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钢筋混凝土结构的耐久性和服役寿命预测

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摘 要:介绍了钢筋混凝土结构在氯离子渗透、碳化和冻融侵蚀作用下的耐久性和服役寿命预测模型。过去几年有关组织或 国际学术委员会提出了大量的混凝土结构耐久性设计模型。为了在混凝土结构耐久性设计过程中,能够安全地使用此类模型, 需要通过分析和比较长期暴露在不同气候条件下的混凝土劣化现场数据,对预测模型的可用性进行验证。在本文中,对混凝 土抗氯离子渗透、碳化和冻融侵蚀的各种模型进行了简要阐述。通过暴露时间超过 20 年的露天场数据,以及约使用了 30 年 的公路桥的现场数据,对包括简单 ERFC 模型、DuraCrete 模型和 ClinConc 模型在内的 3 种氯离子渗透模型进行了评估。同 时,使用暴露 11 年的露天场所的现场数据和 7~13 年的现有建筑的有限数据对一种预测混凝土碳化深度的物理化学模型进行 了评价。针对冻融侵蚀的模型,讨论了临界饱和度测量和实际的饱和度测量中的一些问题。根据对结果的比较,可以发现在 大多数情况下,简单 ERFC 模型在大多数情况下对氯离子渗透的预测值高于实际值,而 DuraCrete 模型的预测值偏低。另外, ClinConc 模型对短期(1 年)和长期(21 年)暴露条件下的预测更合理,预测效果更好。与在挪威获得的暴露级别为 XC3 现场数 据比较,发现 Papadakis 碳化模型可以较好地预测碳化深度;但是,与暴露级别为 XC4 级的现场数据比较发现,该模型低估 了碳化深度。

关键词:混凝土;耐久性;模型;服役寿命;验证
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Durability and Service Life Prediction of Reinforced Concrete Structures

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Abstract: This paper presents some durability and service life models for reinforced concrete structures with regard to chloride ingress, carbonation and frost attack. In the past years a number of models for durability design of concrete structures have been suggested by relevant organisations or international committees. It is necessary to validate these models against long-term field data for their applicability with respect to exposure climate in order to satisfactorily use the models in the durability design and redesign of concrete structures. In this study, various potential models for concrete resistance to chloride ingress, carbonation and frost attack were briefly reviewed. Three models including the simple ERFC, the DuraCrete and the ClinConc, for prediction of chloride ingress were evaluated using the infield data collected from both the field exposure site after over 20 years exposure and the real road bridges of about 30 years old. A physicochemical model for prediction of carbonation depth was evaluated using the infield data collected from the field exposure site after 11 years exposure and the limited data from the real structures with the age of 7-13 years. For the modelling of frost attack, some problems in measurement of critical saturation degree and actual degree of saturation are discussed. According to the comparison results, the simple ERFC overestimates whilst the DuraCrete model underestimate the chloride ingress in most cases. The ClinConc model on the other hand gives reasonable good prediction for both the short-term (one year) and the long-term (21 years) exposure. The Papadakis model for carbonation also gives fairly good prediction of carbonation depth when compared with the Norwegian infield data classified as exposure class XC3, but underestimates the carbonation depths when

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Received date: 2015–04–10. Revised date: 2015–07–18. First author: TANG Luping, Professor. E-mail: tang.luping@chalmers.se compared with the infield data from Norwegian structures in exposure class XC4.

Key words: concrete; durability; modelling; service life; validation

Originality: The work presented in this paper was mainly based on the findings from authors' research projects in the past two decades, with a limited part from the literature for comparison. The projects have been carried out in close cooperation between Chalmers University of Technology and CBI Swedish Cement and Concrete Research Institute, as well as SP Technical Research Institute of Sweden.

1 Introduction

Civil infrastructure is the backbone of our society and its service life plays, therefore, an important role in the development of social sustainability owing to its high costs and serious social and environmental consequences if it fails. Many factors can influence the durability of concrete. Chloride and carbonation induced reinforcement corrosion is perhaps the biggest durability problem of reinforced concrete structures in the world. Frost attack is also a significant durability problem in the Other durability problems include cold regions. alkali-aggregate reactions, sulphate attack, chemical attack, calcium leaching, etc. At the present, the specification of durability is mainly based on the establishment of various constraints to the mixture proportions of the concrete such as cement type and content, water-binder ratio, entrained air-content, or the cover thickness as function of the severity of the exposure. This approach does not consider the actual performance of concrete materials with different types of cement and mineral components added to the cement or directly to the concrete. As towards the sustainable development of society and construction industry, it is a tendency to use performance-based service life design and calculations instead of prescription-based approaches. With the help of more sophisticated durability models safer structures can be designed with expected service life and reduced consumption of materials. In the past years a number of models for service life design have been suggested by relevant national, regional or international committees, mainly dealing with the durability problems of chloride and carbonation induced reinforcement corrosion as well as frost attack. In Sweden, owing to its long coastal line and cold climate with intensive use of de-icing salt, great efforts have been made in development of models for chloride transport in concrete and frost durability of concrete. To validate the models with respect to Swedish climate, efforts have also been made in collecting infield data. This is necessary in order to use the models in service life design or redesign of reinforced concrete structures. This paper will present some durability and service life models and their validation against the infield data with regard to chloride ingress, carbonation depth and frost attack.

2 Durability and service life models

2.1 Models for prediction of chloride ingress

Due to the global problems in chloride-induced corrosion of reinforcement in concrete structures, many prediction models have been proposed in the past decades^[1]. An overview of durability of steel reinforced concrete in chloride environments was given in Ref.[2]. In this overview the role of mineral additions such as fly ash (FA), ultrafine fly ash (UFFA), silica fume (SF), ground granulated blast-furnace slag (GGBFS) and metakaolin (MK), was reviewed. Different test methods for chloride diffusivity and challenges in assessing the durability of concrete from its chloride diffusivity were also discussed. With regard to service life models, very limited models without validation were reviewed in Ref.[2]. It is vitally important that the service life must be validated with the actual infield data in order to be applicable to the actual service life design or redesign. According to Tang L, et al.^[1], the models can be categorized into two groups: empirical and mechanistic. Empirical or semi-empirical models often assume a diffusion process but use total chloride content as the driving force. Obviously, taking the total chloride content as driving force in the transport function is theoretically questionable, because it is only the free chloride ions that can move in the pore solution and contribute to chloride-induced corrosion of reinforcement in concrete. Therefore, mechanistic models often use the free chloride as the driving force and take the non-linear chloride binding into account. In the following sections some often used or mentioned models in the literature will be reviewed.

2.1.1 The simple ERFC model

The abbreviation ERFC denotes the mathematical symbol erfc - Error Function Complement. This model was first proposed in the early 1970's for modelling of chloride ingress in concrete ^[3]. The model uses an erfc solution to Fick's 2nd law of diffusion under the semi-infinite boundary condition:

$$C(x,t) = C_{\rm i} + (C_{\rm s} - C_{\rm i}) \cdot \operatorname{erfc}\left(\frac{x}{2 \cdot \sqrt{D_{\rm a} \cdot t}}\right) \qquad (1)$$

where: C_i is the initial chloride content in the concrete (sometimes this chloride content is negligible), C_s is the surface chloride content, x is the depth, D_a is the apparent diffusion coefficient and t is the exposure duration. In this model the parameters C_s and D_a are assumed constant during the whole period of exposure.

In this model the key parameters are C_s and D_a , which have to be determined by curve-fitting of the chloride ingress profiles from field or laboratory exposure. It has been proven from many experimental data that this simplest model can only describe the chloride ingress under the exposure conditions for a short duration close to the conditions for which the input parameters are determined. As explained later, several modifications to Eq. (1) were proposed to try to expand the applicability range of such type of models.

2.1.2 Mejlbro-Poulsen's model

This mathematical model was developed in Denmark through Danish national project HETEK in the middle of 1990's ^[4]. The model assumes the total chloride as the driving force, and considers both the surface chloride content $C_{\rm s}$ and the apparent diffusion coefficient $D_{\rm a}$ as time-dependent functions, that is,

 $D_{\rm a} = D_{\rm aex} \left(\frac{t_{\rm ex}}{t + t_{\rm av}} \right)^{\alpha}$

and

$$C_{\rm s} = C_{\rm i} + S \left(D_{\rm a} \cdot t \right)^p \tag{3}$$

where: D_{aex} is the apparent diffusion coefficient at the time of exposure t_{ex} , α , S and p are the constants. An analytic solution to Fick's 2nd law with time-dependent C_{s} and D_{a} was given in the form as follows: ^[5]

$$C(x,t) = C_{i} + (C_{s} - C_{i}) \cdot \Psi_{p}\left(\frac{x}{2\sqrt{D_{a} \cdot t}}\right)$$
(4)

where: Ψ is a series of Γ -functions. When p = 0, Eq. (4) becomes the same form as Eq. (1). Because it is impossible to measure D_{aex} at the time of exposure (no ingress profile is available for curve-fitting), the model needs some experimental data from short term exposures (*e.g.* 1 year exposure and at a later storage) to estimate the values of D_{aex} , α , *S* and *p*. Updating from later available infield data may result in different values of these empirical parameters^[6-7]).

2.1.3 DuraCrete model

The DuraCrete project ^[8] recommended the following equation to express the apparent diffusion coefficient in Eq.(1):

$$D_{\rm a} = k_{\rm e,Cl} \cdot k_{\rm c,Cl} \cdot D_{\rm RCM,0} \cdot \left(\frac{t_0}{t + t_{\rm ex}}\right)^{n_{\rm Cl}}$$
(5)

where: $D_{\text{RCM},0}$ is the chloride migration coefficient measured by *e.g.* the Nordtest method NT BUILD 492^[9], at the age $t_0 = 28$ d, $k_{\text{e,Cl}}$ and $k_{\text{c,Cl}}$ are constants considering the influence of environment and curing, respectively, on chloride ingress, t_0 is the reference period (concrete age of 28 d) at which $D_{\text{RCM},0}$ is measured and n_{Cl} is the age factor describing the time-dependency of the apparent diffusion coefficient.

It can be seen that a difference between Eq.s (2) and (5) is that D_{aex} in the former is from the same field exposure conditions as D_{a} , while $D_{\text{RCM},0}$ in the latter is from the laboratory conditions which is different from the actual exposure conditions. The model uses an empirical factor of $k_{\text{e,Cl}}$ to try to bridge the gap between the laboratory and the field conditions. Again, it needs a lot of qualified infield data to establish the proper values of $k_{\text{e,Cl}}$ for actual service life design. The principle of the DuraCrete model was also adopted in a guidance of Concrete Society ^[10] and the fib model code for service life design ^[11], in which the factor $k_{\text{e,Cl}}$ is specified by the following equation:

$$k_{\rm e,Cl} = \exp\left[b_{\rm e}\left(\frac{1}{273 + T_{\rm ref}} - \frac{1}{273 + T_{\rm ref}}\right)\right]$$
 (6)

where: b_e is the regression variable varying between 3 500 and 5 500, with 4 800 as the mean value and 700 as standard deviation, T_{ref} is the reference temperature in °C at which the chloride migration coefficient is measured and T_{real} is the real exposure temperature in °C. 2.1.4 ACI Life 365 Model

In North America, an empirical model has been developed by ACI TC-365 in the beginning of 2000's ^[12]. The model utilizes Fick's 2^{nd} law of time-dependent diffusion as the transport function with the total chloride content *C* as the driving force:

$$\frac{\partial C}{\partial t} = D(t) \frac{\partial^2 C}{\partial x^2} \tag{7}$$

where

(2)

$$D(t) = D_{\rm ref} \left(\frac{t_{\rm ref}}{t}\right)^m \tag{8}$$

where $D_{\rm ref}$ represents the apparent diffusion coefficient at the reference time of exposure t_{ref} and *m* is the constant. In order to prevent the diffusion coefficient indefinitely decreasing with time, the relationship shown in Eq. (7) is only valid up to 30 years. Beyond this time, the value at 30 years (D_{30y}) calculated from Eq. (7) is assumed to be constant throughout the rest of the analysis period. The temperature effect on the apparent diffusion coefficient has also been taken into account in this model. The model selects the rate of chloride build-up and the maximum surface content based on the type of exposure (and structure) and the geographic location. The model also gives various α values for different additions of puozzolanic materials. Obviously, the model is semi-empiric. On the other hand the software of the ACI model has integrated chloride ingress, initiation and propagation of corrosion, repair schedule, and life-cycle costs together, so as to give the user a simple tool for maintenance planning of concrete structures. A numerical approach is followed in the model for the time integration. Therefore, special software is needed for application of the model.

An important difference that often confuses the readers/users of the models, is that, D(t) in equation (8) is different from D_a in Eq.s (2) and (5). The former is the instantaneous diffusion coefficient as conventionally defined in Fick's law, while the latter is the average diffusion coefficient during the period from $t_{\rm ex}$ to $(t + t_{\rm ex})^{[13]}$.

2.1.5 ClinConc model

The model ClinConc (Cl in Concrete) was first developed in the middle of 1990's ^[14-15]. The ClinConc model consists of two main procedures: 1) Simulation of free chloride penetration through the pore solution in concrete using a genuine flux equation based on the principle of Fick's law with the free chloride

concentration as the driving potential, and 2) Calculation of the distribution of the total chloride content in concrete using the mass balance equation combined with non-linear chloride binding. Obviously, the ClinConc model uses free chloride as the driving force and takes non-linear chloride binding into account. Thus it describes chloride transport in concrete in a more scientific way than the empirical or semi-empiric models. Later, this model has been expressed in a more engineer-friendly way ^[16-17] so as to make it possible for applications by practising engineers. The free chloride concentration in the concrete at depth, *x*, is determined using the following equation:

$$\frac{c-c_{\rm i}}{c_{\rm s}-c_{\rm i}} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{\frac{\xi_{\rm D}D_{\rm 6m}}{1-n}} \cdot \left(\frac{t_{\rm 6m}}{t}\right)^n \cdot \left[\left(1 + \frac{t_{\rm ex}}{t}\right)^{1-n} - \left(\frac{t_{\rm ex}}{t}\right)^{1-n}\right] \cdot t}\right)$$
(9)

where: c, c_s and c_i are the concentration of free chlorides in the pore solution at depth x, at the surface of the concrete and initially in the concrete, respectively, D_{6m} = the diffusion coefficient measured by the rapid chloride migration (RCM) test, *e.g.* NT BUILD 492, at the age of t_{6m} , ξ_D is the factor bridging the laboratory measured D_{6m} to the initial apparent diffusion coefficient for the actual exposure environment, n is the age factor accounting for the diffusivity decrease with age, t_{ex} is the age of concrete at the start of exposure and t is the duration of the exposure.

Different from the empirical models, the factors $\xi_{\rm D}$ and n in the ClinConc can be calculated based on the physical properties of concrete including cement hydration, hydroxide content, water accessible porosity, time-dependent chloride binding, and the environmental parameters such as chloride concentration and temperature. The detailed descriptions of the factors $\xi_{\rm D}$ and n are given in ^[16]. The total chloride content is basically the sum of the bound chloride and free chloride and can be calculated based on the relationship between the free and total chloride content, i.e. a chloride binding isotherm ^[18]. It should be noticed that the ClinConc model was primarily developed for the submerged environment, where the chloride solution is constantly in contact with the concrete surface. When the model is used for the atmospheric zone or the road environment, certain modifications are needed.

Both the DuraCrete and the ClinConc models use the diffusion coefficient measured by the RCM test, *e.g.* NT BUILD 492, as an input parameter, but care should be taken that this parameter is tested at different concrete ages, i.*e.* 28 days in the former while 6 months in the latter. Among the above mentioned models, only the ClinConc model treats the material properties and the exposure environment in a separate way.

2.1.6 Other Models

Besides the above mentioned models, there are many other models based on either empirical equations or physical and chemical/electrochemical processes. Some of them are more or less similar to the Life-365 or the DuraCrete model, whilst some of them need special software such as the STADIUM[®] to calculate the complicated mathematical iterations^[19-24]. More information about various models can be found in Ref.[1]. There are also various numerical models such as Multi-Environmental Time Similarity (METS) model^[25], LIFEPROD model^[26], etc.

2.2 Models for prediction of carbonation

The carbonation depth in concrete is conventionally modelled by a function proportional to the square root of exposure time ^[27], that is,

$$x_c(t) = A\sqrt{t} \tag{10}$$

where: $x_c(t)$ = the carbonation depth at the exposure time t and A = the constant depending on many factors such as concentration of CO₂ in the exposure environment, CO₂ diffusion coefficient in concrete and CO₂ binding capacity of concrete.

2.2.1 Physicochemical Model

Based on the physicochemical processes of concrete carbonation the constant A can be described by the following equation ^[28-29]:

$$A = \sqrt{\frac{2D_{e,CO_2} \cdot c_{s,CO_2}}{B}}$$
(11)

where: D_{e,CO_2} is the effective diffusivity of carbon dioxide in the fully carbonated concrete, c_{s,CO_2} is the surface concentration of carbon dioxide, and *B* is the total molar concentration of CaO in concrete, in the form of carbonatable materials, expressed as follows:

$$B = [Ca(OH)_2] + 3[CSH] + 3[C_3S] + 2[C_2S]$$
(12)

In the above equation all the components are referred to their initial concentrations at t = 0. Converting the molar concentration to the mass, Eq. (11) turns into

$$A = \sqrt{\frac{2D_{\rm e,CO_2} \cdot (\varphi_{\rm e,CO_2} / 100)}{0.33C_{\rm CH} + 0.214C_{\rm CSH}}}$$
(13)

where φ_{e,CO_2} is in volume fraction, C_{CH} and C_{CSH} are the contents of calcium hydroxide and the calcium silicate hydrate in concrete (kg/m³), respectively. Since the effective diffusivity D_{e,CO_2} is a function of the porosity and the degree of saturation, which in turn depends on the ambient relative humidity and on the pore-size distribution, this effective diffusivity cannot be determined by a simple method. This effective diffusivity can be expressed by the following empirical equation [³⁰⁻³¹]:

$$D_{\rm e,CO_2} = 6.1 \times 10^{-6} \left(\frac{\varepsilon_{\rm c}}{\frac{W_{\rm C}}{\rho_{\rm C}} + \frac{W_{\rm P}}{\rho_{\rm P}} + \frac{W_{\rm W}}{\rho_{\rm W}}} \right) \cdot (1 - h/100)^{2.2} (14)$$

where: ε_c is the porosity of carbonated concrete, w_C , w_P and w_W are the content of cement, additional material and water, respectively, ρ_C , ρ_P and ρ_W are the density of cement, additional material, and water, respectively, and h is the ambient relative humidity in percentage. Equations were proposed ^[31] for calculation of C_{CH} and C_{CSH} in Eq.(13) and ε_c in Eq.(14) for different types of binder including those blended with silica fume and fly ash.

• For the cement blended with silica fume ($w_{SF} < 0.18$ w_C):

 $C_{\rm CH} = 0.29 \ w_{\rm C} - 1.62 \ w_{\rm SF}$

 $C_{\rm CSH} = 0.57 w_{\rm C} + 2.49 w_{\rm SF}$

 $\varepsilon_{\rm c} = (w_{\rm W} - 0.267 \ C - 0.0278 \ w_{\rm SF})/1000$

• For the cement blended with low calcium fly ash $(w_{\text{FAL}} < 0.23 \text{ C})$:

 $C_{\rm CH} = 0.30 w_{\rm C} - 1.30 w_{\rm SF,L}$

 $C_{\rm CSH} = 0.57 w_{\rm C} + 1.25 w_{\rm SFL}$

 $\varepsilon_{\rm c} = (w_{\rm W} - 0.268 \ w_{\rm C} - 0.177 \ w_{\rm SFL})/1000$

• For the cement blended with high calcium fly ash $(w_{\text{SF,H}} < 0.23 \text{ C})$:

 $C_{\rm CH} = 0.29 \ w_{\rm C} - 0.50 \ w_{\rm SF,LH}$

 $C_{\rm CSH} = 0.57 w_{\rm C} + 0.79 w_{\rm SF,H}$

 $\varepsilon_{\rm c} = (w_{\rm W} - 0.267 \ w_{\rm C} - 0.203 \ w_{\rm SF,H})/1000$

2.2.2 DuraCrete model

The DuraCrete project^[8] recommended the following equation to express the constant A for carbonation depth:

$$A = \sqrt{2c_{\rm s,CO_2} \cdot D_{\rm Ca}} \tag{15}$$

where: D_{Ca} = the carbonation rate which is further expressed as

$$D_{\rm Ca} = k_{\rm e,Ca} \cdot k_{\rm c,Ca} \cdot D_{\rm Ca,0} \cdot \left(\frac{t_0}{t + t_{\rm ex}}\right)^{2n_{\rm Ca}}$$
(16)

where: $D_{Ca,0}$ is the carbonation rate determined in the laboratory using the accelerated carbonation test (ACT), $k_{e,Ca}$ is the environmental factor, $k_{c,Ca}$ is the curing factor, t_0 is the age of the concrete when the ACT test is performed, and n_{Ca} is the age factor. Obviously, the carbonation rate D_{Ca} is a combination of effective diffusivity and CO₂-binding capacity, that is, $D_{Ca} = D_{e,CO_2}$ /*B*.

The principle of the DuraCrete model was also adopted in the fib model code for service life design ^[11], in which the curing factor $k_{c,Ca}$ is specified by the following equation:

$$k_{\rm c,Ca} = \left(\frac{t_{\rm c}}{7}\right)^{b_{\rm c}} \tag{17}$$

where: t_c is the age of curing (in days) and b_c is the exponent with the mean value of -0.567 and the standard deviation of 0.024. The environmental factor $k_{e,Ca}$ in Ref.[11] is specified by the following equation:

$$k_{\rm e,Ca} = \left[\frac{1 - \left(\frac{h_{\rm real}}{100}\right)^{f_{\rm e}}}{1 - \left(\frac{h_{\rm ref}}{100}\right)^{f_{\rm e}}} \right]^{g_{\rm e}}$$
(18)

where: h_{real} is the relative humidity (%) at the carbonated layer, h_{ref} is the reference relative humidity (%) at which the ACT is performed, and f_{e} and g_{e} are the exponents. In Ref.[11], the values of $f_{\text{e}} = 5.0$ and $g_{\text{e}} = 2.5$ are suggested.

In a recent work ^[32] the constant A was further improved by adding a parameter k_e related to environmental factors.

$$A = k_{\rm a} / k_{\rm e} \tag{19}$$

where: k_a is the parameter related to concrete intrinsic factors which is basically the same as Eq. (15) in the DuraCrete model. Based on their results found from field assessment of the relationship between natural and accelerated concrete carbonation resistance ^[33] the values of $k_e = 9.9$ and 15 were suggested for European environmental class XC3 and XC4, respectively.

2.2.3 Other models

In an analytical model ^[34], the differential equation of CO_2 mass balance was solved taking into account the influence of water saturation rate, kinetic effects of portlandite dissolution and surface CO_2 concentration. In this model the computing tool is needed for estimation of water adsorption/desorption isotherm.

There is also a numerical model ^[35] taking into account simultaneously CO₂ concentration, dissolved calcium and liquid water transfers. Computer software is needed to solve such a model.

2.3 Models for prediction of frost attack

2.3.1 Basic principle of modelling

There different models describing the damage mechanisms of concrete under the freeze-thaw action, as summarised in Refs.[36-37]. It is known that the degree

of saturation increases under the action of freeze-thaw cycles. Once the degree of saturation in concrete transgresses the critical level, damage will occur. This is the basic principle for modelling of service life of concrete structures with regard to frost attack. In a typical service life model for internal frost damage in concrete ^[38] both the deterministic and stochastic approaches were used. In the deterministic approach, the basic criterion for frost damage is

$$S_{\rm act} \ge S_{\rm cr}$$
 (20)

where: S_{act} is the actual degree of saturation and S_{cr} is the critical degree of saturation. In the stochastic approach, the probability of the risk of frost damage is

$$P\{\text{frost damage}\} = P\{S_{\text{act}} > S_{\text{cr}}\} = \int_{0}^{\infty} F(S_{\text{cr}}) \cdot f(S_{\text{act}}) dS$$
(21)

where: *P* is the probability, *F* and *f* are the distribution function and frequency function, respectively. Principally, both S_{act} and S_{cr} are time-dependent. When the time-dependent functions of S_{act} and S_{cr} as well as their standard deviations are known, the probability of risk of frost damage can be estimated. Obviously, S_{cr} and S_{act} are two key parameters for estimating frost damage under the service life.

2.3.2 Critical degree of saturation

Theoretically, the critical degree of saturation for a closed container is 0.917. In concrete, however, the value of $S_{\rm cr}$ varies much depending on the pore structures and quality of concrete. An equation to express the critical degree of saturation in concrete was proposed ^[38], that is,

$$S_{\rm cr,min} \leq S_{\rm cr} = 1 - a_{\rm cr} / \varepsilon_{\rm t} \leq S_{\rm cr,max}$$
 (22)

where $S_{cr,min}$ and $S_{cr,max}$ are the lower and upper limit, respectively, a_{cr} is the critical air content, and ε_t is the total porosity. The lower and upper limits are expressed) as follows ^[39]:

$$S_{\rm cr,min} = S_{\rm b} - 0.09 w_{\rm f} / \varepsilon_{\rm t} = 0.917 S_{\rm b} + 0.083 w_{\rm nf} / \varepsilon_{\rm t}$$
 (23)
and

$$S_{\rm cr,min} = 1 - 0.09 w_{\rm f} / \varepsilon_{\rm t} = 0.917 S_{\rm b} + 0.083 w_{\rm nf} / \varepsilon_{\rm t}$$
 (24)

where: $S_{\rm b}$ is the breaking point, so called "knick point" or "nick point", in the water absorption test, which will be discussed later, and $w_{\rm f}$ and $w_{\rm nf}$ are the freezable and non-freezable water, respectively. Assuming that the gel water is non-freezable,

$$w_{\rm nf} = 0.20\alpha_{\rm h} \cdot C \cdot 10^{-3}$$
 (25)

An equation was also suggested ^[39] for estimation of the breaking point S_b :

 $S_{\rm b} = (r - 0.19\alpha_{\rm h}) / [(w/c - 0.19\alpha_{\rm h}) + 1000a \cdot C]$ (26) where: *r* is the water-cement ratio, and *a* is the air porosity in m³/m³.

Since the critical air content a_{cr} is dependent on the air-pore system in concrete including air quantity, size

and spacing factor of the air-pores, the value of $S_{\rm cr}$ in Eq.(22) cannot be simply solved, but give a range of possible values of $S_{\rm cr}$.

2.3.3 Actual degree of saturation

Due to the complicated moisture conditions under the variation of the real climate, it is hardly possible to predict the actual degree of saturation in a real concrete structure. The case of free water available on the concrete surface under the freeze-thaw period represents, nevertheless, the severest exposure condition. Since the capillary suction is a quick process when compared with the water absorption after the breaking point, the degree of saturation based on the long-term capillary absorption is adopted in ^[38], noted as S_{cap} , expressed as

$$S_{\rm cap} = S_{\rm b} + \frac{c \cdot t^d}{w_{\rm sat}} \tag{27}$$

where: c and d are the material dependent coefficients, and w_{sat} is the water content at complete saturation. The coefficient c is mainly dependent on the diffusivity of dissolved air, whilst the exponent d is dependent on the air-pore size distribution. Both the coefficients can be determined by the long-term water absorption test.

Obviously, in this test the water increase in the pore system due to the pumping effect under the freeze-thaw action is not taken into account. Therefore, the degree of saturation based on Eq. (27) may not represent the severest exposure condition.

2.3.4 Some questions in modelling frost attack

Although a complete system has been established in Refs.[38-39]) for calculation of service life of concrete with regard to the frost attack, the knowledge of both the critical and actual degrees of saturation as functions of various influencing factors is still limited. Considering possible influencing factors, we can express the critical degree of saturation by the following function

$$S_{\rm cr} = f\left(\varepsilon_{\rm t}, a_{\rm a}, \alpha_{\rm a}, D_{\rm a}, T_{\rm min}, t_{\rm f}, \cdots\right)$$
(28)

where: a_a , α_a and D_a are the actual air content, actual specific surface and actual spacing factor, respectively, and t_f is the freezing duration time. The first four factors have been quantitatively considered in Fagerlund's model, but the factors T_{min} and t_f have been neglected. Since the amount of unfrozen water in concrete can vary with T_{min} and t_f , the value of S_{cr} may also be dependent on these two factors. It was found ^[40] that the effect of T_{min} on scaling is significant when the T_{min} is in the range of $-10 \ ^{\circ}C$ and $-20 \ ^{\circ}C$ in the slab test. This could be an indication of different critical degrees of saturation at different T_{min} . Under a certain cycle of freeze-thaw, there may exist a relationship between T_{min} and t_f . If we exclude the effect of freezing duration, the first question becomes how to find $f(T_{min})$ for S_{cr} .

On the other hand, the degree of saturation based on equation (27) does not include the water uptake by the pumping effect, as mentioned previously. Then the second question is how to estimate the constants c and d in equation (27) under specific frost conditions.

There are also some computational models coupling both material deterioration and thermodynamic/ mechanical equilibrium ^[41-42].

3 Validation of models against infield data

It is obvious that, no matter which types of models, validation against the infield data is enssential in order to apply the models in the practical durability design or redesign. In this section we will present some validations for models for chloride ingress and carbonation only, since the models for frost attack are far from mature for practical application.

3.1 Validation of models for chloride ingress

It is essentially important to validate various prediction models against both the short-term and the long-term infield data in order to use the models in the practical service life design with acceptable precision. It is, however, not easy to collect the infield data with sufficient information about both the materials (from the birth to the ages of sampling) and the exposure environments. Although some chloride profiles after 100 years of service in Panama Canal were reported ^[43], no further information about concrete (binder content, water-binder ratio, etc.) is available. In an Australian field exposure programme [44] some software based prediction models including the Life-365 and the STADIUM® together with an Excel-based model CSM were evaluated against four types of concrete exposed to a splash zone of Australian western coast for 19 years. The CSM is a model suggested in the guidance of Concrete Society ^[10] which is in principle similar to the DuraCrete model. The comparison results indicated that all the three models underestimate the chloride ingress after a short-term (two years) exposure but revealed varied predictions for the long-term exposure, that is, sometimes similar to the field data but sometimes underestimating or overestimating the chloride ingress. The large variations in the exposure condition, especially the microclimate, could be the important reason to the unsatisfactory predictions.

In Sweden, three models as described in 2.1.1, that is, the simple ERFC model, the DuraCrete model and the ClinConc model, were evaluated using the collected long-term infield data. The other models could not be evaluated due to the difficulties in availability of software or lack of input parameters.

3.1.1 Data over 20 years' exposure in a marine environment

In the beginning of the 1990s, some 40 types of concrete specimens were exposed to seawater at the Träslövsläge field exposure site on the west coast of Sweden^[45]. The specimens were periodically sampled for chloride penetration profiles, which served to provide

"first-hand" information about chloride ingress into concrete and are believed valuable for the examination of modelling for chloride penetration. The Träslövsläge field site is perhaps the first field exposure site in the world for systematic collection of chloride ingress profiles in various types of concrete. Although there are some chloride ingress data, e.g. from one type of concrete with water-binder ratio r 0.4 after exposure under the North Sea tidal zone near the Dornoch bridge, Scotland, for 18 years [46] and from 15 different types of concrete after exposure under the Atlantic tidal zone in La Rochelle, France, for 10 years ^[47], their exposure conditions under the tidal zone made the modelling and validation more complicated. On the other hand, the data from the Träslövsläge field site were taken mainly from the submerged zone, which supplies unique opportunity for validating chloride ingress models under clearer boundary conditions with the longest exposure time (21 vears).

The original mixture proportions of concrete cast in 1992 are published elsewhere ^[45,48-49]. The chloride concentration in the seawater varies from 10 to 18 g Cl per litre, with an average value of about 14 g Cl per litre and the typical water temperature +11 °C as an annual average. The chloride migration coefficients of concrete specimens were tested at an age of 6 months using the RCM test which was adopted as a Nordic standard test NT BUILD 492 ^[9], as described in Ref.[48]. The chloride ingress profiles (as acid soluble chloride) in concrete were measured after different exposure durations from some one year up to 21 years. The detailed descriptions of measurement for chloride profiles are published elsewhere ^[48-49].

It should be noted that both the DuraCrete and the ClinConc models use the diffusion coefficient measured by the RCM test as an input parameter, but care should be taken that this parameter is tested at different concrete ages, i.e. 28 days in the former while 6 months in the latter. However, although in the DuraCrete guidelines ^[8] the concrete age t_0 is specified as 28 days, there should be no difference in the $D_{\rm a}$ values calculated using $D_{\text{RCM28d}}(t_{28d})^n$ and $D_{\text{RCM6m}}(t_{6m})^n$ when the same *n* value is adopted. Therefore, the values of $D_{\rm RCM6m}$ for the concretes exposed at the Träslövsläge field exposure site summarised in Ref.[48]) were used for both the DuraCrete and the ClinConc models. For the simple ERFC model, the input parameters D_a and C_s were taken from the curve-fitting to the infield data after a short-term exposure (one year in this case). The other input parameters for the DuraCrete model were taken from the guidelines recommended by the DuraCrete project [8], whilst those for the ClinConc model were taken or calculated in accordance with the previous studies ^[16,48]. Figures 1 to 3 show three typical examples of the results from concretes with binary and ternary binders which

have been found more and more applications in reinforced concrete structures exposed to chloride environments. It has been found that, when using pure Portland cement as binder, the chloride has already penetrate through the concrete after 10 years' exposure at the Träslövsläge field exposure site. The data from those types of concrete are not relevant for long-term comparison. More detailed comparisons are published elsewhere ^[49]. It can be seen from Figures 1 to 3 that, the simple ERFC overestimates whilst the DuraCrete model underestimate the chloride ingress. The ClinConc model on the other hand gives reasonable good prediction for both the short-term (one year) and the long-term (21 years) exposure.



Fig. 1 Modelled chloride ingress profiles (dense curves) in comparison with the real data (marks) of concrete with 5% silica fume, equivalent w/c 0.30 (efficiency factor 1 for silica fume)



Fig. 2 Modelled chloride ingress profiles (dense curves) in comparison with the real data (marks) of concrete with 20% fly ash, equivalent w/c 0.30 (efficiency factor 0.3 for fly ash)



Fig. 3 Modelled chloride ingress profiles (dense curves) in comparison with the real data (marks) of concrete with 10% fly ash and 5% silica fume, equivalent w/c 0.35 (efficiency factor 0.3 for fly ash and 1 for silica fume)

3.1.2 Prediction of chloride ingress after 100 years' exposure in the seawater

From the above modelled results it can be concluded that the ClinConc model fits fairly well to the measured values from one year up to 21 years' field exposure for most types of concrete. Therefore, it is reasonable to use this model to predict chloride ingress in concrete exposed in Swedish west coast seawater. The predicted profiles are shown in Fig.4. It can be seen from the prediction that, if the chloride threshold value of 1% by weight of binder is assumed, the concrete with plain sulphate resistant Portland cement (SRPC) with water-binder ratio of 0.35 needs a cover thickness of >110 mm to protect the reinforcement for a service life of 100 years. With addition of 5% silica fume and w/b 0.35, it is possible to achieve 100 years' service life with 80 mm cover. The best measure to obtain 100 years' service life with a cover thickness of for example 60 mm is to use either 5% silica fume or 20% fly ash with reduced water-binder ratio ≤ 0.30 , or to use a combination of both fly ash and silica fume (w/b ratio is 0.35). It seems that a water-binder ratio lower than 0.30 does not further reduce chloride ingress. However, the uncertainty in the prediction should be further investigated before this promising model can be applied to the service life design and redesign of reinforced concrete structures exposed to a marine environment.



Fig. 4 Predicted profiles of chloride ingress in concrete with various types of binder and water-binder ratios after 100 years' exposure in Swedish west coast seawater

3.2 Validation of models for carbonation

3.2.1 Infield data of carbonation depths

Although a field assessment of concrete carbonation was made in Portugal ^[33], the data of actual carbonation depths are not publically available. In Norway, some data were measured from Norwegian existing structures after 7–13 years in service ^[50]. The data listed in Table 1 are normalized to w/c 0.6 and exposure age 50 years. In the middle of 1990's, concrete specimens with different types of binder and water-binder ratios were cast and exposed to an exposure site near Swedish town Borås ^[51]. The

specimens at the exposure site were placed on top of loading pallets where they were exposed to water from precipitation only. Obviously, this exposure climate can be classified as exposure class XC4 (cyclic wet and dry), corresponding to a relative humidity of 85%–90%. The measured carbonation depths after exposure of 11 years are listed in Table 2.

| Table 1 | Carbonation | dep | oths on the N | lorwegian | struc | tures |
|---------|--------------|------|-----------------------|-----------|-------|-------|
| | normalized | to | water-cemer | nt ratio | 0.60 | and |
| | exposure age | 50 y | years ^[50] | | | |

| | Carbonation depth/mm | | | | |
|------------------------------|----------------------|--------------------|------------|-----------|--|
| Concrete family | X | C3 | XC4 | | |
| | Average | Std. dev. | Average | Std. dev. | |
| Concrete without silica fume | 15.9 (4)* | 7.0 (45%) | 12.7 (7)* | 4.3 (34%) | |
| Concrete with silica fume | 18.8 (estimated) | 7.5 (estimated) | 15.0 (12)* | 6.1 (41%) | |

* Number of data.

| Table 2 | Carbonation depths measured from the specimens | | | | |
|---------|---|--|--|--|--|
| | exposed at a Swedish exposure site after 11 years | | | | |
| | [51] | | | | |

| | Carbonation depth/mm | | | | | |
|--------------------------|----------------------|------|------|------|------|--|
| Concrete mix | 0.30 | 0.35 | 0.40 | 0.50 | 0.75 | |
| CEM I, upper | 0 | 0 | 0.5 | 0.8 | 2.3 | |
| CEM I, lower | 0 | 0 | 0.8 | 1.7 | 6.1 | |
| CEM I + 5% silica, upper | 0 | 0 | 0.2 | 0.4 | 1.1 | |
| CEM I + 5% silica, lower | 0 | 0 | 0.6 | 0.9 | 3.8 | |
| CEM II/A-LL, upper | 0 | 0 | 0.2 | 0.8 | 2.1 | |
| CEM II/A-LL, lower | 0 | 0 | 0.1 | 0.5 | 1.8 | |
| CEM II/A-S, upper | 0 | 0 | 0.1 | 0.3 | 3.6 | |
| CEM II/A-S, lower | 0 | 0 | 0.8 | 0.8 | 4.1 | |
| CEM I + 30% slag, upper | 0 | 0 | 0.4 | 0.9 | 3.3 | |
| CEM I + 30% slag, lower | 0 | 0 | 1.0 | 1.2 | 8.1 | |
| CEM III/B, upper | 0 | 1.5 | 2.5 | 4.4 | 12.1 | |
| CEM III/B, lower | 1.0 | 2.9 | 1.6 | 3.2 | 9.2 | |

3.2.2 Modelling and comparison

As described in 2.2, the Papadakis physicochemical model ^[28-31] almost does not need any test, while the DuraCrete or fib model ^[11] needs a carbonation rate as input parameter. It is, however, lack of the laboratory data from either the standard natural or accelerated carbonation test. Therefore, only the Papadakis model was used for comparison with the available data of carbonation depths in Table 2, where the mixture proportions are known. The data in Table 1 were also used by interpolating the calculated constant *A* in Eq. (13) for water-binder ratios 0.50 and 0.75 to 0.60.

In the Papadakis model the calculation equations for CH, CSH and ε_c are available for only three types of binder (Portland cement, silica fume and fly ash). Therefore, in the calculation the equations for cement type CEM I were used for the other types of binder. The results are shown in Fig. 5.



Fig. 5 Modelled and measured infield carbonation depths

It can be seen that the Papadakis model gives conservative prediction of carbonation depth in concrete with CEM I (Swedish structural cement for civil engineering), CEM I + 5% SF, and CEM II/A-LL (Swedish building cement), but underestimates the carbonation depth in concrete with slag cement. This model also underestimates the infield data from Norwegian structures in exposure class XC4, but gives fairly good prediction for the data in XC3. Since the actual relative humidity has strong influence on the infield carbonation, the relatively large carbonation depth in XC4 from the Norwegian data may possibly be attributed to the difficulties in distinction between these two classes, as pointed out in Ref.[50]. Therefore, the Papadakis model seems applicable although more data are needed for establishment of the calculation equations for concrete with slag cement.

4 Conclusions

1) The simple ERFC-model significantly overestimates chloride ingress. The DuraCrete model, if the input parameters are properly selected, e.g., the value of D_{RCM} measured at $t_0 = 0.5$ years is used, may give a reasonably good prediction, otherwise it often underestimates chloride ingress. The ClinConc model was previously calibrated against 10 years field data and, therefore, in general gives fairly good predictions for chloride ingress in the real old bridges under the de-icing salt environment with heavy traffic at high speed. This is

a demonstration of importance for a model developer to calibrate his or her prediction model against the field data before the model can be applied to the service life design of real concrete structures.

2) So far, it is lack of sufficient infield data and also laboratory data tested according to the newly standardised test methods for validation of the DuraCrete or fib model. The evaluation with the infield data after 11 vears exposure shows that the Papadakis physicochemical model is relatively simple and gives a conservative prediction of carbonation depth in concrete with CEM I, CEM I + 5% SF, and CEM II/A-LL. The Papadakis model also gives fairly good prediction of carbonation depth when compared with the Norwegian infield data classified as exposure class XC3, but underestimates the carbonation depths when compared with the infield data from Norwegian structures in exposure class XC4. It should be noted that this underestimation may possibly be attributed to the difficulties in distinction between these two classes in the real structures. To apply this model for the concrete with CEM II/A-S or CEM III (slag cement), more data are needed for establishment of the calculation equations.

3) So far, it is premature to apply the prediction models for service life of concrete against frost attack due to the lack of infield data and practical applicable test methods for the input parameters.

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