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Cement and Concrete Research 37 (2007) 589–595
Cement and Concrete Research

On the mathematics of time-dependent apparent chloride diffusion coefficient in concrete

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Received 17 January 2005; accepted 11 January 2007

Abstract

This paper provides an improved mathematical analysis of chloride penetration into concrete employing a time-dependent diffusion coefficient for the solution of Fick's second law of diffusion. In the paper the possible errors caused by the application of oversimplified mathematical expressions used in some models for the evaluation of service life of reinforced concrete structures are discussed. The results from this mathematical analysis demonstrate that some models based on the oversimplified error function complement (ERFC) solutions may easily overestimate the service life by orders of magnitude, especially when the age factor is high. Some chloride profiles after up to 10 years' field exposure were used to compare the oversimplified with the improved models. The results show that both the oversimplified and the improved models fairly well predict the 10 years' chloride ingress in Portland cement concrete, but the oversimplified ERFC model significantly underestimates the chloride ingress in concrete with fly ash.

Keywords: Concrete (E); Diffusion (C); Durability (C); Modeling (E); Transport properties (C)

1. Background

Owing to problems associated with chloride-induced corrosion in reinforced concrete structures, reliable prediction of chloride ingress in concrete is one of the key elements in durability design and redesign of concrete structures. Early work to analyze and extrapolate trends of chloride ingress in concrete was based on Fick's 2nd law, resulting in a prediction model based on an error function complement (ERFC) solution [1]. Since the properties of concrete, especially the surface cover layer, differ very much from the assumptions of a stable, homogeneous, non-reactive material subject to pure diffusion, as assumed for an ERFC solution to Fick's 2nd law, it has been realized that this simplest ERFC model cannot provide a correct analysis for prediction of chloride ingress in concrete. To deal with the complexity of chloride ingress in concrete whose properties change with many factors such as distance from the surface, time, the interactions between chloride and cement hydrates, the influence of moisture transport in parallel with diffusion within the concrete, etc., models based on the actual physical or chemical/electrochemical processes [2–7] would be better than those based on simple Fick's 2nd law. In these physical or chemical/electrochemical models, however, finite lamina time stepped calculation is often needed to solve the sophisticated mathematical equations. A critical review of various approaches to modeling chloride ingress in concrete has been given by Nilsson et al. [8]. In spite of the oversimplified assumptions, the ERFC models are widely used by engineers in practical applications, due to their relatively simple mathematical expressions. The simplest ERFC model, which takes the apparent diffusion coefficient as a constant in time and space, has been proven too conservative due to the lack of consideration of the retarding effect on the diffusion process resulting from chloride binding and refinement of the pore structure over time. Therefore, in some ERFC models the time-dependency of the curve-fitted apparent chloride diffusion coefficient was

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doi:10.1016/j.cemconres.2007.01.006

taken into account by an exponential relationship introducing a so-called age factor. However, this creates a big problem in mathematics of diffusion, as will be discussed later. This paper intends to give the proper mathematical analysis for a time-dependent diffusion coefficient and compare the possible errors caused by some oversimplified mathematical expressions commonly used in the ERFC models.

2. Mathematics of chloride penetration using a time-dependent diffusion coefficient

Takewake and Mastumoto [9] are probably the first who stated the dependency of chloride diffusion coefficient D on the exposure period t and used a purely empiric equation to describe the decrease of diffusion coefficient with time, that is, D is proportional to $t^{-0.1}$. In 1992, Tang and Nilsson [10] from their rapid diffusivity test found that the measured diffusion coefficient in the young concrete dramatically decreased with age and they proposed the mathematical expression for a time-dependent chloride diffusion coefficient based on Crank's mathematics of diffusion [11]:

$$D(t') = a \cdot (t')^{-n} \tag{1}$$

where $D(t')$ is the time-dependent diffusion coefficient, t' is the concrete age, and a and n are constants, with n normally being referred to as the age factor. It should be noted that the constant a has no direct physical meaning but describes a constant product of $D(t')$ and $(t')^n$. With a pair of known diffusion coefficient and age, represented by D_0 and t'_0, Eq. (1) can be rewritten as

$$D(t') = D_0 \cdot (t'_0)^n \cdot (t')^{-n} = D_0 \cdot \left(\frac{t'}{t'_0}\right)^{-n}. \tag{1'}$$

Under the assumptions of 1) homogeneous concrete; 2) constant chloride concentration at the exposure surface; 3) linear chloride binding; 4) constant effect of co-existing ions; and 5) one dimensional diffusion into semi-infinite space, the error function solution to Fick's 2nd law will be:

$$\frac{c}{c_s} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{T}}\right) \tag{2}$$

where c and c_s denote the concentration of dissolved (free) chloride in the pore solution within the concrete cover and at the exposed concrete surface, respectively. The parameter T is defined by:

$$T = \int_{t'_{ex}}^{t+t'_{ex}} D(t')\mathrm{d}t' = \frac{D_0 \cdot (t'_0)^n}{1-n} \cdot \left[(t+t'_{ex})^{1-n} - (t'_{ex})^{1-n}\right] \tag{3}$$

or rearranged as

$$T = \frac{D_0}{1-n} \cdot \left[\left(1+\frac{t'_{ex}}{t}\right)^{1-n} - \left(\frac{t'_{ex}}{t}\right)^{1-n}\right] \cdot \left(\frac{t'_0}{t}\right)^n \cdot t \tag{3'}$$

where t'_{ex} is the age of concrete at the start of exposure and t is the duration of exposure. Note that, to be more explicit, t' denotes the age of concrete and t denotes exposure duration in this paper. Let

$$f(t'_{ex}) = \left[\left(1+\frac{t'_{ex}}{t}\right)^{1-n} - \left(\frac{t'_{ex}}{t}\right)^{1-n}\right] \tag{4}$$

with $f(t'_{ex}) \le 1$ when $0 \le n < 1$ and $t > 0$. Eq. (3) then becomes

$$T = D_0 \cdot \frac{f(t'_{ex})}{1-n} \cdot \left(\frac{t'_0}{t}\right)^n \cdot t = D_a \cdot t \tag{5}$$

where

$$D_a = D_0 \cdot \frac{f(t'_{ex})}{1-n} \cdot \left(\frac{t'_0}{t}\right)^n. \tag{6}$$

Inserting Eq. (5) into Eq. (2) yields an expression similar to the conventional expression for the error function solution to Fick's 2nd law:

$$\frac{c}{c_s} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{D_a \cdot t}}\right) \tag{7}$$

where D_a commonly is referred to as the apparent chloride diffusion coefficient. In general curve-fitting techniques can be used on measured chloride profiles to obtain D_a for different durations of exposure, t.

When chloride concentration in the pore solution, c and c_s (note the lower-case), are replaced by total chloride content in the concrete, C and C_s (note the upper-case), expressed by mass percentage of either concrete or cement, respectively, Eq. (7) becomes the simplest model for chloride ingress in concrete — classified as ERFC model by Nilsson and Carcasses [1]:

$$\frac{C}{C_s} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{D_a \cdot t}}\right) = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{\frac{D_0}{1-n} \cdot \left[\left(1+\frac{t'_{ex}}{t}\right)^{1-n} - \left(\frac{t'_{ex}}{t}\right)^{1-n}\right] \cdot \left(\frac{t'_0}{t}\right)^n \cdot t}}\right). \tag{8}$$

Obviously, Eq. (8) only applies under the implicit assumption that chloride binding is time-independent and linearly proportional to the free chloride concentration c.

It should be noted that the apparent diffusion coefficient D_a in Eqs. (7) or (8) is absolutely not equal to $D(t')$, because $D(t')$ is a function of time that cannot be directly put into the error function solution without time integration as given in Eq. (3), whereas D_a is the result after time integration and can be taken as a "constant" for exposure duration t and put into Eqs. (7) or (8). In this respect, $D(t')$ can be regarded as the diffusion coefficient obtained by a short-term diffusion test of less than, e.g. one or a few days (far less than a year if the unit year is to be used for the service life prediction). The essential difference between D_a and $D(t')$, is often ignored by some researchers, resulting in some ERFC models with oversimplified mathematics, as will be discussed later.

3. Oversimplified mathematics in some ERFC models

In 1994, Mangat and Molloy [12] reported a wide range of experimental data showing that the apparent chloride diffusion coefficient is strongly dependent on the duration of exposure of concrete to a chloride-laden environment. They used an expression similar to Eqs. (2) and (3), but instead of integration from t'_{ex} to $(t+t'_{ex})$ in Eq. (3), they simply integrated the time from 0 to t, and thus derived the following equation for prediction of long-term chloride penetration profiles:

$$\frac{C}{C_s} = 1-\mathrm{erf}\left(\frac{x}{2\sqrt{\frac{D_i}{1-n}\cdot t^{1-n}}}\right) \qquad (9)$$

where D_i was defined as "the effective diffusion coefficient at time t equal to one second" [12]. According to Mangat and Molloy [12], the values of D_i are in the range of 7.08×10^{-9} m^2/s up to 3.04×10^{-2} m^2/s, i.e. far larger than the chloride diffusion coefficient that can be obtained in the diluted bulk solution (2.03×10^{-9} m^2/s). This cannot be correct, because the diffusion coefficient in a porous material should always be less than that in the diluted bulk solution. Consequently, something must be wrong in their extrapolation of the experimental data to "one second" time due to their mathematical simplification, as will be seen later. Nevertheless, if we let $D_i=D_0\cdot(t'_0)^n$, Eq. (9) turns into

$$\frac{C}{C_s} = 1-\mathrm{erf}\left(\frac{x}{2\sqrt{\frac{D_0}{1-n}\cdot\left(\frac{t'_0}{t}\right)^n\cdot t}}\right). \qquad (10)$$

It is obvious that

$$D_{aEq(10)} = \frac{D_0}{1-n}\cdot\left(\frac{t'_0}{t}\right)^n = \frac{D_{aEq(6)}}{f(t'_{ex})} \qquad (11)$$

where $D_{aEq(10)}$ denotes the apparent diffusion coefficient in Eq. (10) and $D_{aEq(6)}$ denotes the one defined in Eq. (6). Clearly, the term $f(t'_{ex})$ is missing in Eq. (10), because in Mangat and Molloy's model [12] the time integration was started from 0, implying that $t'_{ex}=0$, resulting in the term $f(t'_{ex})=1$. Thus, Mangat and Molloy's model is a simplified version of Eq. (6). As shown in Fig. 1, this simplification makes the model mathematically close to the analytical one if $t\gg t'_{ex}$ and $n<0.3$, but may result in an overestimation of the apparent diffusion coefficient, especially when the value of n is high and the exposure period t is not long enough. When the exposure duration $t\to0$, e.g. 1 s as defined in [12], which corresponds to $t/t'_{ex}\approx4\times10^{-7}$ for $t'_{ex}=28$ days, the overestimation of D_a will be as much as several orders of magnitude. This explains why Mangat and Molloy [12] reported improperly large values of diffusion coefficient D_i, paying attention to the fact that the value of n was in the range of 0.44 to 1.34.

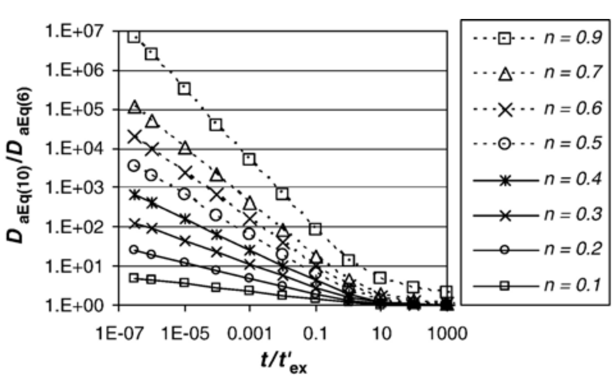

Fig. 1. Relationship between $D_{aEq(10)}$ and $D_{aEq(6)}$.

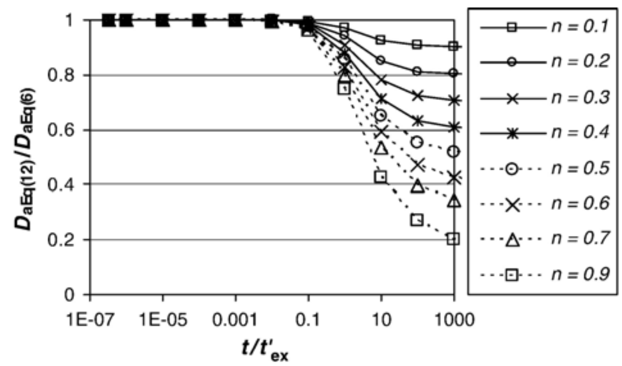

Fig. 2. Relationship between $D_{aEq(12)}$ and $D_{aEq(6)}$.

In 1995, Maage et al. [13] proposed an even simpler0 equation for modeling of chloride penetration, that is,

$$\frac{C}{C_s} = 1-\mathrm{erf}\left(\frac{x}{2\sqrt{D_0\cdot\left(\frac{t'_0}{t'}\right)^n\cdot t}}\right) = 1-\mathrm{erf}\left(\frac{x}{2\sqrt{D_0\cdot\left(\frac{t'_0}{t+t'_{ex}}\right)^n\cdot t}}\right). \qquad (12)$$

However, the authors of [13] seem just simply to have substituted the constant D in the error function solution to Fick's second law by the time-dependent D without adequate clarifying the mathematical basis of diffusion. Thus it follows that

$$D_{aEq(12)} = D_0\cdot\left(\frac{t'_0}{t+t'_{ex}}\right)^n = \frac{1-n}{f(t'_{ex})}\cdot\left(\frac{t}{t+t'_{ex}}\right)^n\cdot D_{aEq(6)} \qquad (13)$$

where $D_{aEq(12)}$ denotes the apparent diffusion coefficient in Eq. (12). Since in normal cases $(t+t'_{ex})\approx t$, the big mathematical mistake in Eq. (12) is the negligence of the term $f(t'_{ex})/(1-n)$, which results in a significant difference between $D_{aEq(12)}$ and $D_{aEq(6)}$, as shown in Fig. 2. With this mathematical oversimplification, Eq. (12) significantly underestimates the apparent diffusion coefficient, which will cause major errors in durability design and redesign of reinforced concrete structures, as will be exemplified in the next chapter.

In the EU project DuraCrete [14] a model similar to Eq. (12) was proposed, with a certain modification resulting from the introduction of two multiplication factors, according to,

$$\frac{C}{C_s} = 1-\mathrm{erf}\left(\frac{x}{2\sqrt{k_c \cdot k_e \cdot D_{RCM} \cdot \left(\frac{t_0}{t+t_{ex}}\right)^n \cdot t}}\right) \tag{14}$$

where k_c is the curing factor, k_e is the environmental factor and D_{RCM} denotes the diffusion coefficient determined by the rapid chloride migration test, i.e. the Nordic standard test method NT BUILD 492. Since both k_c and k_e are constants that modify the diffusion coefficient D_{RCM}, this modification does not change its mathematical characteristics. If we let $D_0 = k_c \cdot k_e \cdot D_{RCM}$, Eq. (14) becomes identical to Eq. (12). It is worthy to remark that, although the constants k_c and k_e may possibly compensate the factor $1/(1-n)$ to some extent, the values of k_c and k_e, presented in the DuraCrete reports [14] do not suggest that this compensation has been included. Therefore, the mathematical expression adopted by the DuraCrete model does not fulfill the underlying differential equation. Consequently, a numerical calculation of the underlying differential equation will yield different results compared to those obtained by using (14).

Until recently, some researchers [8,15–17] realized the mathematical mistake in Eq. (12). Stanish and Thomas [15] in their bulk diffusion tests used the concept of "effective age" and proposed an equation for calculation of the average diffusion coefficient D_{AVG}:

$$D_{AVG} = D_{ref} \cdot (t'_{ref})^n \cdot \frac{(t'_2)^{1-n} - (t'_1)^{1-n}}{(1-n) \cdot (t'_2 - t'_1)} \tag{15}$$

where t'_1 and t'_2 are the age of concrete at start and completion of the bulk diffusion test. Rearranging their equation with $D_{ref} = D_0$, $t'_{ref} = t'_0$, $t'_1 = t'_{ex}$ and $t'_2 = t + t'_{ex}$ yields

$$D_{AVG} = \frac{D_0}{1-n} \cdot \left[\left(1 + \frac{t'_{ex}}{t}\right)^{1-n} - \left(\frac{t'_{ex}}{t}\right)^{1-n}\right] \cdot \left(\frac{t'_0}{t}\right)^n = D_{aEq(6)}. \tag{15'}$$

Very recently, Gulikers [16,17] presented a new modification of the error function solution:

$$\frac{C}{C_s} = 1-\mathrm{erf}\left(\frac{x}{2\sqrt{\frac{D_{i,0}}{1-n} \cdot \left(\frac{t'_0}{t'}\right)^n \cdot \left[t' - t'_{ex} \cdot \left(\frac{t'}{t'_{ex}}\right)^n\right]}}\right). \tag{16}$$

Nilsson et al. [8] also presented a similar equation. In the above equation, t' denotes the concrete age, t'_0 is the reference age and $D_{i,0}$ is the instantaneous value of diffusion coefficient. Thus, the terms inside the square root can be rewritten as

$$T' = D'_a \cdot t = \frac{D_{i,0}}{1-n} \cdot \left(\frac{t'_0}{t + t'_{ex}}\right)^n \cdot \left[(t + t'_{ex}) - t'_{ex} \cdot \left(\frac{t + t'_{ex}}{t'_{ex}}\right)^n\right]. \tag{17}$$

After rearrangement,

$$T' = \frac{D_{i,0} \cdot (t'_0)^n}{1-n} \cdot [(t + t'_{ex})^{1-n} - (t'_{ex})^{1-n}]. \tag{17'}$$

It can be seen that, if the instantaneous value $D_{i,0}$ has the same meaning as D_0, that is, the diffusion coefficient at the age t'_0, Eq. (17′) becomes identical to Eq. (3). Thus, over ten years after the first publication of equations in [10], the mathematical expression of time-dependent diffusion coefficient in [8,15–17] finally comes back to the analytical one.

4. Errors in durability design due to mathematical oversimplification

In the past years the model using Eq. (12) has been used in a number of large construction projects such as the Western Scheldt Tunnel [18,19], and the Green Heart Tunnel in The Netherlands [20], and the Donghai Cross-See Bridge in China [21]. Therefore, it is necessary to evaluate the errors in durability design and redesign caused by the mathematical oversimplification.

4.1. Errors in the estimation of concrete cover

With the required service life t_L, which is normally assumed as the time for initiation of reinforcement corrosion, the thickness of concrete cover can be estimated using the mathematical models as discussed above. In this case the chloride content C in Eqs. (8), (10) and (12) is replaced with the critical content, C_{cr}, for corrosion initiation. Thus the relationships between the cover thicknesses from different models can be derived, as shown in the following equations, using identical values for D_0 as the starting point:

$$\frac{x_{cEq(10)}}{x_{cEq(8)}} = \sqrt{\frac{1}{f(t'_{ex})}} = \sqrt{\frac{D_{aEq(10)}}{D_{aEq(6)}}} \tag{18}$$

and

$$\frac{x_{cEq(12)}}{x_{cEq(8)}} = \sqrt{\frac{1-n}{f(t'_{ex})} \cdot \left(\frac{t_L}{t_L + t'_{ex}}\right)^n} = \sqrt{\frac{D_{aEq(12)}}{D_{aEq(6)}}} \tag{19}$$

where $x_{cEq(8)}$, $x_{cEq(10)}$ and $x_{cEq(12)}$ denote the cover thickness calculated from Eqs. (8), (10) and (12), respectively. As seen in Figs. 3 and 4, when $t'_{ex} = 0.1$ year and $t_L = 100$ years (corresponding to $t_L/t'_{ex} = 1000$), the model with the simplified mathematics of diffusion as Eq. (10) may overestimate the concrete cover by a few percentage up to 40% if values of $n = 0.7$ to 0.9 are used, while the model with the oversimplified mathematics of diffusion as Eq. (12) may underestimate the concrete cover by 15% to 55% if $n = 0.3$–0.9 are used. The overestimation of concrete cover thickness results in a conservative approach, however an underestimated concrete cover thickness may result in serious social and economical consequences due to the reduced service life.

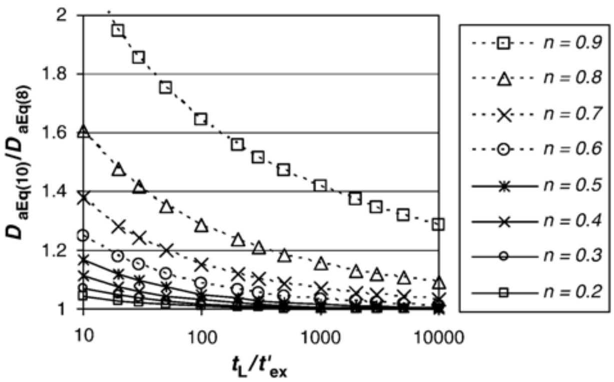

Fig. 3. Relationship between $x_{cEq(10)}$ and $x_{cEq(8)}$.

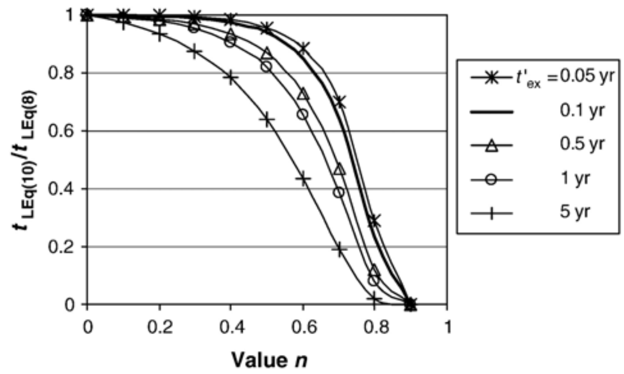

Fig. 5. Relationship between $t_{LEq(10)}$ and $t_{LEq(8)}$.

4.2. Errors in the estimation of service life

Similarly, with the given cover thickness x_c, the relationships between service lives from different models can be derived, as shown in the following equations:

$$t_{LEq(10)} = \left[\left(1+\frac{t'_{ex}}{t_{LEq(8)}}\right)^{1-n} - \left(\frac{t'_{ex}}{t_{LEq(8)}}\right)^{1-n}\right]^{\frac{1}{1-n}} \cdot t_{LEq(8)} \quad (20)$$

and

$$\frac{t_{LEq(12)}}{(t_{LEq(12)}+t'_{ex})^n} = \frac{[t_{LEq(8)}]^{1-n}}{(1-n)} \times \left[\left(1+\frac{t'_{ex}}{t_{LEq(8)}}\right)^{1-n} - \left(\frac{t'_{ex}}{t_{LEq(8)}}\right)^{1-n}\right]. \quad (21)$$

Assuming $t_{LEq(12)} \gg t'_{ex}$ yields

$$t_{LEq(12)} = \left(\frac{1}{1-n}\right)^{\frac{1}{1-n}} \times \left[\left(1+\frac{t'_{ex}}{t_{LEq(8)}}\right)^{1-n} - \left(\frac{t'_{ex}}{t_{LEq(8)}}\right)^{1-n}\right]^{\frac{1}{1-n}} \cdot t_{LEq(8)} \quad (21')$$

where $t_{LEq(8)}$, $t_{LEq(10)}$ and $t_{LEq(12)}$ denote the service life calculated from Eqs. (8), (10) and (12), respectively. Figs. 5 and 6 show the relationships between $t_{LEq(10)}$, $t_{LEq(12)}$ and $t_{LEq(8)}$, assuming $t_{LEq(8)}=100$ years. It can be seen that the model with the simplified mathematics of diffusion as Eq. (10) may underestimate the service life especially when the value of $n>0.5$ or concrete is old at the start of exposure (corresponding to a large t'_{ex}), while the model with the oversimplified mathematics of diffusion as Eq. (12) may overestimate the service life by orders of magnitude if the value of n is large. In the DuraCrete Model [14], values of $n=0.3$ to 0.9 are given. This means that the model using Eq. (12) may overestimate the service life by at least 60% (when $n=0.3$ and $t'_{ex}=0.1$ year), and easily by more than one order of magnitude (when $n>0.63$). As an example, if $D_0=5\times10^{-12}$ m^2/s, $t'_0=t'_{ex}=28$ days, $C_{cr}/C_s=0.1$, $x_c=40$ mm and $n=0.6$, Eqs. (8) and (10) give a service life of 29 and 23 years, respectively, but Eq. (12) gives 227 years! Therefore, the mathematical oversimplification using Eq. (12) can easily result in a large overestimation of service life. It should be noticed that the most important contribution of the DuraCrete model to the durability design and redesign is its probabilistic approach. The oversimplification of the deterministic Eq. (12) can easily be corrected without losing the entire advantage of the probabilistic approach.

5. Comparison between predicted and measured chloride profiles

Chloride profiles measured from two types of concrete continually submerged in seawater at a field site at the Swedish

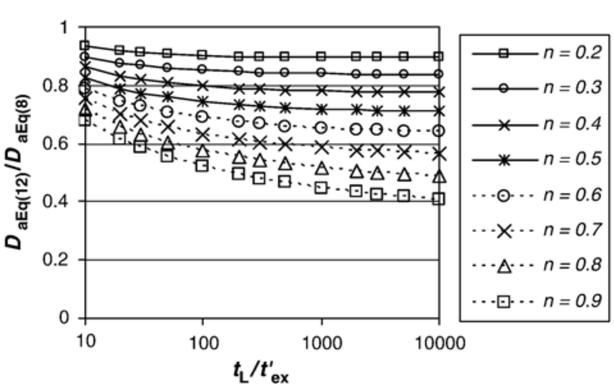

Fig. 4. Relationship between $x_{cEq(12)}$ and $x_{cEq(8)}$.

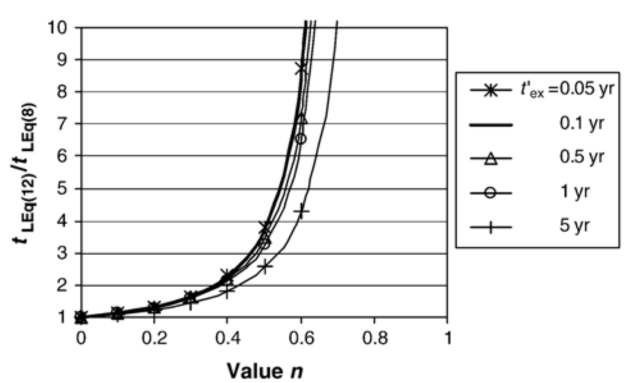

Fig. 6. Relationship between $t_{LEq(12)}$ and $t_{LEq(8)}$.

Table 1
Relevant input data for modeling

Binder type	w/b	R_{28d}, MPa	D_{RCM} or D_0, $\times 10^{-12}$ m^2/s	n according to [14]	C_s according to [14]
100% SRPC	0.30	96	2.5	0.30	3.09
80%SRPC+20%FA	0.30	98	1.5	0.69	3.24

west coast were used to compare the models between the improved mathematics as expressed in Eq. (8) and the DuraCrete formula as expressed in Eq. (14), which is identical to Eq. (12) if $D_0 = k_c \cdot k_e \cdot D_{RCM}$. The detailed information about the field site, the mixture proportions of concrete, the laboratory measurement of chloride migration coefficient and the measurement of chloride profiles was reported elsewhere [22]. The two types of concrete, one with sulfate resistant Portland cement (SRPC) and another blended with 20% fly ash (FA), were chosen in order to evaluate the effect of age factor on the prediction results. Both types of concrete have a water binder ratio of 0.3, belonging to HPC (high-performance concrete). The concrete slabs were exposed to the marine environment at the age $t'_0 = 0.03$ years. The chloride diffusion coefficient D_0 in Eq. (8) or D_{RCM} in Eq. (14) was measured from the parallel specimens stored in the laboratory at the age $t'_0 = 0.5$ years using the Rapid Chloride Migration Test [2] which has later been adopted as a Nordtest method NT BUILD 492 [26]. The mean values of the surface-chloride content C_s were calculated according to the DuraCrete design guidelines [14]. According to the guideline [14], the curing factor $k_c = 0.85$ and the environmental factor $k_e = 1.32$. Other relevant input data used in the modeling are summarized in Table 1. The modeled results are shown in Figs. 7 and 8. It can be seen that the predicted profiles by both Eqs. (8) and (14) are in fairly agreement with the measured ones for Portland cement concrete (Fig. 7). The difference in predicted profiles between Eqs. (8) and (14) is not very large, owing to a relatively low value of age factor ($n = 0.3$). However, for the concrete blended with 20% fly ash, Eq. (14) predicts chloride penetration profiles significant lower than the measured ones. If the critical content, C_{cr}, is 1 mass% of binder for the submerged zone, the actual chloride penetration after 10 years' exposure at the depth of 20 mm has already exceeded the predicted 100 years' penetration

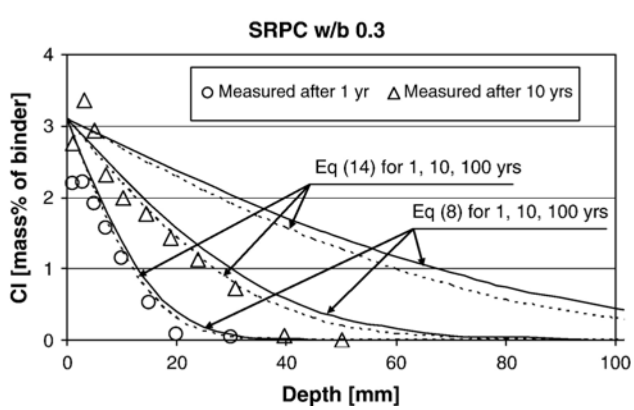

Fig. 7. Measured and predicted chloride profiles in Portland cement concrete.

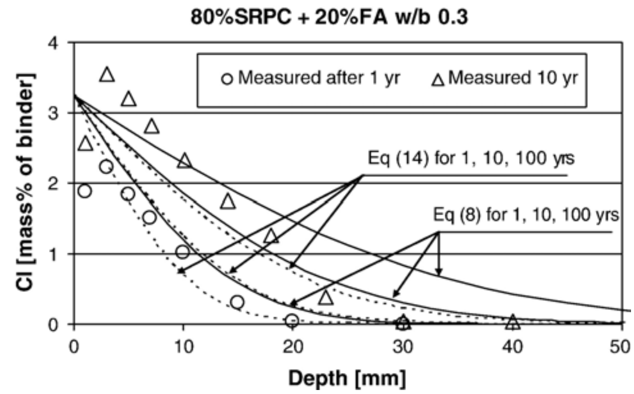

Fig. 8. Measured and predicted chloride profiles in concrete with fly ash.

(Fig. 8), implying that Eq. (14) overestimates the service life by an order of magnitude, similar to the example demonstrated in Section 4.2. With the improved mathematics, Eq. (8) gives relatively better prediction to the 10 years' chloride penetration, even though the shape of the predicted profile is not in good agreement with the actual one, especially the surface-chloride content.

From Figs. 7 and 8 as well as other observations, it has been found that the surface-chloride content C_s also increases with exposure time [22–25], even for concrete exposed under submerged conditions [22,24,25], where the free surface-chloride concentration c_s remains relatively constant over time. Tang and Nilsson [25] attributed the increased surface-chloride content C_s under submerged conditions to the increased chloride binding capacity. The ERFC models assume a constant C_s, which is obviously not the case in reality. Although Eq. (8) describes the time-dependent diffusion in a more proper mathematical way and gives a relatively better prediction, the ignorance of chloride binding is perhaps a vital weakness of the ERFC based models. Further study is certainly needed to improve the ERFC models through more proper estimation of the effect of C_s on the chloride ingress in concrete.

6. Concluding remarks

Based on the more proper mathematical analysis for a time-dependent diffusion coefficient we can conclude that the simplified model such as represented by Eq. (10) may be used for long-term prediction without significant mathematical errors if the age factor n is small (<0.3), however it may underestimate the service life if high values for n are used. From the point view of structural safety, this underestimation may be acceptable because it is on the conservative side, especially when considering the fact that there is still lack of information about the long-term effect of time-dependent chloride diffusion coefficient. However, this model should not be used for obtaining apparent diffusion coefficients from short-term exposures, because in this case the model will tremendously overestimate the apparent diffusion coefficient, as shown in Fig. 1.

The big mathematical oversimplification in some ERFC models using Eq. (12) is mainly due to the negligence of the term $f(t'_{ex})/(1-n)$. As a consequence, the oversimplified ERFC models may easily overestimate the service life by up to orders of magnitude, depending on which age factor is used.

Based on the comparison with the actual ingress profiles measured from two types of concrete exposed under the seawater, it can be concluded that both the oversimplified and the improved models fairly well predict the 10 years' chloride ingress in Portland cement concrete, but the oversimplified ERFC model significantly underestimates the chloride ingress in concrete with fly ash.

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