ON A MODEL OF
CHLORIDE INGRESS INTO CONCRETE
HAVING TIME-DEPENDENT DIFFUSION COEFFICIENT

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ABSTRACT

It is generally accepted that the chloride ingress into concrete by diffusion obeys Fick's second law of diffusion. However, several of the necessary assumptions are not valid for this application in practice. Concrete has a significant development of properties and characteristics, particularly when concrete is young. The capillary pores of the concrete develop with the maturity of the concrete and this fact influences among other parameters the coefficient of chloride diffusion.

This paper discusses the influence of the time-dependent chloride diffusion coefficient of concrete on the chloride ingress by diffusion. It is shown how this influences the chloride profiles and the so-called »square root rule« of ingress of the critical chloride concentration.

Furthermore it is discussed how the need for surface protection of young concrete before exposed to sea water could be determined.

Keywords: *Chloride profile, diffusion, time-dependent coefficient of diffusion, Fick's laws of diffusion, service life of RC-structures in marine environment.*

INTRODUCTION

Concrete is the kind of material which is characterized by an ongoing change of its microstructure, chemically as well as physically. The greatest change takes place immediately after casting when the hydration of the cement starts. However, the micro structural changes will take place after 28 maturity days, and even after years there are notable changes in properties and characteristics of the concrete. After the development of the final microstructure an ageing process will take place, also resulting in a change of properties and characteristics of the concrete.

Thus, speaking about the properties and characteristics of concrete one should always specify not only how these ought to be measured, but also the maturity age of the concrete at which the testing has to be carried out.

Compressive Strength of Concrete

The compressive strength was one of the first properties of concrete to be measured. The compressive strength of concrete develops significantly during a long period, more for some types of concrete than for others. Very early it was decided to test concrete when it had a specified maturity age. For concrete cast with ordinary Portland cement an age of 28 days of wet curing at a temperature of 20 °C was chosen. This is defined as 28 maturity days. The concrete Code of Practice nowadays specifies the concrete to comply with a compressive strength of 28 maturity days, independently of the type of cement.

Previous codes of practice specified the maturity age to 14 days when rapid hardening Portland cement was used. Since 1973 this requirement is not valid in Denmark. The testing age of concrete is now 28 maturity days independent of the cement types. Since 1973 it has become

very common to use Pozzolans like fly ash and silica fume as components of concrete. The increase in compressive strength contributed by e.g. flyash is very low the first 28 maturity days, but later on it can become predominant. This would bring the testing age of concrete up for discussion, but this topic is bryound this paper.

The compressive strength of concrete increases with its maturity. Thus, the bearing capacity of a structural member of a RC-structure will increase as well. This will take place until the ageing of the concrete starts; thereafter, the bearing capacity will decrease.

It stands to reason to require that a RC-structure at an age of 28 maturity days is able to carry the prescribed load with the safety required by the Code of Practice. The later increase in bearing capacity does not influence this fact.

The Diffusion Coefficient of Concrete
Testing of the compressive strength of concrete at a maturity age of 28 days is a very practical decision. The same criterion is often used when the testing age has to be decided for other properties and characteristics of the concrete. However, for many properties and characteristics the maturity of concrete when tested is not always very important as long as the test method and the time of testing are well defined. However, this is only valid when it must be documented that a RC-structure has achieved a property fulfilling a requirement at the time of testing, cf. the compressive strength.

By penetration of aggressive substances into concrete, which may lead to corrosion of the rebars, it is not enough to require that the resistance against penetration has a certain value at the time of testing.The development of the resistance against penetration during the intended lifetime may be just as important. The intended lifetime can be achieved in two different ways:

■ The resistance against penetration is small at e.g. 28 maturity days, but the resistance will increase sufficiently with time in order to reach the intended lifetime.

■ The resistance against penetration is constant with time and small enough in order to reach the intended lifetime.

In this way the compressive strength of concrete differs from its resistance against penetration of e.g. chloride. It is only possible to specify the resistance against penetration of aggressive substances at 28 maturity days, if, and only if, the development of the resistance is known or can be estimated on the safe side. However, the knowledge is limited about the development of the resistance against penetration of chloride into concrete, since the study of this phenomenon began only 20 years ago. Testing chloride penetration into concrete requires long-term studies by laboratory investigation as well as by field inspection.

Despite this, it has been possible to specify requirements for the parameters of chloride ingress of e.g. the concrete in RC-structures of the fixed link across the Great Belt. The reason is that it is possible to estimate the development of the resistance against chloride ingress or on the safe side assume the resistance to be constant.

This paper deals with the »set of rules« which have to be followed, when the lifetime of a RC-structure exposed to a chloride contaminated environment, e.g. sea water, are to be calculated.

The Capillary Porosity of Concrete

The development of the compressive strength of concrete is a result of the fact that the capillary porosity of the concrete decreases with increasing maturity of the concrete. By a general expression found by *Feret* and *Talbot* the compressive strength of concrete is related to the concentration of the solid state of the cementing matrix of the concrete. Thus, the compressive strength of the concrete and the porosity of the concrete are related. Since concrete develops compressive strength with time some of the characteristics of this development will be found in the development of the diffusion coefficient of the concrete.

Portland cement, silica fume, fly ash and slag all contribute to the compressive strength and to the diffusion coefficient in different ways. The effect of fly ash on the compressive strength of concrete mainly shows up after 28 days of maturity and diffusion tests on fly ash concrete show a similar tendency.

CHLORIDE DIFFUSION IN CONCRETE

The most simple presupposition to apply for diffusion of chloride ions in concrete is Fick's first law of diffusion, where the diffusion coefficient is assumed to be constant, i.e. $D = D_o$:

$$F = -D_o \cdot \frac{\partial C}{\partial x}$$

This law expresses that the transport of chloride ions through unit area of a section of the concrete per unit of time (the flux F) is proportional to the concentration gradient of the chloride ions measured normal to the section, i.e. $\partial C/\partial x$. The negative sign in Fick's first law of diffusion arises, because diffusion of chloride ions occurs in the direction opposite to that of increasing concentration of chloride ions.

It is obvious that such a simple assumption could not be valid for the diffusion of chloride ions in concrete. It is possible to mention several phenomena which do *not* obey this simple relation:

■ Concrete is heterogeneous in structure. It consists of aggregates and a cementing matrix having defects. Thus the diffusion coefficient will vary from point to point of the concrete, i.e. the diffusion coefficient D depends on the coordinates (x,y,z) of the concrete.

■ The capillary porosity of the concrete varies with the maturity M of the concrete. Therefore, the diffusion coefficient D also depends on the maturity. Thus, for constant temperature of the concrete the diffusion coefficient depends on the time t since the concrete was cast.

■ The diffusion process, where the random thermal motions of the chloride ions (Brownian movement) tend to reduce the difference in chloride concentration, depends on the temperature, i.e. the diffusion coefficient depends on the temperature T of the concrete.

■ In some cases the diffusion coefficient depends on the concentration of the diffusion substances. Some laboratory tests have shown that the chloride diffusion coefficient D is not independent of the chloride concentration C.

■ Diffusion of chloride ions only takes place in the pore liquid of the capillary pores of the concrete, if these pores are filled or almost filled with pore liquid. The range of pore sizes is from appx. 2 nm to 5 µm in diameter. If the capillary pores contain excess water from the mix and/or imbibing water from outside, the diffusion process can take place. However, if the concrete dries out the coarse pores wille be empty before the finer pores. Thus, the

amount of capillary pores available for diffusion will depend on the humidity of the concrete, and therefore the chloride diffusion coefficient of concrete depends on the humidity of the concrete, *RH*.

This variety and complexity of variables on which the chloride diffusion coefficient depends makes it complicated to apply Fick's first diffusion law. Furthermore, it is doubtful whether Fick's second law of diffusion in its most simple form applying a constant chloride diffusion coefficient is valid for the diffusion process in concrete. However, it has been possible to apply Fick's second law with a constant diffusion coefficient, e.g. by the test method APM 302, cf. [Frederiksen, 1992 p.22]. The reason is that most of the variables are kept constant during the test, and the influence of time on the diffusion coefficient during the testing time is negligble.

On the other hand, if Fick's second law is applied over a longer period, e.g. for the calculation of the lifetime of a RC-structure, it has to be taken into account that the chloride diffusion coefficient depends on the maturity of the concrete.

This paper deals only with the diffusion process, when the diffusion coefficient depends on the time during which diffusion has taken place, but not on any of the other variables, i.e. $D = D(t)$. Some laboratory diffusion tests indicate that the chloride binding is also dependent on time. However, here it is assumed that the chloride binding is constant, i.e. independent on time.

Fick's first general law of diffusion

In 1855 A. Fick formulated the laws of diffusion by direct analogy with the equation of heat conduction presented by Fourier in 1822. However, the application of Fick's laws on chloride processes in concrete appears many years later, cf. [Collepardi, 1970 and 1972]. Thus, the study of chloride diffusion processes in concrete technology is still fairly young.

The presupposition of Fick's diffusion theory is that the transport of chloride ions through unit area of a section of the concrete per unit of time (the flux F) is proportional to the concentration gradient of the chloride ions measured normal to the section, i.e. $\partial C/\partial x$. i.e.

$$F = -D \cdot \frac{\partial C}{\partial x}$$

The negative sign in Fick's first law of diffusion arises because diffusion of chloride ions occurs in the direction opposite to that of increasing concentration of chloride ions, cf. figure 1. The constant of proportionality D is called the diffusion coefficient. This paper only deals with cases where D depends on the time for which diffusion has been taking place but not on any other variables, i.e. $D = D(t)$. Is the diffusion coefficient constant $D = D_o$, the relation is usually referred to as Fick's first law of diffusion. If this is not the case, the relation is usually referred to as Fick's first general law of diffusion.

There are cases where such simple relation should not be applied. The diffusion process may be irreversible or has a history-dependence. In such cases Fick's law of diffusion is not valid, and the diffusion process is referred to as a »non-Fickian« or »anomalous« diffusion process. However, no observation so far indicates that the chloride diffusion in concrete should be characterized as »anomalous« diffusion.
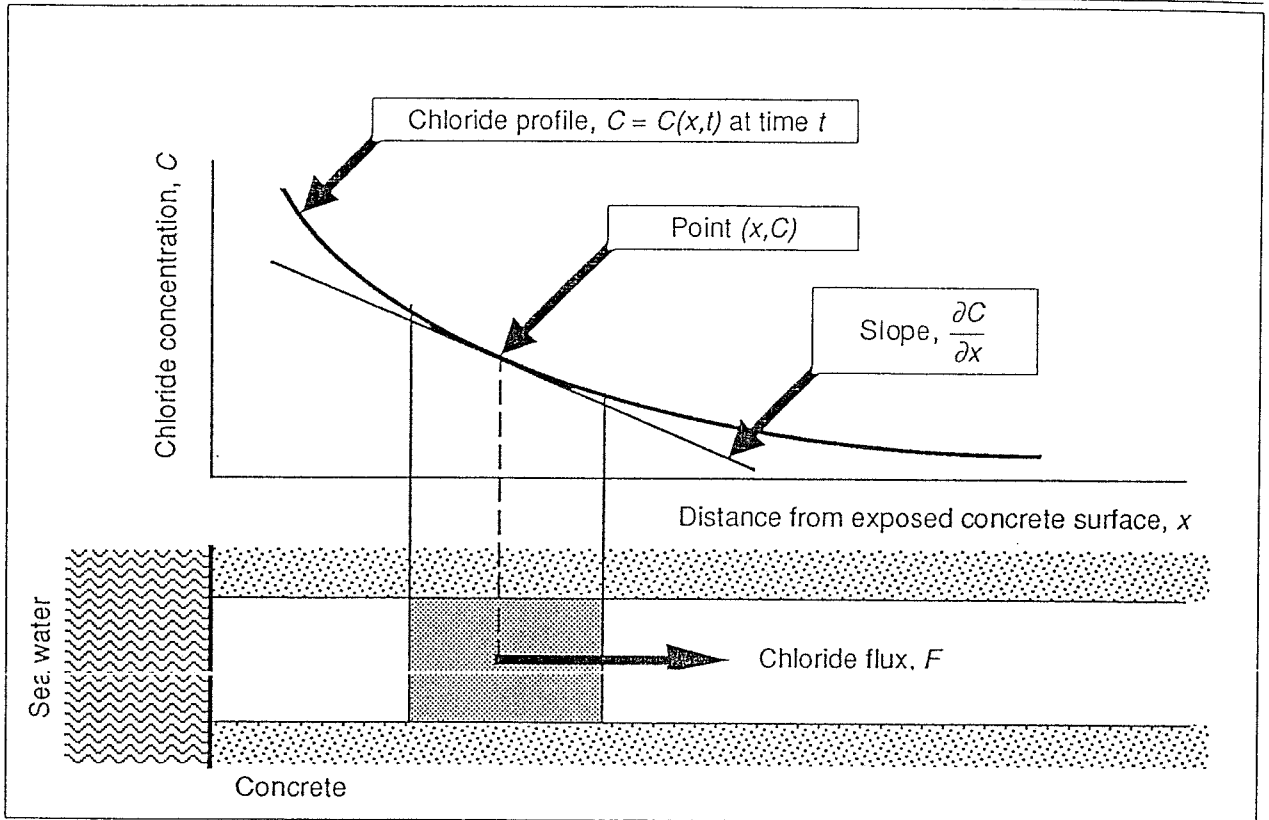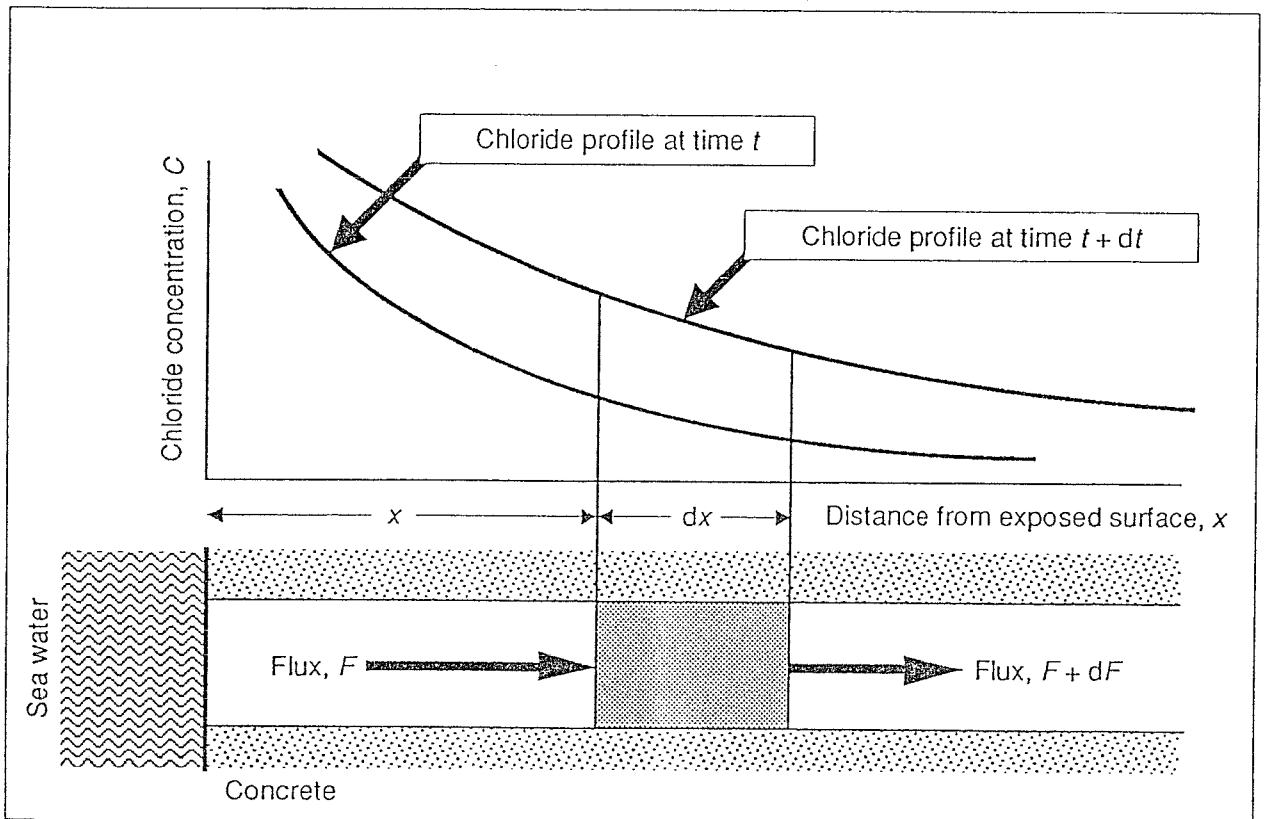
Figure 1. Fick's first general law of diffusion expresses, that the flux of chloride ions in concrete is proportional to the chloride concentration gradient normal to the section.

Figure 2. Fick's first general law of diffusion expresses, that the change in flux per unit in the x-axis is equal to the change in

Fick's second general law of diffusion

When chloride diffuse into concrete a change of the chloride concentration C occurs at any time t in every point x of the concrete, i.e. a non-steady state of diffusion.

In order to simplify the problems only one-dimensional diffusion is dealt with here, i.e. there is a gradient of chloride concentration only along the x-axis, cf. figure 1 and 2. Many problems of chloride ingress can be solved by the application of this simplification in practice.

Consider an element parallel to the chloride diffusion into a semi-infinite volume of concrete. For convenience the cross-section of the element is taken as $dA = 1$. Thus, between the two consecutive sections at a distance of dx the volume is $dV = dx$. Per unit time, $dt = 1$, the amount of chloride which diffuses into this volume dV is by definition the flux F, cf. figure 2.

In the same way the amount of chloride which diffuses out of the volume dV is the flux at the abscissa $x + dx$. The flux changes along the x-axis with $\partial F/\partial x$ per unit of the x-axis. Thus, during the time $dt = 1$ the increase of chloride in the volume dV yields:

$$\frac{\partial C}{\partial t} \cdot dx = F - \left(F + \frac{\partial F}{\partial x} \cdot dx\right) = -\frac{\partial F}{\partial x} \cdot dx$$

By applying Fick's first general law of diffusion this expression reduces simply to:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \cdot \frac{\partial C}{\partial x}\right)$$

Here it is assumed that the chloride diffusion coefficient of the concrete depends on the time for which diffusion has taken place but *not* on any other variables, i.e. $D = D(t)$. In this special case Fick's second law of diffusion yields:

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

In order to apply Fick's second law in this form for concrete exposed to chloride during a longer period of time, one ought to know the development of the chloride diffusion coefficient with time, i.e. the function $D = D(t)$. If only few observations exist in a specific case it is possible to estimate an upper and lower bound for the variation of $D = D(t)$.

ANALYTICAL SOLUTION

Solutions to Fick's second general law of diffusion in the following form:

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

always exist in the cases where a solution for a constant $D = D_o$ exists.

Method of Substitution

This is verified by introducing the following substitution:

$$dI(t) = D(t) \cdot dt$$

It is seen that the substitution $I = I(t)$ is defined by the following expression:

$$I(t) = \int_0^t D(\tau) \cdot d\tau$$

Introducing $dI = D(t) \cdot dt$ into Fick's second general law reduces it to the following expression:

$$\frac{\partial C}{\partial I} = \frac{\partial^2 C}{\partial x^2}$$

The solutions for a constant $D = 1$ can therefore be used to find the chloride-profile $C = C(x,I)$, i.e. as function of x and $I = I(t)$. In order to find the chloride profile $C = C(x,t)$ to a given time t the value of $I = I(t)$ shall be found and used in the solution. This will be demonstrated in the following pages.

A Special Case

For a well-known case, i.e. a semi-infinite volume of concrete which is exposed to a constant (time-independent) chloride contaminated environment (e.g. sea water), the solution for $D = 1$, cf. [Poulsen, 1990 p.39], yields:

$$C(x,I) = C_i + (C_s - C_i) \cdot \text{erfc} \frac{x}{\sqrt{4 \cdot I(t) \cdot 1}}$$

where the value of $I(t)$ should correspond to the time t to which the chloride profile refers to. By this it is obvious, that the chloride profile has the shape of an error function independent of the chloride diffusion coefficient to be time-dependent or constant. Thus, it is not possible to determine if the chloride diffusion coefficient of the concrete is time-dependent or constant just by the shape of the chloride profile.

The Geometrical Interpretation of the Substitution $I(t)$

The substitution $I = I(t)$ is defined as the definite integral from 0 to t of $D = D(t)$. Thus $I = I(t)$ may be described as the area between the curve $D = D(t)$ and the x-axis from 0 to t, cf. figure 3. However, it is more convenient to introduce the mean value D_{mid} of the chloride diffusion coefficient in the interval from 0 to t, defined by the following formula:

$$D_{mid} = \frac{1}{t} \int_0^t D(\tau) \cdot d\tau$$

By introducing the relationship $I(t) = t \cdot D_{mid}$, the chloride profile yields:

$$C(x,t) = C_i + (C_s - C_i) \cdot \text{erfc} \frac{x}{\sqrt{4 \cdot t \cdot D_{mid}}}$$

It should be noticed that since $D = D(t)$ varies with time t so will D_{mid} vary with time. This result leads to the following simple rule of calculating the chloride profile, when the chloride diffusion coefficient is time-dependent:

The mean value of the chloride diffusion coefficient D_{mid} during the exposure time from 0 to t is calculated and used to replace the chloride diffusion coefficient D_o in the the expression for the chloride profile calculated under the condition that the chloride diffusion coefficient D_o remains constant.
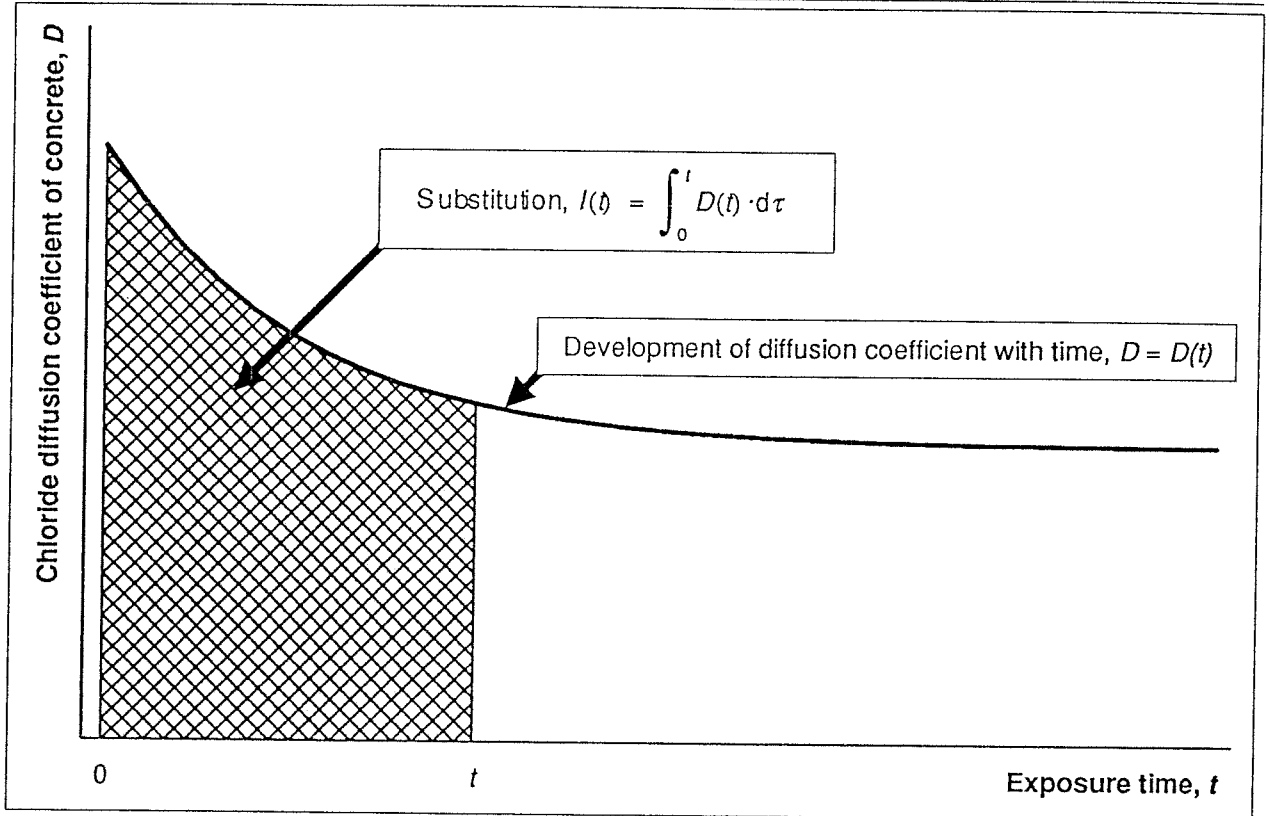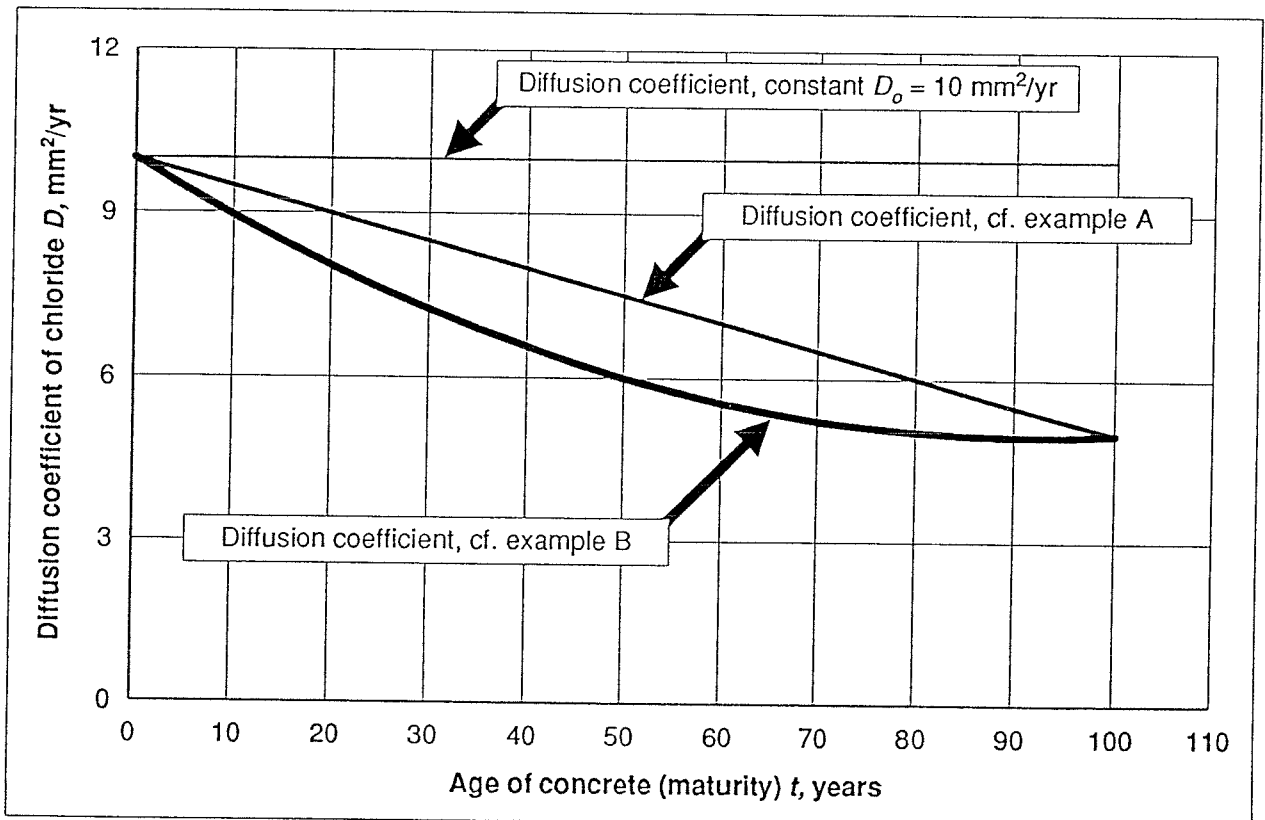
The graph shows chloride diffusion coefficient D on the vertical axis against exposure time t on the horizontal axis, with the following labels:

Substitution, $I(t) = \int_0^t D(t) \cdot d\tau$

Development of diffusion coefficient with time, $D = D(t)$

Figure 3. The chloride diffusion coefficient D of concrete decreases with the maturity of the concrete, i.e. with time t, D = D(t). An explanation of the applied substitution I = I(t) could be the shaded area during the exposure time, here from 0 to t.

Figure 4. The development of the diffusion coefficient D = D(t) applied for the examples.

The graph shows diffusion coefficient of chloride D (mm²/yr) on the vertical axis against age of concrete (maturity) t, years on the horizontal axis, with the following labels:

Diffusion coefficient, constant $D_o = 10$ mm^2/yr

Diffusion coefficient, cf. example A

Diffusion coefficient, cf. example B

Ingress of the Critical Chloride Concentration C_{cr}

On condition that the chloride diffusion coefficient of the concrete remains constant, i.e. $D = D_o$, the critical chloride concentration will ingress according to the »square root formula«, cf. [Poulsen, 1985 p.85]:

$$x_{cr} = K_1 \cdot \sqrt{t}$$

Since $D = D(t)$ will never be strictly monotonic increasing on $[0, t]$, it will be on the safe side to use the »square root formula«, applying $D_o = D(0)$. However, the time-dependence can easily be taken into account by the corresponding formula:

$$x_{cr} = K_c \cdot \sqrt{I(t)}$$

where $I(t) = t \cdot D_{mid}$. Here K_c is a constant dependent on the characteristic chloride concentration of the concrete in the following way:

$$K_c = 2 \cdot \text{erfc}^{-1}\left(\frac{C_{cr} - C_i}{C_s - C_i}\right)$$

Example A and B illustrate the application of the formulae and illustrate the influence which a time-dependent chloride diffusion coefficient may have on the ingress of chloride into concrete.

EARLY EXPOSURE OF CONCRETE TO SEA WATER

The chloride diffusion coefficient of concrete will change its value from that of fresh concrete when cast to that of concrete, where hydration and development of properties have stabilized. The largest change in the value of the chloride diffusion coefficient will take place during the first appx. 28 maturity days after casting. Hence, concrete should not be exposed to sea water too early. However, young concrete could be exposed to sea water if certain precautions are taken. Guidance for such precautions may be found in the early Danish Code of Practice concerning sea water exposed RC-structures, cf. [Danish Society of Civil Engineers, 1926 p.4]. Here, the section I, clause 8 states: »*The curing time, until the concrete is exposed to sea water, shall be at least 6 weeks assuming that ordinary Portland cement is used. If the concrete surface is tarred or protected in another way, only the strength requirement determines the exposure time*«.

The concrete mix proportions ought to be designed in such a way that the concrete fulfills a requirement of a maximum ingress of the critical chloride concentration during the intended life-time when exposed to sea water, when it is not younger than 28 days of maturity. If it is neccesary to expose concrete to sea water, when it is younger than 28 maturity days, its surface should be protected by a decent membrane. This membrane should keep out the chloride ions from the concrete, until the concrete reaches a sufficient or required maturity.

This membrane could be a cheap one and need not be more durable than to serve its simple function until the concrete has reached the required maturity. This membrane should be chosen by a functional test method, e.g. like the AEC test method APM 302 for the determination of chloride ingress into concrete, cf. [Frederiksen, 1992 p.22] and [Sørensen, 1992 p.20].

EXAMPLES

Example 1 in [Poulsen, 1990 p.41] assumes that the parameters of the chloride diffusion process remain constant:

- Diffusion coefficient, D_o = 10 mm²/year.

- The surface chloride concentration (the chloride binding), C_s = 1,2 % of mass powder.

- The initial chloride concentration of the concrete, C_i = 0,1 % of mass powder.

Figure 7 in [Poulsen, 1990 p.41] shows chloride-profiles determined under these conditions. Among the chloride profiles shown the 100-years chloride profile is also found.

Example A. It is assumed that C_s remains constant at least in a 100 years' time. On the other hand it is assumed that the chloride diffusion coefficient $D(t)$ is strictly monotonic decreasing on the time interval [0, t] from D_o = 10 mm²/yr at the beginning of the exposure start until D_{100} = 5 mm²/yr 100 years later. Here it is assumed that the reduction is equal per year, cf. figure 4. According to this $D(t)$ can be written as follows:

$$D(t) = 10 \cdot (1 - 0{,}005 \cdot t) = 10 - 0{,}05 \cdot t$$

By definite integration of $D(t)$ from 0 to t the substitution $I(t)$ is found to be:

$$I(t) = 10 \cdot t - 0{,}025 \cdot t^2$$

For t =100 years $I(100)$ = 750 mm². This means that the mean value of the chloride diffusion coefficient during the t = 100 years yields:

$$D_{mid} = 750/100 = 7{,}5 \text{ mm}^2/\text{yr}$$

The chloride-profiles after 100 years of exposure are shown in figure 5 for as well a constant value of D_o = 10 mm²/yr as a decreasing chloride diffusion coefficient obeying a mean value of the chloride diffusion coefficient of D_{mid} = 7,5 mm²/yr at the end of the exposure time of 100 years. Figure 6 shows the ingress of the critical chloride concentration C_{cr} = 0,4 % of mass powder versus the exposure time t of the concrete.

Example B. Now it is assumed that the chloride diffusion coefficient $D(t)$ decreases obeying a parabolic variation with time t. At the start of the chloride exposure, i.e. t = 0 the value is D_o = 10 mm²/yr. After 50 years of exposure the value is $D(50)$ = 6 mm²/yr and after 50 years of exposure the value is $D(100)$ = 5 mm²/yr. By applying Simpson's rule for numerical integration $I(100)$ is found to be:

$$I(100) = \frac{\Delta t}{3} \cdot (D_0 + 4 \cdot D_{50} + D_{100}) = \frac{50}{3} \cdot (10 + 4 \cdot 6 + 5) = 650 \text{ mm}^2$$

For t =100 years $I(100)$ = 650 mm². This means that the mean value of the chloride diffusion coefficient during the t = 100 years yields:

$$D_{mid} = 650/100 = 6{,}5 \text{ mm}^2/\text{yr}$$

The chloride-profiles after 100 years of exposure under these conditions are shown in figure 5. Figure 6 shows the ingress of the critical chloride concentration C_{cr} = 0,4 % of mass powder versus the exposure time t of the concrete.
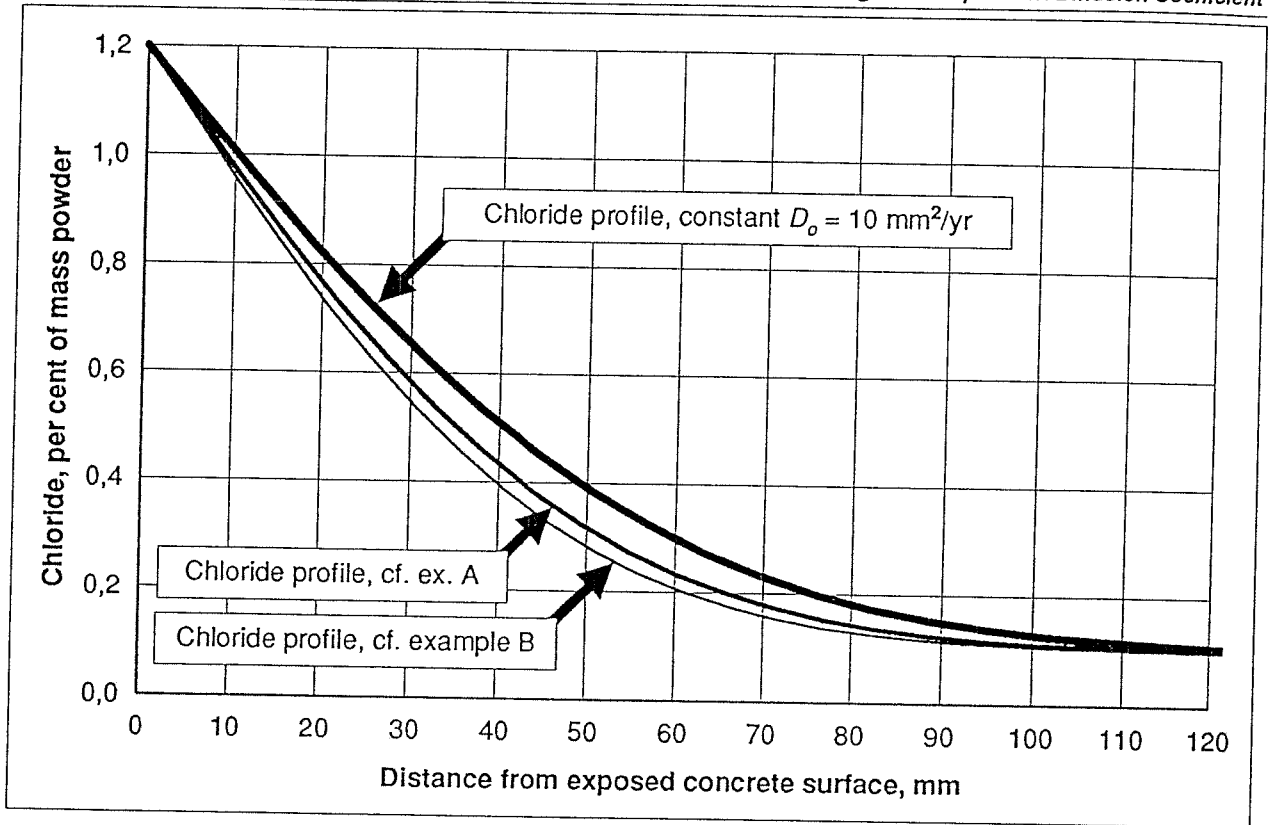
Figure 5. Chloride profiles of concrete after 100 years of exposure under various conditions.

Figure 6. Ingress of critical chloride concentration into concrete under various conditions. Thick line represents concrete with constant diffusion coefficient. Medium line represents conditions given in example A. Medium line represents conditions given in example B.
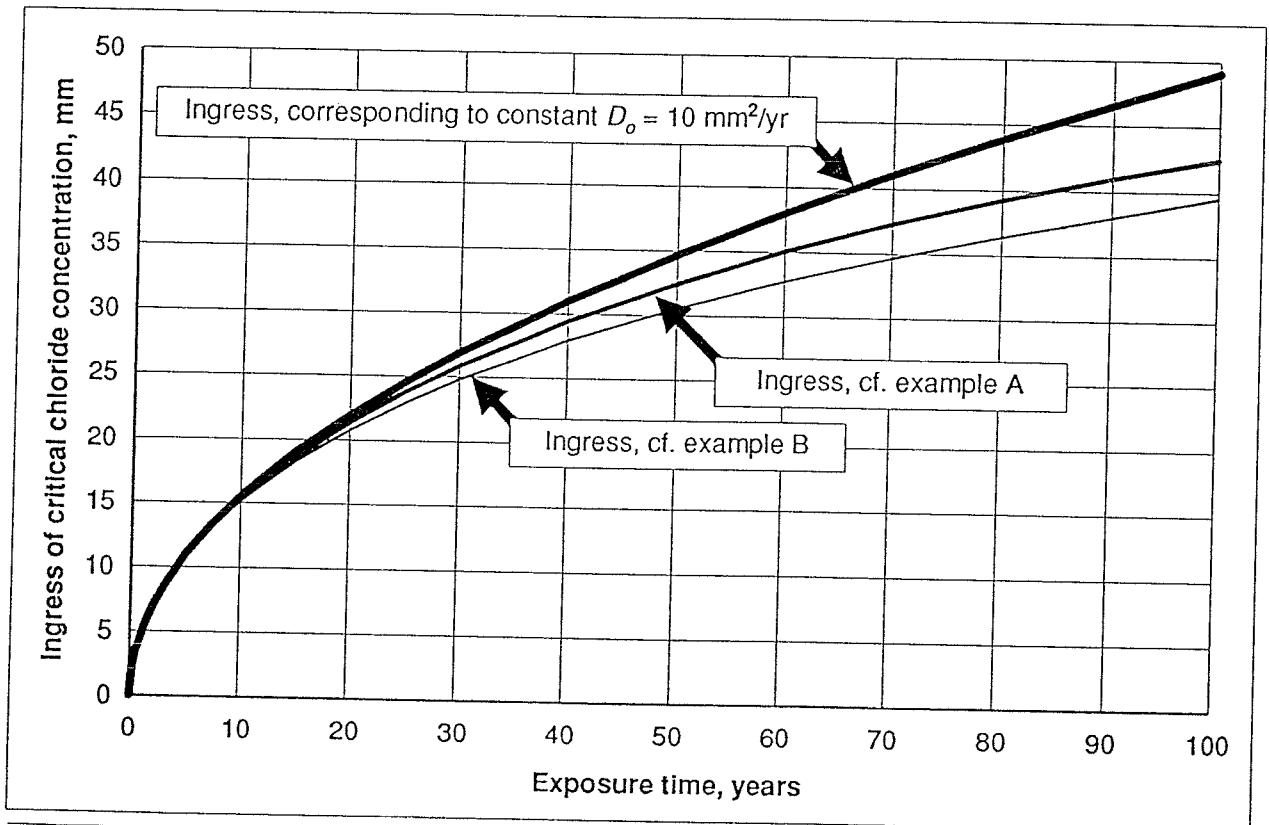
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PENETRAZIONE DEI CLORURI E VITA DI SERVIZIO DELLE STRUTTURE IN CALCESTRUZZO ARMATO IN AMBIENTE MARINO

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CHLORIDE INGRESS INTO AND LIFETIME OF MARINE REINFORCED CONCRETE STRUCTURES

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