LUND INSTITUTE OF TECHNOLOGY
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Division of Building Materials

Fick's 2nd law - Complete solutions for chloride ingress into concrete

– with focus on time dependent diffusivity and boundary condition

Jens Mejer Frederiksen
Leif Mejlbro
Lars-Olof Nilsson

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Lund Institute of Technology
Division of Building Materials
Box 118
SE-221 00 Lund, Sweden

Telephone: 46-46-2227415
Telefax: 46-46-2224427
www.byggnadsmaterial.lth.se

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Preface

In the ideal world there would be no need for this report. The reasons for making the analysis were purely due to misuse and misunderstandings of how to apply known mathematics in a correct manner when dealing with chloride ingress evaluation, modelling and prediction. The analysis did, however, bring forth a more clear understanding and terminology.

In fact, the intermediate results were quite unexpected and more general than foreseen. The most positive result of the study was the opportunity to make a sound, simple and "correct" approximation of the calculation of chloride profiles where simultaneous time dependent surface concentration and diffusivity can be treated in a correct manner by a slight modification of the classical error function solution. Without this analysis we would never have found that result!

We hope that the report will settle the discussions we have appointed and that a few readers will take the time needed to study our findings.

December 7, 2009

Jens Mejer Frederiksen

Leif Mejlbro

Lars-Olof Nilsson

Introduction

This report focuses on models of chloride ingress into concrete that are based on mathematical solutions of Fick's second law. In recent years a lot of confusion has been identified concerning these models. In some cases time-dependencies of diffusivity have been used in a mathematically incorrect way. In other cases field and laboratory data from one way of describing the time-dependency of these diffusivity has been used in models that are based on another model.

This is now clarified in this report. Some of the clarifications are completely new, concerning the relationship between the age exponents in the time-dependency of the "instantaneous" and the "achieved" diffusivity. This part is due to a problem not foreseen by *Poulsen & Mejlbro*(2006), and it is due to some mathematical imprecise formulations by others and it may be an appropriate amendment for the book [13] by *Poulsen & Mejlbro* (2006) to be complete.

The need and the idea for the report were made clear after a series of discussions, the first one being initiated by Dr. *Tang Luping*, SP/CTH, Sweden, and Mr. *Joost Gulikers*, RWS, The Netherlands, after input from Prof. *Lars-Olof Nilsson*, LTH, Sweden. Initiative for a first meeting to resolve this was taken by Ms. *Birit Buhr*, COWI, Denmark, after a notification by Mr. *Thomas Frølund*, COWI, Denmark. Additional participants in this first meeting were *Carola Edwardsen, Mette Sloth, Jens Mejer Frederiksen, Leif Mejlbro, Ervin Poulsen, Steen Rostam* and *Michael H. Faber* from Denmark, *Peter Schiessl* from Germany and *Joost Gulikers* from The Netherlands.

After the first meeting it was clear that significant misunderstanding remained. In another set of meetings this was clarified in depth from discussions between *Jens Mejer Frederiksen, Leif Mejlbro* and *Lars-Olof Nilsson.* The mathematical clarification was made by prof. emeritus *Leif Mejlbro*, DTU, Denmark, and this report was edited by all three os us, *Jens Mejer Frederiksen*, COWI (from July 2006 to March 2007)/ALECTIA (from March 2007), Denmark, *Lars-Olof Nilsson*, LTH, Sweden, and *Leif Mejlbro*, DTU, Denmark.

Chapter 1

Background

Mathematical models for prediction of chloride ingress have developed since the early 1990s in order to adapt better to the observations from exposure in natural environments like sea water and de-icing salt exposures. The approach first applied by *Collepardi et al.* in 1970 [3] has been dominating – and still is – when chloride ingress into concrete is modelled or analyzed. *Collepardi's* approach (the "Collepardi Model") was to use the error function solution to Fick's second law, i.e. assuming that the boundary condition and the diffusivity both are constants.

In the late 1980s, observations in the laboratory and in the field showed that the chloride ingress did not develop in time as it would be predicted by the "Collepardi Model". Discussions arose on whether sufficient connectivity of the pore system of e.g. high performance concrete was present, and *Sørensen* [15] studied this intensively from a theoretical point of view. If so, this would restrict the chloride ingress and hence compromise the use of mathematical diffusion models for prediction of chloride ingress into concrete. *Sørensen* demonstrated on computer modelled systems with limited connectivity that the ingress would appear as ordinary ingress profiles, but they *could not* develop in time as estimated by the "Collepardi Model" (with constant diffusivity and boundary condition) because of the limited pore system. In fact, this theory has never been rebutted.

In 1993 *Poulsen* [11] suggested that the diffusivity calculated according the the "Collepardi Model" was regarded as the integral (or the average) of the point-wise diffusivity. The idea to do this originated from observations made by *Maage et al.* [8], and *Takewaka et al.* [16]. One of the consequences of the diffusivity being a function of time was that the dependency needed to be observed on the same concrete in the same environment, before a prediction of the future chloride ingress could be made. This situation has not yet changed, so there is still a need of data from observations.

Since the mid 1990s it has been the state-of-the-art to apply solutions to Fick's second law, where the diffusivity is considered to be time dependent. This has led to different approaches. Analytical solutions on one hand and numerical solutions on the other hand.

Amongst the analytical solutions it has erroneously [17] been claimed recently that the approach taken by the *DuraCrete Model* [5] was based on the application of an instantaneous diffusivity which could lead to erroneous results. Therefore, a discussion arose on how the time-dependency of the chloride diffusivity should be handled in a mathematically correct manner. This discussion is still confusing and contains mathematical errors, cf. e.g. [10] and [17]. Also in numerical solutions of Fick's second law, cf. e.g. [7], similar mathematical mistakes are made when using field data as input to a time-dependent instantaneous diffusivity.

In order to elucidate this, the comprehensive solutions of the problem of transport of chloride by diffusion into concrete are recapitulated in this report. It should, however, already here be stated that the *DuraCrete Model* is *not* considering an instantaneous (or point-wise) diffusivity, but instead an achieved (or averaged) diffusivity, so there is *no mathematical error* in this model.

The mathematical description needs some ideal (abstract) functions which cannot be measured in practice, while the functions which can be estimated by safe measurements in practice cannot be applied directly in the ideal world of Mathematics. Fortunately, there is a correspondence between the two descriptions, and unfortunately, this correspondence is far from always understood and is therefore often neglected, which may cause some strange results, which will be demonstrated in this report.

The models dealt with in the following do not intend to model the actual physical and chemical processes involved in the chloride ingress into concrete. The aim of the models is solely to describe the *result* of these physical and chemical processes of this transport, i.e. the chloride profiles. For practical application the models are all dependent of calibration against good measurements from the environment and the concrete type in question.

Chloride ingress into concrete is a slow process. Preferable the ingress of the corrosion initiating amount of chloride takes place over several decades. Due to this slow process, and the experiences with premature deterioration of chloride exposed concrete structures, engineers have found a need for improvements of as well the understanding of the chloride ingress process as such and of the chosen concrete quality. In fact, the ability of producing concrete of high quality has improved faster than the improvements of models for chloride ingress.

Models for chloride ingress into concrete structures are studied either in the laboratory or in the field – on real structures or by exposing laboratory manufactured specimens under natural conditions. What is the more realistic depends on what one is looking for. Factors influencing chloride ingress in the early stage after the exposure has begun, are often not regarded as interesting neither for the long term prediction of a chloride profile nor for the understanding of the interaction between chloride and premature concrete.

Early observations of chloride ingress can, however, lead to a misinterpretation of the stipulated service life of a structure. Laboratory tests during production control can exhibit values that may seem to be unacceptable if a too conservative prediction model is applied. A similar situation arises if the chloride profile of a new structure is measured only a few years after the exposure started and hence long time before the service life is expected to end.

Observations of chloride profiles made on structures that have been in service for many years are often missing a connection to early data. This makes further extrapolations uncertain and hence the estimation of the residual service lifetime uncertain.

The advantage of using mathematical models for prediction of the rate of chloride ingress is that we have the possibility to gain experience by studying the behaviour of concrete produced under modern conditions with modern materials. The disadvantage is of course that we can only study the ingress process in the early phases for up to about 20 years before the test programme is left behind by the development in the concrete industry.

The time gap between the periods we can study intensively (0–20 years) and the periods we have interest for (50–300 years) is extremely large. This puts a great responsibility on the modelers, because the choice of wrong models (too optimistic or too conservative) will lead to high expenses, either at the time of construction or at the time of repair/reconstruction. Due to the interest rate, the more optimistic models will often be preferred, because the net present value of future expenses is small. The optimal model may be one giving the smallest net present value – i.e. the lowest cost of construction plus operation and maintenance.

These general considerations apply differently for structures to be constructed and for structures already in service. This is due to the number of adjustable parameters – a lot more parameters can be adjusted before construction than after. The demanded precision of a model for the two purposes is therefore different, but nevertheless it is preferable to use only one mathematical model for both time periods (0–20 years of 50–300 years).

Till now, observations of achieved diffusivity decreasing with the exposure time of the concrete have been widely accepted and published. These findings lead to more optimistic models for the chloride ingress into concrete. On the other hand, several observations indicate that also the apparent/achieved surface concentration is time dependent – a tendency for an increasing apparent surface concentration with time is observed. This may lead to less optimistic models.

In this report we shall try to present a mathematically correct model that is applicable on chloride exposed concrete structures. The aim is to have one "master model" in which as well laboratory test data as field observations can be made useful. The model can with as little bias as possible be calibrated to observed data (preferable a pool of good data being the "prior" for other data from an environment (represented by the "prior")) and thereby obtain a model that will give "the mean value of our at any time present experience" rather than a value biased by personal judgements.

The way to avoid the previous misunderstandings is clearly to define what the assumptions are, and not to mix "apples and pears". The latter may be the most difficult part because one needs to make clear of what nature a parameter is and when to make a mathematical transformation to get from one category to another one.

Our contribution is to present, based on Fick's second law, the mathematical models, solutions and their application. Thereby we hope to have highlighted that misunderstandings in the application of these models are crucial for the result – as it would be for any other model.

A large number of alternative models are being used for chloride ingress. Some of them are utilizing research front knowledge on Physics and Chemistry, but are still too complicated to use in practical applications [10].

Using Fick's second law as a mass balance equation for chloride in concrete, we acknowledge that one or a few important assumptions are made [10]. The Physics and Chemistry are significantly simplified:

1) the flux of chloride ions is solely described by Fick's first law with a diffusion coefficient D_{F_2} and the total chloride content C as the flux potential,
   or

2) the flux of chloride ions is solely described by Fick's first law with a diffusion coefficient D_{F_1} and the "free" chloride content c as the flux potential,
   and

3) the binding capacity dC/dc is a constant, i.e. does not change with the concentration.

These assumptions mean that the diffusivity D in the rest of this report is equal to the diffusivity D_{F_2} in Fick's second law, where

$$D_{F_2} = \frac{D_{F_1}}{dC/dc}.$$

Other ions than chloride are totally neglected. The interaction between the chloride in the solution and chloride in the matrix is described in a very simplified way. To include all ions and other physical and chemical effects, completely different solution methods are required. This is described in [10].

Chapter 2

Fick's second law – traditional solutions

In Appendix A we have derived Fick's second law under very modest physical assumptions. Therefore, we may in most cases model the transport by diffusion of heat, moisture and chloride in a porous material by Fick's second law of diffusion. The interested reader is here referred to Appendix A for more details, including a discussion of why it is so difficult to avoid Fick's second law. We shall, however, not repeat this discussion, so we take for granted that the *pure mathematical formulation* of ingress into a one-dimensional half infinite space is given by the following initial/boundary value problem for a parabolic partial differential equation (the *heat equation*) of constant coefficients, and a boundary condition, which is a function of time t,

$$\begin{cases} \dfrac{\partial C}{\partial t} = \dfrac{\partial^2 C}{\partial x^2}, & x > 0, \quad t > 0, \\[2ex] C(0,t) = C_s(t), & t > 0, \\[2ex] C(x,0) = 0, & x > 0. \end{cases} \tag{2.1}$$

Here, C denotes the concentration, t is the time, and x is the distance from the exposed surface, and the index s denotes the surface.

In (2.1), no diffusivity is yet introduced, and it is considered purely in a mathematical way with no physical dimension involved. The *unique* solution of (2.1) is according to e.g. [1] given by

$$C(x,t) = -2 \int_0^t \frac{\partial K}{\partial x}(x, t-\tau)\, C_s(\tau)\, \mathrm{d}\tau, \qquad x > 0, \quad t > 0,$$

where

$$K(x,t) = \frac{1}{2\sqrt{\pi t}} \exp\left(-\frac{x^2}{4t}\right), \qquad t > 0, \quad x \in \mathbb{R}.$$

Hence, the solution is given by

$$(2.2)\quad C(x,t) = \frac{x}{2\sqrt{\pi t}} \int_0^t \frac{1}{\tau\sqrt{\tau}}\, C_s(t-\tau) \exp\left(-\frac{x^2}{4\tau}\right) \mathrm{d}\tau,$$

a formula, which is well fit for theoretical considerations, but definitely not for practical applications. We notice that the unique solution of the problem (2.1) is given by (2.2), which was mathematically derived some 100–150 years ago. With the exception of the cases mentioned below, one never really cared for how to compute (2.2) in practice.

According to an early edition of *Crank* [4] it should only be possible to compute (2.2) explicitly when

$$C_{s,0}(t) = C_{s,0}, \qquad C_{s,1/2}(t) = C_{s,1/2}\sqrt{t} \qquad \text{or} \qquad C_{s,1}(t) = C_{s,1}\, t,$$

which can also be written in the form

$$(2.3)\quad C_{s,p}(t) = C_{s,p}\, t^p, \qquad \text{where } p \in \left\{0\,,\, \frac{1}{2}\,,\, 1\right\}.$$

It can, however, be shown that it follows implicit from *Crank* [4] and *Carslaw & Jaeger* [2] (and it was corrected in a later edition of [4]) that it can actually be computed explicitly whenever $2p \in \mathbb{N}_0$, i.e.

$$C_{s,p}(t) = C_{s,p}\, t^p, \qquad \text{where } p \in \left\{0\,,\, \frac{1}{2}\,,\, 1\,,\, \frac{3}{2}\,,\, 2\,,\, \frac{5}{2}\,,\, \dots\right\}.$$

For $p = 0$ and $C_{s,0}(t) = C_{s,0}$ we get in particular the so-called (complementary) *error function solution*,

$$(2.4)\quad C(x,t) = C_{s,0}\, \mathrm{erfc}\left(\frac{x}{2\sqrt{t}}\right),$$

where the function “erfc” is defined by

$$\begin{aligned} \mathrm{erfc}(z) &= 1 - \frac{2}{\sqrt{\pi}} \int_0^z \exp\left(-u^2\right)\, \mathrm{d}u = \frac{2}{\sqrt{\pi}} \int_z^{+\infty} \exp\left(-u^2\right)\, \mathrm{d}u \\ (2.5)\qquad &= 1 - \frac{2}{\sqrt{\pi}} \sum_{n=0}^{+\infty} \frac{(-1)^n}{(2n+1)n!}\, z^{2n+1}. \end{aligned}$$

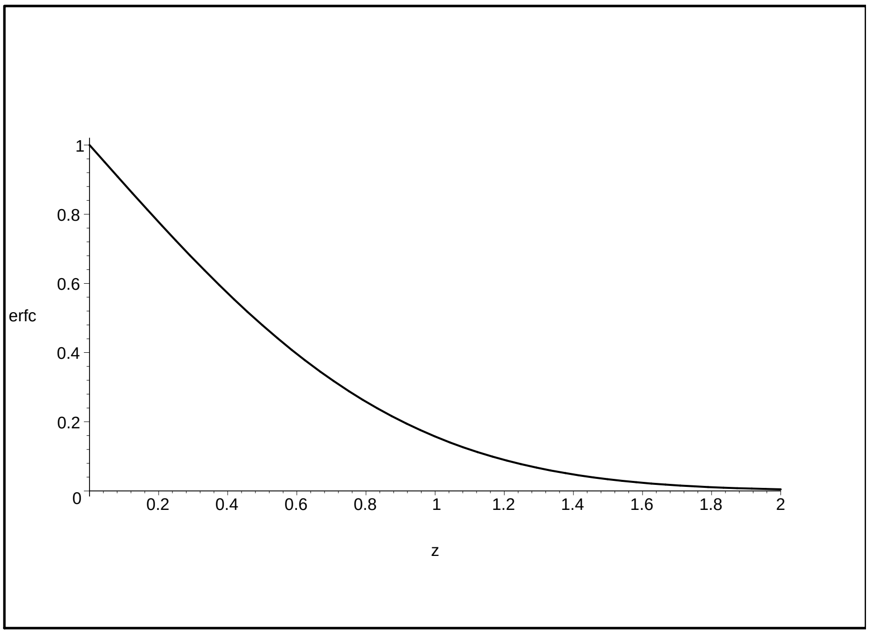

Figure 2.1: The graph of erfc(z), cf. (2.5).

In this connection it will also be relevant to show its counterpart, namely the graph of the simplest possible solution, where we for simplicity choose $x = 2$. Thus, we shall only consider the graph of the function $\mathrm{erfc}(1/\sqrt{t})$, cf. Figure 2.2.

For completeness we now introduce a constant diffusivity $D > 0$ into (2.1). Then we recognize Fick's second law as it was originally used for modelling chloride ingress,

$$\text{(2.6)}\quad \begin{cases} \dfrac{\partial C}{\partial t} = D\,\dfrac{\partial^2 C}{\partial x^2}, & x > 0, \quad t > t_{ex}, \\[2ex] C(0,t) = C_{s,0}, & t > t_{ex}, \\[2ex] C\left(x, t_{ex}\right) = 0, & x > 0, \end{cases}$$

where $C_{s,0}$ is a constant, and t_{ex} is the time of first exposure. The solution (2.4) is then turned into the *"error function solution"* of Fick's second law,

$$\text{(2.7)}\quad C(x,t) = C_{s,0}\,\mathrm{erfc}\left(\frac{x}{2\sqrt{D\cdot(t-t_{ex})}}\right), \qquad x > 0, \quad t > t_{ex}.$$

We note that if we calibrate Figure 2.2, such that we write $x^2/\{4D\}$ instead of 1 on the horizontal axis, then the graph of (2.7) is again given by Figure 2.2.

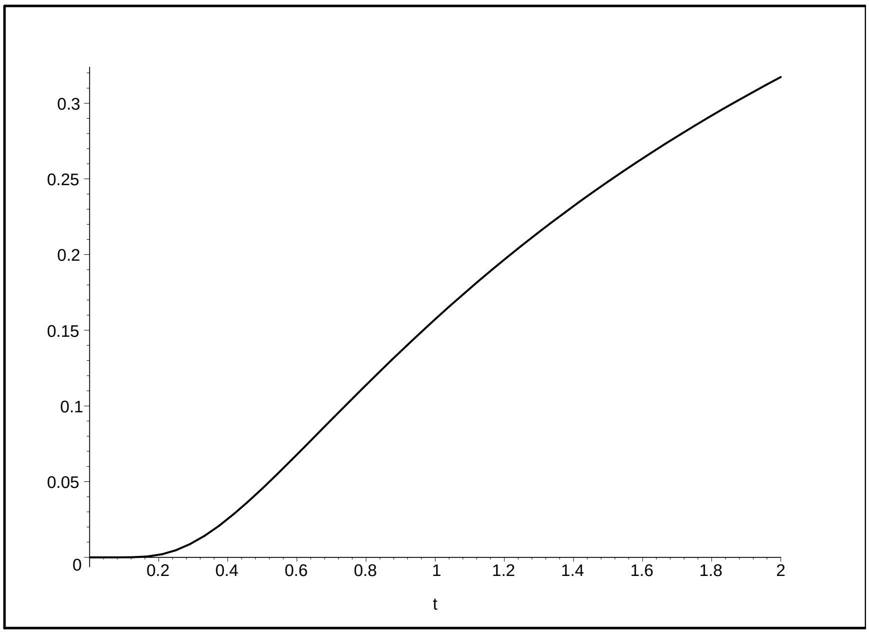

Figure 2.2: The graph of the solution $C(2,t) = \mathrm{erfc}(1/\sqrt{t})$ at the depth $x = 2$. Different scales on the axes. This figure is actually generic in the sense that we can obtain every possible chloride profile from this figure by only changing the units on the axes. The abstract time is taken along the horizontal axis, i.e. "$t = 1$" corresponds to "$x/\sqrt{4Dt} = 1$" in the general case, where the diffusivity is $D = 1$, and the chloride concentration between 0 and 1 is along the vertical axis. We shall not go further into this graphical application in this report.

Chapter 3

The Ψ_p-functions

In spite of the statement of *Crank* [4] it was shown by *Mejlbro* [9] that if one introduces some special functions, Ψ_p, only depending on p, it nevertheless becomes possible to solve (2.1) assuming (2.3) explicitly by using a very simple procedure.

We shall in this chapter only define these functions and note that they in spite of their apparent complicated structure in fact are very easy to implement in practice. We leave for a moment their applications in the solution of (2.1) and (2.3) to the following chapter. The interested reader is referred to either *Mejlbro* [9] or *Poulsen & Mejlbro* [13] for further properties of the Ψ_p-functions.

The Ψ_p-functions are defined as follows,

$$(3.1)\quad \Psi_p(z) = \sum_{n=0}^{+\infty} \frac{p^{(n)}(2z)^{2n}}{(2n)!} - \frac{\Gamma(p+1)}{\Gamma(p+0.5)} \sum_{n=0}^{+\infty} \frac{(p-0.5)^{(n)}(2z)^{2n+1}}{(2n+1)!},$$

where $\Gamma(y)$ is the Gamma function defined by

$$\Gamma(y) := \int_0^{+\infty} u^{y-1} e^{-u}\,\mathrm{d}u, \qquad \text{for } y > 0,$$

and the *factorial power*, e.g. $p^{(n)}$ in (3.1), is defined by

$$(3.2)\quad p^{(0)}=1; \quad p^{(1)}=p; \quad p^{(2)}=p(p-1); \quad \dots \quad ; p^{(n)}=p(p-1)(p-2)\cdots(p-n+1),$$

where $p^{(n)}$ contains $n \geq 1$ decreasing factors. Note that the parameter p the exponent in (3.2) is the same p as in (2.3).

One can also describe Ψ_p for $p \geq -0.5$ as the unique solution of the ordinary *initial value problem*

$$(3.3)\quad \Psi_p''(u) + 2u\,\Psi_p'(u) - 4p\,\Psi_p(u) = 0, \qquad \Psi_p(0) = 1, \qquad \Psi_p'(0) = -2\,\frac{\Gamma(p+1)}{\Gamma\left(p+\frac{1}{2}\right)}.$$

The proof of (3.3) can be found in *Poulsen & Mejlbro* [13].

It follows in particular from either (3.1) or (3.3) combined with (2.5) that we have the important identification

$$\Psi_0(z) = \operatorname{erfc}(z).$$

Putting

$$z := \frac{x}{2\sqrt{D \cdot t}}, \qquad D > 0 \text{ constant},$$

it will be shown in the next chapter that if the boundary condition is a constant times t^p, then $t^p \Psi_p(z)$ in general plays a similar rôle in the solution of Fick's second law, as $\operatorname{erfc}(z) = t^0 \Psi_0(z)$ does in the case of a constant boundary condition. For that reason it is quite natural to call the $\Psi_p(z)$ the *generalized (complementary) error functions.*

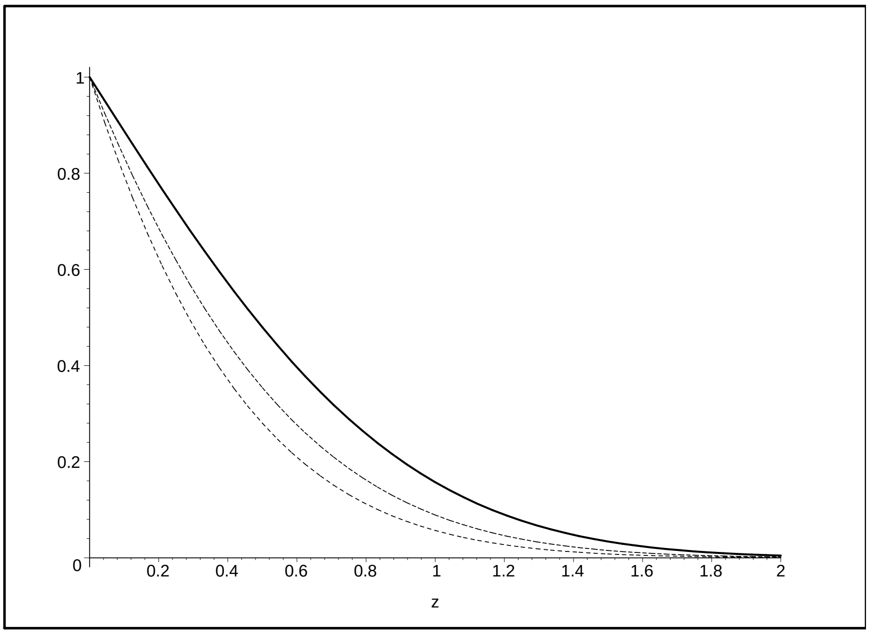

Figure 3.1: The graphs of the functions Ψ_p, for $p = 0$ (= $\operatorname{erfc}(z)$, thick line), for $p = \frac{1}{2}$ (dashed line) and $p = 1$ (dotted line).

Chapter 4

The abstract (mathematical) Fick's second law for $C_p(0,t) = t^p$

The idea of an alternative solution of the problem (2.1) of constant diffusivity is to benefit from the linearity, so we can use the principle of superposition of partial solutions. We therefore search some special problems, which can be used as building stones in the general solution. Of these, only the error function solution (2.7) has been applied isolated in practice as a first approximation. However, by adding linear combinations of these special solutions one obtains an extremely flexible model, which includes the error function solution as a very special case.

In order to obtain the right mathematical solution from the very beginning we here strip the usual Fick's second law of all its physical dimensions and formally put the diffusivity $D = 1$. Thus, in this chapter – and only in this chapter – we shall not interpret t as the time variable and x as the length variable. They are just dimensionless mathematical variables.

The solutions of these special problems, where we choose $C_s(t) = t^p$, $p \geq 0$, and $C_i = 0$, will be denoted by $C_p(x,t)$. They are therefore defined as the unique bounded solution of the special initial/boundary value problem

$$(4.1) \quad \begin{cases} \dfrac{\partial C_p}{\partial t} = \dfrac{\partial^2 C_p}{\partial x^2}, & x > 0, \quad t > 0, \\[2ex] C_p(0,t) = C_{p,s}(t) = t^p, & t > 0, \quad p \geq 0 \quad \text{(constant)}, \\[2ex] C_p(x,0) = 0, & x > 0. \end{cases}$$

It was proved by *Mejlbro* [9] that the unique solution of (4.1) is given by

$$(4.2)\quad C_p(x,t) = t^p \Psi_p\left(\frac{x}{2\sqrt{t}}\right), \qquad \left[= \frac{x}{2\sqrt{\pi t}} \int_0^t (t-\tau)^p \, \frac{1}{\tau\sqrt{\tau}} \exp\left(-\frac{x^2}{4\tau}\right) \mathrm{d}\tau\right].$$

The expression in the squared parentheses is the integral of (2.2) which is no longer needed, because the simple procedure is just to multiply the power function t^p of the boundary condition by the factor $\Psi_p(x/\sqrt{4t})$, where the index p is the same as the exponent of the simple boundary condition.

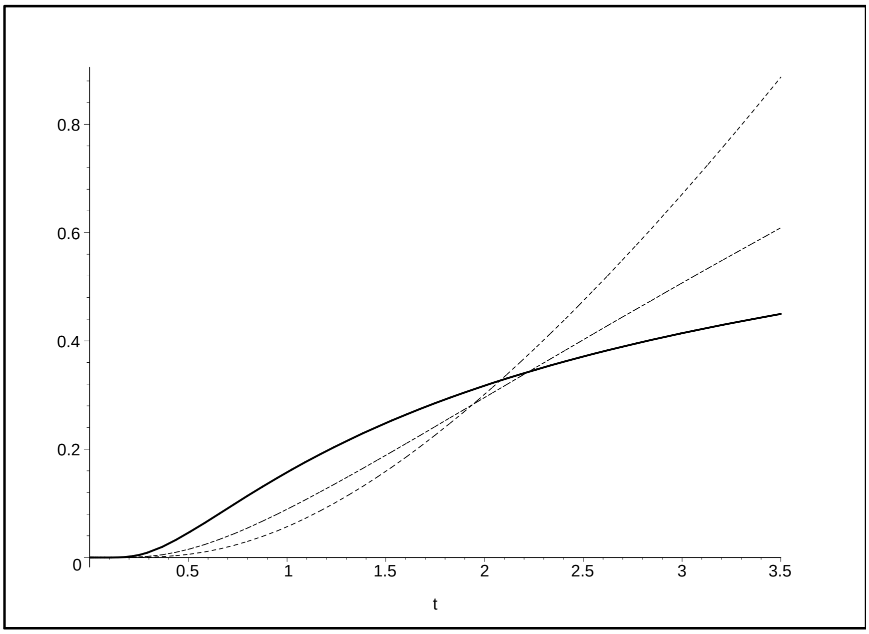

Figure 4.1: The graphs of the solutions $C_p(2,t) = t^p \cdot \Psi_p(1/\sqrt{t})$, at the depth $x = 2$ for $p = 0$ (i.e. $\mathrm{erfc}(1/\sqrt{t})$, full line), for $p = \frac{1}{2}$ (dashed line) and for $p = 1$ (dotted line). Notice that the graphs intersect, and that $\mathrm{erfc}(1/\sqrt{t})$ is dominating for small t, while $\Psi_1(1/\sqrt{t})$ becomes dominating for large t. Cf. also Figure 2.2.

For general fixed $x > 0$ we scale the time unit of the figure, such that "$t = (x/2)^2$" is represented by 1 on the time scale on the figure, and we have with this remark shown that the figure can be applied for general $x > 0$.

As observed above we have $\Psi_0(z) = \mathrm{erfc}(z)$, so we shall only get a solution containing $\mathrm{erfc}(z)$ when the exponent $p = 0$. If this is not the case, then erfc cannot enter the exact solution, though it may be possible to find a reasonable approximation by erfc using the methods of Chapter C.5 in Appendix C.

Figure 4.1 also gives the hint that when the error function solution is not satisfactory, then one should in the next approximation choose $C_s(t)$ as simple as possible, e.g.

$$C_s(t) = S \cdot t^p,$$

or in general,

$$C_i(t) = C_i + S \cdot t^p, \qquad \text{if } C(0,x) = C_i.$$

This means that the HETEK model, cf. Appendix B.5, is a very natural generalization from the (complementary) error function model, also called the *Collepardi Model.*

Remark 4.1 Once (4.1) has been solved by (4.2), it is not hard by superposition to find an approximating solution of the more general problem (2.1), provided that the boundary condition $C_s(t)$ is continuous in t. However, in order not to confuse the reader for the time being, as long as the easy solution technique (4.2) of problem (4.1) is not well-known, we have decided not to bring the full solution formula in this report. $\diamondsuit$

Chapter 5

Introduction of time-dependent diffusivity

We now introduce a diffusivity $D(t) > 0$ depending of time t and consider the more realistic problem

$$\text{(5.1)} \quad \begin{cases} \dfrac{\partial C}{\partial t} = \dfrac{\partial}{\partial x}\left\{D(t)\,\dfrac{\partial C}{\partial x}\right\} = D(t)\,\dfrac{\partial^2 C}{\partial x^2}, & x > 0, \quad t > t_{ex}, \\ C(0,t) = C_s(t), & t > t_{ex}, \\ C\left(x, t_{ex}\right) = 0, & x > 0, \end{cases}$$

where t_{ex} denotes the time of first exposure. Such a model was suggested by *Takewaka et al.* [16], and later by *Poulsen* [11].

In order not to get into trouble with the physical dimensions later on we may, whenever necessary, assume that we have chosen a time unit and a length unit etc. and that all variables in (5.1) are measured with respect to these chosen units. This trick will make the problem (5.1) dimensionless.

It is here of paramount importance for the understanding of where the pitfalls are in this theory that we recognize that the differential equation of (5.1) is referring to *points* $(x,t) \in \mathbb{R}_+ \times \,]t_{ex}, +\infty[$. In fact, we shall later also consider another, closely related diffusivity which very often is confused with the present one in (5.1). We shall therefore here give it a name. We call $D(t)$ from the differential equation of (5.1) the *instantaneous* (or *point-wise*) diffusivity. We consider the instantaneous diffusivity $D(t)$ as an *ideal function*, which somehow can be specified for each given and fixed time $t \geq 0$. We see that it enters in a natural way in the differential equation of (5.1), which is also point-wise in its structure, while the other diffusivity to be introduced later, the so-called *average diffusivity*, is *not* suited for the differential equation of (5.1). There are, however, a couple of drawbacks in the properties of the instantaneous $D(t)$. It is very difficult to measure within a given prescribed tolerated error $\varepsilon > 0$, and it does not enter the solution in a nice way. We shall come back to this later, because the other diffusivity fulfils these requirements.

The notation of (5.1) is that t denotes the real time, and that t_{ex} is the age at exposure. This means that the duration of the exposure is always represented by an interval, e.g.: The concentration is measured at a given time t_{in} (most often simply written as "t"). The duration of the exposure is then the length $t_{in} - t_{ex}$ of the exposure time interval $[t_{ex}, t_{in}]$. Following *Poulsen* [11] we shall in most of this report *not* put t_{ex} equal to 0 (zero). We note that we often have $t_{in} \gg t_{ex}$ and therefore $t_{in} - t_{ex} \approx t_{in}$.

If we change the variable in the following way

$$(5.2) \quad T = T(t) := \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau, \qquad t > t_{ex} > 0,$$

then the problem, equation (5.1), is transformed into

$$(5.3) \quad \begin{cases} \dfrac{\partial \tilde{C}}{\partial T} = \dfrac{\partial^2 \tilde{C}}{\partial x^2}, & x > 0, \quad T > 0, \\[2ex] \tilde{C}(0,T) = C_s(t) = \tilde{C}_s(T), & T > 0, \\[2ex] \tilde{C}(x,0) = 0, & x > 0, \end{cases}$$

where we have applied the notation of the "one-to-one" correspondence

$$\tilde{C}(x,T) = \tilde{C}\left(x, \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau\right) = C(x,t), \qquad \text{i.e.} \qquad C(x,t) = C\left(x, t(T)\right) = \tilde{C}(x,T),$$

because (5.2) is monotone, so the inverse $t = t(T)$ exists and is unique. In this way we have transferred the problem and the solution of it back to a known one, namely (2.1), so we immediately get the solution expressed in the new variable T. The only difference is that we are now forced to consider the *integral of the diffusivity* over the exposure time interval $[t_{ex}, t_{in}]$ instead of $D \cdot (t - t_{ex})$, when D is constant.

We note in particular in the special case where the boundary condition $C_s(t) = C_{s,0} > 0$ is constant that (5.1) is reduced to the simpler problem

$$(5.4) \quad \begin{cases} \dfrac{\partial C}{\partial t} = D(t)\,\dfrac{\partial^2 C}{\partial x^2}, & x > 0, \quad t > t_{ex}, \\[2ex] C(0,t) = C_{s,0}, \qquad \text{constant}, & t > t_{ex}, \\[2ex] C\left(x, t_{ex}\right) = 0, & x > 0. \end{cases}$$

Using the transformation (5.2) we get the following simplification of (5.3),

$$\begin{cases} \dfrac{\partial \tilde{C}}{\partial T} = \dfrac{\partial^2 \tilde{C}}{\partial x^2}, & x > 0, \quad T > 0, \\ \tilde{C}(0, T) = C_{s,0}, & T > 0, \\ \tilde{C}(x, 0) = 0, & x > 0, \end{cases}$$

the solution of which is

$$C(x,t) = \tilde{C}(x,T) = C_{s,0}\,\mathrm{erfc}\left(\frac{x}{2\sqrt{T}}\right) = C_{s,0}\,\mathrm{erfc}\left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right). \tag{5.5}$$

Chapter 6

Time-dependent diffusivity and time-dependent surface concentration

We saw in Chapter 5 that the work of *Takewaka et al.* [16] and later *Poulsen* [11] suggested the introduction of a diffusivity $D(t)$ depending on time t. For some reasons which will be explained in a later chapter they chose $D(t)$ such that

$$\frac{1}{t - t_{ex}} \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau := D_{\mathrm{aex}} \left\{ \frac{t_{ex}}{t} \right\}^{\alpha}, \qquad t > t_{ex} \quad 0 \leq \alpha < 1.$$

However, although it was a step forward, it could not be used in all cases to predict the chloride ingress into concrete. Then *Uji et al.* [18] suggested in 1990 *for constant diffusivity* that also the surface concentration of chloride profiles might be regarded as a continuous increasing function like (6.1) below

$$(6.1) \quad C_s(t) = C_0(t) = C(0,t) = S\,\sqrt{t},$$

where S denotes a "surface chloride content coefficient" of the unit $1/\sqrt{\text{time}}$. As mentioned earlier in this report, *Crank* [4] presented the solution of Fick's second law in this special case.

Other investigations showed immediately that the square root function would not always fit the actual data, but the fact that the surface chloride content changed with time was again and again found to be the reality. For these reasons a more flexible structure was asked for.

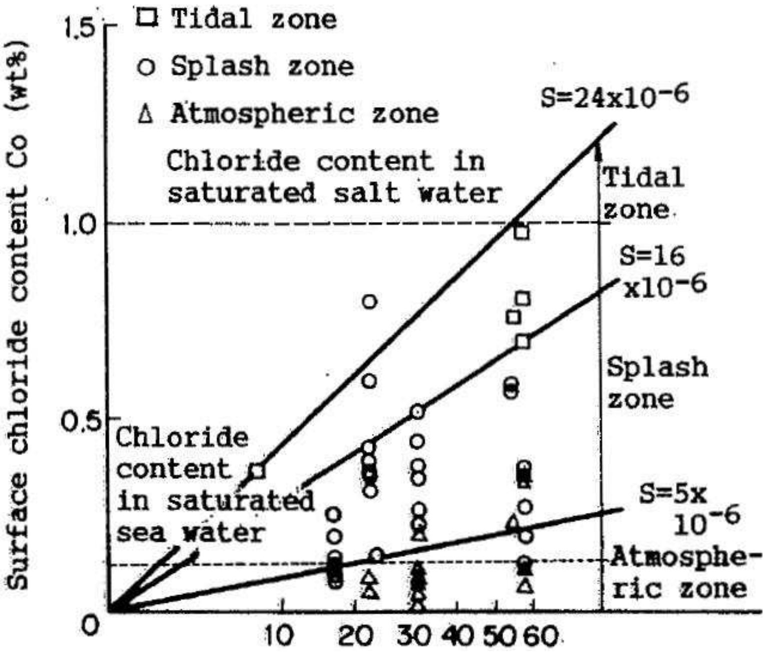

Figure 6.1: From *Uji et al.* [18], (figure 5). The figure shows the "Relationship between surface chloride content and the years in service "for the inspected structures". The time scale is square root of time. This is a natural choice, and it will be generalized in Appendix C. The observed grouping of the local environments: Tidal zone — Splash zone — Atmospheric zone, are marked with the straight lines where the different values of the parameter S are given.

When we combine *Takewaka's* and *Uji's* ideas, the problem is described by

$$\begin{cases} \dfrac{\partial C}{\partial t} = D(t)\,\dfrac{\partial^2 C}{\partial x^2}, & x > 0, \quad t > t_{ex}, \\[2ex] C(0,t) = C_s(t), & t > t_{ex}, \\[2ex] C\left(x, t_{ex}\right) = 0, & x > 0. \end{cases}$$

By the change of variable (5.2) from Chapter 5, i.e.

$$T = T(t) := \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau, \qquad 0 < t_{ex} < t,$$

we build the diffusivity $D(t)$ into the new variable T, so the problem is transformed into the basic problem of (2.1) in the new variable T instead of t. In particular, we see that the boundary condition is now written

$$C_s(t) = C_s(t(T)) = \tilde{C}_s(T).$$

Our solution method described in Chapter 4 relies on the assumption that we can transform the problem into the generic equation (4.1). Therefore, we shall assume that the boundary condition above has *the simple structure in the new variable* T,

$$C_{s,p}(t) = \tilde{C}_{s,p}(T) = T^p = \left\{ \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau \right\}^p . \tag{6.2}$$

It follows from Chapter 4 that this particular problem has a unique solution, which can be found by introducing (6.1) into (4.2), when t is replaced by $T := \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau$,

$$\begin{aligned} C(x,t) = \tilde{C}(x,T) &= \left\{ \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau \right\}^p \Psi_p \left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}} \right) \\ &= C_{s,p}(t) \cdot \Psi_p \left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}} \right) . \end{aligned} \tag{6.3}$$

Example 6.1 For the time being no data is available, so in order to get a qualitative understanding of what happens, when we combine the two models, we have for convenience put $t_{ex} = 0$ and chosen $D(t)$, such that

$$\int_0^t D(\tau)\,\mathrm{d}\tau := t \cdot \frac{1}{t^\alpha},$$

i.e. we are using a slightly different model of $D(t)$ than the one given above, and we also assume that the constant $D_{\text{aex}} = 1$. We shall fix $p = \frac{1}{2}$ and we choose for simplicity $x = 2$, such that $x/2 = 1$, hence we consider the analogue of (6.3) given by

$$C_{\alpha,\frac{1}{2}}(2,t) := \left\{ \int_0^t D(\tau)\,\mathrm{d}\tau \right\}^p \Psi_p \left(\frac{x}{2\sqrt{\int_0^t D(\tau)\,\mathrm{d}\tau}} \right) = t^{(1-\alpha)/2} \cdot \Psi_p \left(t^{-(1-\alpha)/2} \right) . \tag{6.4}$$

Keeping $p = \frac{1}{2}$ and $x = 2$ fixed, the graphs of $C_{\alpha,\frac{1}{2}}(2,t)$ are given on Figure 6.2 for $\alpha = 0$, $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{3}{4}$. It is seen that in the (abstract time) interval $]0,1[$ on the abscissa axis the curves are given from below in the order $\alpha = 0$, $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{3}{4}$. They all intersect at $t = 1$, and for $t > 1$ the order is reversed, i.e. from below, $\alpha = \frac{3}{4}$, $\frac{1}{2}$, $\frac{1}{4}$ and 0. We also see that the differences are quite dramatic for the different values of α. Clearly, if we also vary p, we obtain by combining these two ideas a very flexible model, which is coined in the HETEK model, cf. Appendix B.5.

For general x, formula (6.4) is written

$$C_{\alpha,\frac{1}{2}}(x,t) = t^{(1-alpha)/2} \cdot \Psi_p\left(\frac{x}{2} \cdot t^{-(1-\alpha)/2}\right) = \frac{x}{2} \cdot u^{(1-\alpha)/2}\Psi_p\left(u^{-(1-\alpha)2}\right),$$

where we have put $u^{(1-\alpha)/2} = \frac{2}{x} \cdot t^{(1-\alpha)/2}$, i.e. $u = (2/x)^{2/(1-\alpha)} \cdot t$. Therefore, if we change scales on the axis of Figure 6.2, writing $(2/x)^{2/(1-\alpha)}$ instead of 1 on the horizontal axis, and $x/2$ instead of 1 on the vertical axis, we also obtain Figure 6.2 in the general situation. Hence, Figure 6.2 with $x = 2$ may be considered as giving a qualitative picture of what happens, when p and x are kept fixed, while α varies. $\Diamond$

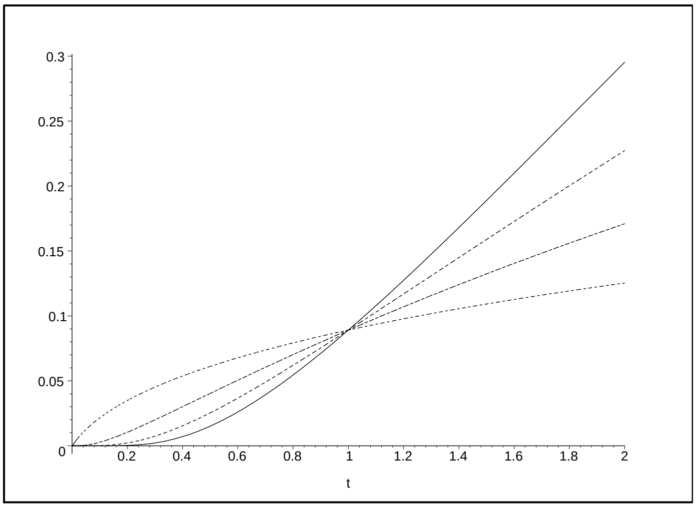

Figure 6.2: The graphs of four solutions of (6.4) for $p = \frac{1}{2}$, $x = 2$ and $\alpha = 0$, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$ illustrating a case of time-dependent diffusivity and surface chloride content.

In more general cases, we can of course again use the principle of superposition.

In other words, it is convenient to express $C_s(t)$ as a sum of power functions of the type

$$(6.5) \quad \left\{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau\right\}^p .$$

It suffices of course in the first approximation to use a constant times (6.5). It may be added here that we in this way get the motivation for the HETEK model, cf. e.g. Appendix B.5.

Chapter 7

Different diffusivities – definitions

The time-dependent diffusivity $D(t)$ in Fick's second law (5.1) is not used directly in analytical solutions. The other occurring diffusivities need to be clearly defined, and the relationships between them must be identified, to avoid misuse and misunderstanding.

7.1 The average diffusivity $D_{\mathbf{av}}(t)$

When we compare (2.6) and (5.1) with (6.2) and their solutions (2.7) and (6.3), we see that the variable in (2.7) is

$$\frac{x}{2\sqrt{D \cdot (t - t_{ex})}}, \qquad D \text{ constant},$$

while it in (6.3) is

$$\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}, \qquad D(t) \text{ time dependent}.$$

We note that if D is constant, then

$$\int_{t_{ex}}^{t} D\,\mathrm{d}\tau = D \cdot (t - t_{ex})\,,$$

so the two expressions are actually of the same type. It is therefore tempting to give these two arguments the same structure. Thus, we introduce a new function $D_{av}(t)$ by

$$(t - t_{ex})\,D_{av}(t) := \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau, \qquad t > t_{ex},$$

or

$$D_{av}(t) := \frac{1}{t - t_{ex}} \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau, \qquad t > t_{ex}, \tag{7.1}$$

which clearly can be interpreted as the *average* of the diffusivity $D(t)$ over the interval $t_{ex} < \tau < t$. We shall therefore call this new function $D_{av}(t)$ the *average diffusivity.* To distinguish $D(t)$ from $D_{av}(t)$ we call $D(t)$ the *instantaneous* or *point-wise diffusivity.*

A very good reason for using the average diffusivity $D_{av}(t)$ is that e.g. the solution (6.3) can then be written in two ways,

$$\begin{aligned} (7.2)\quad C(x,t) &= \left\{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau\right\}^{p} \Psi_p\left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right) \\ (7.3)\qquad\qquad &= \{(t-t_{ex})\,D_{av}(t)\}^{p}\,\Psi_p\left(\frac{x}{2\sqrt{(t-t_{ex})\,D_{av}(t)}}\right). \end{aligned}$$

If we here model the *instantaneous diffusivity*, i.e. we assume a simple structure of $D(t)$, it follows from (7.1) that the expression of the unique solution is far from simple, because we shall still integrate $D(t)$ in (7.2). If, however, from our measured data we choose to model the *average diffusivity* instead, then $D_{av}(t)$ is given a simple structure, and we shall just insert the chosen $D_{av}(t)$ into (7.3) without any further integration.

As mentioned previously, the *average diffusivity* $D_{av}(t)$ was introduced by (7.1), i.e.

$$D_{av}(t) := \frac{1}{t-t_{ex}}\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau, \qquad t > t_{ex}.$$

Now, assume that we have modelled $D_{av}(t)$ by some continuously differentiable function, for convenience also called $D_{av}(t)$. Then

$$\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau = (t-t_{ex})\,D_{av}(t),$$

where the right hand side is a continuously differentiable function. Hence, we *reconstruct* the corresponding instantaneous diffusivity by the formula (7.4) below, which is obtained by differentiation,

$$(7.4)\quad D(t) = D_{av}(t) + (t-t_{ex})\,D_{av}{}'(t), \qquad t > t_{ex}.$$

There is a general agreement that $D_{av}(t)$ is decreasing, so $D_{av}{}'(t) < 0$. This implies by (7.4) that we for such decreasing $D_{av}(t)$ always have that $D(t) < D_{av}(t)$, so for that reason alone one must be very careful never to confuse the two diffusivities.

Let us now consider the problem

$$
(7.5)\quad \begin{cases} \dfrac{\partial C}{\partial t} = D(t)\,\dfrac{\partial^2 C}{\partial x^2}, & x > 0, \quad t > t_{ex}, \\[2ex] C(0,t) = C_i + S \cdot \left\{ \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau \right\}^p, & t > t_{ex}, \\[2ex] C\left(x, t_{ex}\right) = C_i, & x > 0, \end{cases}
$$

which is a simple special case of (5.1), so its solution is easily derived from (6.3), i.e.

$$
(7.6)\quad C(x,t) = C_i + S \cdot \left\{ \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau \right\}^p \Psi_p \left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}} \right).
$$

We see that if the *average diffusivity* $D_{av}(t)$ is modelled, then (7.5) and (6.4) are transformed into the problem

$$
(7.7)\quad \begin{cases} \dfrac{\partial C}{\partial t} = \left\{ D_{av}(t) + \left(t - t_{ex}\right) D_{av}{}'(t) \right\} \dfrac{\partial^2 C}{\partial x^2}, & x > 0, \quad t > t_{ex}, \\[2ex] C(0,t) = C_i + S \cdot \left\{ \left(t - t_{ex}\right) D_{av}(t) \right\}^p, & t > t_{ex}, \\[2ex] C\left(x, t_{ex}\right) = C_i, & x > 0, \end{cases}
$$

the solution of which is

$$
C(x,t) = C_i + S \cdot \left\{ \left(t - t_{ex}\right) D_{av}(t) \right\}^p \Psi_p \left(\frac{x}{2\sqrt{\left(t - t_{ex}\right) D_{av}(t)}} \right).
$$

Therefore, by modelling $D_{av}(t)$, we obtain a simple solution (because $D_{av}(t)$ is assumed given) at the expense of a complicated differential equation.

The pitfall here is that one is inclined to model the *instantaneous diffusivity* $D(t)$ instead of the *average diffusivity* $D_{av}(t)$. By correct computations one should then end up with the messy formula (7.2), which in practice is not nice to apply for a given simple $D(\tau)$. It is even worse, if one confuses the two diffusivities $D(t)$ and $D_{av}(t)$. Then the "result" will be wrong as will be explained in the next sections.

Given a model for $D_{av}(t)$, then

$$
D(t) = D_{av}(t) + \left(t - t_{ex}\right) D_{av}{}'(t).
$$

The correct stated problem of Fick's second law is then (7.7), but one would in practice of course prefer the following mixed variant

$$
(7.8) \quad \begin{cases} \dfrac{\partial C}{\partial t} = D(t)\,\dfrac{\partial^2 C}{\partial x^2}, & \text{(instantaneous)}, \\[2ex] C(0,t) = C_i + S \cdot \{(t - t_{ex})\, D_{av}(t\}^p\,, & \text{(average)}, \\[2ex] C\,(x, t_{ex}) = C_i, & \end{cases}
$$

where we have emphasized that the instantaneous diffusivity given above only enters the differential equation, while the average diffusivity enters both the boundary condition and the solution.

7.2 The achieved diffusivity $D_{ach}(t)$

The term "achieved diffusivity", a name already coined by *Ervin Poulsen* [11], refers to the regression parameter D that is quantified by curve-fitting equation (2.7) (an error function "solution") to a measured chloride profile. That regression parameter D is then "achieved" from exposure data, by assuming that D is the average diffusivity in the time-interval $[t_{ex}, t_{in}]$, where t_{in} is the time when the chloride profile was measured. For different ages t_{meas} a time-dependent $D_{ach}(t)$ is obtained. Consequently, if $p = 0$, then the regression parameter that is obtained is a measure of the average diffusivity $D_{av}(t)$ in equation (7.1).

7.3 Model for the time-dependent average diffusivity

It was mentioned in the Introduction and Chapter 5 that *Takewaka et al.* [16] suggested handling the change in time for the (average) diffusivity as a power function as given in (7.9),

$$
(7.9) \quad D_{av}(t) = D_{\text{av,ex}} \left\{ \frac{t_{ex}}{t} \right\}^{\alpha}.
$$

Here, $D_{\text{av,ex}}$ and α are constants, where $D_{\text{av,ex}}$ is the reference diffusivity ($D_{\text{av,ex}} > 0$) at the beginning of the exposure t_{ex}, and $0 \leq \alpha < 1$ (note that $\alpha < 1$) is a dimension-free parameter. *Takewaka et al.* based their suggestion on an analysis of chloride profiles from natural exposure, i.e. the derived the diffusivities in the traditional way by using *Collepardi's Model* [3].

A number of other authors have published the same tendency, namely that the achieved or average diffusivity decreases with the time of exposure. When the diffusivity is plotted versus the logarithm of time, the data often fit quite well to a straight line, so a function like (7.9) will describe the data well for t away from t_{ex}.

The empirical formula (7.9) is the same in the models of *LIGHTCON* [8], *Mejlbro* [9], *Poulsen* [12], *DuraCrete* [5], etc. — The basis parameter D_0 is an average diffusivity (i.e. measured over a time interval) and $\alpha \in [0,1[$ is a dimension-free parameter describing the decrease in time of the averaged diffusivity $D_{av}(t)$.

We shall in the next section discuss the case of (7.9) and also show that we by a small change of the definition (7.9) may obtain even more convenient formulæ.

We have also noted previously that experience shows that we in general can assume that $D_{av}(t)$ is decreasing in t, which again implies that

$$D(t) = D_{av}(t) + (t - t_{ex})\, {D_{av}}'(t) < D_{av}(t) \qquad \text{for } t > t_{ex}.$$

We can therefore expect that a confusion of $D(t)$ and $D_{av}(t)$ may have quite a dramatic effect on the solution. This is actually true, and it will be demonstrated in the next sections.

7.4 Alternative model 1 for $D_{av}(t)$

We end this chapter by introducing two alternative models of $D_{av}(t)$. If we instead of (7.9) choose the model

$$\text{(7.10)} \quad D_{av}(t) = \tilde{D}_{\text{av,ex}} \left\{ \frac{t_{ex}}{t - t_{ex}} \right\}^{\alpha}, \qquad t > t_{ex}, \qquad 0 \le \alpha < 1,$$

then of course $D_{av}(t) \to +\infty$ for $t \to t_{ex}+$. The reader may wonder why we introduce $+\infty$ for $t = t_{ex}$. This is of no importance, because it is shown in Appendix A that *the flow of chloride ions is non-Fickean for $t > t_{\text{ex}}$ close to t_{ex}*, so none of the models in this report, including the error function model, is reliable for t close to t_{ex}, i.e. for

$$\text{(7.11)} \quad t_{ex} < t < t_{ex} + \text{ const.} \cdot \frac{4D}{x^2},$$

where the constant is still to be found empirically. We may therefore choose $D_{av}(t)$ in this interval, such that the result becomes reliable for $t > t_{ex} + \text{ const.} \cdot 4D/x^2$, and such that it at the same time is easy to handle. Therefore, we may allow (7.10) as a model of $D_{av}(t)$, because none of the models makes sense for $t = t_{ex}$ for other reasons. A more detailed description is given in Appendix D.

7.5 Alternative model 2 for $D_{av}(t)$

The *DuraCrete* model [5] for chloride ingress uses a time-dependent average diffusion coefficient $D_{av}(t_{ex}; t)$, which is slightly different from (7.9),

$$D_{av}(t_{ex}; t) = D_0 \left\{ \frac{t_0}{t} \right\}^{\alpha},$$

where t_0 is the age, when D_0 is measured. Usually D_0 is quantified by measuring a D_{RCM} in 24 hours with a rapid chloride migration test at an age of $t_0 = 28$ days. Then D_0 is found by correcting the D_{RCM} with an "environmental factor" k_e, i.e.

$$D_0 = k_e \cdot D_{\mathrm{RCM}}.$$

Since the age t_0 of testing is different from the age t_{ex} at exposure, this is another way of describing $D_{av}(t_{ex}; t)$. The parameter t_{ex} does not even appear in the equation, in spite of the exponent α being evaluated from exposure tests with a certain age at exposure, usually different from 28 days.

The relationship between this alternative way of describing the average diffusion coefficient is of course

$$D_0 = D_{\mathrm{av,ex}} \left\{ \frac{t_{ex}}{t_0} \right\}^{\alpha}.$$

This gives a simple relationship between the $D_{\mathrm{av,ex}}$ derived from exposure tests and the D_0 determined from a rapid chloride migration test.

Chapter 8

Instantaneous diffusivity $D(t)$ versus average diffusivity $D_{av}(t)$

8.1 Introduction

We shall once more emphasize the differences between $D(t)$ and $D_{av}(t)$. It is obvious that care must be taken when we convert from one diffusivity to another one.

In order to clarify how the practical application of the models above should be handled to be consistent with mathematics, we shall try to clarify how each parameter should be understood – and thereby avoid both wrong interpretations of results (e.g. chloride profiles from real structures) and wrong use of the derived parameters, e.g. the use of the age parameter α in finite element models.

When we consider the relation between the point-wise, or instantaneous, diffusivity $D(t)$, and the average diffusivity $D_{av}(t)$ we get the following equations which define the mathematical relationships between the average diffusivity and the point-wise diffusivity:

$$\left\{\begin{array}{ll} D_{av}(t) := \dfrac{1}{t - t_{ex}} \int_{t_{ex}}^{t} D(\tau)\, \mathrm{d}\tau, & \\ & t > t_{ex}, \\ D(t) = D_{av}(t) + (t - t_{ex})\, D_{av}{}'(t). & \end{array}\right.$$

We recall that problem (7.5), i.e.

$$\left\{\begin{array}{lll} \dfrac{\partial C}{\partial t} = D(t)\, \dfrac{\partial^2 C}{\partial x^2}, & x > 0, & t > t_{ex}, \\ C(0,t) = C_i + C_s(t), & t > t_{ex}, & \\ C\left(x, t_{ex}\right) = C_i, & x > 0, & \end{array}\right.$$

is then *precisely the same* as the strange looking equation

$$\begin{cases} \dfrac{\partial C}{\partial t} = \left\{D_{av}(t) + (t - t_{ex})\, D_{av}{}'(t)\right\} \dfrac{\partial^2 C}{\partial x^2}, & x > 0, \quad t > t_{ex}, \\[2ex] C(0,t) = C_i + C_s(t), & t > t_{ex}, \\[2ex] C\,(x, t_{ex}) = C_i, & x > 0, \end{cases}$$

with the same solution, and it is *different from* the erroneous equation

$$\begin{cases} \dfrac{\partial C}{\partial t} = D_{av}(t)\, \dfrac{\partial^2 C}{\partial x^2}, & x > 0, \quad t > t_{ex}, \\[2ex] C(0,t) = C_i + C_s(t), & t > t_{ex}, \\[2ex] C\,(x, t_{ex}) = C_i, & x > 0, \end{cases}$$

with *different* (and in our context wrong) solution, where we have replaced the instantaneous $D(t)$ erroneously by the average $D_{av}(t)$. That it indeed is wrong, is easily checked by simply inserting the supposed solution into the differential equation.

In order to study the isolated effect when we have a *point-wise* diffusivity being time dependent and also a boundary condition being time dependent, we shall again start by considering one of our building stones. Hence we consider the very special problem (with indexed solution):

$$(8.1) \quad \begin{cases} \dfrac{\partial C_p}{\partial t} = \dfrac{\partial}{\partial x}\left\{D(t)\, \dfrac{\partial C_p}{\partial x}\right\}, & x > 0, \quad t > t_{ex}, \qquad \text{(instantaneous)}, \\[2ex] C_p(0,t) = \left\{(t - t_{ex})\, D_{av}(t)\right\}^p, & t > t_{ex}, \qquad \text{(achieved)}, \\[2ex] C_p\,(x, t_{ex}) = 0, & x > 0, \end{cases}$$

so the concentration is normalized.

We notice that even though we start with at *point-wise* diffusivity in the differential equation, we have to consider the *average* diffusivity, if we want to model the surface boundary condition in a way that will lead us to a solution of the type (6.3). Furthermore, in order to solve (8.1) we need to chance the variable as in (5.2), and we eventually get the solution (7.3) with $C_i = 0$ and $S = 1$,

$$C_p(x,t) = \tilde{C}_p(x,T) = \left\{(t - t_{ex})\, D_{av}(t)\right\}^p \Psi_p \left\{\frac{x}{2\sqrt{(t - t_{ex})\, D_{av}(t)}}\right\}, \qquad \text{(achieved)},$$

where the *average* diffusivity applies.

8.2 Modelling $D_{av}(t)$

Using (7.9), i.e.

$$D_{av}(t) = D_{\text{av,ex}} \left\{ \frac{t_{ex}}{t} \right\}^{\alpha},$$

and applying the previously found relationship

$$D(t) = D_{av}(t) + (t - t_{ex})\, D_{av}{}'(t) < D_{av}(t) \qquad \text{for } t > t_{ex},$$

we see that the relationship between the average and the point-wise diffusivity in this special case is given by

$$(8.2)\;\; D(t) = D_{\text{av,ex}} \left((1-\alpha) \left\{ \frac{t_{ex}}{t} \right\}^{\alpha} + \alpha \left\{ \frac{t_{ex}}{t} \right\}^{\alpha+1} \right).$$

It follows immediately from (7.9) and (8.2) that

$$D(t) = \left\{ 1 - \alpha + \alpha \cdot \frac{t_{ex}}{t} \right\} D_{av}(t) \approx (1-\alpha) D_{av}(t) \qquad \text{for large } t.$$

The relationship is illustrated in Figure 8.1.

These results show that $D(t)$ and $D_{av}(t)$ are very different (unless α is close to 0), so they must not be interchanged.

Clearly, since $D(t)/D_{av}(t) \to 1 - \alpha$ for $t \to +\infty$, we shall get very different results if we by accident put $D_{av}(t)$ into the diffusion differential equation instead of $D(t)$.

8.3 Modelling $D(t)$

For completeness we mention that if we instead of the average diffusivity introduced the *point-wise* diffusivity (assuming that it was possible to measure it within given limits) in the form

$$(8.3)\;\; D(t) = D_0 \left\{ \frac{t_{ex}}{t} \right\}^{n},$$

where we have replaced α in (7.9) by n in order to distinguish between the two models, when they are compared, then we derive that the *average* diffusivity is given by

$$(8.4)\;\; D_{av}(t) = \frac{t_{ex}}{t - t_{ex}} \cdot \frac{D_0}{1-n} \left(\left\{ \frac{t}{t_{ex}} \right\}^{1-n} - 1 \right),$$

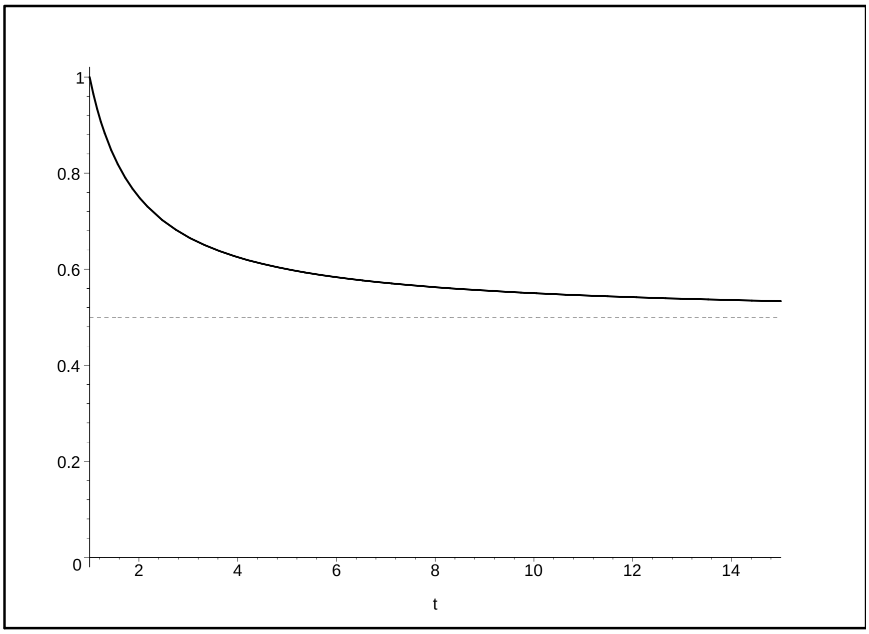

Figure 8.1: Graph for $\alpha = \frac{1}{2}$ of the quotient

$$\frac{D(t)}{D_{av}(t)} = \frac{1}{2}\left\{1 + \frac{1}{t}\right\} \approx \frac{1}{2} \qquad \text{for large } t,$$

(full line) and its asymptote (dotted line).

which does not fit well into the structure of the solution, or into the procedure of either (2.4) or (4.2).

Here it must be emphasized that the analysis above shows that the problems become very different, according to whether we use (7.9) or (8.3) as our assumption. However, both descriptions make formally sense, and there is no mathematical error in either of the two derived models (8.2) and (8.3). There are probably larger measurement problems in establishing (8.3) than in (7.9), and there are definitely much larger mathematical problems in the analytical solution process, if we adopt the nice structure (8.3) of the instantaneous diffusivity, instead of choosing to model the average diffusivity by (7.9). But it must be admitted that it is very strange that the problem (8.1) should be described by both the instantaneous and the average diffusivities at the same time, if one also wants an easy solution procedure.

Numerical solutions are also easier to find, if we choose the model (7.9).

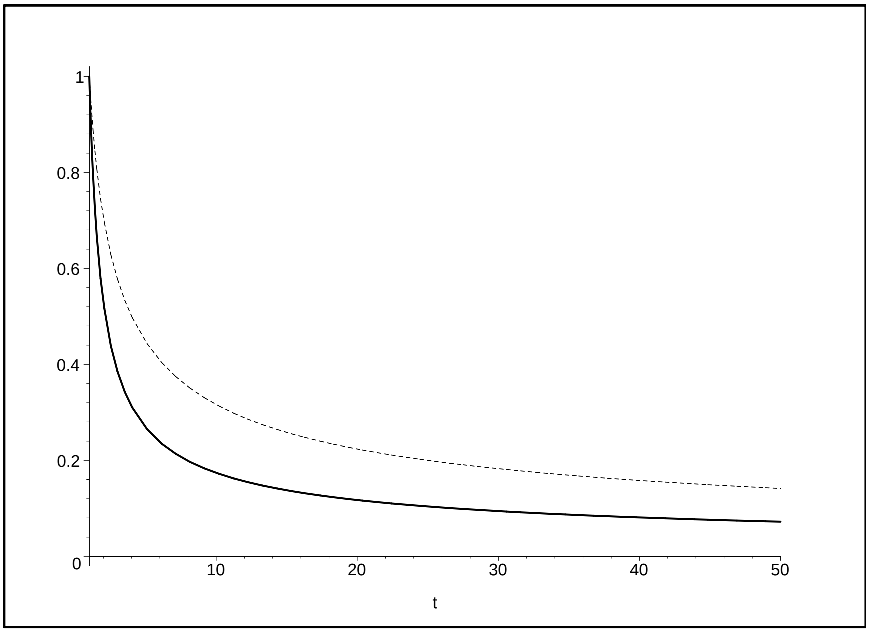

Figure 8.2: The graphs for $p = \frac{1}{2}$ of $D_{av}(t) = 1/\sqrt{t}$, (dotted line) and the corresponding

$$D(t) = \frac{1}{2}\left\{\frac{1}{\sqrt{t}} + \frac{1}{t\sqrt{t}}\right\}, \qquad \text{(full line).}$$

Chapter 9

Age exponents in time-dependent diffusivities

9.1 Age exponents n and α for the instantaneous and the average diffusivity

Some papers use the model (7.9), while others use (8.3) instead, cf. Section 8.3. Therefore, we felt that it is necessary also to derive the relationship between the exponents α of (7.9) and n of (8.3) in order to get some form of "translation" from one model to the other. The relationship is given by

$$(9.1)\quad n = f(\alpha, t) = \alpha + \frac{\ln\left\{(1-\alpha) + \alpha\,\dfrac{t_{ex}}{t}\right\}}{\ln\left(\dfrac{t_{ex}}{t}\right)} = \alpha + \frac{\ln\{(1-\alpha) + \alpha \cdot u\}}{\ln u},$$

where $0 < u := \dfrac{t_{ex}}{t} < 1$. Thus it is obvious that

1) The correspondence between α and n is not a simple function.

2) The correspondence is time dependent.

3) The parameter α is always smaller than n.

4) If the time dependency of the point-wise diffusivity is calculated by the use of the parameter α belonging to the averaging diffusivity, then the time dependent point-wise diffusivity will at every time t become bigger than it should be.

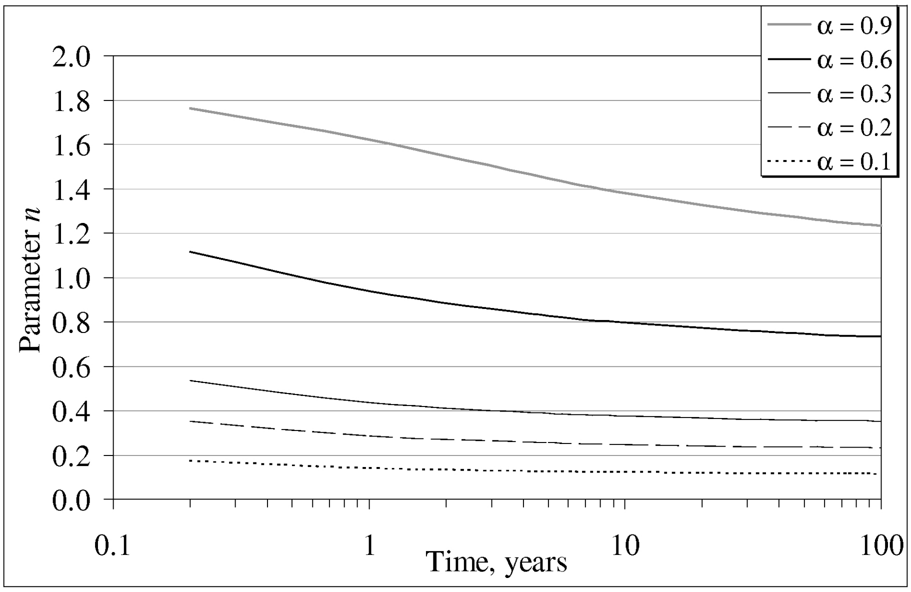

Figure 9.1: The relationship between the two "age exponents" from equation (9.1).

9.2 Age exponents for the average and the achieved diffusivity

If we assume that the average diffusivity can be described by equation (7.9), i.e.

$$D_{av}\left(t_{ex};t\right)=D_{\text{av,ex}}\left\{\frac{t_{ex}}{t}\right\}^{\alpha},$$

and that the surface chloride concentration $C_s(t)$ is time-dependent as described by equation (6.2), then the chloride profiles $C(x,t)$ can be predicted using the Ψ-functions as in equation (6.3). If this is assumed to describe correctly the true chloride ingress, then it is important to know what possible errors are made if the erfc model is used for curve-fitting measured chloride profiles, without considering the time-dependency of the surface chloride level.

Since the time-dependency of the C_s value means that the chloride profiles are somewhat more "curved" than the erfc model is able to describe, cf. Figure 9.3, there must be a clear difference between a chloride profile and a corresponding erfc curve used for curve-fitting. The first question that arises is whether the age exponents for the two diffusivities are different and, if so, what the relationship looks like. This is here analyzed in two different ways, first a numerical analysis and then an analytical one.

9.3 Numerical analysis of age exponents for the average and the achieved diffusivity

The numerical analysis is performed in the following way:

1) The average diffusivity $D_{av}(t_{ex};t)$ is assumed to follow equation (7.9), with an age exponent called α_{ψ}, cf. Figure 9.2.

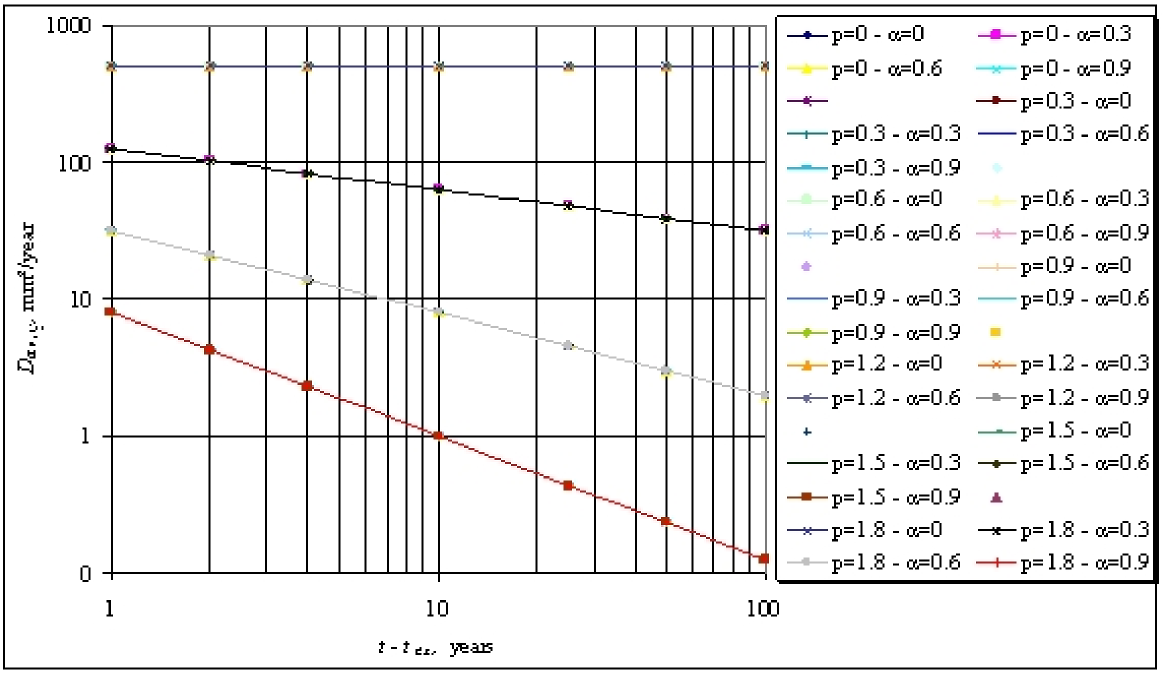

Figure 9.2: The input data for the numerical analysis; the time-dependent average diffusivity according to Equation (7.9) with a series of age exponent values α_{ψ}. The different values of p have no influence on the $D_{\mathrm{av},\psi}$, only on the surface chloride content $C_s(t)$.

2) The surface chloride content $C_s(t)$ is assumed to follow equation (6.2) with the parameter p.

3) Chloride profiles $C(x,t)$ are predicted analytically from equation (6.3) for exposure times between 1 and 100 years for a series of values of the age exponent α_{ψ} and the parameter p. A value of $D_{\mathrm{av,ex},\psi} = 500$ mm^2/year is chosen.

4) The chloride profiles are curve-fitted by a regression analysis to the erfc model,

equation (5.5) with the two regression parameters C_{sa} and $D_{\text{av,erfc}}\,(t_{ex};t)$ for a number of exposure times t. An example is shown in Figure 9.3.

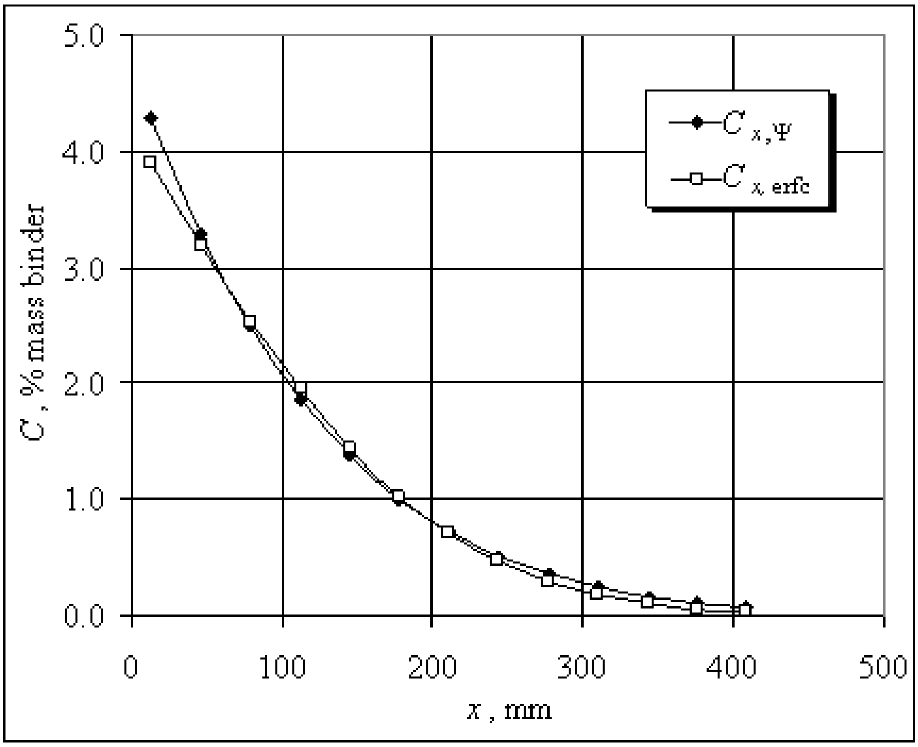

Figure 9.3: An example of the curve-fitting procedure for $\alpha = 0$ and $p = 1.2$.

5) From this curve-fitting, a series of achieved diffusivities $D_{\text{av,erfc}}\,(t_{ex};t)$ are obtained for the various exposure times for each combination of age exponent α_{ψ} and p values, cf. Figure 9.4.

6) Each series of these achieved diffusivities $D\ _{\text{av,erfc}}\,(t_{ex};t)$ are then fitted to the time-dependency similar to equation (7.9), but with the age exponent called α_{erfc} and the diffusivity parameter called $D_{\text{av,ex, erfc}}$.

7) The two age exponents α_{ψ} and α_{erfc} are finally compared.

The input data for this numerical analysis is shown in Figure 9.2.

For each series of α_{ψ} and p-values these achieved diffusivities $D_{\text{av,erfc}}\,(t_{ex};t)$ are fitted to the time-dependency similar to equation (7.9), but with the age exponent called α_{erfc} and the diffusivity parameter called $D_{\text{av,ex,erfc}}$. The two age exponents α_{erfx} and α_{ψ} are compared in Figure 9.6.

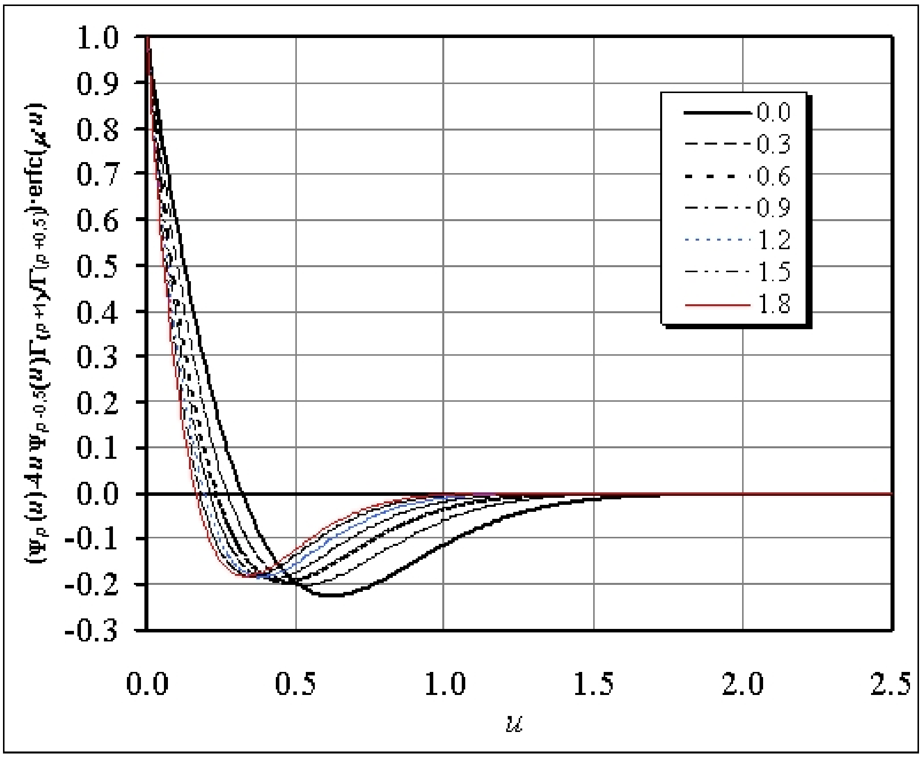

Figure 9.4: A graphical representation of the minimizing problem of equations (9.2), (9.3) and (9.4). The solution is found when the integral of the curve is zero.

From the numerical analysis it seems as if the age exponents are equal! The differences in Figure 9.6 for $\alpha_\psi = 0$ are due to uncertainties in the curve-fitting when the diffusivity is assumed to be constant. These results are further validated by an analytical analysis, cf. Section 9.4 below and Appendix C.

9.4 Analytical analysis of age exponents for the average and the achieved diffusivity

The numerical analysis in Section 9.3 is complemented with an analytical analysis, cf. Appendix C. The principle used is to minimize the differences between chloride profiles obtained from the two models, as in a curve-fitting procedure, i.e. minimize the differences between the two functions $C_\psi(x,t)$ and $C_{\mathrm{erfc}}(x,t)$ of (9.2) and (9.3) below. The initial chloride content C_i is here set to zero and the symbols are somewhat

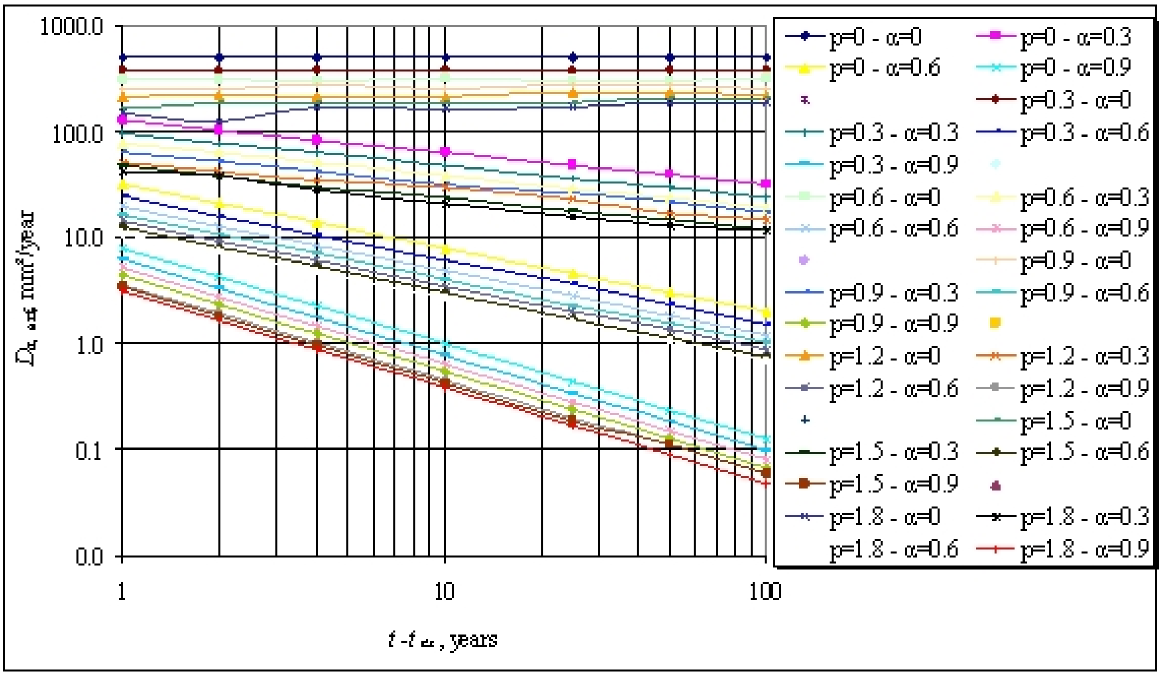

Figure 9.5: The output data for the numerical analysis; the time-dependent achieved diffusivity for the series of age exponent values α_ψ and p values.

different from those in Appendix C,

$$(9.2)\quad \begin{cases} C_\psi(x,t) = C_s(t,p)\cdot\Psi_p\left(\dfrac{x}{2\sqrt{D_{\text{av},\psi}\cdot(t-t_{ex})}}\right), \\[2ex] D_{\text{av},\psi} = D_{\text{av,ex},\psi}\cdot\left\{\dfrac{t_{ex}}{t}\right\}^{\alpha_\psi}, \end{cases}$$

where $D_{\text{av},\psi}$ is the average diffusivity in Fick's second law, and

$$(9.3)\quad \begin{cases} C_{\text{erfc}}(x,t) = C_{\text{sa}}\cdot\text{erfc}\left(\dfrac{x}{2\sqrt{D_{\text{av,erfc}}\cdot(t-t_{ex})}}\right), \\[2ex] D_{\text{av,erfc}} = D_{\text{av,ex,erfc}}\cdot\left\{\dfrac{t_{ex}}{t}\right\}^{\alpha_{\text{erfc}}}, \end{cases}$$

where $D_{\text{av,erfc}}$ is the time-dependent "achieved diffusivity" in the error function solution of Fick's second law with a constant surface chloride content C_{sa}.

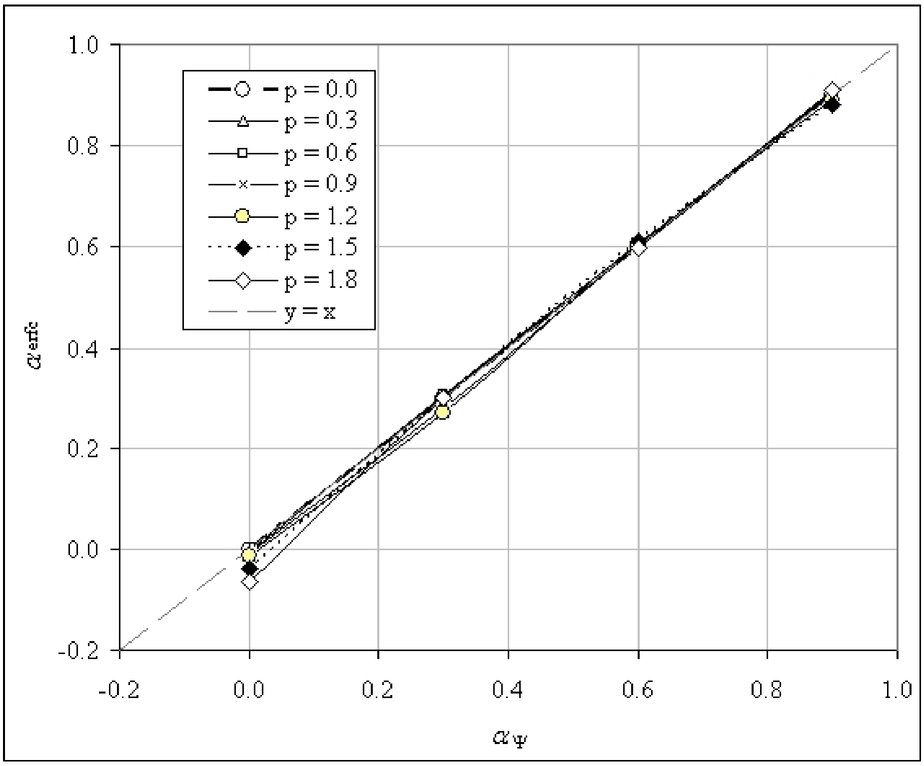

Figure 9.6: A comparison between the age exponents in the average (α_ψ) and the achieved diffusivity (α_{erfc}).

Equations (9.2) and (9.3) constitute a “special case” where the diffusivities are expressed by special functions. In Appendix C this problem is solved for a general case, where the time-dependent average diffusivity could be expressed by general equations. Finally, the solution of the special case of the equations (9.2) and (9.3) is found.

As seen in Appendix C, the minimizing problem can be expressed through

$$(9.4)\quad \int_0^{+\infty} \left\{ \Psi_p(u) - 4u \cdot \frac{\Gamma(p+1)}{\Gamma(p+0.5)} \cdot \Psi_{p-0.5}(u) \right\} \operatorname{erfc}(\mu_p \cdot u)\, \mathrm{d}u = 0,$$

also illustrated in Figure 9.4.

The solution is found to be independent of t, see Equation (9.5),

$$(9.5)\quad D_{\text{av,erfc}}(t) = \frac{1}{\mu_p^2} D_{\text{av},\psi}(t),$$

where μ_p only depends on p and not on t! The factor μ_p is quantified in Chapter 10 as well as by the tables of Appendix C.8.

In the special case, as expressed by equations (9.2) and (9.3), it is proved mathematically in Appendix C that the relationship between the two age exponents becomes remarkably simple:

(9.6) $\alpha_{\text{erfc}} = \alpha_{\psi}$.

The relationship between the absolute values of the two diffusivities is shown in Chapter 10.

Chapter 10

Average diffusivity $D_{av,\psi}(t)$ versus achieved diffusivity $D_{av,\mathrm{erfc}}(t)$

The results of Chapter 9 showed that the achieved diffusivity $D_{\mathrm{av,erfc}}(t)$ is different from the average diffusivity $D_{\mathrm{av},\psi}(t)$, even though the two age exponents are identical! This is further discussed in the present chapter.

10.1 Numerical analysis

According to the numerical analysis of Section 9.3 the relationship between the two diffusivities can be evaluated. The output data in Figure 9.2 and the input data in Figure 9.5 are compared in Figure 10.1.

There is a significant effect of the parameter p on the relationship, and none on the age exponent α, i.e. a significant effect on the time-dependency of the surface chloride content $C_s(t)$. For large p values the achieved diffusivity may be as small as some 30 % of the average diffusivity! Values of p between 0.3 and 1.1 in the submerged have been observed in the submerged zone from 10-years field exposure tests.

As mentioned in Section 9.3 there is a scatter for $\alpha = 0$, due to large uncertainties in the curve-fitting procedure for constant D values.

10.2 Analytical analysis

From the analytical analysis described in Section 9.4 with the results (9.5) and (9.6) it is quite clear that the relationship between the achieved and the average diffusivity is reduced to a relationship between the parameters

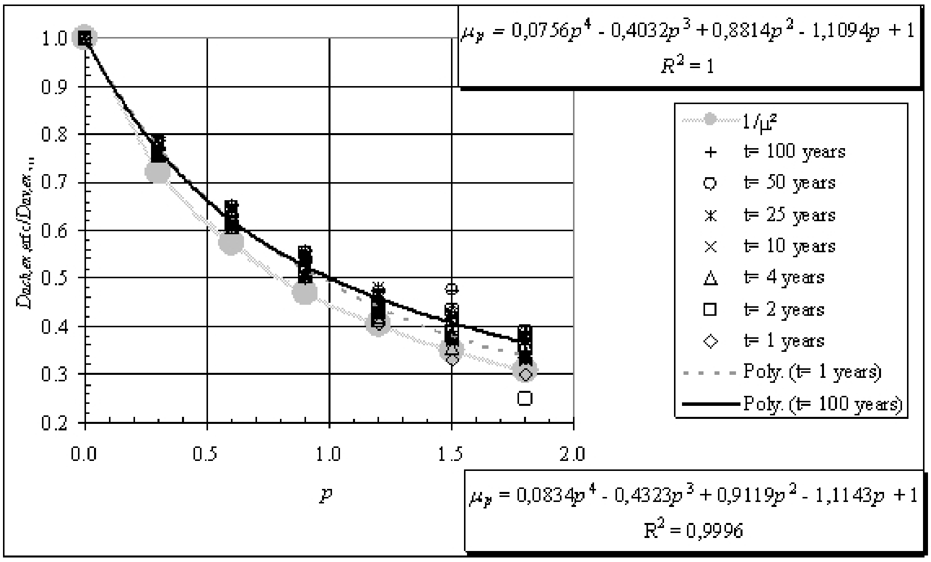

Figure 10.1: The relationship between the parameters $D_{\text{ach,ex}}$ and $D_{\text{av,ex}}$ in the achieved and average diffusivity, respectively, from the numerical analysis.

$$(10.1)\quad D_{\text{av,ex,erfc}} = \frac{1}{\mu_p^2}\, D_{\text{av,ex},\psi}.$$

The values of μ_p are found by using the minimizing procedure available in Excel to solve Equation (9.4), shown graphically in Figure 9.4. The results are shown in Figure 10.2, as values of μ_p and of $1/\mu_p^2$.

The results from the analytical analysis correspond very well with the results of the numerical analysis, cf. Figures 9.4 and 10.1.

Consequently, the analysis shows that there is a significant effect of the time-dependency of the surface chloride content on the results obtained from a curve-fitting procedure where this is neglected. These findings lead to significant consequences for many practical applications. This is quantified in Chapter 11.

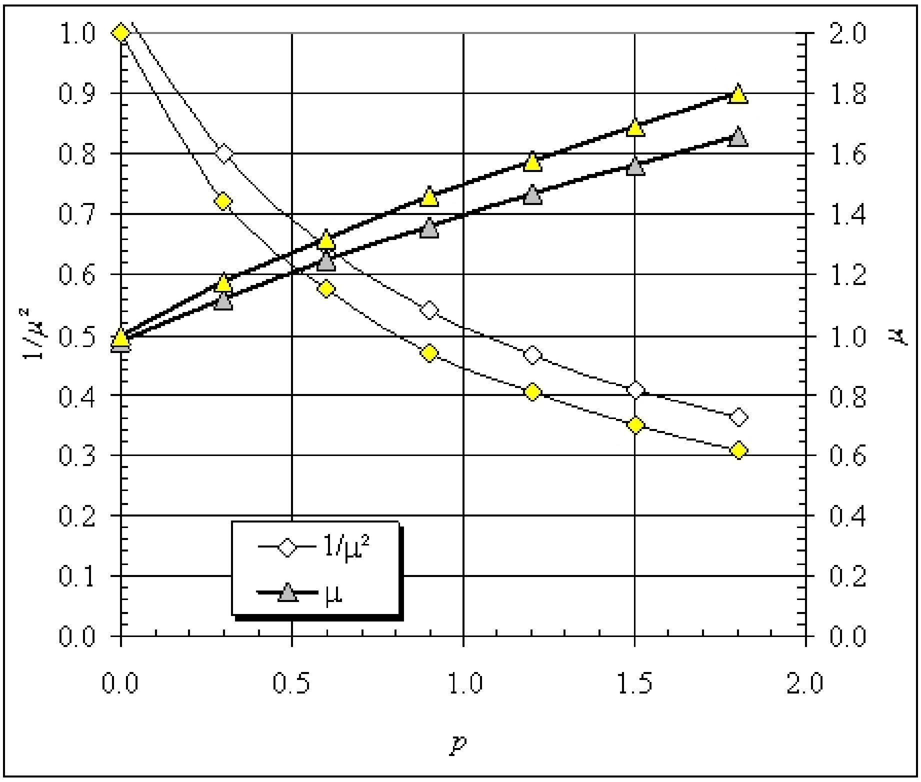

Figure 10.2: The relationship $1/\mu_p^2$ between the parameters $D_{\text{ach,ex}}$ and $D_{\text{av, ex}}$ in the achieved and average diffusivity, respectively, from the numerical analysis, cf. Equation (10.1). The two sets of curves correspond to whether we are using (C.17) or (C.19) in the iteration process. The two formulæ are equivalent, but (C.19) has better numerical properties than (C.17).

Chapter 11

Numerical examples of consequences

A number of chloride ingress models do not consider the time-dependency of the surface chloride content $C_s(t)$. High quality exposure data, where this effect is not hidden by a large scatter, demonstrate the effect very well. An early example is shown in Figure 6.1.

In spite of this, the parameters in those models are quantified by assuming the surface chloride content C_s to be constant in time. From the analysis of the sections 10.1 and 10.2 it is now quite clear that this will lead to significant errors in the parameter values, especially those parameters that are related to the parameter $D_{\text{aex,ex}}$.

By using short term exposure data, and neglecting the time-dependency of the value of C_s, a value of $D_{\text{av,ex}}$ could be obtained which is 1.5-2 times too low. This causes significant errors when applying such a model for extrapolations. Service lives being 1.5-2 times too long could be obtained!

Predictions with the erfc-model, using regression parameters from curve-fitting exposure data up to a certain exposure time, may be very erroneous.

11.1 Assumptions

The assumptions used are the following. Chloride ingress is correctly described by the Ψ model with a time-dependent surface chloride content given by the parameter p. After an exposure time of $t_{in} - t_{ex}$ a chloride profile is "measured", without any errors at all. That chloride profile is curve-fitted to the erfc model, which gives the two regression parameters $D_{\text{ach}}\,(t_{in})$ and $C_{\text{sa}}\,(t_{in})$. We have already a series of data at shorter exposure times, which means that we can evaluate the time-dependency

$$D_{\mathrm{ach}}(t) = D_{\mathrm{ach,erfc}} \cdot \left\{ \frac{t_{ex}}{t} \right\}^{\alpha} .$$

11.2 Predictions

For predicting the chloride ingress after the last exposure time we first use the surface chloride content C_{sa} at the last "measurement" and $D_{\mathrm{aex,erfc}}$ and α in the time-dependent diffusivity equation above. The prediction is made until an age of the "end of the service life" t_{TL}, with $D_{\mathrm{ach}}\,(t_{\mathrm{LT}})$ and C_{sa}. The chloride ingress is predicted with the erfc model as the chloride content at a depth of x_{cr} (e.g. the depth of the reinforcement). This is called the *ordinary estimate.*

The chloride concentration at the depth x_{cr} at time t_{LT} is then predicted by means of the Ψ model, with $D_{av}\,(t_{\mathrm{LT}})$ and $C_s(t)$. This is called the Ψ_p *estimate.*

The relation between the *ordinary estimate* and the Ψ_p *estimate* is then shown as functions of $(t_{in} - t_{ex})$ for $\alpha = 0.0$, 0.3 and 0.6, and for $p = 0.3$, 0.6, 0.9, 1.2 and 1.5. For $p = 0$ the *erfc estimate* is of course equal to the Ψ_p *estimate.*

11.3 Results

One example of the comparison is shown in Figure 11.1, for a cover depth x_{cr} of 45 mm and a service life t_{LT} of 100 years.

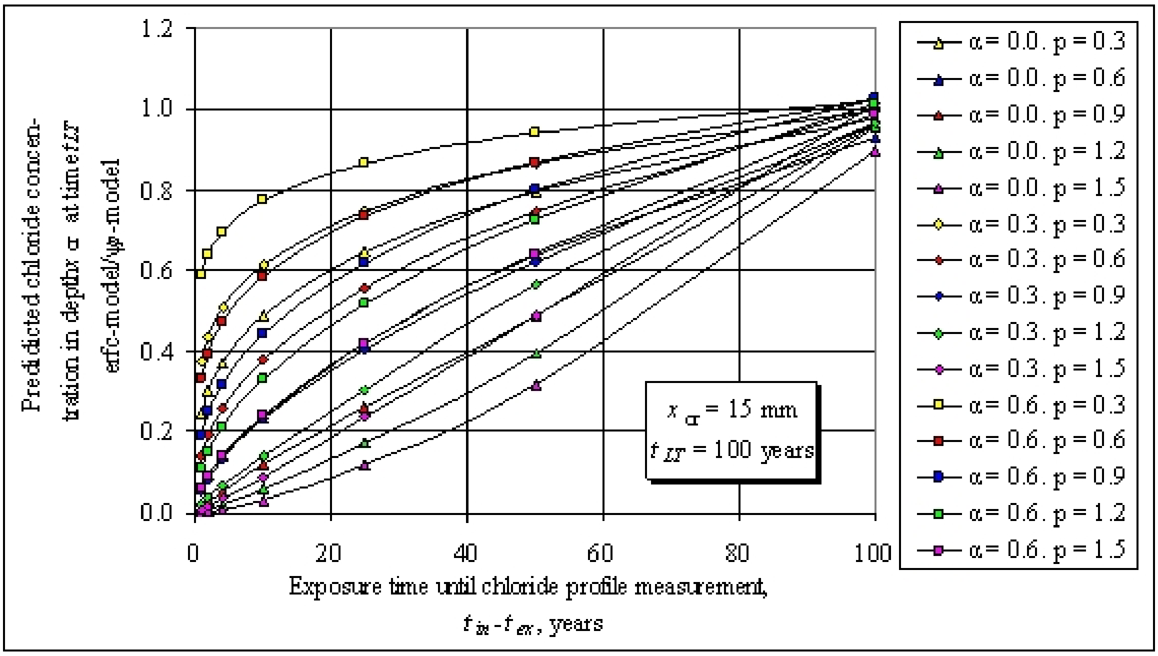

Figure 11.1: Comparison of the erfc estimate and the Ψ_p estimate for a cover depth of 45 mm and a service life of 100 years, from data up to different inspections times t_{in}.

Chapter 12

The $\lambda\mu$-modification of the erfc solution to approximate the Ψ solution

Finally, we shall consider the possibility of approximating a Ψ-solution by a modified erfc-solution, since erfc-functions are more widely available in e.g. spreadsheet programs etc.. In spite of what has been said previously, this is actually possible. Surprisingly, this possibility was discovered by making the analysis in this report, and as the climax of this report this result is briefly sketched out below. The mathematical derivation of this modification and approximation is given in Appendix C.

The Ψ-solution is shown before, cf. equation (6.3) and equation (9.2). Its structure may be written in the following way

(12.1) $C_{\Psi_p}(x,t) = C_s(t,p) \cdot \Psi_p\left(z\right),$

where

$$C_s(t,p) = S \cdot (D_{av,\Psi} \cdot (t - t_{ex}))^p$$

and

$$z = \frac{x}{2\sqrt{D_{\mathrm{av},\Psi_p} \cdot (t - t_{ex})}}.$$

As shown by the rather complicated mathematical elucidation in Appendix C, it turns out that an approximation of equation (12.1) to an erfc-solution only requires two universal modification factors to be included. We denote these factors λ_p and μ_p as they only depend on the parameter p, i.e. they are independent of the time and the magnitude of the diffusivity. They are tabulated in Appendix C, and good polynomial approximations for these factors are given below.

The advantage of this approximation is that the approximation allows for a surface boundary concentration increasing with time according to the exact same models for C_s as used in the Ψ-model. Thus, the possibility for taking an increasing surface boundary concentration into account can be made using the erfc-function instead of the Ψ_p-functions (the generalised erfc-functions).

The parameters p and S are decisive for the way the surface boundary condition increases with time.

From the curve-fitting example in Figure 9.3 it is obvious that in order to obtain a better approximation the erfc-profile must be somewhat more curved. This is achieved by introducing the factor μ_p^2 in the argument for the erfc-function. The modification factor μ_p for the argument in the erfc-function varies between approximately 0.3 and 1, depending on the p-value, cf. Figure 10.2.

The additional modification factor λ_p is multiplied on the *value* of the erfc-function.

Values of λ_p are given by the equations (C.22) or (C.23) in Appendix C, and shown to depend only on p. The values are shown in Figure 12.1 to vary between 1.00 to some 0.92.

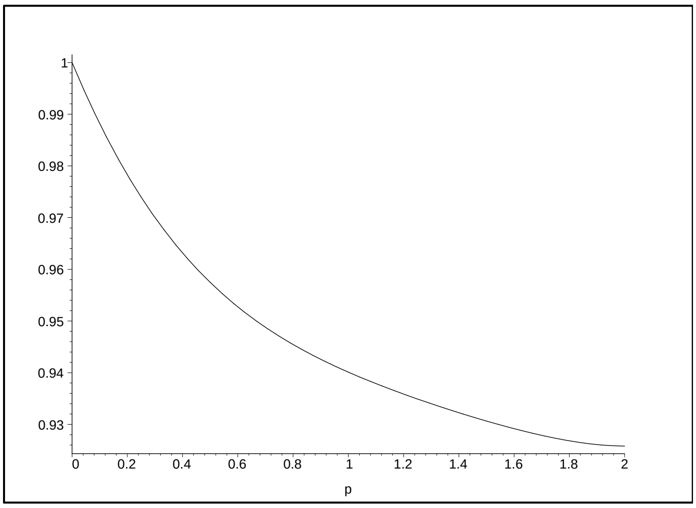

Figure 12.1: The correction factor λ_p of $C_{\text{sa}}(t)$ in the erfc-approximation, from equation (C.22). The approximation formula here is

$$\lambda_p = 1 - 0.1287p + 0.1104p^2 - 0.0509p^3 - 0.0093p^4,$$

and $R^2 = 0.9998$. Note that the vertical scale goes from 0.93 to 1.

With these two factors included, the erfc-approximation is

$$(12.2)\quad C_{\text{approx}}(x,t) = C_{\text{sa}}(t) \cdot \operatorname{erfc}\left(\mu_p \cdot Z\right) = \lambda_p \cdot C_s(t,p) \cdot \operatorname{erfc}\left(\mu_p \cdot Z_p\right).$$

The small errors in this approximation are quantified in Appendix C.
The disadvantage of using this approximation is that values close to the surface and near the deep (horizontal) part of the chloride profile cannot be calculated with the required accuracy. The unmodified erfc-argument, z must lie in the interval

$$0.0625 < z = \frac{x}{2\sqrt{D_{\text{av},\Psi_p} \cdot (t - t_{ex})}} < 2.$$

In practice this means that the chloride profile must be represented by points in that interval. Points outside the same interval are more or less wasted.

Calculations equivalent to those made in Chapters 9 and 10 were made using the modified erfc-solution.

Chapter 13

Conclusions

The solutions of Fick's second law, for chloride ingress into concrete, have to be treated with care. There are various solutions, depending on the assumptions that are made. Since the diffusivity and the surface chloride content both are time-dependent, the traditional solutions are not valid, neither for curve-fitting exposure data nor for predictions.

The main conclusions of the work presented in this report are:

1) Since it has become the state-of-the-art to consider the diffusivity to be time-dependent, we must always carefully specify, if we are considering the "instantaneous diffusivity" $D(t)$, or the "average diffusivity" $D_{av}(t)$. As demonstrated in this report it is disastrous for the result, if these two different, though equivalent diffusivities are confused and put in the wrong places in either the formulation of Fick's second law, or in the solution formula.

2) The age exponent n (of the "instantaneous diffusivity" $D(t)$) and α (of the "average diffusivity" $D_{av}(t)$) are quite different and must never be confused. The time dependent relationship between them has been quantified.

3) In realistic cases with a value of $\alpha \approx 0.6$ the error on the age exponent will be a factor of 1.25! Having in mind that the age exponent is the overall dominant parameter in chloride ingress modelling with a time dependent diffusivity such an error therefore is unacceptable.

4) The age exponent α of diffusivity derived from exposure data by use of the traditional erfc-solution with a time-dependent diffusivity, is actually equal to the age exponent α of the diffusivity derived by use of the more advanced Ψ_p-solution! Even though the time-dependency of the surface chloride content is neglected when evaluating the achieved diffusivity, the age exponent will still be correct.

5) This is not true for the other parameters in the models.

6) The time-dependent achieved diffusivity from curve-fitting chloride profiles, without considering the time-dependency of the surface chloride concentration, is very different from the "average diffusivity"! In realistic cases where the value of p is 0.4-1.1 the error on the derived diffusivity will be a factor 1.5-2.

7) This means that in the past a significant error has often been introduced in the diffusivity obtained from exposure data! And therefore, in e.g. the *DuraCrete model*, the environmental factor is quantified erroneously! Consequently, service-life predictions in such cases may be too optimistic and up to two times overestimated!

8) Most observations of chloride ingress over time indicate that the surface chloride content is time-dependent. Consequently, any model for chloride ingress must include such a description. The Ψ-model (cf. [6], [9], [12]) gives a mathematically correct solution to Fick's second law for these conditions.

9) A solution using the (λ, μ)-modification of the erfc function as suggested for the first time in this report has shown to be a mathematically sound way to overcome any computational difficulties with the Ψ-model. This is exemplified in the report.

If any future time-dependency of the surface chloride content is neglected when modelling chloride ingress into concrete, the service life will be significantly overestimated! As long as we are missing chloride ingress models expressing a fundamental understanding of the physical and chemical processes involved, prediction models must be founded on long term chloride ingress data of high quality.

Any chloride prediction is of course of little value if knowledge on chloride threshold values for initiation of steel in concrete are missing. For the time being more focus on the decisive parameters for chloride threshold values are needed in order to make service life modelling meaningful – both for new structures and for existing structures.

In order to base future design and reassessment of chloride exposed concrete structures on firm knowledge rather than solely on experience more research, development, data and test methods in this field are needed.

Appendix A

Fick's laws of diffusion

A.1 Introduction

When one considers chloride ingress into concrete, Fick's second law is a very important model. It is, however, difficult to solve in general, and there is also a serious problem of adopting the most convenient diffusion coefficient for given measured data, so one has only considered some special cases of Fick's second law in the literature. Because the measured data far from always does fit anyone of these known special cases, these apparent failures have unfortunately created a tendency among some engineers to reject Fick's second law in general. We shall in this chapter of the Appendix show that this is a very hasty conclusion. In fact, it will be demonstrated that if

1) the flow of chloride ions is slow, i.e. it is a flow without vortices so it can be described by a gradient field,
2) and Fick's first law is assumed to hold,

then the flow also obeys Fick's second law for some (known or unknown) diffusion coefficient $D(x,t)$.

Therefore, if one rejects Fick's second law, then either one has chosen a wrong diffusion coefficient, or the flow contains vortices, so it cannot be described by a gradient field, or Fick's first law must be rejected.

The sections following after the argumentation mentioned above will deal with some special variants of Fick's second law from the literature and their unique solutions.

A.2 Scalar potential, diffusion coefficient and flux

In order to do things right we shall here start in full generality by considering a flow of chloride ions in a three-dimensional space. Once we have derived the necessary results for our purposes, we shall specialize and restrict ourselves to the simpler one-dimensional case.

Let $0 \leq C(\mathbf{x}, t) \leq 1$ denote the density of chloride ions at the point $\mathbf{x} := (x_1, x_2, x_3) \in \Omega$ in the given region $\Omega \subseteq \mathbb{R}^3$ at time t. Since the flow of chloride ions in general is very slow, we may without loss of generality assume that the flow is without vortices, hence it can be described as a gradient field with a corresponding *scalar potential* H. A sound physical assumption is that H is *proportional to the density* $C(\mathbf{x}, t)$, i.e. the scalar potential is of the structure

$$\text{(A.1)} \quad H = D(\mathbf{x}, t, \cdots)C(\mathbf{x}, t)$$

for some factor $D(\mathbf{x}, t, \cdots)$ depending on $\mathbf{x}$ and t, and possibly some other variables like e.g. the temperature, or pH-value, or the density $C(\mathbf{x}, t)$ itself, etc.. The equation (A.1) formally defines the function $D(\mathbf{x}, t, \cdots)$, which naturally is called the *(instantaneous) diffusion coefficient* of Ω, so in some sense it describes the physical properties of Ω at the point $(\mathbf{x}, t)$. We note in particular that the rôle of the diffusion coefficient in (A.1) is to transform the random microscopic diffusion, chemical, etc. processes at $\mathbf{x}$ into a simple macroscopic *model*, which describes the overall trend of the flow at the point $(\mathbf{x}, t)$, neglecting the confusing and irrelevant random processes which only will blur the description.

Since $D(\mathbf{x}, t, \cdots)$ is considered as a *model*, the strategy is always to choose it as simple as possible and only adjust it to more complicated variants, when one particular version does not fit with the observations made.

Given the scalar potential H by (A.1), the *flow* of the chloride ions is then described by the vector field $\mathbf{V} = (V_1, V_2, V_3)$, which is obtained by taking the gradient of the potential H. It is in potential theory always customary to change the sign. Hence, the *flow* is described by

(A.2)
$$\mathbf{V} := -\mathbf{grad}\ H = -\left(\frac{\partial H}{\partial x_1}, \frac{\partial H}{\partial x_2}, \frac{\partial H}{\partial x_3}\right) = -\left(\frac{\partial(D \cdot C)}{\partial x_1}, \frac{\partial(D \cdot C)}{\partial x_2}, \frac{\partial(D \cdot C)}{\partial x_3}\right).$$

At the point $(\mathbf{x}, t)$ the vector $\mathbf{V}(\mathbf{x}, t)$ indicates the direction of the flow through the point $\mathbf{x}$ at time t, and the length $\|\mathbf{V}(\mathbf{x}, t)\|$ of $\mathbf{V}(\mathbf{x}, t)$ indicates the speed of the flow through $\mathbf{x}$ at time t. Hence, $\mathbf{V}(\mathbf{x}, t)$ can be interpreted as the velocity of the flow at time t and at the point $\mathbf{x}$.

We shall next introduce the *flux* of the flow given by (A.2) through a point $\mathbf{x}$ on a surface S in Ω, where we furthermore assume that S is smooth at $\mathbf{x}$, so a unit normal vector $\mathbf{n} = \mathbf{n}(\mathbf{x})$, $\|\mathbf{n}\| = 1$, of S exists at $\mathbf{x}$. We define the *flux* of the vector field $\mathbf{V}$, given by (A.2), through S at $\mathbf{x}$ and time t as

$$\text{(A.3)}\quad F_S(\mathbf{x}, t) = \mathbf{n}(\mathbf{x}) \cdot \mathbf{V}(\mathbf{x}, t), \qquad \mathbf{n}(\mathbf{x}) \text{ perpendicular to } S \text{ at } \mathbf{x},$$

where the dot denotes the scalar product of two vectors.

We note that if the surface S_1 is perpendicular to e.g. the x_1-axis, and $\mathbf{x} = (x_1, 0, 0) \in S_1$ is a point on both S_1 and the x_1-axis, then we may choose $\mathbf{n}(\mathbf{x}) = (1, 0, 0)$. Then it follows from (A.3) and (A.2) that

$$\text{(A.4)}\quad F_{S_1}(x_1, 0, 0) = -\frac{\partial}{\partial x_1}(D \cdot C),$$

and similarly for the other two axes. By adding all contributions we conclude that we in general have

$$\frac{\partial C}{\partial t} = -\mathrm{div}\,\{\mathbf{grad}(D \cdot C)\} = -\Delta(D \cdot C),$$

where Δ is the Laplacian,

$$\Delta = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2}.$$

This remark shows that we without loss of generality may constrict ourselves to only considering the one-dimensional case. The reduced model is the familiar positive half-line $\mathbb{R}_+$ on the real axis, so (A.1), (A.2), (A.3) and (A.4) reduce to the simpler one-dimensional model

$$\begin{cases} H = D(x, t, \cdots)C(x, t), & x > 0,\ t > 0, \quad \text{potential,} \\ F(x, t, \cdots) = -\dfrac{\partial}{\partial x}\{D(x, t, \cdots)C(x, t)\}, & x > 0,\ t > 0, \quad \text{flux.} \end{cases}$$

Summary. Considering the one-dimensional case we have in this section only assumed that the flow of chloride ions is given by a *scalar potential* H, which is proportional to $C(x, t)$. The factor of proportion $D(x, t, \cdots)$ is the *instantaneous diffusion coefficient.* The *flux* at $x \in \mathbb{R}_+$ at time $t > 0$ is then given by

$$\text{(A.5)}\quad F = -\frac{\partial}{\partial x}\{D \cdot C\}.$$

A.3 Fick's first law and non-Fickean flows

When we compute the right hand side of (A.5), we get the flux

$$\text{(A.6)}\quad F = -D(x,t,\cdots)\,\frac{\partial C}{\partial x} - \frac{\partial D}{\partial x}\,C(x,t).$$

As mentioned previously, $D(x,t,\cdots)$ gives a macroscopic model of the microscopic random processes. In most cases we apply our model on an object which is almost homogeneous in its chemical composition and structure, so one would expect $D(x,t,\cdots)$ not to vary much in x, i.e. $\partial D/\partial x$ must be very small. Under this assumption (A.6) can be written

$$\text{(A.7)}\quad F \approx -D(x,t,\cdots)\,\frac{\partial C}{\partial x}, \qquad \text{or just} \quad F = -D\,\frac{\partial C}{\partial x} \quad \text{for short.}$$

Thus, by *assuming almost homogeneity of the concrete on the half-line representing the concrete* we have proved the essential step of

Fick's first law. *The flow in concrete of chloride ions through a unit area of a section of the concrete per unit of time (i.e. the flux F) is proportional to the density gradient of the chloride ions measured normally to the section.*

We shall in the next section show that *if we accept Fick's first law as our model, then Fick's second law is easily derived from this first law.* Therefore, if a flow cannot be modelled by some version of Fick's second law, then we are forced to reject (A.7) and go back to the analysis of (A.6) or (A.5).

We define the flow to be *non-Fickean*, if Fick's first law does not apply, i.e. when (A.7) does not hold. Thus, for non-Fickean flows, $|\partial D/\partial x|$ is either very large, or $D(x,t,\cdots)$ may even be discontinuous at x, so the partial derivative with respect to x does not exist. The latter is e.g. the case, when $x = 0$ is the boundary point, or $x = x_0 > 0$ separates two parts of the concrete of different chemical composition or geometrical structure, like essentially more pores to the left at x_0 than to the right.

A.4 Fickean flows and Fick's second law

Once Fick's first law has been accepted as the model of a given flow, we say that we have a *Fickean flow.* For completeness we mention that the Fickean flows again formally can be subdivided into the following two classes:

1) The Fickean flow is called a *simple Fickean flow* if the diffusion coefficient $D(x,t)$ does only depend on x and t, possibly in the form of the density $C(x,t)$ of the chloride ions, in which case we get a non-linear equation later on. All investigations in the literature are dealing with examples of simple Fickean flows.

2) In reality no Fickean flow is simple, because they are characterized by $D(x, t, \cdots)$ also depending on some other variables, like e.g. the temperature, the pH-value etc.. For each such new variable we must go back to the physical considerations in order to set up an additional differential equation. However, the few investigations available indicate that $D(x, t, \cdots)$ always at least depends on the temperature, though the fluctuations in the temperature do not influence the overall trend. By this we mean that if the temperature T is the same at $t = t_1$ and $t = t_2 > t_1$ at some fixed point, and $C(x, t_1, T)$ is known, then $C(x, t_2, T)$ can be predicted by the chosen model of Fick's second law by simply assuming that the temperature is kept fixed for $t_1 < t < t_2$. This extra variable, the temperature, only changes the balance between the chloride atoms and the chloride ions and have nothing to do with the ingress of chloride ions from the outside world.

As the model always should be kept as simple as possible, we shall only consider the *simple Fickean flows* in the following.

The next result, the *mass balance equation* is a general result which is proved without any assumption of the flow being Fickean or non-Fickean.

The mass balance equation. *The change in chloride per unit time is equal to the change of flux per unit length.*
In the one-dimensional case this is expressed mathematically in the form

$$\text{(A.8)} \quad \frac{\partial C}{\partial t} = -\frac{\partial F}{\partial x}.$$

In fact, consider an element parallel to the chloride diffusion into a semi-infinite volume of concrete. We choose for convenience the element of area of the cross-section perpendicular to the x-axis as $dA = 1$. Between two consecutive sections at the distance dx the volume of the tube becomes $dV = dx$. The amount of chloride per unit time, $dt = 1$ which diffuses into this volume dV is by definition the flux F. Similarly, the amount of chloride which diffuses out from the volume dV is the flux at the abscissa $x + dx$. Hence, the flux changes along the x-axis at the amount of $\partial F / \partial x$ per unit on the x-axis. During the time $dt = 1$ the increase of chloride in the volume becomes

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

and (A.8) follows without any further assumption.

Combining the equations (A.4) and (A.8) we see that if we only assume that the flow is given by a gradient field, then we must have the equation

$$\text{(A.9)} \quad \frac{\partial C}{\partial t} = \frac{\partial^2}{\partial x^2} \{D(x, t) C(x, t)\},$$

no matter whether we consider a Fickean or non-Fickean flow. However, one does not consider (A.9) in the literature, because it in general is difficult to solve mathematically. The mathematical solution methods become easier, if we can replace (A.9) by

$$\text{(A.10)}\quad \frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left\{D(x,t)\,\frac{\partial}{\partial x}\,C(x,t)\right\}.$$

It is for that reason that we have emphasized the importance of *Fick's first law.* In fact, when we combine (A.7) and (A.8) we immediately get (A.10). This is *Fick's second law,* which thus is derived from Fick's first law.

Fick's second law. *The change in chloride content per unit time is equal to the change per unit length of the product of the diffusion coefficient D and the density gradient of the chloride ions.*
In one dimension this is expressed by (A.10), i.e.

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

We shall here emphasize that if the flow contains vortices, then we still get equation (A.9), which in structure is of the same type as (A.10). The only difference is that $D(x,t)$ is put at different places in the two equations. Therefore, equations of this type cannot be avoided, unless we consider really violent flows.

Appendix B

A catalogue of models based on Fick's second law

B.1 Introduction

We shall in the following only consider (simple) Fickean flows, hence the differential equation is given by Fick's second law, or more precisely by the equation (A.10) in one dimension. In order to obtain a unique mathematical solution we have to specify the initial conditions and the boundary conditions. If t_{ex} denotes the time of first exposure, then the typical initial/boundary problem for Fick's second law is written

$$\text{(B.1)} \quad \begin{cases} \dfrac{\partial C}{\partial t} = \dfrac{\partial}{\partial x}\left\{D(x,t)\,\dfrac{\partial}{\partial x}\,C(x,t)\right\}, & x>0,\ t>t_{ex}, \quad \text{differential equation,} \\[2ex] C(0,t) = \varphi(t), & x=0,\ t\geq t_{ex} \quad \text{boundary condition,} \\[2ex] C\left(x,t_{ex}\right) = \chi(x), & x\geq 0,\ t=t_{ex}, \quad \text{initial condition,} \end{cases}$$

where $\varphi(t)$ and $\chi(x)$ are prescribed functions. Note that $D(x,t)$ here could be replaced by $D(x,t,C(x,t))$, where the diffusion coefficient also depends on the concentration of the chloride. This gives us a nonlinear partial differential equation, which does not look too nice for a first approach, so we shall avoid this case in the following. Then under very weak mathematical assumptions (which are always fulfilled in the engineering sciences) this initial/boundary problem (B.1) has a unique solution. The problem is "only" to find it.

We see in this model that we shall choose – or if possible, specify by measurements – the three functions $D(x,t)$, $\varphi(t)$ and $\chi(x)$. It turns up that the initial condition $\chi(x)$ is the least important for both mathematical and engineering reasons. If the concrete is homogeneous in composure then it should be a constant, and this constant reappears as the same constant in the solution formula.

In this chapter we shall list some of the most commonly used special models based on the general Fick's second law. We emphasize in order to avoid misunderstandings that if some of the following models – and even if all of them – do not fit in practice, one cannot conclude that Fick's second law does not hold. One should instead try to generalize the classical models below to also cover a given case which cannot be described by one of these special examples of models of Fick's second law.

B.2 Collepardi's model

The most reasonable approach for setting up a model is to ask the following question

What is the simplest form of the problem (B.1) above?

The answer is *Collepardi*'s model [3] from the beginning of the 1970s, in which he put $D(x,t) = D_0 > 0$ and $\varphi(t) = C_s$ and $\chi(x) = C_i$ all constants. Hence, (B.1) reduces to

Collepardi's model (also called *the error function model*):

$$\text{(B.2)} \quad \begin{cases} \dfrac{\partial C}{\partial t} = D_0 \dfrac{\partial^2 C}{\partial x^2} & x > 0,\ t > t_{ex}, \quad \text{differential equation,} \\ C(0,t) = C_s, & x = 0,\ t \geq t_{ex} \quad \text{boundary condition,} \\ C\left(x, t_{ex}\right) = C_i, & x \geq 0,\ t = t_{ex}, \quad \text{initial condition.} \end{cases}$$

Its familiar unique solution, which most civil engineers have used as a model, is given by the complementary error function below

$$\text{(B.3)} \quad C(x,t) = C_i + (C_s - C_i)\, \mathrm{erfc}\left(\frac{x}{2\sqrt{D_0 \cdot (t - t_{ex})}}\right), \qquad x \geq 0,\ t \geq t_{ex}.$$

B.3 Takewaka and Matsumoto's model

Collepardi's model was a big step forward in understanding the dynamics of flows of chloride ions into concrete. However, it did not last long, before one realized that it had some shortcomings by putting $D(x,t)$, $\varphi(t)$ and $\chi(x)$ all constants. *Takewaka & Matsumoto* [16] pointed out in 1988 that one would get a better model (the next iteration) by assuming that $D(x,t) = D(t) > 0$ is a function in t alone. Hence, we get

Takewaka a nd Matsumoto's model:

$$\begin{cases} \dfrac{\partial C}{\partial t} = D(t)\,\dfrac{\partial^2 C}{\partial x^2} & x > 0,\ t > t_{ex}, \qquad \text{differential equation,} \\[2ex] C(0,t) = C_s, & x = 0,\ t \geq t_{ex} \qquad \text{boundary condition,} \\[2ex] C\left(x, t_{ex}\right) = C_i, & x > 0,\ t = t_{ex}, \qquad \text{initial condition,} \end{cases} \tag{B.4}$$

the solution of which is easily proved to be

$$C(x,t) = C_i + \left(C_s - C_i\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right), \qquad x \geq 0,\ t \geq t_{ex}. \tag{B.5}$$

One particular important case of this model was later used in the HETEK model with the *average diffusion coefficient* $D_{\mathrm{av}}(t)$ given by

$$D_{\mathrm{av}}(t) := \frac{1}{t - t_{ex}} \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau = D_{\mathrm{aex}} \left\{\frac{t_{ex}}{t}\right\}^{\alpha}, \qquad t > t_{ex}, \qquad 0 \leq \alpha < 1. \tag{B.6}$$

B.4 The Ψ_p-function model

Another modification was suggested by *Swamy et al.* [14], and also by *Uji et al.* [18], who obtained better results, when the boundary condition was assumed to be a power function of exponent 1/2, 1, 3/2, etc.. This led *Mejlbro* [9] to examine the more general case of putting $\varphi(t) = t^p$, where just $p \geq -1/2$. In order not to have too many irrelevant constants at large, *Mejlbro* considered the simplified model

Mejlbro's model:

$$\begin{cases} \dfrac{\partial C_p}{\partial t} = \dfrac{\partial^2 C_p}{\partial x^2} & x > 0,\ t > 0 \qquad \text{differential equation,} \\[2ex] C_p(0,t) = t^p, & x = 0,\ t \geq 0,\ p \geq -\frac{1}{2}, \qquad \text{boundary condition,} \\[2ex] C_p(x,0) = 0, & x \geq 0,\ t = 0, \qquad \text{initial condition,} \end{cases} \tag{B.7}$$

where $D = 1$, $t_{ex} = 0$ and $\chi(x) = 0$. In order to emphasize that $C_p(x,t)$ is the solution of a very special (and generic) problem only depending on one parameter, namely the exponent p, we have added the index p to the solution.

Mejlbro [9] defined in this connection the class of *generalized error functions* $\Psi_p(u)$, which could be found independently of (B.7), where $\operatorname{erfc}(u) = \Psi_0(u)$ is a special case, and where the solution of (B.7) was obtained by multiplying the boundary condition t^p by the function $\Psi_p(u)$, where $u = x/\{2\sqrt{t}\}$. Thus, the solution of (B.7) becomes

(B.8)
$$C_p(x,t) = t^p\,\Psi_p\left(\frac{x}{2\sqrt{t}}\right), \qquad \text{in particular} \qquad C_0(x,t) = \operatorname{erfc}\left(\frac{x}{2\sqrt{t}}\right) \quad \text{where } t^0 = 1.$$

Clearly, *Mejlbro*'s model could by linearity be extended to the more general

(B.9)
$$\begin{cases} \dfrac{\partial C}{\partial t} = D(t)\,\dfrac{\partial^2 C}{\partial x^2} & x > 0,\ t > t_{ex} & \text{differential equation,} \\[2ex] C(0,t) = C_i + S\Big(\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau\Big)^p, & x = 0,\ t \geq t_{ex},\ p \geq -\frac{1}{2}, & \text{boundary condition,} \\[2ex] C\left(x, t_{ex}\right) = C_i, & x \geq 0,\ t = t_{ex}, & \text{initial condition,} \end{cases}$$

where $S > 0$ is a constant. The solution of (B.9) is easily found by combining the previous results,

$$\text{(B.10)}\quad C(x,t) = C_i + S\left(\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau\right)^p \Psi_p\left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right), \qquad x \geq 0,\ t > t_{ex}.$$

Equation (B.9) and its solution (B.10) is to date the most general version of Fick's second law using a simple solution method. It should here be mentioned that there exists some very difficult solution procedures for the more general problem (B.1). These are unfortunately not of practical use for the time being. The theory above could also be enhanced by adding two or more problems for different p of (B.9) from which one obtains the solution by superposition. However, as long as (B.9) and (B.10) are not common knowledge, there is no need here to bring this extension.

B.5 The HETEK model

Mejlbro's investigation above was originally aimed at solving the HETEK model, created by *Frederiksen et al.* [6]. This is an important special case of *Mejlbro*'s model, because one has only to specify five constants in its application. Since the *average diffusion coefficient* $D_{\text{av}}(t)$ is used here, the strict formulation of the HETEK model may look strange at the first glance. The different rôles of the average and the instantaneous diffusion coefficients are discussed elsewhere in this report, so we shall not repeat this discussion.

The HETEK model:

We choose the *average diffusion coefficient* $D_{\text{av}}(t)$, such that

$$\text{(B.11)}\quad D_{\text{av}}(t) := \frac{1}{t - t_{ex}} \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau = D_{\text{aex}} \left\{ \frac{t_{ex}}{t} \right\}^{\alpha}, \qquad \text{for } t > t_{ex},$$

where $D_{\text{aex}} > 0$ and $\alpha \in [0, 1[$ are constants. When we multiply by $t - t_{ex}$ and then differentiate the result, it follows easily from (B.11) that the *instantaneous diffusion coefficient* $D(t)$ is given by

$$\text{(B.12)}\quad D(t) = D_{\text{aex}} \left\{ \frac{t_{ex}}{t} \right\}^{\alpha} \left(1 - \alpha + \alpha \cdot \frac{t_{ex}}{t} \right).$$

Since

$$\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau = D_{\text{aex}}\,(t - t_{ex}) \left\{ \frac{t_{ex}}{t} \right\}^{\alpha},$$

it follows that the HETEK model is best formulated in the following way

(B.13)

$$\begin{cases} \dfrac{\partial C}{\partial t} = D_{\text{aex}} \left\{ \dfrac{t_{ex}}{t} \right\}^{\alpha} \left(1 - \alpha + \alpha \cdot \dfrac{t_{ex}}{t} \right) \dfrac{\partial^2 C}{\partial x^2}, & x > 0,\ t > t_{ex} \qquad \text{diff. eq.,} \\ C(0, t) = C_i + S \left(D_{\text{aex}}\,(t - t_{ex}) \left\{ \dfrac{t_{ex}}{t} \right\}^{\alpha} \right)^{p}, & x = 0,\ t > t_{ex}, \qquad \text{bd. cond.,} \\ C\left(x, t_{ex}\right) = C_i, & x \geq 0,\ t = t_{ex}, \qquad \text{init. cond.,} \end{cases}$$

because the solution of (B.13) is found in a very simple way,

$$\text{(B.14)}\quad C(x, t) = C_i + S \left(D_{\text{aex}}\,(t - t_{ex}) \left\{ \frac{t_{ex}}{t} \right\}^{\alpha} \right)^{p} \Psi_p \left(\frac{x}{2\sqrt{D_{\text{aex}}\,(t - t_{ex}) \left\{ \dfrac{t_{ex}}{t} \right\}^{\alpha}}} \right),$$

for $x \geq 0$, $t > t_{ex}$. The introduction of the exponent α more or less compensates for the fact that the flow is non-Fickean close to the boundary.

Note that the HETEK model only contains five unknown parameters, namely the constants D_{aex}, α, p, S and C_i. Furthermore, one should not rely on measurements corresponding to t close to t_{ex}, where we cannot trust the model, because the flow is here non-Fickean.

In fact, it was mentioned in section A.3 that the flow is always non-Fickean near the boundary, e.g. for $0 < x < \Delta$. Diffusion is a slow process, so during some small time interval $t_{ex} < t < t_{ex} + \delta$, where $\delta > 0$ depends of Δ as well as in some sense of the diffusion coefficient $D(x,t)$, most of the chloride ions of the process will still remain in the non-Fickean x-interval $[0,\Delta]$, so the process is non-Fickean shortly after $t = t_{ex}$. This is only proving the *existence* of such a constant δ. Its size is not known for the time being and is for further study. However, a qualified guess is that $\delta \approx t_{ex}$, so we guess that the flow is non-Fickean for $t_{ex} \leq t \leq 2t_{ex}$, and Fickean for $t > 2t_{ex}$.

Since the flow always is non-Fickean for t very close to the time of first exposure t_{ex}, when most of the ions from the flow are very close to the boundary, we cannot rely on the description given by the model for such t. Therefore, we can allow $D(t)$ and $D_{\text{av}}(t)$ to be very large close to t_{ex} and even infinity at $t = t_{ex}$, as long as $(t - t_{ex})\, D_{\text{av}}(t) \to 0$ for $t \to t_{ex}$. This idea was already considered by the creators of the HETEK model as a possibility, but unfortunately rejected, “because the diffusion coefficient cannot be infinite”. As indicated above, since the flow is non-Fickean in the beginning of the exposure, when the chloride ions are still close to the boundary, this is not a serious objection, because on never considers the model, when $t_{ex} < t < 2t_{ex}$. We can therefore set up the following modified HETEK model, which is easier to handle in practice:

The modified HETEK model:

We here replace (B.11) by

$$\text{(B.15)}\quad D_{\text{av}}(t) = D^*_{\text{aex}}\,(t - t_{ex})^{-\alpha}, \qquad t > t_{ex}.$$

Then

$$\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau = D^*_{\text{aex}}\,(t - t_{ex})^{1-\alpha},$$

and

$$D(t) = (1-\alpha)D_{\text{av}}(t) = (1-\alpha)D^*_{\text{aex}}\,(t - t_{ex})^{-\alpha},$$

so the problem is written in the form

$$\text{(B.16)}\quad \begin{cases} \dfrac{\partial C}{\partial t} = \dfrac{(1-\alpha)D^*_{\text{aex}}}{(t - t_{ex})^{\alpha}}\,\dfrac{\partial^2 C}{\partial x^2}, & x > 0,\ t > t_{ex}, \quad \text{diff. eq.}, \\[2ex] C(0,t) = C_i + S\left\{D^*_{\text{aex}}\,(t - t_{ex})^{1-\alpha}\right\}^p, & x = 0,\ t > t_{ex}, \quad \text{bd. cond.}, \\[2ex] C(x, t_{ex}) = C_i, & x > 0,\ t = t_{ex}, \quad \text{init. cond..} \end{cases}$$

Clearly, (B.16) is less complicated than the original HETEK model (B.13). Also the solution

(B.17)

$$C(x,t) = C_i + S\left\{D^*_{\text{aex}}\,(t-t_{ex})^{1-\alpha}\right\}^p\,\Psi_p\left(\frac{x}{2\sqrt{D^*_{\text{aex}}\,(t-t_{ex})^{1-\alpha}}}\right), \quad x>0,\ t>t_{ex},$$

of (B.16) is simpler than (B.14), and it can furthermore be proved that (B.16) and (B.14) are almost equal, when t is large compared with t_{ex}. In this case we also have only five unknown parameters, which should be specified by measurements.

Although the HETEK model is specified by only five constants, it is not hard to show by computer simulation, cf. e.g. Figure 6.2, that it covers a lot of cases, which have not yet been studied in details.

Remark B.1 Finally, it should be mentioned that if the auxiliary variable T, which intrinsically is entering the problem, is given by

$$T := D^*_{\text{aex}}\,(t-t_{ex})^{1-\alpha},$$

then we can always express the original variable t explicitly in T,

$$t = t_{ex} + \left\{\frac{T}{D^*_{\text{aex}}}\right\}^{1/(1-\alpha)},$$

a fact, which is quite useful in the practical computations (not shown here). This is not possible in the original HETEK model, where T is given by

$$T = D_{\text{aex}}\,(t-t_{ex})\cdot\left\{\frac{t_{ex}}{t}\right\}^{\alpha},$$

which is an equation that in general cannot be explicitly solved with respect to t. ◊

B.6 Conclusions

It has been argued that it in general is very difficult to reject Fick's second law as a model for chloride ingress into concrete.

A general initial/boundary value problem (B.1) for Fick's second law is given, and some special cases are discussed with their solutions.

Note, however, that none of the special initial/boundary value problems shown here exhaust all possibilities of general problem (B.1), although the HETEK model may cover many cases. The reason is that even the models presented here are not too well-known in public. It should be mentioned that if the diffusion coefficient $D(t)$ only depends on t and is continuous in t, then the problem (B.1) can be solved with this diffusion coefficient by extending the methods of *Mejlbro*'s model by e,g, using *Weierstraß's approximation theorem.*

Appendix C

Comparison of $C(x,t)$ and $C_{approx}(x,t)$

C.1 Introduction

Traditionally engineers prefer to use the well-known error function solution instead of the more correct Ψ_p-solutions, because one is not yet quite familiar with the latter ones. However, if one is not careful in the setup, one can easily obtain some very wrong predictions. In this chapter of the Appendix we shall in details discuss the difference between the exact solution $C(x,t)$ and the approximating error function solution $C_{\text{erfc}}(x,t)$. We shall even find a reasonable approximation of the correct solution by a "twisted" error function solution, where we shall need the tables of Section C.8, where we guess from the graphs that the relative error of such an approximation is of the size of λ_p for T large, given in one of the above mentioned tables. These results are here published for the first time.

C.2 Specification of the assumptions

We shall consider Fick's second law in its special form

$$\text{(C.1)}\quad \begin{cases} \dfrac{\partial C}{\partial t} = D(t)\,\dfrac{\partial^2 C}{\partial x^2}, & x>0, \quad t>t_{ex} \\[2ex] C(0,t) = C_i + S\cdot\left\{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau\right\}^p, & t>t_{ex}, \\[2ex] C\left(x,t_{ex}\right) = C_i, & x>0, \end{cases}$$

where $p\geq 0$ and $C_i>0$ and $S>0$ are constants, and the diffusion coefficient $D(t)>0$ is a function of time t alone.

Remark C.1 When $D(t) = D > 0$ is a constant and $p = 0$, then we get the usual complementary error function solution, so the classical case is included in this model. As argued in the main body of this report it has long been recognized that the diffusion coefficient in practice is a function of t. The first successful examples are of the type $D(t) \sim$ constant times $t^{-\alpha}$, where $\alpha \in]0,1[$ is a constant.
The structure of the term $S \cdot \left\{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau\right\}^p$ of the boundary condition is chosen for convenience. It can be shown that it is $\sim$ a constant times t^p. By choosing the "neighbouring" $\left\{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau\right\}^p$ instead of the simpler function t^p we obtain an easy solution formula (C.2) below. $\Diamond$

It follows from the general theory that the *unique* solution of (C.1) is given by

$$\text{(C.2)}\quad C(x,t) = C_i + S \cdot \left\{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau\right\}^p \Psi_p\left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right).$$

Notice that if $D(t) = D > 0$ is a constant, and $p = 0$ in (C.1), then (C.2) becomes the classical solution

$$\begin{aligned} C(x,t) &= C_i + S \cdot \{D \cdot (t - t_{ex})\}^0 \cdot \Psi_0\left(\frac{x}{2\sqrt{D \cdot (t - t_{ex})}}\right) \\ &= C_i + S \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{D \cdot (t - t_{ex})}}\right), \end{aligned}$$

because $\Psi_0 = \operatorname{erfc}$.

We shall in the following assume Fick's second law in the form (C.1) and its uniquely determined solution (C.2). Or more precisely, we *pretend* that we by some measurements only know the graphs of the chloride profiles (C.2), and then we shall approximate these graphs by known classical solutions. Finally, we shall compare the derived solution with the exact solution (C.2).

Let us assume that we do not know $D(t)$, S, p and C_i of (C.1), and that we by measurements only know a finite number of finite parts of the chloride profiles given by (C.2). A traditional civil engineer would then by the latter measured data using e.g. regression analysis construct an approximating solution by adopting the usual complementary error function as the underlying structure function. Thus, our civil engineer would find an approximating solution of the form

$$\text{(C.3)}\quad C_{\text{approx}}(x,t) = C_{\text{i,approx}} + C_{\text{s,approx}} \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D_{\text{approx}}(\tau)\,\mathrm{d}\tau}}\right).$$

This approximating function $C_{\text{approx}}(x,t)$ is implicitly constructed, such that its difference from the exact solution $C(x,t)$ is "more or less" minimized in "mean square". We shall later return to the precise meaning of this apparently vague statement. Here we just note that we by statistical methods explicitly can find the constants $C_{\text{i,approx}}$ and $C_{\text{s,approx}}$ and the *approximating diffusion coefficient* $D_{\text{approx}}(t)$ from our measured data. Hence, $C_{\text{i,approx}}$ and $C_{\text{s,approx}}$ and $D_{\text{approx}}(t)$ in (C.3) can be assumed known in the following.

Remark C.2 Note that the introduction of the approximating diffusion coefficient $D_{\text{approx}}(t)$ in (C.3) relies heavily on the fact that a solution of Fick's second law always is depending on the variable

$$u := \frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}},$$

so we adopt the same structure of the approximating solution. ◊

It will in the following be convenient to refer to a new function $\mu_p(t) > 0$, which is defined by

$$\text{(C.4)}\quad \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau = \{\mu_p(t)\}^2 \int_{t_{ex}}^{t} D_{\text{approx}}(\tau)\,\mathrm{d}\tau.$$

Remark C.3 As mentioned above we have already derived $D_{\text{approx}}(t)$ from our measured data. If we can find $\mu_p(t)$ explicitly, then we also know $\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau$, from which we obtain $D(t)$ itself by a differentiation. The function $\mu_p(t)$ is therefore important for our reconstruction of the original problem (C.1), if this is possible.

That $\mu_p(t)$ also depends on the index p is due to the fact that since (C.3) is approximating a Ψ_p-solution (C.2), the *approximating diffusion coefficient* $D_{\text{approx}}(t)$ must necessarily depend on p. Since $D(t)$ is independent of p, we conclude that $\mu_p(t)$ is also depending on p. Clearly, the definition (C.4) indicates that one may expect that $\mu_p(t)$ is a function of t. The surprising result is that $\mu_p(t) = \mu_p$ *does neither depend on* $D(t)$ *nor on* t, *but only on* p. This is an unexpected and deep result, the proof of which is given in Section C.4. ◊

It follows from (C.4) that (C.3) can now be written in the form

$$\text{(C.5)}\quad C_{\text{approx}}(x,t) = C_{\text{i,approx}} + S_{\text{approx}} \cdot \operatorname{erfc}\left(\mu_p(t) \cdot \frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right),$$

where we for later *theoretical* reasons have switched back to the (yet unknown) diffusion coefficient $D(t)$.

Another convenient notation in the following is

$$\text{(C.6)}\quad S_p(t) := S\cdot\left\{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau\right\}^p .$$

Then the exact solution (C.2) is written

$$\text{(C.7)}\quad C(x,t) = C_i + S_p(t)\cdot\Psi_p\left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right).$$

Remark C.4 Clearly, (C.7) and (C.5) are formally of the same structure. When $p = 0$, formula (C.7) reduces to

$$C(x,t) = C_i + S_0(t)\cdot\operatorname{erfc}\left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right),$$

which is already expressed by an error function solution, so they must coincide in this case. Hence, if $p = 0$, then

$$C_{\text{i,approx}} = C_i, \qquad S_{\text{approx}} = S_0(t) \quad \text{a constant}, \qquad \gamma_0(t) = 1. \qquad \Diamond$$

Problem C.1 *For given $p \geq 0$, find the best approximation of the form (C.5) and (C.2) [or equivalently of (C.7)] in some sense of minimizing in mean square.*

C.3 Analysis of Problem C.1

As usual, mean square approximation means mathematically that one shall minimize the improper plane integral

$$\int_0^{+\infty}\left\{\int_{t_{ex}}^{+\infty}\left\{C_{\text{approx}}(x,t) - C(x,t)\right\}^2\mathrm{d}t\right\}\mathrm{d}x$$

with respect to the unknown constants $C_{\text{i,approx}}$ and S_{approx}, and the unknown function $\mu_p(t)$, cf. (C.5). This is, however, not possible, because the inner integral with respect to t is clearly infinite when $p > 0$. In fact, it follows for every fixed $x > 0$ that $C(x,t) \to +\infty$ for $t \to +\infty$, while $C_{\text{approx}}(x,t)$ is always bounded.

The problem is not well-posed in this setup. Fortunately, there is a slightly different approach which can be applied with success. We shall allow the “constant”

$S_{\text{approx}} = S_{\text{approx}}(t)$ to be *a function of* t, and then consider t as a constant. We shall therefore more modestly minimize

$$\text{(C.8)} \quad \int_0^{+\infty} \{C_{\text{approx}}(x,t) - C(x,t)\}^2 \,\mathrm{d}x \qquad \text{for every fixed } t > t_{ex}.$$

Amazingly, this problem can be solved.

Since we consider $t \geq t_{ex}$ as a constant parameter, we can make the change of variable $x \longleftrightarrow u$ by the definition

$$\text{(C.9)} \quad u := \frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}u}}.$$

Then (C.8) is computed in the following way

$$\begin{aligned}
&\int_0^{+\infty} \{C_{\text{approx}}(x,t) - C(x,t)\}^2 \,\mathrm{d}x \\
&\quad = \int_0^{+\infty} \left\{ C_{\text{i,approx}} + S_{\text{approx}}(t)\,\mathrm{erfc}\left(\mu_p(t)\, \frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\mathrm{d}\tau}} \right) \right. \\
&\qquad\qquad \left. -C_i - S_p(t)\,\Psi_p\left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}} \right) \right\}^2 \mathrm{d}x \\
&\quad = 2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau} \cdot \int_0^{+\infty} \{C_{\text{i,approx}} - C_i + S_{\text{approx}}(t) \cdot \mathrm{erfc}\,(\mu_p(t) \cdot u) - S_p(t)\Psi_p(u)\}^2 \,\mathrm{d}u.
\end{aligned}$$

Thus we have reduced the problem to minimizing

$$\text{(C.10)} \quad \int_0^{+\infty} \{C_{\text{i,approx}} - C_i + S_{\text{approx}}(t) \cdot \mathrm{erfc}\,(\mu_p(t) \cdot u) - S_p(t) \cdot \Psi(u)\}^2 \,\mathrm{d}u$$

for every fixed $t > t_{ex}$.

Since $S_{\text{approx}}(t)$ and $S_p(t)$ are to be considered as finite constants for fixed $t > t_{ex}$, and $\mathrm{erfc}\,(\mu_p(t) \cdot u)$ and $\Psi_p(u)$ are bounded functions of u, we conclude that we not so surprisingly must have

$$C_{\text{i,approx}} = C_i.$$

In fact, if $C_{\text{i,approx}} \neq C_i$, then (C.10) would again become infinite. Hence, instead of the impossible Problem C.1 we shall solve

Problem C.2 *For given* $p \geq 0$ *and*

$$S_p(t) := S \left\{ \int_{t_{\text{ex}}}^{t} D(\tau)\, d\tau \right\}^p ,$$

minimize for every fixed $t > t_{\text{ex}}$ *the function*

$$\text{(C.11)} \quad \Phi\left(S^*, \gamma\right) := \int_0^{+\infty} \left\{ S^* \cdot \mathit{erfc}(\gamma \cdot u) - S_p(t) \cdot \Psi_p(u) \right\} du$$

with respect to (S^*, γ).

We note that if (S^*, γ) is a solution of Problem C.2, then

$$S_{\text{approx}}(t) = S^* \qquad \text{and} \qquad \mu_p(t) = \gamma.$$

C.4 Solution of Problem C.2

The function $\Phi\left(S^*, \gamma\right)$ defined by (C.11) is differentiable, and it can be proved that we may differentiate the integrand under the integral sign. The function is positive, and it is not hard to prove – though quite tedious – that the minimum exists and that it is attained at an inner point (S^*, γ), i.e. $0 < S^* < +\infty$ and $0 < \gamma < +\infty$. It follows from *Elementary Calculus* that the minimum is attained at a stationary point, i.e. the system of equations of the minimum is given by the two equations

$$\text{(C.12)} \quad 0 = \frac{\partial \Phi}{\partial S^*} = 2 \int_0^{+\infty} \left\{ S^* \operatorname{erfc}(\gamma \cdot u) - S_p(t)\, \Psi_p(u) \right\} \operatorname{erfc}(\gamma \cdot u) \mathrm{d}u,$$

$$\text{(C.13)} \quad 0 = \frac{\partial \Phi}{\partial \gamma} = 2 \int_0^{+\infty} \left\{ S^* \operatorname{erfc}(\gamma \cdot u) - S_p(t)\, \Psi_p(u) \right\} \cdot \left\{ -\frac{2}{\sqrt{\pi}}\, u \, \exp\left(-\gamma^2 u^2\right) \right\} \mathrm{d}u.$$

We multiply (C.12) by $\gamma/2$. Then we get by a rearrangement and the change of variable $\zeta := \gamma \cdot u$ in the integral not containing $\Psi_p(u)$,

$$\text{(C.14)} \quad S^* \int_0^{+\infty} \{\operatorname{erfc}(\zeta)\}^2 \mathrm{d}\zeta = S_p(t) \cdot \gamma \cdot \int_0^{+\infty} \Psi_p(u) \operatorname{erfc}(\gamma \cdot u) \mathrm{d}u.$$

We note that

$$\frac{\partial}{\partial u} \operatorname{erfc}(\gamma \cdot u) = \frac{2}{\sqrt{\pi}}\, \gamma \, \exp\left(-\gamma^2 u^2\right) = \frac{\gamma}{u} \left\{ -\frac{2}{\sqrt{\pi}}\, u \, \exp\left(-\gamma^2 u^2\right) \right\} = \frac{\gamma}{u} \frac{\partial}{\partial u} \operatorname{erfc}(\gamma \cdot u).$$

If (C.13) is multiplied by γ^2, then by the same change of variable $\zeta = \gamma \cdot u$ as above,

$$\text{(C.15)}\quad 2S^* \int_{\zeta=0}^{+\infty} \zeta \,\mathrm{erfc}(\zeta)\,\mathrm{d}(\mathrm{erfc}(\zeta)) = 2S_p(t) \int_{\zeta=0}^{+\infty} \zeta \cdot \Psi_p\left(\frac{\zeta}{\gamma}\right) \mathrm{d}\{\mathrm{erfc}(\zeta)\}.$$

The left hand side of (C.15) becomes by integrating by parts,

$$\begin{aligned} 2S^* \int_{\zeta=0}^{+\infty} \zeta \cdot \mathrm{erfc}(\zeta)\,\mathrm{d}\{\mathrm{erfc}(\zeta)\} &= S^* \int_{\zeta=0}^{+\infty} \zeta \,\mathrm{d}\left\{(\mathrm{erfc}(\zeta))^2\right\} \\ = S^* \left\{ [\zeta \cdot (\mathrm{erfc}(\zeta))^2]_0^{+\infty} - \int_0^{+\infty} \{\mathrm{erfc}(\zeta)\}^2 \mathrm{d}\zeta \right\} &= -S^* \int_0^{+\infty} \{\mathrm{erfc}(\zeta)\}^2 \mathrm{d}\zeta, \end{aligned}$$

which is equal to the left hand side of (C.14) of the opposite sign. Hence, it follows from this computation and (C.14) and (C.15) that

$$-2S_p(t) \int_{\zeta=0}^{+\infty} \zeta \cdot \Psi_p\left(\frac{\zeta}{\gamma}\right) \mathrm{d}\{\mathrm{erfc}(\zeta)\} = +S_p(t) \cdot \gamma \int_0^{+\infty} \Psi_p(u)\,\mathrm{erfc}(\gamma \cdot u)\,\mathrm{d}u,$$

or, when we divide by $S_p(t) > 0$ and integrate by parts,

$$\begin{aligned} \gamma \int_0^{+\infty} \Psi_p(u)\,\mathrm{erfc}(\gamma \cdot u)\,\mathrm{d}u &= -2 \int_{\zeta=0}^{+\infty} \zeta \cdot \Psi_p\left(\frac{\zeta}{\gamma}\right) \mathrm{d}\{\mathrm{erfc}(\zeta)\} \\ &= -2 \left\{ \left[\zeta \cdot \Psi_p\left(\frac{\zeta}{\gamma}\right) \cdot \mathrm{erfc}(\zeta) \right]_0^{+\infty} - \int_0^{+\infty} \left\{ \Psi_p\left(\frac{\zeta}{\gamma}\right) + \frac{\zeta}{\gamma} \cdot \Psi_p'\left(\frac{\zeta}{\gamma}\right) \right\} \mathrm{erfc}(\zeta)\,\mathrm{d}\zeta \right\} \\ &= 2\gamma \int_0^{+\infty} \left\{ \Psi_p(u) + u \cdot \Psi_p'(u) \right\} \cdot \mathrm{erfc}(\gamma \cdot u)\,\mathrm{d}u. \end{aligned}$$

Since $\gamma > 0$, we conclude that

$$\text{(C.16)}\quad \int_0^{+\infty} \Psi_p(u)\mathrm{erfc}(\gamma \cdot u)\,\mathrm{d}u = 2 \int_0^{+\infty} \left\{ \Psi_p(u) + u \cdot \Psi_p'(u) \right\} \mathrm{erfc}(\gamma \cdot u)\,\mathrm{d}u,$$

which is reduced to

$$\text{(C.17)}\quad \int_0^{+\infty} \left\{ \Psi_p(u) + 2u \cdot \Psi_p'(u) \right\} \cdot \mathrm{erfc}\left(\mu_p(t) \cdot u\right)\,\mathrm{d}u = 0.$$

Clearly, the right hand side of (C.17) does not depend on t, and since t formally only appears in $\mu_p(t)$, it is easy to conclude that $\gamma_p'(t) = 0$, so

$$\text{(C.18)}\quad \mu_p(t) = \mu_p \qquad \text{is independent of } t.$$

The identity (C.17) can now be written

$$\text{(C.19)}\quad \int_0^{+\infty} \left\{\Psi_p(u) + 2u \cdot \Psi_p'(u)\right\} \cdot \operatorname{erfc}\left(\mu_p \cdot u\right) \, \mathrm{d}u = 0.$$

We note that even if the variable of integration u given by (C.9) depends on t and $D(t)$, it is a so-called "dummy variable" in (C.19), so it is removed by the integration, since the limits of the integral do not depend on t or $D(t)$. Hence, equation (C.19) is independent of $D(t)$ and t. Thus, in principle (C.19) can be used to find μ_p as a function of p.

In practice this is not an easy task, because both $\Psi_p(u)$ and $\Psi_p'(u) \sim \Psi_{p-0.5}(u)$ occur in (C.19). Instead, it follows from an integration by parts of the right hand side of (C.16) that

$$\begin{aligned}
\int_0^{+\infty} \Psi_p(u) \operatorname{erfc}(\gamma \cdot u) \, \mathrm{d}u &= 2 \int_0^{+\infty} \left\{\Psi_p(u) + u \cdot \Psi_p'(u)\right\} \cdot \operatorname{erfc}(\gamma \cdot u) \, \mathrm{d}u \\
&= 2 \int_0^{+\infty} \frac{d}{du} \left\{u \cdot \Psi_p(u)\right\} \cdot \operatorname{erfc}(\gamma \cdot u) \, \mathrm{d}u \\
&= 2 \left[u \cdot \Psi_p(u) \cdot \operatorname{erfc}(\gamma \cdot u)\right]_0^{+\infty} - 2 \int_0^{+\infty} u \cdot \Psi_p(u) \cdot \frac{d}{du}\{\operatorname{erfc}(\gamma \cdot u) \, \mathrm{d}u \\
&= \frac{4}{\sqrt{\pi}} \int_0^{+\infty} u \cdot \Psi_p(u) \cdot \gamma \cdot \exp\left(-\gamma^2 u^2\right) \mathrm{d}u.
\end{aligned}$$

Hence, (C.19) is equivalent to

$$\text{(C.20)}\quad \int_0^{+\infty} \Psi_p(u) \cdot \left\{\operatorname{erfc}\left(\mu_p \cdot u\right) - \frac{4}{\sqrt{\pi}} \cdot u \cdot \mu_p \cdot \exp\left(-\mu_p^2 u^2\right)\right\} \mathrm{d}u = 0,$$

which is easier to use numerically, when we find $\gamma = \mu_p$ as a function of p.

Remark C.5 Note that (C.18) is easy to derive from (C.17) and difficult from the equivalent formula (C.20), while $\gamma = \mu_p$ is easier to compute from (C.20) than from (C.17). ◊

Finally, it follows from (C.14) and (C.6) that

$$\begin{aligned}
S^* &= S_p^*(t) = S_p(t) \cdot \mu_p \cdot \frac{\int_0^{+\infty} \Psi_p(u) \operatorname{erfc}\left(\mu_p u\right) \, \mathrm{d}u}{\int_0^{+\infty} \{\operatorname{erfc}(\zeta)\}^2 \mathrm{d}\zeta} \\
\text{(C.21)}\quad &= S \cdot \left\{\int_{t_{ex}}^{t} D(\tau) \, \mathrm{d}\tau\right\}^p \cdot \mu_p \cdot \frac{\int_0^{+\infty} \Psi_p(u) \operatorname{erfc}\left(\mu_p u\right) \, \mathrm{d}u}{\int_0^{+\infty} \{\operatorname{erfc}(\zeta)\}^2 \mathrm{d}\zeta}.
\end{aligned}$$

We immediately derive the important result that *the quotient*

$$\text{(C.22)}\quad \lambda_p := \frac{S^*(t)}{S_p(t)} = \mu_p \cdot \frac{\int_0^{+\infty} \Psi_p(u)\mathrm{erfc}\left(\mu_p u\right)\, \mathrm{d}u}{\int_0^{+\infty} \{\mathrm{erfc}(\zeta)\}^2 \mathrm{d}\zeta}$$

only depends on p and not on t [or $D(t)$]. Since $S_p(t)$ is increasing in t for fixed p, the same is true for $S_p^*(t)$.

It is not hard to prove by a partial integration that

$$\int \{\mathrm{erfc}(t)\}^2 \mathrm{d}t = t\{\mathrm{erfc}(t)\}^2 - \frac{2}{\sqrt{\pi}}\,\mathrm{erfc}(t)\cdot\exp\left(-t^2\right) + \sqrt{\frac{2}{\pi}}\cdot\mathrm{erfc}\left(\sqrt{2}\,t\right),$$

so the denominator of (C.22) becomes

$$\int_0^{+\infty} \{\mathrm{erfc}(t)\}^2 \mathrm{d}t = \frac{2}{\sqrt{\pi}} - \sqrt{\frac{2}{\pi}} = \sqrt{\frac{2}{\pi}}\left(\sqrt{2}-1\right) = \sqrt{\frac{2}{\pi}}\,\frac{1}{\left(\sqrt{2}+1\right)},$$

and (C.22) is simplified to

$$\text{(C.23)}\quad \lambda_p = \sqrt{\frac{\pi}{2}}\cdot\left(\sqrt{2}+1\right)\cdot\mu_p\cdot\int_0^{+\infty} \Psi_p(u)\mathrm{erfc}\left(\mu_p u\right)\,\mathrm{d}u,$$

which makes it easier to compute in practice.

These observations can now be applied in the following way. Let us for simplicity assume that $C_i = 0$ in (C.1), so the exact solution is given by

$$C(x,t) = S_p(t)\,\Psi_p\left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right),$$

while the best approximating error function "solution" is given by

$$C_{\text{approx}}(x,t) = S_p^*(t)\cdot\mathrm{erfc}\left(\mu_p\cdot\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right).$$

We see that we have the same expression

$$\text{(C.24)}\quad u = \frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}} := \frac{1}{T}$$

occurring in both expressions, so the relative error of using $C_{\text{approx}}(x,t)$ instead of the exact solution $C(x,t)$ is derived from the quotient

$$\text{(C.25)}\quad \frac{C_{\text{approx}}(x,t)}{C(x,t)} = \frac{S_p^*(t)}{S_p(t)} \cdot \frac{\operatorname{erfc}\left(\dfrac{\mu_p}{T}\right)}{\Psi_p\left(\dfrac{1}{T}\right)} = \lambda_p \cdot \frac{\operatorname{erfc}\left(\dfrac{\mu_p}{T}\right)}{\Psi_p\left(\dfrac{1}{T}\right)}.$$

A comparison of the graphs of $\Psi_p\left(\dfrac{1}{T}\right)$ and $\lambda_p \cdot \operatorname{erfc}\left(\dfrac{\mu_p}{T}\right)$ for some values of p indicates that the relative error of applying the approximating function $\lambda_p \cdot \operatorname{erfc}\left(\dfrac{\mu_p}{T}\right)$ instead of the exact solution $\Psi_p\left(\dfrac{1}{T}\right)$ is at most λ_p. Hence, it is important to compute tables of μ_p and λ_p, using the implicit formulæ (C.20) and (C.23). These are given in Section C.8, page 98 at the end of Chapter C.

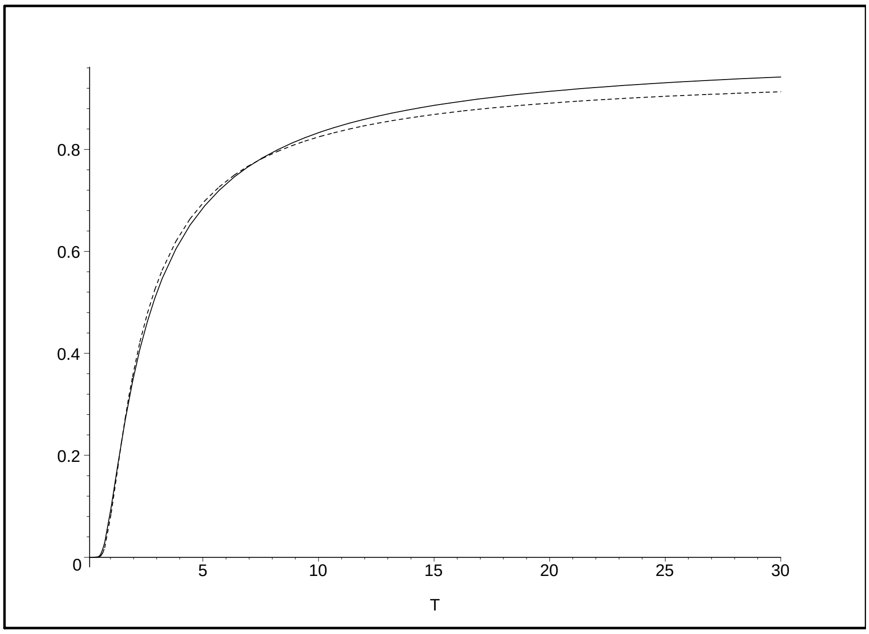

Figure C.1: The graphs of $\Psi_{0.5}(1/T)$ (full line) and the approximation $0.9577\operatorname{erfc}(1.2399/T)$ (dotted line).

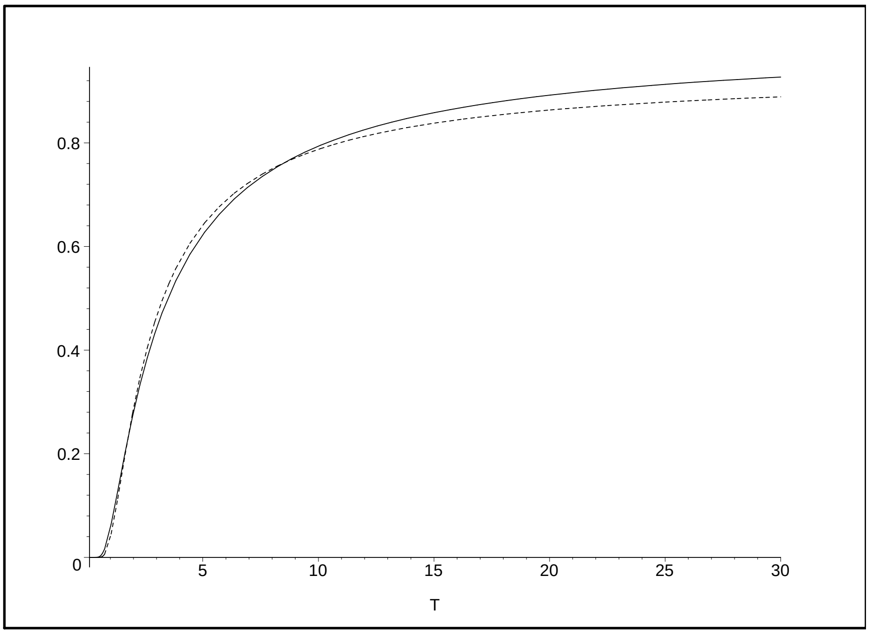

Figure C.2: The graphs of $\Psi_1(1/T)$ (full line) and the approximation $0.9400\mathrm{erfc}(1.4481/T)$ (dotted line).

C.5 The general results

Given Fick's second law in the special form

$$\begin{cases} \dfrac{\partial C}{\partial t} & = & D(t)\,\dfrac{\partial^2 C}{\partial x^2}, & x>0, \quad t>t_{ex} \\ C(0,t) & = & S\cdot\left\{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau\right\}^{p} := S_p(t), & t>t_{ex}, \\ C\left(x,t_{ex}\right) & = & C_i, & x>0, \end{cases}$$

the exact solution of which is given by

$$C(x,t) = S\cdot\left\{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau\right\}^{p} \psi_p\left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right) = S_p(t)\cdot\Psi_p\left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right).$$

This exact solution is approximated by a function of the type

$$C_{\mathrm{approx}}(x,t) = \lambda_p(t)\cdot S_p(t)\cdot\mathrm{erfc}\left(\mu_p(t)\cdot\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right).$$

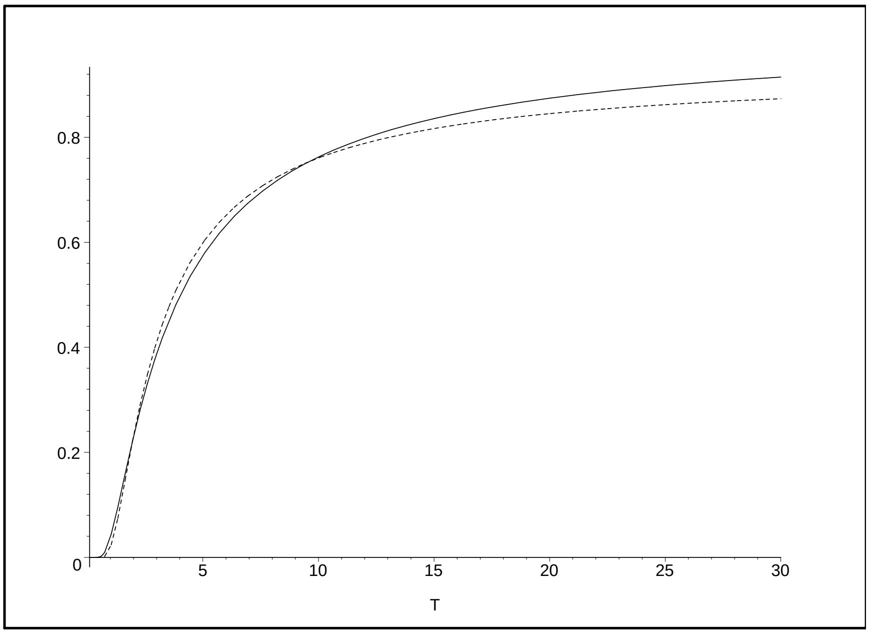

Figure C.3: The graphs of $\Psi_{1.5}(1/T)$ (full line) and the approximation $0.9305\mathrm{erfc}(1.6330/T)$ (dotted line).

The main results are

1) *The function $\mu_p(t) := \mu_p$ is constant in the variable t, and increasing in the parameter p. It is numerically found from the implicit expression (C.20), i.e.*

$$\int_0^{+\infty} \Psi_p(u) \cdot \left\{ erfc\left(\mu_p \cdot u\right) - \frac{4}{\sqrt{\pi}} \cdot u \cdot \mu_p \cdot \exp\left(-\mu_p^2 u^2\right) \right\} du = 0.$$

2) *The "approximating diffusion coefficient" $D^*(t)$ is given by*

$$D^*(t) = \frac{1}{\mu_p^2} D(t),$$

and the relationship between the averaged diffusion coefficient $D_{\mathrm{av}}(t)$ and the achieved diffusion coefficient $D_{\mathrm{ach}}(t)$ is similarly given by

$$D_{\mathrm{ach}}(t) = \frac{1}{\mu_p^2} D_{\mathrm{av}}(t),$$

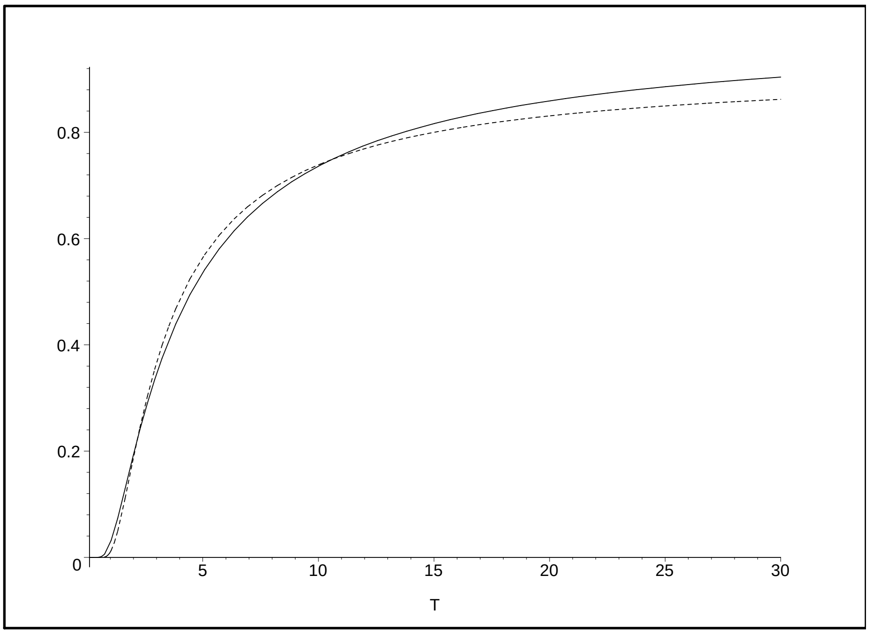

Figure C.4: The graphs of $\Psi_2(1/T)$ (full line) and the approximation $0.9247\mathrm{erfc}(1.8004/T)$ (dotted line).

3) The factor $\lambda_p(t)$ of the approximating solution is constant in the variable t and a decreasing function in the parameter p. It is given by

$$\frac{C_{approx}(x,t)}{C(x,t)} = \lambda_p \cdot \frac{\operatorname{erfc}\left(\mu_p \dfrac{x}{2\sqrt{\int_{t_{\mathrm{ex}}}^{t} D(\tau)\,d\tau}}\right)}{\Psi_p\left(\dfrac{x}{2\sqrt{\int_{t_{\mathrm{ex}}}^{t} D(\tau)\,d\tau}}\right)} = \lambda_p \cdot \frac{\operatorname{erfc}\left(\frac{\mu_p}{T}\right)}{\Psi_p\left(\dfrac{1}{T}\right)},$$

where

$$T := \frac{2}{x}\sqrt{\int_{t_{\mathrm{ex}}}^{t} D(\tau)\,\mathrm{d}\tau}.$$

We note that the square root occurs naturally, which is the already mentioned generalization of Uji's observation, cf. also Figure 6.1. It is numerically determined from the implicit relation

$$\lambda_p = \sqrt{\frac{\pi}{2}} \cdot \left(\sqrt{2}+1\right) \cdot \mu_p \cdot \int_0^{+\infty} \Psi_p(u)\,\operatorname{erfc}\left(\mu_p u\right)\,du.$$

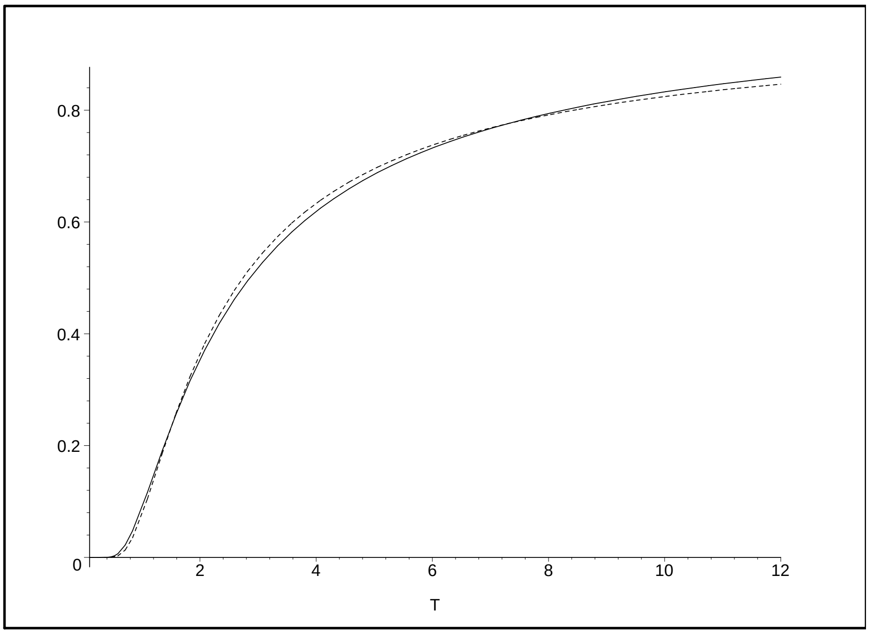

Figure C.5: The graphs of $\Psi_{0.5}(1/T)$ (full line) and the approximation $0.9577\,\mathrm{erfc}(1.2399/T)$ (dotted line) for $0 < T < 12$.

4) There are graphical indications of that the relative error of using $C_{approx}(x,t)$ instead of $C(x,t)$ is smaller than $1-\lambda_p$, for large T, cf. Figures C.1–C.4. In the case where $2 < T < 16$ the approximations are even much better, cf. Figures C.5–C.8

C.6 An important special case

It is customary to model the averaged diffusion coefficient $D_{\mathrm{av}}(t)$ by a power function, i.e.

$$D_{\mathrm{av}} = \frac{1}{t - t_{ex}} \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau := D_{\mathrm{aex}} \cdot \left\{ \frac{t_{ex}}{t} \right\}^{\alpha},$$

from which we derive by a differentiation that the point-wise diffusion coefficient is given by

$$D(t) = D_{\mathrm{av}}(t) + (t - t_{ex})\, D'_{\mathrm{av}}(t).$$

Then it follows by the general results in the previous section that

$$D^*_{\mathrm{av}}(t) = D^*_{\mathrm{aex}} \left\{ \frac{t_{ex}}{t} \right\}^{\alpha^*} = \frac{1}{\mu_p^2}\, D_{\mathrm{av}}(t) = \frac{D_{\mathrm{aex}}}{\mu_p^2} \left\{ \frac{t_{ex}}{t} \right\}^{\alpha},$$

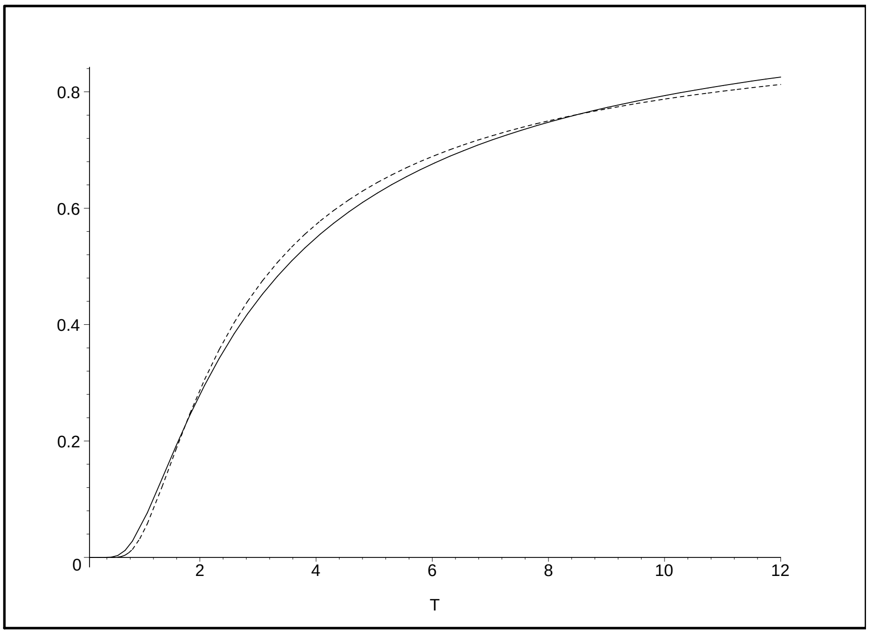

Figure C.6: The graphs of $\Psi_1(1/T)$ (full line) and the approximation $0.9400\,\mathrm{erfc}(1.4481/T)$ (dotted line) for $0 < T < 12$.

so by identification,

$$D^*_{\text{aex}} = \frac{1}{\mu_p^2}\,D_{\text{aex}} \qquad \text{and} \qquad \alpha^* = \alpha.$$

C.7 The limits of the approximation (C.26) when $2 < T < 16$.

When we consider the Figures C.5–C.8) we see that the modified erfc approximation

$$\text{(C.26)}\quad C_{\text{approx}}(x,t) = \lambda_p \cdot S_p(t) \cdot \mathrm{erfc}\left(\mu_p \cdot \frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right)$$

has a very small *relative error*, when it is compared with the correct solution

$$\text{(C.27)}\quad C(x,t) = S_p(t) \cdot \Psi_p\left(\frac{x}{2\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau}}\right)$$

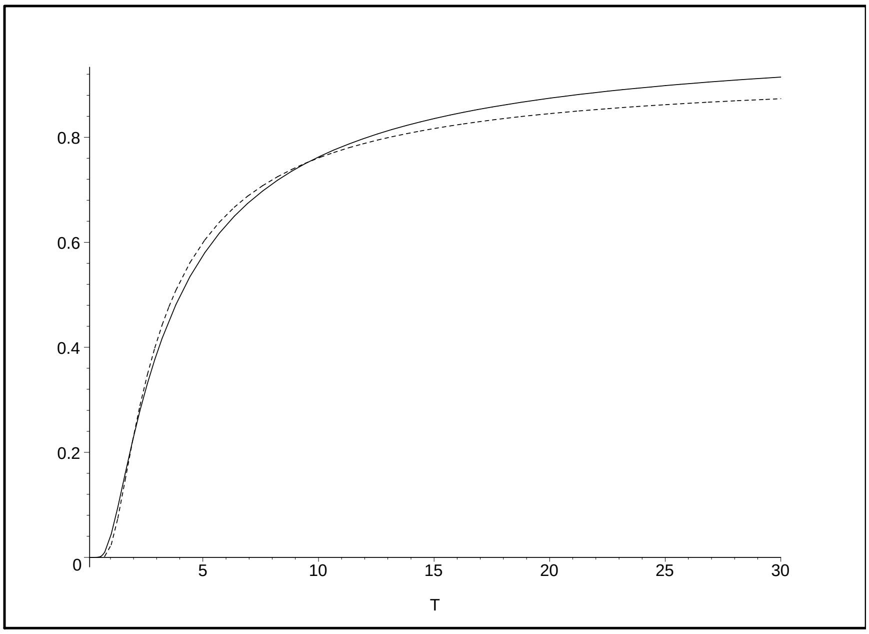

Figure C.7: The graphs of $\Psi_{1.5}(1/T)$ (full line) and the approximation $0.9305\,\mathrm{erfc}(1.6330/T)$ (dotted line) for $0 < T < 12$.

for $2 < T < 16$. It is indicated in Appendix C that the relative error for large $T \in \mathbb{R}_+$ is $\leq 1 - \lambda_p$, but if we restrict ourselves to this smaller interval $2 < T < 16$, then the relative error becomes much smaller. It is therefore worth while to investigate under what circumstances the variable T lies in this desirable and moderate interval $2 < T < 16$.

Since

$$\text{(C.28)}\quad T = \frac{2}{x}\sqrt{\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau} > 0 \qquad \text{for } t > t_{ex},$$

it follows that $2 < T < 16$, if

$$\text{(C.29)}\quad x^2 < \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau < 64x^2.$$

Assume that $D(t) \leq D^*$ for some constant $D^* > 0$. Then

$$\int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau \leq D^* \cdot (t - t_{ex}) \leq D^* \cdot t,$$

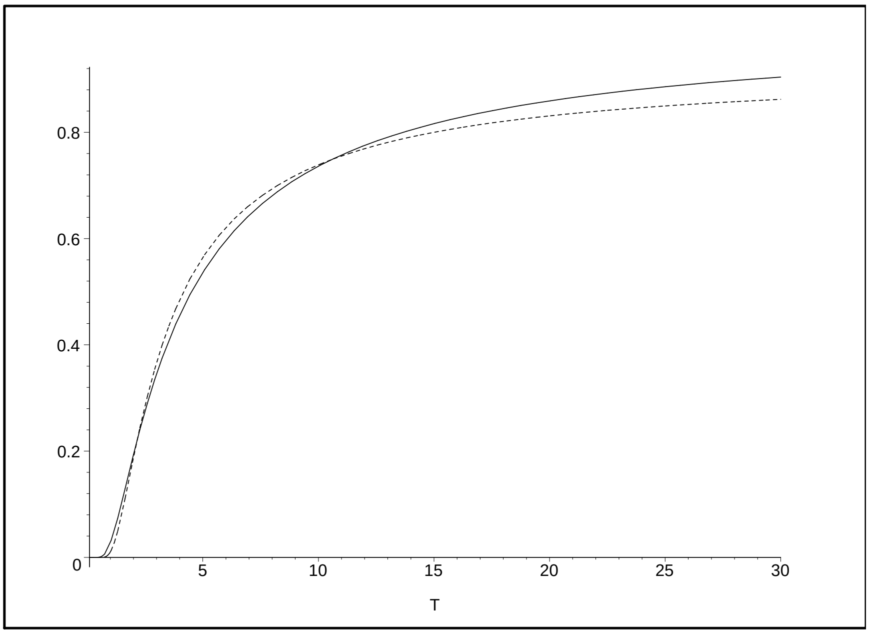

Figure C.8: The graphs of $\Psi_2(1/T)$ (full line) and the approximation $0.9247\,\mathrm{erfc}(1.8004/T)$ (dotted line) for $0 < T < 12$.

so the right hand side of (C.29) is fulfilled, if

$$\text{(C.30)}\quad t < \frac{64x^2}{D^*} = t_0\left(x, D^*\right) = t_0.$$

Thus, for $t_{ex} < t < t_0\left(x, D^*\right)$ we may in the first approximation successfully use the modified erfc "solution" (C.26), and in this way avoid the Ψ_p function.

In Table C.1 we have computed the upper bound t_0 yr from (C.30) for various values of x mm and D^* mm^2/yr.

In Table C.2 and Table C.3 we have computed the relative error

$$\frac{C_{\text{approx}}(x,t) - C_\Psi(x,t)}{C_\Psi(x,t)} \cdot 100\ \%,$$

of the approximative solution $C_{\text{approx}}(x,t)$, when $1 \leq T \leq 16$, from which follows that the relative approximation is very poor for $T = 1$ and not for $2 \leq T \leq 16$, and in many cases even for $2 \leq T < +\infty$.

$D^* \setminus x$	5.00	10.00	20.00	30.00	40.00	50.00	75.00	100.00
5	180.00	720.00						
10	90.00	360.00						
15	60.00	240.00	960.00					
20	45.00	180.00	720.00					
25	36.00	144.00	560.00					
50	18.00	72.00	288.00	648.00				
100	9.00	36.00	144.00	324.00	576.00	900.00		
150	6.00	24.00	96.00	216.00	384.00	600.00		
200	4.50	18.00	72.00	162.00	288.00	450.00		
250	3.60	14.40	57.60	129.60	230.40	360.00	810.00	
300	3.00	12.00	48.00	108.00	192.00	300.00	675.00	
350	2.57	10.29	41.14	92.57	164.57	257.14	578.57	
400	2.25	9.00	36.00	81.00	144.00	225.00	506.25	900.00
450	2.00	8.00	32.00	72.00	128.00	200.00	450.00	800.00
500	1.80	7.20	28.80	64.80	115.20	180.00	405.00	720.00
600	1.50	6.00	24.00	54.00	96.00	150.00	337.50	600.00
700	1.29	5.14	20,57	46.29	82.29	128.57	289.29	514.29
800	1.13	4.50	18.00	40.50	72.00	112.50	253.13	450.00
900	1.00	4.00	16.00	36.00	64.00	100.00	225.00	400.00
1000	0.90	3.60	14.40	32.40	57.60	90.00	202.50	360

Table C.1: Table of the upper bound $t_0 = 36x^2/D^*$ for the time t (in years), for which the modified erfc approximation (C.26) can be applied with a small relative error. This approximation can be successfully applied, when $D(t) \leq D^*$ and $t_{ex} < t \leq t_0\,(x, D^*)$ When $t_0 > 1000$ years, it is omitted.

C.8 Tables of μ_p and λ_p

The tables below were first found by using numerical methods on the formulæ (C.20) and (C.22). Once the tables were calculated we derived the following approximating polynomials, which may also be useful,

(C.31) $\lambda_p \approx 1 - 0.1287\,p + 0.1104\,p^2 - 0.0509\,p^3 + 0.0093\,p^4$

and

(C.32) $\mu_p \approx 1 + 0.5194\,p - 0.0876\,p^2 + 0.0185\,p^3 - 0.0022\,p^4.$

$p \backslash T$	1	2	3	4	5	6	7	8	9	10
0.1	-2.11	0.97	0.79	0.48	0.23	0.04	-0.11	-0.23	-0.32	-0.40
0.2	-4.74	1.73	1.50	0.96	0.50	0.15	-0.13	-0.36	-0.54	-0.69
0.3	-7.74	2.31	2.16	1.43	0.81	0.31	-0.08	-0.39	-0.65	-0.86
0.4	-11.03	2.73	2.74	1.89	1.12	0.50	0.02	-0.38	-0.70	-0.96
0.5	-14.50	3.02	3.27	2.33	1.44	0.72	0.15	-0.31	-0.69	-1.00
0.6	-18.10	3.17	3.75	2.74	1.76	0.95	0.30	-0.22	-0.65	-1.01
0.7	-21.79	3.20	4.16	3.14	2.07	1.18	0.47	-0.11	-0.59	-0.98
0.8	-25.50	3.14	4.53	3.51	2.38	1.43	0.65	0.02	-0.49	-0.93
0.9	-29.19	2.98	4.86	3.86	2.68	1.67	0.84	0.17	-0.39	-0.86
1.0	-32.85	2.73	5.13	4.19	2.98	1.91	1.04	0.32	-0.27	-0.77
1.1	-36.43	2.40	5.37	4.49	3.25	2.14	1.22	0.47	-0.16	-0.68
1.2	-39.92	2.09	5.57	4.78	3.52	2.37	1.42	0.63	-0.03	-0.58
1.3	-43.32	1.56	5.74	5.05	3.78	2.61	1.61	0.79	0.11	-0.47
1.4	-46.59	1.05	5.87	5.29	4.03	2.83	1.80	0.95	0.24	-0.36
1.5	-49.76	0.49	5.97	5.52	4.26	3.04	1.99	1.11	0.38	-0.24
1.6	-52.78	-0.12	6.05	5.73	4.49	3.25	2.18	1.27	0.51	-0.13
1.7	-55.68	-0.77	6.10	5.93	4.71	3.46	2.36	1.44	0.66	-0.00
1.8	-58.49	-1.47	6.11	6.11	4.91	3.65	2.54	1.59	0.79	0.11
1.9	-61.07	-2.19	6.11	6.28	5.12	3.86	2.72	1.75	0.94	0.24
2.0	-63.57	-2.95	6.08	6.43	5.31	4.04	2.89	1.91	1.07	0.36

Table C.2: The relative error in % of the modified erfc approximation for $1 \leq T \leq 10$ and $0.1 \leq p \leq 2.0$.

$p \backslash T$	11	12	13	14	15	16	∞
0.1	-0.48	-0.53	-0.58	-0.63	-0.66	-0.70	-1.23
0.2	-0.81	-0.92	-1.01	-1.09	-1.16	-1.22	-2.22
0.3	-1.04	-1.19	-1.32	-1.43	-1.53	-1.62	-3.02
0.4	-1.18	-1.37	-1.53	-1.68	-1.80	-1.91	-3.68
0.5	-1.27	-1.49	-1.68	-1.85	-2.00	-2.13	-4.23
0.6	-1.31	-1.56	-1.78	-1.98	-2.14	-2.29	-4.70
0.7	-1.31	-1.60	-1.84	-2.06	-2.25	-2.41	-5.10
0.8	-1.29	-1.60	-1.87	-2.10	-2.31	-2.49	-5.44
0.9	-1.25	-1.58	-1.87	-2.13	-2.35	-2.55	-5.74
1.0	-1.19	-1.55	-1.86	-2.13	-2.36	-2.57	-6.00
1.1	-1.13	-1.51	-1.84	-2.12	-2.37	-2.60	-6.24
1.2	-1.05	-1.45	-1.80	-2.10	-2.36	-2.60	-6.45
1.3	-0.96	-1.38	-1.74	-2.06	-2.34	-2.58	-6.63
1.4	-0.87	-1.31	-1.68	-2.01	-2.31	-2.56	-6.80
1.5	-0.77	-1.23	-1.62	-1.96	-2.27	-2.53	-6.95
1.6	-0.67	-1.14	-1.55	-1.91	-2.22	-2.50	-7.09
1.7	-0.57	-1.05	-1.47	-1.84	-2.16	-2.45	-7.21
1.8	-0.47	-0.97	-1.40	-1.78	-2.12	-2.41	-7.33
1.9	-0.36	-0.87	-1.31	-1.70	-2.05	-2.36	-7.43
2.0	-0.25	-0.78	-1.24	-1.64	-1.99	-2.31	-7.53

Table C.3: The relative error in % of the modified erfc approximation for $0.1 \leq p \leq 2.0$ and for $11 \leq T \leq 16$ (and $1 - \lambda_p$ when $T = +\infty$).

p	+0.00	+0.01	+0.02	+0.03	+0.04	+0.05	+0.06	+0.07	+0.08	+0.09
0.0	1.0000	1.0052	1.0103	1.0155	1.0206	1.0257	1.0308	1.0359	1.0409	1.0460
0.1	1.0510	1.0560	1.0610	1.0660	1.0710	1.0759	1.0808	1.0858	1.0907	1.0955
0.2	1.1004	1.1053	1.1101	1.1149	1.1197	1.1245	1.1293	1.1341	1.1389	1.1436
0.3	1.1483	1.1530	1.1577	1.1624	1.1671	1.1717	1.1763	1.1810	1.1856	1.1902
0.4	1.1948	1.1993	1.2039	1.2084	1.2130	1.2175	1.2220	1.2265	1.2310	1.2354
0.5	1.2399	1.2443	1.2487	1.2532	1.2576	1.2620	1.2663	1.2707	1.2751	1.2794
0.6	1.2837	1.2881	1.2924	1.2967	1.3009	1.3052	1.3095	1.3137	1.3180	1.3222
0.7	1.3264	1.3306	1.3348	1.3390	1.3432	1.3473	1.3515	1.3556	1.3598	1.3639
0.8	1.3680	1.3721	1.3762	1.3802	1.3843	1.3884	1.3924	1.3964	1.4005	1.4045
0.9	1.4085	1.4125	1.4165	1.4205	1.4244	1.4284	1.4323	1.4363	1.4402	1.4441
1.0	1.4481	1.4519	1.4558	1.4597	1.4636	1.4675	1.4713	1.4752	1.4790	1.4828
1.1	1.4867	1.4905	1.4943	1.4981	1.5019	1.5056	1.5094	1.5132	1.5169	1.5207
1.2	1.5244	1.5281	1.5319	1.5356	1.5393	1.5430	1.5468	1.5504	1.5541	1.5577
1.3	1.5614	1.5650	1.5686	1.5722	1.5759	1.5795	1.5831	1.5867	1.5903	1.5939
1.4	1.5975	1.6011	1.6047	1.6086	1.6118	1.6153	1.6189	1.6224	1.6259	1.6294
1.5	1.6330	1.6365	1.6400	1.6434	1.6469	1.6504	1.6539	1.6573	1.6608	1.6642
1.6	1.6677	1.6711	1.6746	1.6780	1.6814	1.6848	1.6882	1.6916	1.6950	1.6984
1.7	1.7018	1.7051	1.7085	1.7119	1.7152	1.7185	1.7219	1.7253	1.7286	1.7319
1.8	1.7353	1.7385	1.7419	1.7452	1.7485	1.7517	1.7550	1.7583	1.7616	1.7648
1.9	1.7681	1.7714	1.7746	1.7779	1.7811	1.7843	1.7876	1.7908	1.7940	1.7972
2.0	1.8004									

Table C.4: Table of μ_p.

p	+0.00	+0.01	+0.02	+0.03	+0.04	+0.05	+0.06	+0.07	+0.08	+0.09
0.0	1.0000	0.9986	0.9972	0.9960	0.9947	0.9935	0.9922	0.9911	0.9899	0.9888
0.1	0.9877	0.9866	0.9855	0.9845	0.9835	0.9825	0.9815	0.9806	0.9796	0.9787
0.2	0.9778	0.9770	0.9761	0.9752	0.9744	0.9736	0.9728	0.9721	0.9713	0.9706
0.3	0.9698	0.9691	0.9684	0.9677	0.9671	0.9664	0.9657	0.9651	0.9645	0.9638
0.4	0.9632	0.9626	0.9620	0.9615	0.9609	0.9604	0.9598	0.9593	0.9588	0.9582
0.5	0.9577	0.9572	0.9567	0.9562	0.9558	0.9553	0.9548	0.9544	0.9539	0.9535
0.6	0.9530	0.9526	0.9522	0.9517	0.9514	0.9510	0.9506	0.9502	0.9498	0.9494
0.7	0.9490	0.9487	0.9483	0.9480	0.9476	0.9472	0.9469	0.9466	0.9463	0.9459
0.8	0.9456	0.9453	0.9450	0.9446	0.9443	0.9440	0.9437	0.9434	0.9432	0.9429
0.9	0.9426	0.9423	0.9420	0.9418	0.9415	0.9412	0.9410	0.9407	0.9404	0.9402
1.0	0.9400	0.9397	0.9394	0.9392	0.9390	0.9388	0.9385	0.9383	0.9381	0.9378
1.1	0.9376	0.9374	0.9372	0.9370	0.9368	0.9366	0.9364	0.9361	0.9359	0.9357
1.2	0.9355	0.9353	0.9352	0.9350	0.9348	0.9346	0.9344	0.9342	0.9341	0.9339
1.3	0.9337	0.9335	0.9333	0.9331	0.9330	0.9328	0.9326	0.9325	0.9323	0.9322
1.4	0.9320	0.9318	0.9317	0.9316	0.9314	0.9312	0.9311	0.9309	0.9308	0.9306
1.5	0.9305	0.9304	0.9302	0.9301	0.9299	0.9298	0.9297	0.9295	0.9294	0.9292
1.6	0.9291	0.9290	0.9289	0.9287	0.9286	0.9285	0.9283	0.9282	0.9281	0.9280
1.7	0.9279	0.9277	0.9276	0.9275	0.9274	0.9273	0.9272	0.9271	0.9269	0.9268
1.8	0.9267	0.9266	0.9265	0.9264	0.9263	0.9262	0.9261	0.9260	0.9259	0.9258
1.9	0.9257	0.9256	0.9255	0.9254	0.9253	0.9252	0.9251	0.9250	0.9249	0.9248
2.0	0.9247									

Table C.5: Table of λ_p.

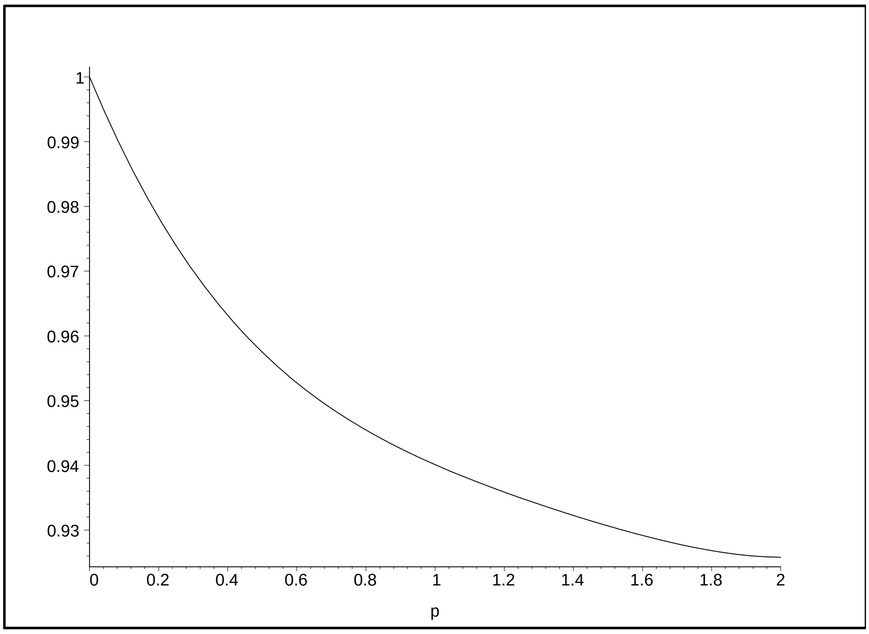

Figure C.9: The graph of μ_p and its polynomial approximation.

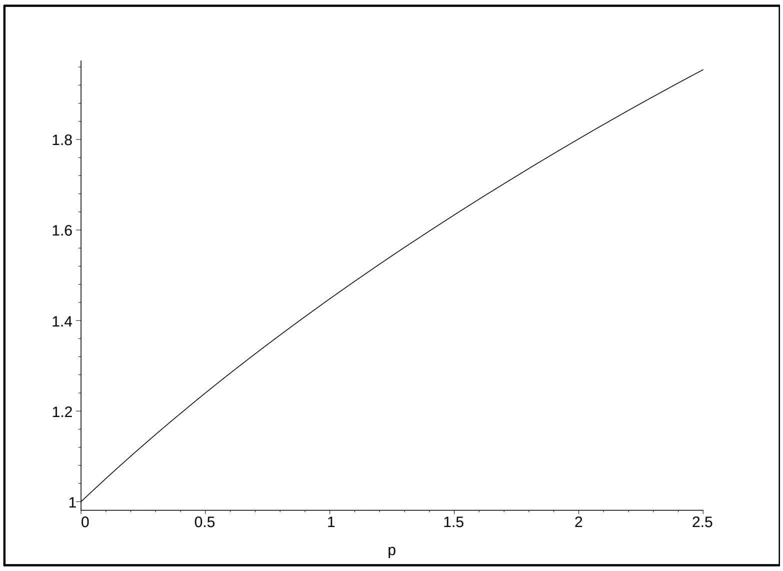

Figure C.10: The graph of λ_p and its polynomial approximation.

Appendix D

Alternative model 1 for $D_{av}(t)$

For completeness we return to the alternative model 1 for $D_{av}(t)$, already mentioned in Section 7.4. We choose the model

$$\text{(D.1)}\quad D_{av}(t) = \tilde{D}_{\text{av,ex}} \left\{ \frac{t_{ex}}{t - t_{ex}} \right\}^{\alpha}, \qquad t > t_{ex}, \qquad 0 \le \alpha < 1.$$

Then the change of variable (5.2) becomes

$$\begin{aligned} T &:= \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau = (t - t_{ex})\, D_{av}(t) = \tilde{D}_{\text{av,ex}}\,(t - t_{ex}) \cdot \left\{ \frac{t_{ex}}{t - t_{ex}} \right\}^{\alpha} \\ \text{(D.2)} \quad &= \tilde{D}_{\text{av,ex}} \cdot t_{ex}^{\alpha} \cdot (t - t_{ex})^{1-\alpha}, \qquad t > t_{ex}. \end{aligned}$$

It follows from the assumption $0 \le \alpha < 1$ that $0 < 1 - \alpha \le 1$, hence we can find the inverse of (D.2), which is given by

$$\text{(D.3)}\quad t = t_{ex} + \left\{ \frac{T}{\tilde{D}_{\text{av,ex}} \cdot t_{ex}^{\alpha}} \right\}^{1/(1-\alpha)} = t_{ex} + \text{ const. } T^{1/(1-\alpha)}, \qquad T \ge 0.$$

In other words, by choosing the model (D.1) instead of (7.9) it becomes possible explicitly to find the inverse $t = t(T)$ as a function (D.3) of T.

Notice that if we allowed $\alpha = 1$, then (D.2) would degenerate to $T =$ constant, and we could not use T as a new variable. Thus, we have to exclude $\alpha = 1$.

Using the same model (D.1), problem (7.5) is then written with obvious modifications of notation,

$$\text{(D.4)}\quad \begin{cases} \dfrac{\partial C}{\partial t} = D(t)\,\dfrac{\partial^2 C}{\partial x^2}, & x > 0, \quad t > t_{ex}, \\[2ex] C(0,t) = C_i + S_{\alpha,p}\cdot (t - t_{ex})^{(1-\alpha)p}, & t > t_{ex}, \\[2ex] C\,(x, t_{ex}) = C_i, & x > 0, \end{cases}$$

where

$$\text{(D.5)}\quad D(t) = (1-\alpha)\tilde{D}_{\text{av,ex}} \left\{ \frac{t_{ex}}{t - t_{ex}} \right\}^{\alpha} = (1-\alpha) D_{av}(t) \quad \text{and} \quad S_{\alpha,p} = S \cdot \tilde{D}^{p}_{\text{av,ex}} \cdot t_{ex}^{\alpha p}.$$

The solution of (D.4) is then

$$\text{(D.6)}\quad C(x,t) = C_i + S_{\alpha,p}\,(t - t_{ex})^{1-\alpha} \cdot \Psi_p \left(\frac{x}{2\sqrt{S_{\alpha,p}\,(t - t_{ex})^{1-\alpha}}} \right),$$

which is easier to handle in practice than (7.9), where [cf. the definition of $D_{av}(t)$]

(D.7)

$$T := \int_{t_{ex}}^{t} D(\tau)\,\mathrm{d}\tau = (t - t_{ex})\,D_{av}(t) = D_{\text{av,ex}} \cdot t_{ex} \left(\left\{ \frac{t}{t_{ex}} \right\}^{1-\alpha} - \left\{ \frac{t_{ex}}{t} \right\}^{\alpha} \right), \qquad t > t_{ex}.$$

Notice that none of the two models is wrong. They are *different* from each other and therefore must give different results.

The advantages of using (D.1) instead of (7.9) are as follows:

1) We refer the model of diffusivity to the time of first exposure and not to the time of casting.

2) The change of variable (D.2), i.e.

$$T = \tilde{D}_{\text{av,ex}} \cdot t_{ex}^{\alpha} \cdot (t - t_{ex})^{1-\alpha}, \qquad t > t_{ex}., \qquad 0 \le \alpha < 1,$$

is simpler in its structure than (D.7).

3) The inverse of (D.2) is explicitly given by (D.3), i.e.

$$t = t_{ex} + \left\{ \frac{T}{\tilde{D}_{\text{av,ex}} \cdot t_{ex}^{\alpha}} \right\}^{1/(1-\alpha)} = t_{ex} + \text{ const. } T^{1/(1-\alpha)}, \qquad T \ge 0,$$

while the inverse of (D.7) can only be found explicitly for $\alpha = 0, \frac{1}{2}$, (and with some knowledge of *Cardano's* formulæ, also for $\alpha = \frac{1}{3}, \frac{2}{3}$, and $\alpha = \frac{1}{4}, \frac{3}{4}$, but the formulæ of these four additional values of α are extremely difficult to implement).

4) Since the inverse of (D.2) is explicitly given by (D.3), so $t = t(T)$ is a known function, it will in the future be possible to extend problem (D.4) to cases, where the boundary condition is more general like

   $$C(0,t) = C_i + S_p(t), \qquad t > t_{ex}, \quad n \leq \alpha < 1,$$

   by simply inserting $t = t(T)$ and then approximate the new function in the variable T. In the case of (7.9), this is only possible for the very special values of α already mentioned in 3) above.

5) The structure of solution for the model (D.2), i.e. (D.6), is simpler than the solution when (7.9) is chosen as our model.

6) The relationship between $D(t)$ and $D_{av}(t)$ is very simple for the model (D.2), namely

   $$D(t) = (1-\alpha)D_{av}(t), \qquad t > t_{ex}, \quad 0 \leq \alpha < 1.$$

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