on curing methods: water, membrane and aeration. For OPC and SF concretes, aerated curing is beneficial in reducing the $C_{\rm S}$, whereas water curing is beneficial for PFA and GGBS concretes. However, D does not seem to be much affected by curing duration.

- (3) For the exposure to tidal and splash zones, D and C_S were affected by the height from sea level (i.e. degree of contact to seawater). As the height increases from sea level, both D and C_S increase. For airborne chloride environments, the exposed time and the distance from sea are key factors to C_S , but the level of C_S at a given D was negligibly low to impose a corrosion risk, compared to tidal/splash or submerged region.
- (4) Environmental conditions like climate significantly affect chloride transport. Concrete structures exposed to a marine environment near the Equator produced a remarkably high C_S , compared to the C_S from the high latitudes. The higher C_S in the tropical area is due to an enhanced ionic transport and high concentration of chlorides.
- (5) Air void content in concretes influences D and C_S . An increase in air voids resulted in increased D and decreased C_S . A large air void content (due to poor compaction, for example) increases pore structure formation, which provides more open pathways for chloride transport.
- (6) A refined model for C_S which considers time-dependent characteristics of chloride build-up and binding capacity is proposed in this study. This model provides a more realistic build-up of C_S , compared to a few basic models for C_S accumulation in an aerated condition. However, further refinement of the model and verification with long-term exposure data is necessary for practical prediction of chloride profiles in concrete structures exposed to marine environments.

Acknowledgements

The authors would like to acknowledge financial supports from a project on Standardization of Performance based Construction Specifications and Design and a Centre for Concrete Corea, Korea.

References

- Federal Highway Administration. Building more durable bridges. Washington DC: FOCUS Federal Highway Administration; September, 2001. p. 6.
- [2] BRE Centre for Concrete Construction. Guide to the maintenance, repair and monitoring of reinforced concrete structures. DME report No. 4. Watford, UK; 2001.
- [3] Page CL. Mechanism of corrosion protection in reinforced concrete marine structure. Nature 1975;256:514–5.
- [4] Page CL, Treadaway KWJ. Aspects of the electrochemistry of steel in concrete. Nature 1982;297:109–15.
- [5] Gjørv OE, Vennesland Ø. Evaluation and control of steel corrosion in offshore structures. In: Scanlon JM, editor. Concrete durability. ACI SP 100; 1987. p. 1575–1602.
- [6] Berke NS, Sundberg KM. The effect of admixtures and concrete mix designs on long-term concrete durability in chloride environments. In: Corrosion-89, NACE conference. Texas, US; 1989. p. 386.
- [7] Kropp J. Chlorides in concrete. In: Kropp J, Hilsdorf HK, editors. Performance criteria for concrete durability, E&FN SPON; 1995. p. 138-64.

- [8] Keer JG. Surface treatments. In: Mays G, editor. Durability of concrete structures, E&FN SPON; 1992. p. 146–65.
- [9] Hooton RD, Geiker MR, Bentz EC. Effects of curing on chloride ingress and implications on service life. ACI Mater J 2002;99:201–6.
- [10] Funahashi M. Predicting corrosion free service life of a concrete structure in a chloride environment. ACI Mater J 1990;87:581–7.
- [11] Clear KC. Time to corrosion of reinforcing steel in concrete slab, vol.3. Report No. FHWA-RD-76-70. Federal Highway Administration;1986
- [12] West RE, Hime WG. Chloride profiles in salty concrete. Mater Performance 1985;24:29–36.
- [13] Bamforth PB, Price WF. Factors influencing chloride ingress into marine structures. In: Dhir RK, Jones MR, editors. Concrete 2000; 1993. p. 1105–18.
- [14] Bentz EC, Evans CM, Thomas MDA. Chloride diffusion modelling for marine exposed concretes. In: Page CL, Bamforth PB, Figg JW, editors. Corrosion of reinforcement in concrete construction. Cambridge, UK: The Royal Society of Chemistry Publication; 1996. p. 136-45
- [15] Buenfeld NR, Shurafa-Daoudi MT, McLoughlin IM. Chloride transport due to wick action in concrete. In: Nilsson LO, Oliver JP, editors. Chloride penetration into concrete. Paris, France: RILEM Publication; 1997. p. 302–24.
- [16] Crank J. The mathematic of diffusion. 2nd ed. Oxford Science Publication; 1983.
- [17] ACI Committee 365. Service-life prediction: state of the art report. Manual of concrete practice, Part 5. American Concrete Institute; 2000.
- [18] Andrade C, Diez JM, Alonso C. Mathematical modelling of a concrete surface skin effect on diffusion in chloride contaminated media. Adv Cement Based Mater 1997;6:36–44.
- [19] Gjørv OE, Vennesland Ø. Diffusion of chloride ions from seawater into concrete. Cement Concrete Res 1979;9:229–38.
- [20] Uji K, Matsuoka Y, Maruya T. Formation of an equation for surface chloride content of concrete due to permeation of chloride. In: Page CL, Treadaway KWJ, Bamforth PB, editors. Corrosion of reinforcement in concrete. London, UK: Elsevier Applied Science; 1990. p. 258-67.
- [21] Liam KC, Roy SK, Northwood DO. Chloride ingress measurements and corrosion potential mapping study of a 24-year-old reinforced concrete jetty structure in a tropical marine environment. Mag Concrete Res 1992;44:205–15.
- [22] Kudoh K, Hirotani A, Moriwake A, Yasuda M. Study on durability of a repaired concrete structure in Tokyo bay. In: Malhotra VM, editor. Evaluation and rehabilitation of concrete structures and innovations in design. ACI 128, Hong Kong; 1991. p. 1293–307.
- [23] Morinaga S. Life prediction of reinforced concrete structures in hot and salt-laden environments. In: Walker MJ, editor. Concrete in hot climates, E&FN SPON; 1992. p. 155–64.
- [24] Mustafa MA, Yusof KM. Atmospheric chloride penetration into concrete in semitropical marine environment. Cement Concrete Res 1994;24:661–70.
- [25] Mohammed TU, Yamaji T, Hamada H. Chloride diffusion, microstructure and mineralory of concrete after 15 years of exposure in tidal environment. ACI Mater 2002;99:256–63.

- [26] Troconis de Rincón OTO, Castro P, Moreno EI, Torres-Acosta AA, Morón de Bravo O, Arrieta I, et al. Chloride profiles in two marine structures – meaning and some predictions. Build Environ 2004;39:1065–70.
- [27] Oh BH, Cha SW, Jang BS, Jang SY. Development of highperformance concrete having high resistance to chloride penetration. Nucl Eng Des 2002;212;221–31.
- [28] Schiessl P, Breit W. Local repair measures at concrete structures damaged by reinforcement corrosion. In: Page CL, Bamforth PB, Figg JW, editors. Corrosion of reinforcement in concrete construction. Cambridge, UK: The Royal Society of Chemistry Publication; 1996. p. 525–34.
- [29] Hussain SE, Rasheeduzafar S. Corrosion resistance performance of fly ash blended cement concrete. ACI Mater J 1994;91:264–73.
- [30] Maruya T, Tangtermsirikul S, Matsuoka Y. Modeling of chloride ion movement in the surface layer of hardened concrete. Concrete Library of JSCE, No. 32; 1998. p. 69–84.
- [31] Dhir RK, El-Mohr MAK, Dyer TD. Chloride binding in GGBS concrete. Cement Concrete Res 1996;26:1767–73.
- [32] Luo R, Cai Y, Wang C, Huang X. Study of chloride binding and diffusion in GGBS concrete. Cement Concrete Res 2003;33:1–7.
- [33] Bamforth PB. The derivation of input data for modeling chloride ingress from eight-years UK coastal exposure trials. Mag Concrete Res 1999;51:87–96.
- [34] Buenfeld NR, Okundi E. Effect of cement content on transport in concrete. Mag Concrete Res 1998;50:339–51.
- [35] Glass GK, Buenfeld NR. The influence of chloride binding on the chloride induced corrosion risk in reinforced concrete. Corros Sci 2000:42:329–44.
- [36] TWRL. Marine durability survey of the Tongue Sand Tower. Concrete in the oceans. Technical Report No. 5. Cement and Concrete Association; 1980. p. 84–92.
- [37] Standard Specification for Durability of Concrete. Japan Society of Civil Engineers; 1999. p. 11–3.
- [38] Glass GK, Yang R, Dickhaus T, Buenfeld NR. Backscattered electron imaging of the steel-concrete interface. Corros Sci 2001;43:605–10.
- [39] Ann KY, Song HW. Chloride threshold level for corrosion of steel in concrete. Corros Sci, in press.
- [40] Amey SL, Johnson DA, Miltenberger MA, Farzam H. Predicting the service life of concrete marine structures: an environmental methodology. ACI Struct J 1998;95:205–14.
- [41] Garboczi EJ. Computational materials science of cement-based materials. Mater Struct 1993;26:191–5.
- [42] Winslow DN, Cohen MD, Bentz DP, Snyder KA, Garboczi EJ. Percolation and pore structure in mortars and concrete. Cement Concrete Res 1994;24:25–37.
- [43] Ann KY. Enhancing the chloride threshold level for steel corrosion in concrete. PhD thesis. Imperial College of Science Technology and Medicine, University of London; 2005.
- [44] Meira GR, Andrade C, Padaratz IJ, Alonso C, Borba Jr JC. Chloride penetration into concrete structures in the marine atmospheric zone relationship between deposition of chlorides on the wet candle and chlorides accumulated into concrete. Cement Concrete Compos 2007;29(9):667–76.