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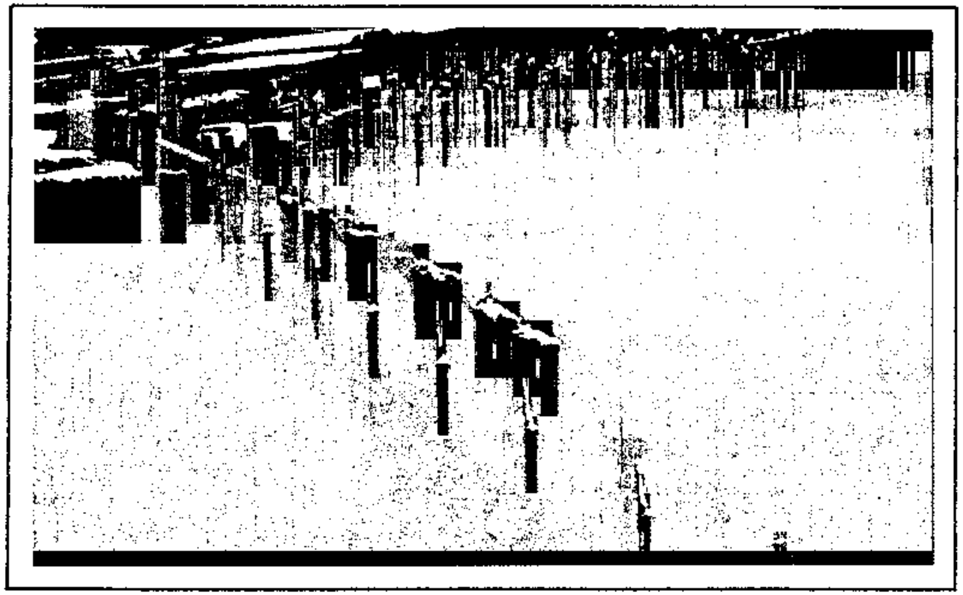

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Estimation of Chloride Ingress and Service Life Prediction in RC Structures Exposed to Marine Environment

by Ervin Poulsen

Synopsis: In 1996 Mejlbro [1] and Poulsen [2] published a mathematical model of the chloride ingress into concrete by diffusion. The model was based upon a solution of Fick's second law of diffusion [3] in such a way that the achieved chloride diffusion coefficient and the chloride content of the exposed concrete surface, i.e. the boundary condition, could be time-dependent. This model was inspired by several observations and data from marine RC structures published by Takewaka et al [4], Uji et al [5] and Swamy et al [6].

The mathematical model was chosen to depend on four basic parameters which described the environment and the concrete's response to the exposure of it. In this way it was possible to calibrate the mathematical model to observations obtained from marine RC structures and from concrete specimens exposed at marine exposure stations such that it was still possible to obtain an analytical solution to the prediction of the service lifetime of a marine RC structure [2] and the design of the rebar cover [7] and [8].

In 1995 the Road Directorate in Denmark launched a number of research projects among which the project »Test Methods for Chloride Resistance of High Quality Concrete« made it possible to calibrate the mathematical model by 15 different concretes comprising 4 types of cement, 2 types of silica fume, 2 types of fly ash and with a range of the ratio of water to binder from 0.25 to 0.75 by mass, [9], [10], [11], 12] and [13].

This paper presents the result of the calibration of the mathematical model of chloride ingress into concrete of marine RC structures. Furthermore, a formula for the service lifetime prediction is presented, and it is illustrated how this formula should be applied in practice.

Keywords: Chloride ingress, Fick's second law, time-dependent diffusion coefficient, time-dependent surface chloride concentration, threshold chloride content, marine exposure, service life prediction.

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INTRODUCTION

Until Collepardi et al, [14] and [15], published their model of chloride ingress into concrete by diffusion, no mathematical model of chloride ingress into concrete was available. Therefore, during the "pre-Collepardi period," the determination of the concrete composition and the rebar cover necessary for the maintenance of a required service lifetime were mainly based upon experience and rules of thumb. During this period the 1-2-3 rule of rebar cover was declared valid for indoor, out of doors and marine environment, respectively. However, in some countries rebar covers of 1, 2 and 3 inches were used while in others the cover was 1, 2 and 3 cm.

A great step forward was taken when the mathematical model of chloride ingress into concrete by diffusion was introduced in the early 1970s by Collepardi et al. This introduction revolutionized the analysis and design of marine RC structures. Mario Collepardi studied ceramics in the late 1960s. Diffusion processes of ceramics at high temperatures according to Fick's second law of diffusion were well-known at that time from Crank's text book [16] on »The Mathematics of Diffusion« (first edition 1956). Collepardi's study of chloride diffusion in cement paste and concrete was only academic at that time [17]. His study was published in English in the Journal of the American Ceramic Society in 1972, and changed all further studies of chloride ingress into concrete. .

The solution of Fick's second law of diffusion described by Collepardi et al was applied by several authors on condition that the chloride diffusion coefficient and the chloride content of the near-to-surface layer of the exposed concrete remain constant. When applied to old marine RC structures this assumption is acceptable, but for younger structures and especially for newly cast structures this assumption would lead to gross deviation from what is found in practice.

Extensive inspection of marine concrete structures, especially in Japan, [4], [5], [6], led to the proposal that the chloride diffusion coefficient and the chloride content of the near-to-surface layer of the exposed concrete were time-dependent beside depending on the concrete composition, the chloride intensity of the marine environment and workmanship (casting, compaction, curing).

The solution of Fick's second law of diffusion only existed for a variation of the surface chloride content with time [16] as a constant, the square root of time and a linear dependency on time.

THE MEJLBRO-POULSEN MODEL

Until recently no analytical solution of Fick's second law of diffusion was available when the boundary condition was time-dependent except in special cases. The missing analytical solution of Fick's second law of diffusion with time-dependent surface chloride concentration and time-dependent diffusion coefficient was found by Mejlbro [1] in 1996 making it possible to describe the chloride ingress into concrete in more details than before, [2] and [12].

The Mejlbro-Poulsen model of chloride ingress into concrete has, therefore, formed one of the bases of the Danish research programme named HETEK on the chloride ingress into marine and deiced RC structures. HETEK is the Danish abbreviation for »**H**igh quality concrete, the **E**ntrepreneur's **TEC**hnology«. The model was verified by a comparison with observations obtained from the Träslövsläge Marine Exposure Station situated near Varberg in Sweden.

Chloride Ingress into Concrete

The Mejlbro-Poulsen model is described in all details in [1] and [2]. Thus, only a few comments will be stressed here.

It was found that the achieved chloride content of the near-to-surface layer of the exposed concrete surface C_{sa} not only depended on time but also on the properties of the concrete and the chloride intensity of the environment [5], [6] and [12]. Thus, Mejlbro [1] proposed that C_{sa} ought to be described by the following family of functions:

$$C_{sa} = C_i + S_p \times \left\{ \left(\frac{t}{t_{ex}} - 1 \right) \times \frac{D_a}{D_{aex}} \right\}^p \tag{1}$$

Here:

C_i denotes the initial chloride content of the concrete.

S_p is a factor depending on concrete and environment, cf. [12].

p is an exponent depending on concrete and environment, cf. [12].

t denotes the time (concrete age) measured from the time of casting (origon).

t_{ex} denotes the time of the first chloride exposure.

D_a denotes the achieved chloride diffusion coefficient, [18] and [1], defined by:

$$D_a = \frac{1}{t - t_{ex}} \int_{t_{ex}}^{t} D(u)du \tag{2}$$

where:

D denotes the true chloride diffusion coefficient of the concrete.

Extensive inspection of marine RC structures in Japan [4] led to the proposal that the achieved (i.e. measured) diffusion coefficient D_a varies versus time as a power function (Takewaka's law), i.e.:

$$D_a = D_{aex} \times \left(\frac{t_{ex}}{t}\right)^{\alpha} \qquad (3)$$

Here:

D_{aex} denotes the value of the diffusion coefficient at time $t = t_{ex}$.

α is an exponent which varies between 0 and 1, cf. [4] and [19].

When applying Takewaka's law (3) the chloride concentration of the exposed concrete surface obeys the following simple expression:

$$C_{sa} = C_i + S_p \times \tau^p \qquad (4)$$

where:

$$\tau = \left(\frac{t}{t_{ex}}\right)^{1-\alpha} - \left(\frac{t_{ex}}{t}\right)^{\alpha} \qquad (5)$$

Applying (3) and (4) the solution of Fick's second law of diffusion yields [1]:

$$C(x,t) = C_i + S_p \times \tau^p \times \Psi_p\left(\frac{0.5x}{\sqrt{\tau \times t_{ex} D_{aex}}}\right) \qquad (6)$$

where $C(x,t)$ is the chloride concentration of the concrete at distance x from the exposed concrete surface at time t and $\Psi_p(z)$ are the Mejlbro's Ψ-functions [1] which are a generalized erfc-function and defined as:

$$\Psi_p(z) = \sum_{n=0}^{+\infty} \frac{p^{(n)}(2z)^{2n}}{(2n)!} - \frac{\Gamma(p+1)}{\Gamma(p+0.5)} \sum_{n=0}^{+\infty} \frac{(p-0.5)^{(n)}(2z)^{2n+1}}{(2n+1)!} \qquad (7)$$

The notation used in (7) is:

$$p^{(n)} = p \times (p-1) \times (p-2) \times \ldots \times (p-n+1) \qquad (8)$$

with n factors and $n \geq 1$. For $n = 0$, $p(0) = 1$. In (7) the notation $\Gamma(y)$ denotes the Gamma function defined as:

$$\Gamma(y) = \int_0^{+\infty} u^{y-1} \exp(-u) du \qquad (9)$$

for $y \geq 0$. The functions $\Psi_p(z)$ can be determnined by means of a spread sheet, e.g. Microsoft Excel 5.0, and a simple pocket programme for HP-42S is given in [1], where also the Ψ-functions are tabulated.

The Träslövsläge Marine Exposure Station

In order to determine how the four parameters of concrete chloride diffusivity, α, D_{aex}, S_p and p depend on the concrete composition and the various marine environments, i.e. submerged in seawater, marine splash and marine atmosphere, observations of the chloride ingress into concrete specimens at the Träslövsläge Marine Exposure Station on the Swedish west coast were studied. At this exposure

station several concrete specimens representing 15 Nos. of different types of concrete had been exposed for up to 2.4 years at the time of this study, leading to 83 Nos. of chloride profiles comprising 475 Nos. of chloride determinations. The following parameters were studied:

- 4 types of cement (Swedish Slite, Anlägg, Degerhamn and Danish low alkali sulphate resisting portland cement).
- 2 types of silica fume (slurry 1:1 and condensed silica fume).
- 2 types of fly ash (Swedish and Danish).
- Water/binder ratios: 0.25 - 0.75 by mass (i.e. 0.25, 0.30, 0.35, 0.40, 0.50, 0.75).

CHLORIDE PROFILES

The basis of how to characterize the chloride diffusivity of concrete is the chloride profile, i.e. the graph of the chloride concentration of the concrete versus the distance from the chloride exposed surface. In order to be able to handle the information represented by the chloride profile in a simple way, a chloride profile is described by the following three parameters assuming the chloride ingress into the concrete to obey Fick's second law of diffusion:

- The ordinate C_{sa} of the chloride profile at the exposed surface $x = 0$, i.e. the achieved surface chloride concentration.
- The asymptote C_i of the chloride for $x \to \infty$, i.e. the chloride concentration of the undisturbed (non-exposed) concrete.
- The achieved chloride diffusion coefficient D_a, cf. (2).

Chloride profile of Concrete Exposed to Seawater

Fig. 1 shows typical chloride profiles from one of the specimens (No. 1-50) corresponding to various periods of seawater exposure. The specimens were exposed to seawater when 14 days old (t_{ex} = 0.038 yr) at the Träslövsläge Marine Exposure Station. The concrete contains Swedish Anläggs Cement of 370 kg/m^3 concrete, w/c = 0.50 and aggregates having a maximum size of $d_{\max}$ = 20 mm. The exposed surface of the concrete was cast against formwork. The following is learned from this example:

- C_{sa}, which is the ordinate of the chloride profile at $x = 0$, is time-dependent.
- The chloride profiles show a hump at a distance of appx. $x = 0.5 \times d_{\max}$.

This can be explained in the following way: concrete is a heterogeneous medium, and the chloride from the seawater penetrates concrete through the cement matrix assuming that the aggregates do not allow the chloride to pass. This is the common case of marine concrete. When concrete is cast against formwork the void fraction of the coarse aggregates (filled with cement matrix) ranges from 100 % at surface to a minimum at $x = 0{,}5 \times d_{\max}$, cf. Fig. 2.

Fig. 3 shows a chloride profile from a marine RC structure which has been submerged in seawater for 20 years. The unit of the ordinate of the chloride profile is % by mass concrete. The chloride has penetrated the concrete to about 80 mm from the exposed surface. This made it possible to obtain the detailed shape of the profile by grinding and analyzing layers having a thickness of 1 mm. As seen the profile reflects the presence of the aggregates in the concrete. The aggregates used did not contain calcite (checked by thin section analysis) and the portland cement used at the time of casting (Danish Rapid Hardening portland cement) contained 65 % by mass of CaO. Thus, by the calcium-profile, cf. Fig. 4, the chloride profile showed in Fig. 5 was obtained. Here the unit of the ordinate of the chloride profile is % by mass binder (cement).

Parameters of the chloride profiles

When C_i is assumed to be a constant, it is seen that a chloride profile is described by two parameters D_a and C_{sa}. In order to model the time-dependency of these parameters a minimum of two parameters each is necessary. This means that the chloride ingress into concrete is described by four parameters.

Parameters D_{aex} and α. Takewaka's law (3) shows that D_a is a power function of time. Thus, by plotting D_a versus t/t_{ex} in a double logarithmic coordinate system a straight line is obtained. From this line the geometrical meaning of the parameters can be explained as follows, cf. Fig. 6:

- D_{aex} is the ordinate at the abscissa $t/t_{ex} = 1$, i.e. $t = t_{ex}$.
- α is the (numerical) value of the slope of the straight line.

Parameters S_p and p. Mejlbro's proposal for C_{sa}, cf. (4), shows that $C_{sa} - C_i$ is a power function of the parameter τ, cf. (5). Thus, by plotting $C_{sa} - C_i$ versus τ in a double logarithmic coordinate system a straight line is obtained. From this line the geometrical meaning of the parameters can be explained as follows, cf. Fig. 6:

- S_p is the ordinate at the abscissa $\tau = 1$.
- p is the slope of the straight line.

PARAMETERS ESTIMATED FROM CONCRETE MIXTURE

Since a wide range of different concretes were tested at the Träslövsläge Marine Exposure Station, it should be possible to to determine formulae for the basic parameters in relation to the concrete composition. These relations seem to be rather complicated, but at the present stage only simple relations have been tried, since only data from the examination of concrete exposed up to 2.4 years were available. However, new sets of observations will be available during 1997 – and these data may change the formulae here presented. However, the whole idea presented will be applicable for data from other marine exposure stations and, therefore, of interest to the reader.

Derived Parameters

It was found that it was too complicated to find the relation between the concrete composition and the basic parameters. Instead, four derived parameters were introduced, namely:

- C_1 the surface chloride concentration C_{sa} at the time $t = 1$ year.
- C_{100} the surface chloride concentration C_{sa} at the time $t = 100$ years.
- D_1 the chloride diffusion coefficient D_a at the time $t = 1$ year.
- D_{100} the chloride diffusion coefficient D_a at the time $t = 100$ years.

Efficiency Factors

In order to determine the influence of the concrete composition on these derived parameters the equivalent w/c is introduced as:

$$\mathrm{eqv}\{w/c\} = \frac{W}{C + f_F \times F + f_S \times S} \tag{10}$$

where:

W is mass of water per unit volume of concrete, e.g. kg/m^3 of concrete.
C is mass of cement per unit volume of concrete, e.g. kg/m^3 of concrete.
F is mass of fly ash per unit volume of concrete, e.g. kg/m^3 of concrete.
S is mass of silica fume per unit volume of concrete, e.g. kg/m^3 of concrete.
f_F is efficiency factor for fly ash with respect to the property in question.
f_S is efficiency factor for silica fume with respect to the property in question.

Formulae for Derived Parameters

Frederiksen [12] has proposed the following formulae for the derived parameters:

$$C_1 = k_b \times \mathrm{eqv}\{w/c_b\} \tag{11}$$

$$C_{100} = k_t \times C_1 \tag{12}$$

$$D_1 = k_D \times \exp\left(-\sqrt{\frac{10}{\mathrm{eqv}\{w/c_D\}}}\right) \tag{13}$$

$$D_{100} = \frac{D_1}{\exp[k_\alpha \times (1 - 1.5 \times \mathrm{eqv}\{w/c_D\})]} \tag{14}$$

The factors k_b, k_t, k_D and k_α represent the types of environment, and their values are given in Table 1. The efficiency factors f_F and f_S of $\mathrm{eqv}\{w/c_b\}$ and $\mathrm{eqv}\{w/c_D\}$, cf. (10), are presented in Table 2. The unit of C_1 and C_{100} is % by mass binder and the unit of D_1 and D_{100} is mm^2/yr.

Fig. 7 and 8 show the values of D_1 and C_1, found from interpolation of observations versus the estimated values calculated from Frederiksen's formulae (11) to (14). An acceptable agreement is obtained.

Values of D_{100} and C_{100} must be found from extrapolation of observations. If only few observations are available at early ages D_{100} and C_{100} will show gross deviations. Fig. 9 shows the determination of D_1 and D_{100} from just two observations, each given by their confidence intervals. By interpolation of all combinations likely to occur it is seen that the deviation of D_1 determined by interpolation has the same order of magnitude as the observations. It is also seen that the deviation of D_{100} determined by extrapolation will show gross deviation. To overcome this problem it is necessary to inspect the test specimens many times during the early period. Of the 15 concretes tested at Träslövsläge Marine Exposure Station only 5 concretes are covered by three observations and 10 concretes are covered by just two observations. The next set of observations will be available during 1997.

Fig. 10 and 11 show the values of D_{100} and C_{100}, found from extrapolation of observations versus the estimated values calculated from Frederiksen's formulae (11) to (14). Gross deviation is expected and observed.

From Derived to Basic Parameters

The four basic parameters D_{aex}, α, S_p and p of the chloride diffusivity and the local environment of the concrete, defined by (3), (4) and (5), can be found from the knowledge of D_1, D_{100}, C_1, and C_{100} by a step-by-step determination in the following way:

Step 1. Calculate the parameter:

$$\theta = \frac{1}{2} \times \log_{10}\left(\frac{1}{t_{ex}}\right) \tag{15}$$

Step 2. Calculate:

$$\alpha = \frac{1}{2} \times \log_{10}\left(\frac{D_1}{D_{100}}\right) \tag{16}$$

Step 3. Calculate:

$$D_{aex} = D_1 \times \left(\frac{D_1}{D_{100}}\right)^{\theta} \tag{17}$$

Step 4. Calculate:

$$p = \frac{\log_{10}\left(\dfrac{C_{100}}{C_1}\right)}{\log_{10}\left(\dfrac{100 - t_{ex}}{1 - t_{ex}} \times \dfrac{D_{100}}{D_1}\right)} \tag{18}$$

Step 5. Calculate:

$$S_p = C_1 \times \left\{\left(\frac{D_1}{D_{100}}\right)^{\theta} \times \frac{t_{ex}}{1 - t_{ex}}\right\}^{p} \tag{19}$$

These formulae are known as Mejlbro's transformation formulae. The formulae are suitable for calculation by means of a spread sheet or a programmable pocket calculator.

PREDICTION OF SERVICE LIFETIME

When the service lifetime of a new marine RC structure has to be predicted several concepts are possible, e.g.:

- The basic parameters may be estimated on the basis of personal experience, a data base, references in the literature or examination of neighbouring marine RC structures to the structure planned.
- The derived parameters may be found by Frederiksen's formulae for C_1, C_{100}, D_1 and D_{100}, cf. (11) to (14), and transformed into the basic parameters α, D_{aex}, S_p and p by Mejlbro's transformation formulae (15) to (19).
- The basic parameters may be found on the basis of in-situ pre-testing the concrete proposed to the local marine environmental class in question.

The determination of the parameters describing the long time development of the chloride ingress into concrete will always be made with an uncertain prediction, and one has to rely on parameters assumed to be constant really are constant during the service lifetime, e.g. the threshold value of chloride in concrete.

Definition of Service Lifetime

The service lifetime of a marine RC structural member is here defined as the initiation period, i.e. the time from mixing (casting) the concrete until the chloride concentration at the reinforcement has reached the threshold level corresponding to the concrete and it's local marine environment and starts corroding.

No part of the propagation stage is taken into account, even if there is a reserve of reinforcement. The chloride attack on reinforcement results not only in a decrease of the cross-section of the rebars, but it also introduces brittleness to the reinforcement [20]. Ductility of RC structures is one of the important bases of the structural design (even if the theory of linear elasticity is applied). However, marine RC structures like bridges and jetties are exposed to dynamic loads and ought to be ductile, e.g. as required by the Danish Code of Practice.

The repair of RC structures suffering from disintegration caused by chloride attack is difficult and costly. The rehabilitation during its initiation stage is generally small compared with rehabilitation during the propagation stage. Thus, the end of the initiation period is often »the point of no return«.

Threshold Value of Chloride in Concrete

No simple transformation exists of short term corrosion data from the laboratory and marine exposure stations to threshold values which are applicable to determine the long term behaviour of marine RC structures. Here, the results of the HETEK project are applied and the reader is referred to this work [12].

Frederiksen [12] has proposed the following formula for the threshold value of chloride in concrete, depending on the concrete composition and the local marine environment:

$$C_{\mathrm{cr}} = k_{\mathrm{cr}} \times (1.2 - \mathrm{eqv}\{w/c_{\mathrm{cr}}\}) \tag{20}$$

where the equivalent ratio of water to cementious materials $\mathrm{eqv}\{w/c_{\mathrm{cr}}\}$ is defined by (10). The environmental factor k_{cr} is given in Table 1 and the efficiency factors f_F and f_S are given in Table 2. Eq. (20) is valid for rebar cover ≥ 25 mm and crack width ≤ 0.1 mm.

Service Lifetime Formula

When the basic parameters α, D_{aex}, S_p and p are given the chloride profile can be calculated at any time from:

$$C(x,t) = C_i + (C_{sa} - C_i) \times \Psi_p(z) \tag{21}$$

where:

$$z = \frac{0.5x}{\sqrt{\tau \times t_{ex} D_{aex}}} \tag{22}$$

In order to determine the initiation period it is convenient to write (21) as follows:

$$C(x,t) = C_i + S_p \times \left(\frac{0.5x}{\sqrt{t_{ex} D_{aex}}} \right)^{2p} \times \Lambda_p(z) \tag{23}$$

where z is given by (22) and:

$$\Lambda_p(z) = \frac{\Psi_p(z)}{z^{2p}} \tag{24}$$

The functions $\Lambda_p(z)$ are tabulated versus z and p by Mejlbro [1].

When knowing the basic parameters, the cover c of the reinforcement and the threshold value C_{cr}, the initiation time t_{cr} can be determined by solving the following equations :

$$C_{\mathrm{cr}} = C_i + S_p \times \left(\frac{0.5c}{\sqrt{t_{ex} D_{aex}}} \right)^{2p} \times \Lambda_p(z_{\mathrm{cr}}) \tag{25}$$

$$z_{\mathrm{cr}} = \frac{0.5c}{\sqrt{\tau_{\mathrm{cr}} \times t_{ex} D_{aex}}} \tag{26}$$

$$\tau_{\mathrm{cr}} = \left(\frac{t_{\mathrm{cr}}}{t_{ex}} \right)^{1-\alpha} - \left(\frac{t_{ex}}{t_{\mathrm{cr}}} \right)^{\alpha} \approx \left(\frac{t_{\mathrm{cr}}}{t_{ex}} \right)^{1-\alpha} \tag{27}$$

When $t_{\mathrm{cr}} >> t_{\mathrm{ex}}$ the initiation period yields:

$$t_{\mathrm{cr}} = t_{ex} \times \left(\frac{0.5c}{\sqrt{t_{ex} D_{aex}} \times \mathrm{inv}\Lambda_p(y_{\mathrm{cr}})} \right)^{\frac{2}{1-\alpha}} \tag{28}$$

where $\mathrm{inv}\Lambda_p$ is the inverse Λ-function and:

$$y_{\mathrm{cr}} = \frac{C_{\mathrm{cr}} - C_i}{S_p} \times \left(\frac{\sqrt{t_{ex} D_{aex}}}{0.5c} \right)^{2p} \tag{29}$$

DISCUSSION AND CONCLUSION

Deterministic prediction of the service lifetime of a marine RC structure is rather complex, i.e. many parameters are involved, and they have a non-linear influence which makes it difficult to determine it by pre-testing the concrete. However, here the lifetime is described as a function of five decisive parameters.

The influences of the properties of the concrete and its response to the marine environment are neither fully understood nor determined.

The basic parameters presented must be calibrated against observed chloride ingress into concrete of old marine RC structures before application of this method.

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REFERENCES

[1] **Leif Mejlbro**: »The Complete Solution of Fick's Second Law of Diffusion with Time-dependent Diffusion Coefficient and Surface Concentration«. Durability of Concrete in Saline Environment. Cementa. Danderyd Sweden 1996.

[2] **Ervin Poulsen**: »Estimation of Chloride Ingress into Concrete and Prediction of Service Lifetime with Reference to Marine RC Structures«. Durability of Concrete in Saline Environment. Cementa. Danderyd Sweden 1996.

[3] **Adolf E. Fick**: Poggendorff's Annalen der Physik. **94**, 59. 1855.

[4] **K. Takewaka** et al: »Quality and Cover Thickness of Concrete based on the Estimation of Chloride Penetration in Marine Environment«. ACI, SP-109. Detroit USA 1988.

[5] **K. Uji** et al: »Formulation of an Equation for Surface Chloride Content due to Permeation of Chloride«. Proceedings of the third International Symposium on »Corrosion of Reinforcement in Concrete Construction«. Elsevier Applied Science, London UK 1990.

[6] **R.N. Swamy** et al: »A Critical Evaluation of Chloride Penetration into Concrete in Marine Environment«. Proceedings of the Conference on »Corrosion and Corrosion Protection of Steel in concrete«. University of Sheffield, Vol. 1. Sheffield UK 1994.

[7] **Ervin Poulsen**: »Design of Rebar Covers in Marine Concrete Structures, Deterministic Approach«. Proceedings of the International RILEM Workshop on »Chloride Penetration into Concrete«. RILEM Publication, E-mail: sg@rilem.ens-cachan.fr. France 1995.

[8] **Ervin Poulsen** et al: »Design of Rebar Covers in Marine RC Structures«. Proceedings of the Odd E. Gjørv Symposium on »Concrete for Marine Structures«. St. Andrews-By-The-Sea Canada 1996.

[9] **Jens M. Frederiksen** (edt.) et al: »HETEK, Chloride Penetration into Concrete«. State-of-the-Art, Transport Processes, Corrosion Initiation, Test Methods and Prediction Models«. Report No. 53:1996. The Danish Road Directorate. Copenhagen Denmark 1996.

[10] **Jens M. Frederiksen** (edt.) et al: »HETEK, the Effect of the *w/c* Ratio on Chloride Transport into Concrete – Immersion, Migration and Resistivity Tests«. Report No. 54:1996. The Danish Road Directorate. Copenhagen Denmark 1996.

[11] **Jens M. Frederiksen** (editor) et al: »HETEK, Investigation of Chloride Penetration into Bridge Columns Exposed to De-icing Salt«. Report No. 82:1996. The Danish Road Directorate. Copenhagen Denmark 1996.

[12] **Jens M. Frederiksen** (editor) et al: » HETEK, a System of Estimation of Chloride Ingress into Concrete, Theoretical Background«. Report No. 83:1997. The Danish Road Directorate. Copenhagen Denmark 1997.

[13] **Jens M. Frederiksen** (editor) et al: » HETEK, Manual for the Design, Execution and Maintenance of Reinforced Concrete Infrastructures Exposed to Chloride«. Report No. 87:1997. The Danish Road Directorate. Copenhagen Denmark 1997.

[14] **Mario Collepardi** et al: »The Kinetics of Chloride Ions Penetration in Concrete (in Italian)«. Il Cemento, Vol. 67. Italy 1970.

[15] **Mario Collepardi** et al: »Penetration of Chloride Ions into Cement Pastes and Concrete«. Journal of American Ceramic Society, Vol. 55. USA 1972.

[16] **John Crank:** »The Mathematics of Diffusion«. Second Edition (first edition 1956). Clarendon Press. Oxford UK 1975.

[17] **Mario Collepardi:** »Private communication«. ENCO. Spresiano Italy 1997.

[18] **Ervin Poulsen:** »On a Model of Chloride Ingress into Concrete having Time-dependent Diffusion Coefficient«. Nordic Miniseminar on Chloride Penetration into Concrete Structures. Gothenburg Sweden 1993.

[19] **Magne Maage** et al: »Practical Non-steady State Chloride Transport as a Part of a Model for Predicting the Initiation Period«. Proceedings of the International RILEM Workshop on »Chloride Penetration into Concrete«. RILEM Publication, E-mail: sg@rilem.ens-cachan.fr. France 1995.

[20] **Shigeru Morinaga:** »Remaining Life of Reinforced Concrete Structures after Corrosion Cracking«. Proceedings of the Seventh International Conference on Durability of Building Materials and Components, Stockholm Sweden, Vol. 1. E & FN Spon. UK 1996.

Table 1. Values of environment factors used in Frederiksen's formulae (11) to (14).

Environment	k_b	k_t	k_D	k_α	k_{cr}
Marine atmosphere	2.20	7.0	10,000	4.60	0.50
Marine splash	3.70	4.5	15,000	0.45	0.75
Submerged	5.15	1.5	25,000	2.75	2.00

Note. The environmental factors k_α and k_t are non-dimensional while the unit of the environmental factor k_b is »% by mass binder« and the unit of k_D is »mm^2/yr«. The environmental factors are defined by equation (11) to (14). The environmental factors are found by a multiple regression analysis on data from the Träslövsläge Marine Exposure Station.

Table 2. Values of efficiency factors for calculation of the equvivalent *w/c* of concrete.

Binder	eqv{w/c_b}	eqv{w/c_D}	eqv{w/c_{cr}}
Cement, f_C=	+1.00	+1.00	+1.00
Silica fume, f_S=	–1.50	+7.00	–3.50
Fly ash, f_F=	+0.75	+1.00	–1.00

Note. The efficiency factors are all non-dimensional. The efficiency factors are defined by equation (10) and are found by a multiple regression analysis on data from the Träslövsläge Marine Exposure Station. An efficiency factor of a pozzolan is defined as the value of *w/c* for a corresponding concrete, where the pozzolan is replaced by such an amount of portland cement that this concrete (with otherwise identical constituent materials) has the same chloride diffusivity as the given concrete.

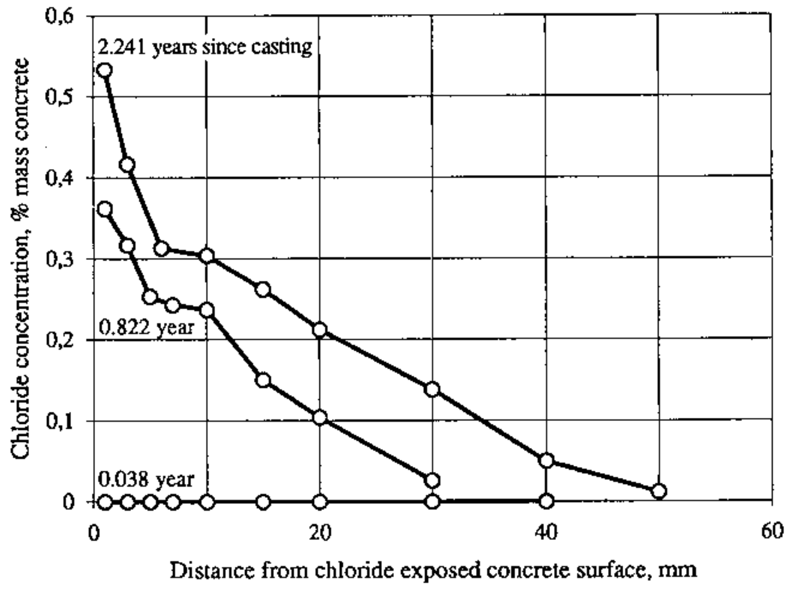

Fig. 1. Typical chloride profiles of concrete submerged in seawater at various periods of exposure. It is seen that the chloride content of the concrete surface and the diffusion coefficient vary with the exposure time. The chloride profiles show a hump at a distance from the exposed concrete surface of appx. 50 % of the maximum aggregate size.

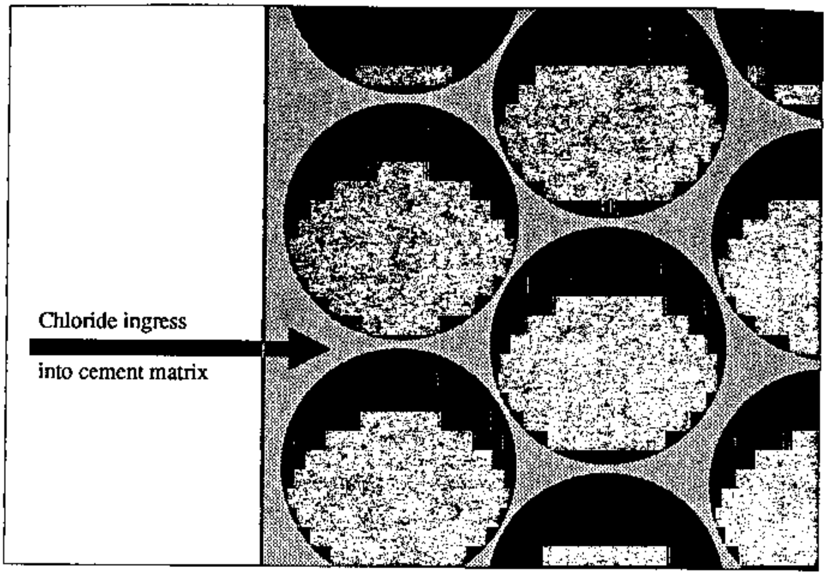

Fig. 2. When concrete is cast against formwork the void fraction of the coarse aggregates (filled with binding matrix) ranges from 100 % at surface to a minimum at 50 % of the maximum aggregate size.

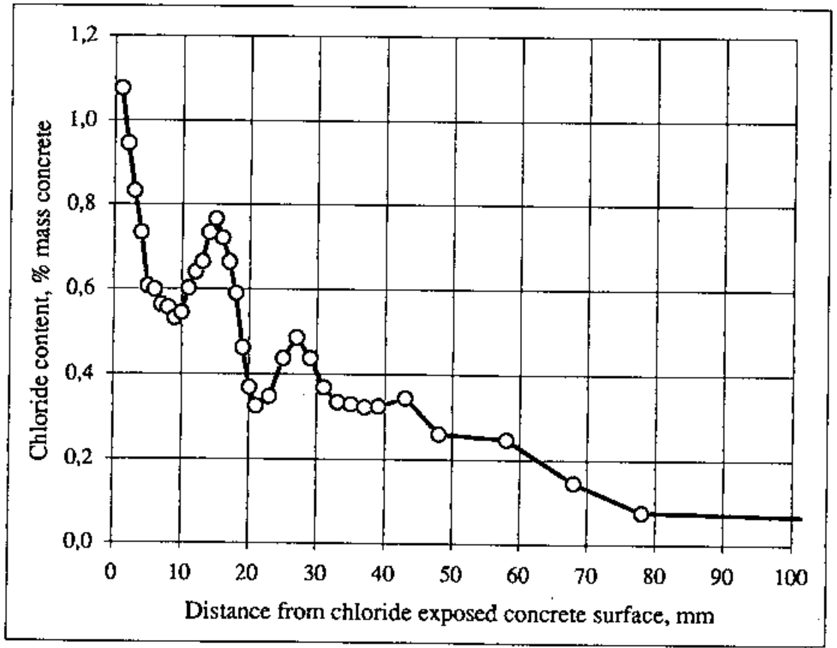

Fig. 3. A chloride profile from a marine RC structure which has been submerged in seawater (Nuuk, Greenland) for 20 years. The unit of the ordinate is % by mass concrete. As seen the profile reflects the presence of the coarse aggregate in the concrete. A detailed shape was made possible by the analysis of 1 mm thick layers.

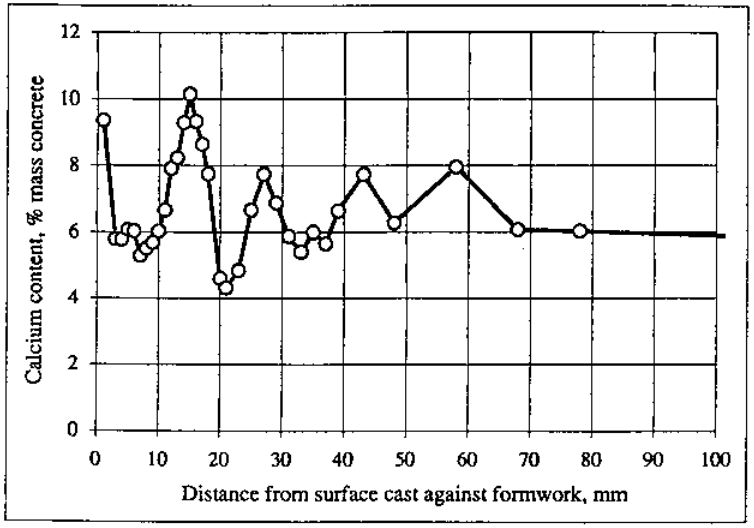

Fig. 4. A calcium-profile of the concrete determined from the same dust-samples as the chloride profile shown in Fig. 3, By assuming that the cement contains 65 % by mass of CaO it is possible to determine the cement profile. Thus, the calcium profile is proportional to the distribution of the cement matrix since the aggregates contain no calcite.

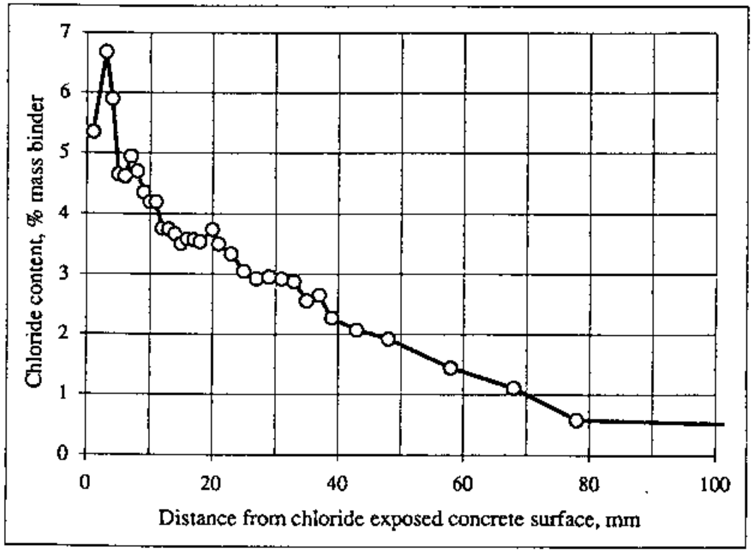

Fig. 5. The chloride profile shown in Fig. 3 transformed by means of the calcium-profile shown in Fig. 4 in such a way that the unit of the ordinate of the chloride profile yields % by mass binder (cement). An effect of leaching is visible at the near-to-surface layer of the concrete.

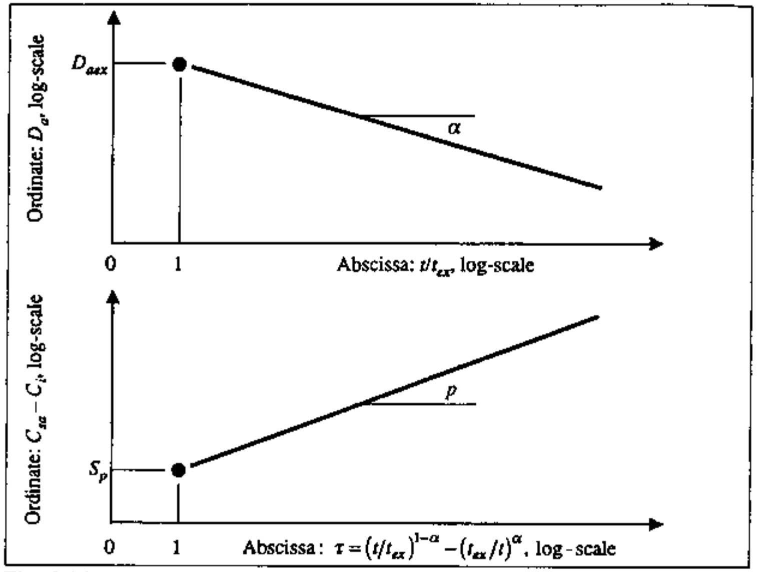

Fig. 6. The basic parameters D_{aex} and α (Takewaka's law (3)) have a geometrical meaning as shown in the upper diagram. The basic parameters S_p and p (Mejlbro's proposal (4)) have a geometrical meaning as shown in the bottom diagram.

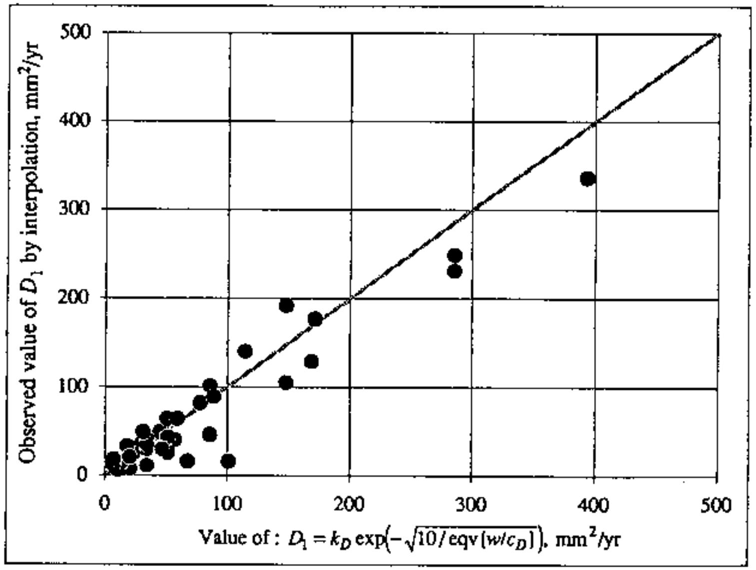

Fig. 7. The observed value of D_1 determined by interpolation of measurements versus the values of D_1 determined by Frederiksen's formula (13). An acceptable agreement is obtained.

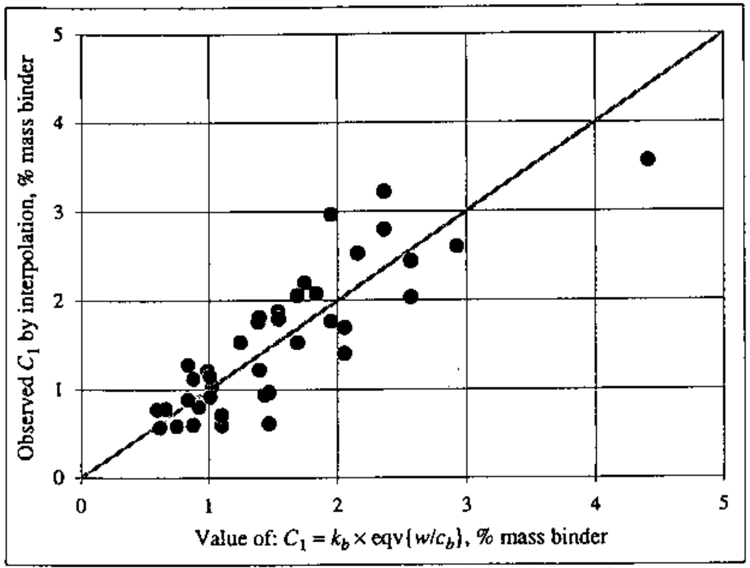

Fig. 8. The observed value of C_1 determined by interpolation of measurements versus the values of C_1 determined by Frederiksen's formula (11). An acceptable agreement is obtained.

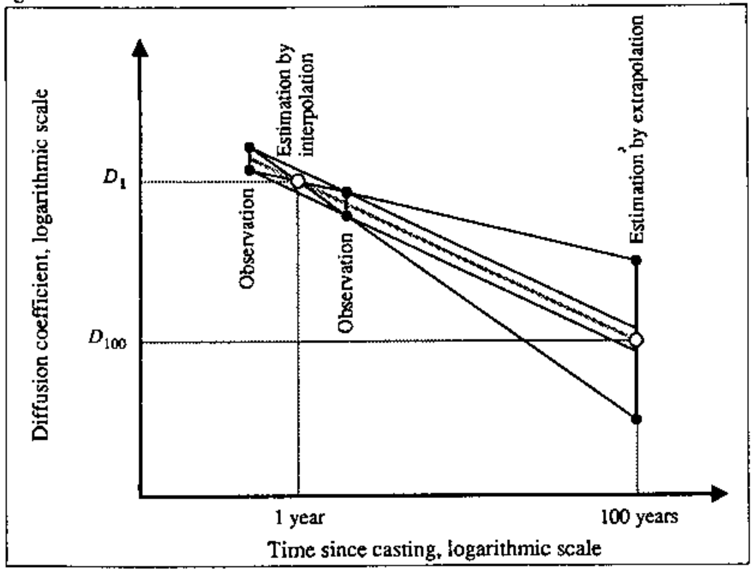

Fig. 9. The determined value of D_1 determined by interpolation of measurements will generally show deviation of the same order of magnitude as the observations themselves, while the determined value of D_{100} determined by extrapolation of the measurements will generally show gross deviation.

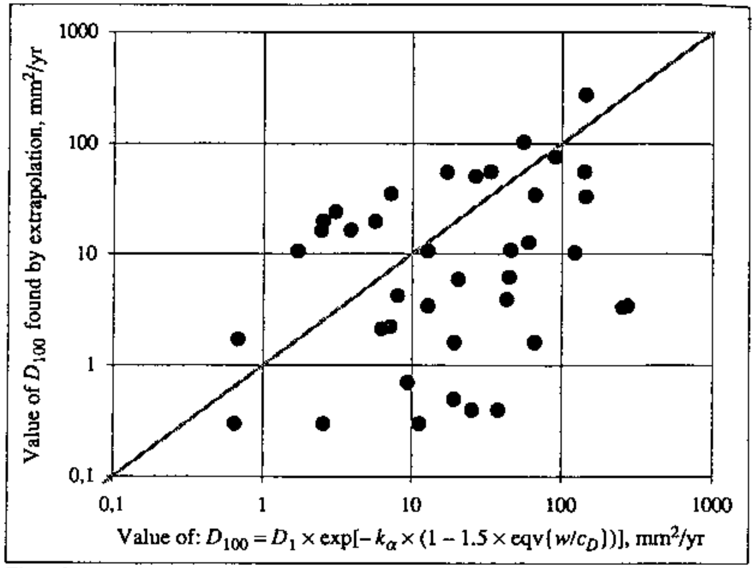

Fig. 10. The determined values of D_{100} found by extrapolation of measurements versus the values of D_{100} determined by Frederiksen's formula (14). A gross deviation is expected and observed.

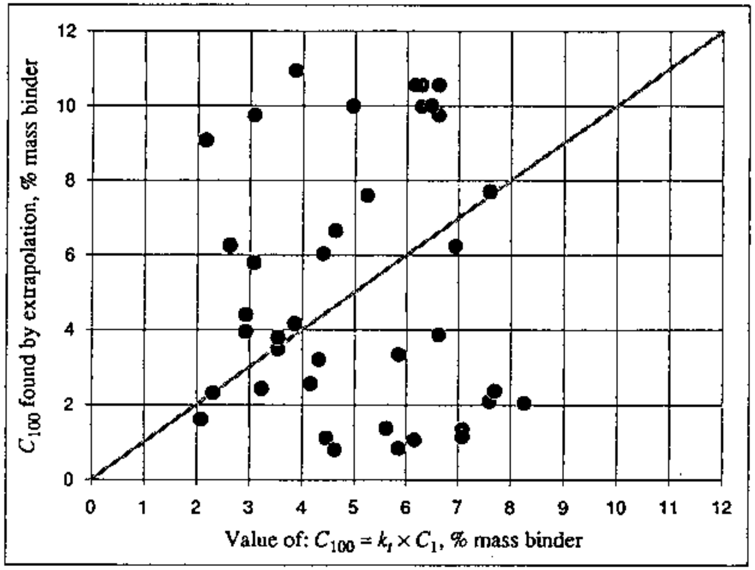

Fig. 11. The determined values of C_{100} found by extrapolation of measurements versus the values of C_{100} determined by Frederiksen's formula (12). A gross deviation is expected and observed.

Concrete: c, W, C, F, S, C_i

Environment: LEC, t_{ex}

	Environment factors				
Local environment class	k_b	k_t	k_D	k_α	k_{cr}
Marine atmosphere zone	2.20	7.0	10,000	4.60	0.50
Marine splash zone	3.70	4.5	15,000	0.45	0.75
Submerged in seawater	5.15	1.5	25,000	2.75	2.00

$$\mathrm{eqv}\{w/c_D\} = \frac{W}{C + 1.0 \times F + 7.0 \times S}$$

$$\mathrm{eqv}\{w/c_b\} = \frac{W}{C + 0.75 \times F - 1.5 \times S}$$

$$D_1 = k_D \times \exp\left(-\sqrt{\frac{10}{\mathrm{eqv}(w/c_D)}}\right)$$

$$C_1 = k_b \times \mathrm{eqv}\{w/c_b\}$$

$$D_{100} = \frac{D_1}{\exp[k_\alpha \times (1 - 1.5 \times \mathrm{eqv}\{w/c_D\})]}$$

$$C_{100} = k_t \times C_1$$

$$\theta = \frac{1}{2} \times \log_{10}\left(\frac{1}{t_{ex}}\right)$$

$$\alpha = \frac{1}{2} \times \log_{10}\left(\frac{D_1}{D_{100}}\right)$$

$$D_{aex} = D_1 \times \left(\frac{D_1}{D_{100}}\right)^{\theta}$$

$$p = \frac{\log_{10}\left(\frac{C_{100}}{C_1}\right)}{\log_{10}\left(\frac{100 - t_{ex}}{1 - t_{ex}} \times \frac{D_{100}}{D_1}\right)}$$

$$S_p = C_1 \times \left\{\left(\frac{D_1}{D_{100}}\right)^{\theta} \times \frac{t_{ex}}{1 - t_{ex}}\right\}^{p}$$

$$\mathrm{eqv}\{w/c_{cr}\} = \frac{W}{C - 1.0 \times F - 3.5 \times S}$$

$$C_{cr} = k_{cr} \times (1.2 - \mathrm{eqv}\{w/c_{cr}\})$$

$$y_{cr} = \frac{C_{cr} - C_i}{S_p} \times \left(\frac{\sqrt{t_{ex} D_{aex}}}{0.5c}\right)^{2p}$$

$$z_{cr} = \mathrm{inv}\,\Lambda_p(y_{cr})$$

Predicted initiation period: $\mathrm{est}\{t_{cr}\} = t_{ex} \times \left(\frac{0.5c}{y_{cr} \times \sqrt{t_{ex} D_{aex}}}\right)^{\frac{2}{1-\alpha}}$

Fig. 12. Input form and collection of formulae for the prediction of initiation service lifetime of concrete exposed to marine environment based on the Mejlbro-Poulsen model applying Frederiksen's formulae for estimating diffusivity and threshold value.