THE CHLORIDE DIFFUSION CHARACTERISTICS OF CONCRETE
Approximative determination by linear regression analysis

Ervin Poulsen
AEC Rådgivende Ingeniører A/S.
Holte Midtpunkt 23-3,
DK-2840 Holte, Denmark.

ABSTRACT

The chloride ingress into concrete has been shown to obey Fick's second law of diffusion, cf. /2/, /4/ and /5/. The complexity of the equation derived from Fick's second law of diffusion is a hindrance when the chloride diffusion characteristics have to be determined by laboratory tests. Only non-linear curve-fitting is available, e.g. by applying the Gauss-Newton method.

However, a simple approximation makes it possible to determine the chloride diffusion characteristics by linear curve-fitting and the paper describes how it is possible to obtain a good estimate by applying a small pocket-computer.

Keywords. Chloride profile, diffusion, approximation, curve-fitting.

1.INTRODUCTION

Penetration of chloride into concrete is assumed to occur owing to several types of transport processes, i.e. permeation, imbibition and diffusion. The ingress of the chloride ions into the concrete from its environment will increase the chloride concentration of the concrete in its surface layers. The graph of the chloride concentration versus the distance perpendicular to the concrete surface is called the chloride profile. A chloride profile changes with time since more chloride will penetrate from the environment and the chloride already in the concrete tends to penetrate further into the concrete towards less chloride concentration.

Chloride penetration into concrete by permeation, imbibition and diffusion obeys different laws and shall be treated mathematically in different ways. The total quantity of chloride ions entering the concrete through a unit area of the surface varies with the transport process and normally chloride diffusion seems to be the predominant transport process of the penetration of chloride into the concrete for marine structures, cf. /5/.

2. THE PROCESS OF DIFFUSION

Chloride diffusion is the process by which chloride is transported from one part of wet concrete to another through the capillary pores as a result of random motion of the chloride ions. The chloride ions diffuse towards the part of the concrete having a lower concentration of chloride.

The mathematical theory of normal diffusion in an isotropic substance is based upon the hypothesis that the rate of transfer of a diffusion substance through a unit area of a section of the medium is proportional to the concentration gradient measured normal to the section, i.e.

$$F = -D \cdot \frac{\partial C}{\partial x} \tag{1}$$

This is referred to as *Fick's first law of diffusion*. Here D is the diffusion coefficient, and the negative sign denotes that the transfer of substance occurs in the direction of decreasing concentration.

Diffusion processes which do not obey Fick's law are called non-Fickian diffusion or anomalous diffusion.

The above given definition of normal diffusion is the basis for the calculation of the diffusion processes. However, for non-steady conditions it is convenient to apply the following expression:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \cdot \frac{\partial C}{\partial x}\right) \tag{2}$$

when a one-dimensional case is considered. This expression is derived from Fick's first law of diffusion, cf. /3/ and /7/. For the special condition, when $D = D_o$ is a constant, equation (2) yields:

$$\frac{\partial C}{\partial t} = D_o \cdot \frac{\partial^2 C}{\partial x^2} \tag{3}$$

This is referred to as *Fick's second law of diffusion*.

3. ON THE CHLORIDE DIFFUSION INTO CONCRETE

In the case of chloride diffusion into concrete it must be remembered that concrete is neither an isotropic medium nor a homogeneous material. All concrete consists of paste, aggregrates and defects. In most cases aggregates are considered to be impermeable to chloride ingress while diffusion of chloride ions can easily take place through the paste and the defects.

However, for many problems encountered in practice it is sufficient to consider concrete as a quasi homogeneous material the diffusion of chloride ions of which can be considered to obey Fick's laws of diffusion.

The chloride diffusion coefficient of concrete will not only vary with the properties and characteristics of the concrete, i.e.

- The water/cement-ratio of the concrete.
- The type of the cementitious materials.

but also with the condition of the concrete, i.e.

- The maturity of the concrete (degree of hydration).

- The effectiveness of the curing (hydration, cracks and defects).

and the environmental conditions, i.e.

- The temperature of the environment and the concrete.
- The chloride concentration of the environment.

In general the chloride diffusion coefficient of a given concrete with saturated pores depends on the maturity age M of the concrete, the location in the concrete, i.e. the distance x from the exposed concrete surface, and the temperature T of the concrete. Thus, the chloride diffusion coefficient can be written as:

$$D = D(x, M, T) \tag{4}$$

If concrete is sufficiently cured its dependence on x can be neglected. In laboratory tests it is possible to keep T constant and in short-term laboratory tests the influence of M can be neglected if the concrete is not green. Thus, for practical purposes chloride diffusion into concrete can be approximated by a Fickian diffusion on the assumption that the chloride diffusion coefficient is constant. Many civil engineering problems can be solved in this way with sufficient accuracy. However, one must never forget that these assumptions are approximations and may yield to wrong conclusions in extreme situations.

4. THE MATHEMATICAL MODEL

A very common case in engineering practice is the chloride diffusion into a volume of concrete, assumed to behave as a semi-infinite medium. In this case the solution to Fick's second law of diffusion, equation 3, yields:

$$C(x,t) = C_i + (C_s - C_i) \cdot \mathrm{erfc}\frac{x}{\sqrt{4 \cdot t \cdot D_o}} \tag{5}$$

Here,

$C(x,t)$ denotes the chloride profile, i.e. the chloride concentration of the concrete versus the distance x from the exposed surface at the time t, since the chloride exposure started.

C_i denotes the initial chloride concentration of the concrete (to be found deep in the concrete).

C_s denotes the chloride concentration of the concrete surface.

D_o denotes the chloride diffusion coefficient (here assumed to be a constant).

The function $y = \mathrm{erfc}(z)$ is referred to as the error-function complement defined by the following expression:

$$\mathrm{erfc}(z) = 1 - \mathrm{erf}(z) \tag{6}$$

where the error function erf(z) is defined by

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \cdot \int_0^z \exp(-\zeta^2) \cdot d\zeta \tag{7}$$

The table of the error-function complement is found in mathematical handbooks. Thus it is easy to calculate a chloride profile, when the parameters of chloride ingress C_s, D_o and C_i are known, cf. /7/.

5. THE COVERCRETE AND THE HEARTCRETE

The concrete near to the surface of a structural member forms the protection of the rebars. This concrete cover (covercrete) can be very much poorer than the concrete in the interior of a structural member (heartcrete) due to a high concentration of defects. When found, the defects of the covercrete are often caused by the work site effects of poor workmanship and insufficient curing.

The defects can be classified as cracks and separation of constituents of the concrete. Such defects occur on both the macro and the micro scale.

The chloride diffusion characteristics depend on the constituents and the mix proportions of the concrete as well as on the concentration of the defects in the concrete. Thus, it is important to distinguish between the diffusion characteristics of the covercrete and the heartcrete of a structural member of reinforced concrete.

Furthermore, it is impossible to achieve realistic values of the chloride diffusion characteristics by testing labcrete; only realcrete will lead to reliable test results, including the greater variation in practice.

6. EXPERIMENTAL DETERMINATION OF CHLORIDE DIFFUSION PARAMETERS

Concrete cores with a diameter of approximately 100 mm are drilled from a concrete full-scale trial casting. When the diffusion properties of the heartcrete are to be determined the covercrete of the cores is removed by cutting at least 150 mm from the surface part of the core. When the diffusion properties of the covercrete are to be determined it is important to make a correction for the variation of the concentration of the paste with the distance from the surface, e.g. by determination of the calcium profile. The paste concentration of the concrete is higher in the covercrete than in the heartcrete, cf. /1/, due to the systematic variation of aggregates versus the distance from the concrete surface.

The whole surface of the core, except for the top and the bottom parts, shall be covered by an epoxy or a polyurethane coating in order to prevent chloride ingress when exposed to a liquid containing a high concentration of chloride. The exposure must last 35-65 days or at least long enough for the chloride ingress into the concrete to exceed approximately 10-15 mm. The exposure temperature must be fixed during the chloride ingress test, since chloride diffusion depends on the temperature.

It is possible to determine the chloride profile of the concrete by milling off powder from the core and by carrying out a chloride analysis of the powder.

7. NON-LINEAR CURVE-FITTING OF A CHLORIDE PROFILE

Quantitative measurements of the chloride concentration of concrete versus the distance from the exposed concrete surface determine the chloride profile in concrete exposed to a solution of chloride. From this chloride profile the three parameters C_s, D_o and C_i shall be determined by means of regression analysis. However, the mathematical expression of the chloride profile given by equation (5) is a transcendental function in x and t. This means that a non-linear regression analysis must be applied.

This fact makes it rather inconvenient to determine C_s, D_o and C_i and it requires a computer programme in order to run the process. Furthermore, it is neccessary to estimate a set of C_s, D_o and C_i before starting the iteration procedure.

In the following a way of finding a suitable set of C_s, D_o and D_i is shown. In many cases a guess like this is found to be fully satisfactory for the estimation of the chloride diffusion parameters for many engineering purposes.

8. AN APPROXIMATION OF THE CHLORIDE PROFILE

Both rational approximation as well as infinite series expansions have often been suggested in order to make an easy calculation of the error function complement erfc(z). However, for engineering purposes a very simple approximation makes it possible to overcome the difficulties described above. The following is such an approximation:

$$\mathrm{erf}(z) \approx \left(1-\frac{z}{\sqrt{3}}\right)^2 \qquad (8)$$

valid in the interval $0 \le z < \sqrt{3}$. For $z \ge \sqrt{3}$ the following approximation $\mathrm{erfc}(z) \approx 0$ is applied. By the approximation, equation (8), the chloride profile yields the following expression:

$$C(x,t) \approx C_i + (C_s - C_i) \cdot \left(1-\frac{x}{\sqrt{12 \cdot t \cdot D_o}}\right)^2 \qquad (9)$$

valid in the interval $0 \le x < \sqrt{12 \cdot t \cdot D_o}$. For $x \ge \sqrt{12 \cdot t \cdot D_o}$ the chloride profile yields $C(x,t) \approx C_i$.

It is convenient to arrange equation 9 in the following way:

$$\frac{x}{\sqrt{12 \cdot t \cdot D_o}} + \sqrt{\frac{C(x,t)-C_i}{C_s - C_i}} = 1 \qquad (10)$$

By introducing the substitutions:

$$u = \frac{x}{\sqrt{12 \cdot t \cdot D_o}} \qquad (11)$$

and

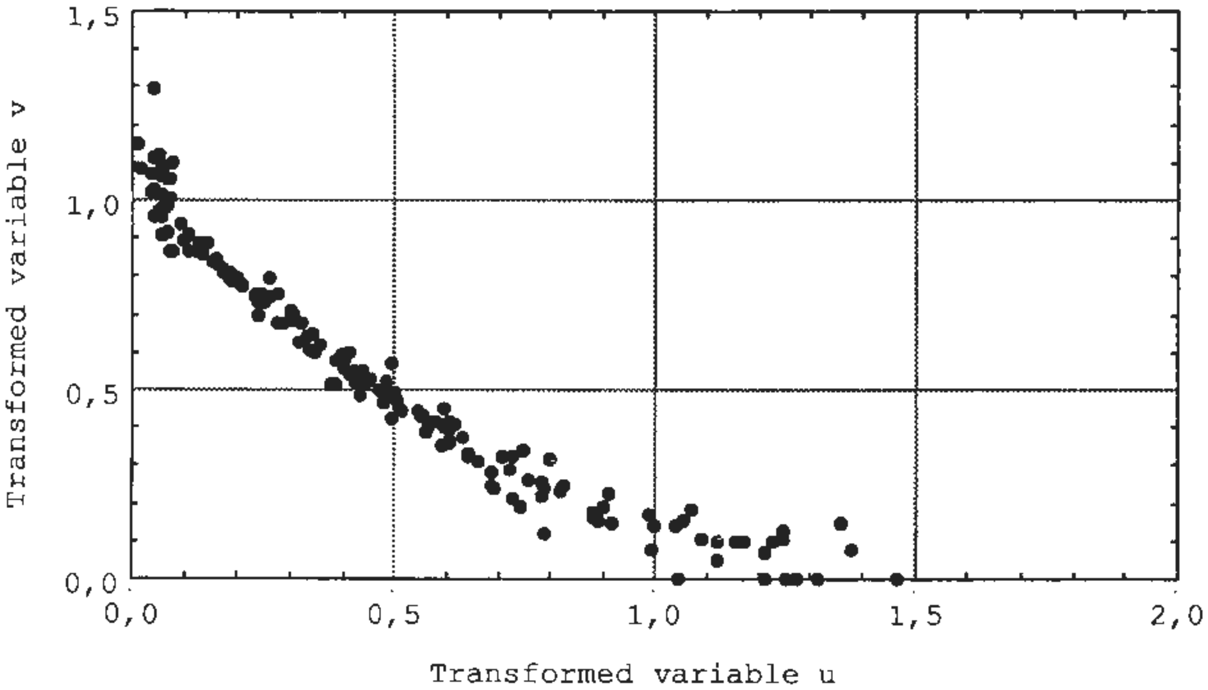

Figure 1. This diagramme shows test data from 20 nos. of chloride profiles, representing 204 nos. of chloride analysis. The distances x from the exposed surface are transformed into the abscissae u and the chloride concentrations are transformed into the ordinates v by means of (11) and (12) respectively. When negative values occur from the analysis the ordinates v are replaced by 0.000. For 0.1 ≤ u ≤ 0.9 the transformed data can be represented by a straight line.

$$v = \sqrt{\frac{C(x,t) - C_i}{C_s - C_i}} \tag{12}$$

it is seen that the graph of equation (10) is a straight line when v is plotted against u. Figure 1 shows test results from several chloride profiles where the observations have been transformed in this way.

Such linearization of chloride profiles has its limits. It is seen that the approximation $u + v = 1$ is valid in practice inside the interval:

$$0.1 \leq u \leq 0.9 \tag{13}$$

The reason for the limit $u \geq 0.1$ is a relatively higher chloride concentration at the exposed surface, probably caused by lack of surface cleaning, i.e. the surface pores are still partially full of chloride.

The reason for the limit $u \leq 0.9$ is that the approximation given by equation 8 also has its limit.

9. LINEAR CURVE-FITTING OF A CHLORIDE PROFILE

The approximation equation (9) makes it possible to carry out the curve-fitting of chloride profiles by means of a linear regression analysis. For this purpose equation (9) shall be arranged as follows:

$$\sqrt{C(x,t) - C_i} = \sqrt{C_s - C_i} - x \cdot \sqrt{\frac{C_s - C_i}{12 \cdot t \cdot D_o}} \tag{14}$$

By applying the following substitutions:

$$y = \sqrt{C(x,t) - C_i} \tag{15}$$

$$q = \sqrt{C_s - C_i} \tag{16}$$

and

$$\alpha = -\sqrt{\frac{C_s - C_i}{12 \cdot t \cdot D_o}} = -\frac{q}{\sqrt{12 \cdot t \cdot D_o}} \tag{17}$$

it is possible to write equation (9) in the following way:

$$y = \alpha \cdot x + q \tag{18}$$

This is the usual form in which a result of a linear regression analysis is represented. Thus, the routine for the determination of the chloride diffusion parameters C_i, C_s and D_o from the test results is as follows:

1. The value of C_i is determined as the mean value of test results from the heartcrete, i.e. of at least 2 nos. of test results.

2. All the measured concentrations of chloride shall be transformed into a new variable:

$$y = \sqrt{C(x,t) - C_i} \tag{19}$$

3. All of the variables not fulfilling the limits $0.1 \le u \le 0.9$ are rejected for the following regression analysis. This rejection must be estimated since the limits depend on the not known value of D_o. When D_o is determined the limits shall be checked, cf. point 6.

4. A linear curve-fitting is carried out for the plot of the remaining variables (x,y).

5. From the fitted line $y = \alpha \cdot x + q$, i.e. from the determined values of α and q, the chloride concentration at the surface C_s shall be determined by the formula:

$$C_s = q^2 + C_i \tag{20}$$

   The chloride diffusion coefficient D_o shall be determined by the following formula:

$$D_o = \frac{(q/\alpha)^2}{12 \cdot t} \tag{21}$$

6. The limits $0.1 \le u \le 0.9$, cf. point 3, shall be checked and accepted.

Samples of concrete nos.	Distance from exposed surface to sample x mm	Chloride concentration C per cent of mass concrete	Curve-fitting. Values of $y = \sqrt{C(x,t) - C_i}$
1	0,40	0,440	-
2	1,30	0,306	0,5532
3	2,25	0,227	0,4764
4	3,00	0,145	0,3808
5	3,80	0,094	0,3066
6	4,80	0,051	0,2258
7	6,15	0,025	0,1581
8	7,90	0,011	-
9	9,35	0,005	-
10	48,25	0,001	-
11	53,20	0,001	-

Table 1. The first three columns show test data for a chloride profile determined by means of the test procedure APM 302, cf. /6/. The last column shows the calculation of the transformed variable y, used for the regression analysis. Test values not fulfilling the limits, cf. (13), are not calculated.

10. A NUMERICAL EXAMPLE

Table 1 shows test data for a chloride profile determined by means of the test procedure APM 302, cf. /6/, following the description given in section 6. The exposure time was 65.9 days corresponding to $t = 0.18$ yr. The specimen was exposed to a liquid containing chloride ions of a concentration of 107.7 g/liter of liquid. The exposure temperature was $T = 25$ °C.

The value of the initial chloride concentration of the concrete is determined as the mean value of the test results nos. 10 and 11, cf. table 1. Thus, the value

$$C_i = 0.001 \text{ per cent of mass concrete} \tag{22}$$

is found.

In order to fulfil the requirement $0.1 \leq u \leq 0.9$, cf. equation 13, it is estimated that the tests results no. 1 and nos. 8-11 must be rejected. Figure 2 shows the linear regression analysis carried out for the remaining 6 nos. of test results.

Here, the following values $q = 0.650$ and $\alpha = -0.085$ are found. Thus the value of the chloride concentration at the surface C_s is

$$C_s = q^2 + C_i = 0.650^2 + 0.001 = 0.424 \text{ per cent of mass concrete} \tag{23}$$

and the value of the chloride diffusion coefficient D_o yields

$$D_o = \frac{(q/\alpha)^2}{12 \cdot t} = \frac{(0.650/0.085)^2}{12 \cdot 0.18} = 27 \text{ mm}^2/\text{yr} \tag{24}$$

In order to prove that the limits of equation 13 are fulfilled, the limits of the distance x are found. The lower limit yields:

$$x_{min} = 0.1 \cdot \sqrt{12 \cdot t \cdot D_o} = 0.1 \cdot \sqrt{12 \cdot 0.18 \cdot 27} = 0.8 \text{ mm} \tag{25}$$

and the upper limit yields:

$$x_{max} = 0.9 \cdot \sqrt{12 \cdot t \cdot D_o} = 0.9 \cdot \sqrt{12 \cdot 0.18 \cdot 27} = 6.9 \text{ mm} \tag{26}$$

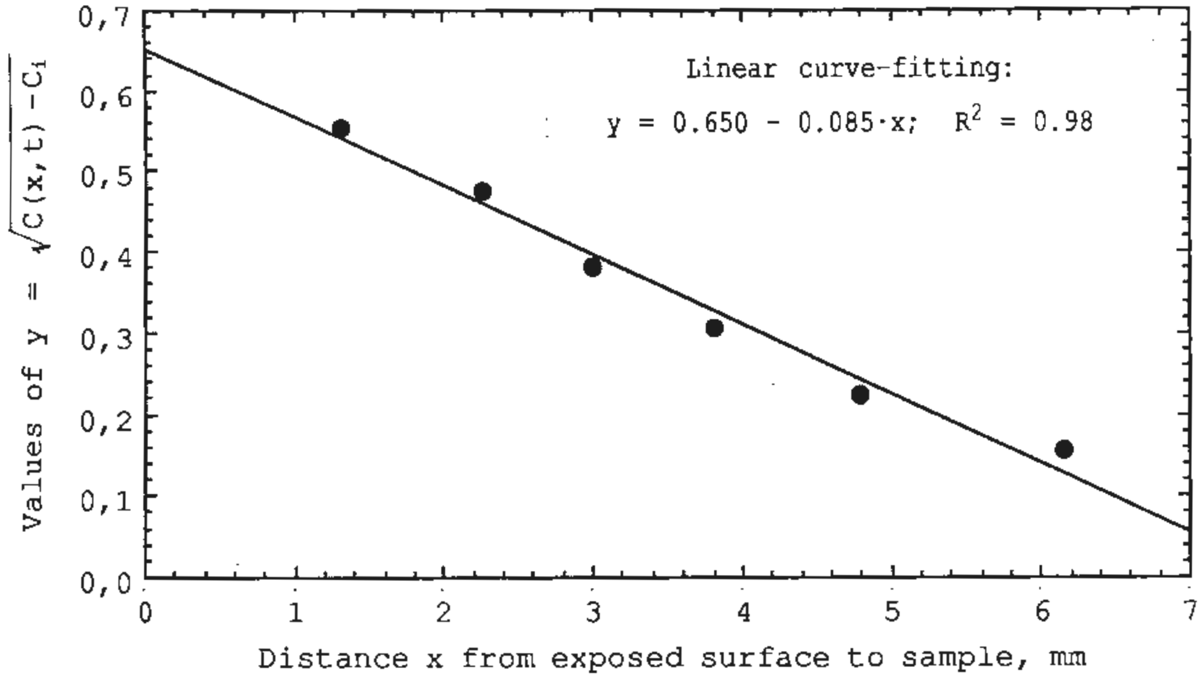

Figure 2. Linear regression analysis of the transformed variables, cf. table 1, fulfilling the limits required, cf. (13). It is possible to carry out the linear regression analysis by means of a pocket-computer as a standard procedure. The value of C_i *is needed for the analysis and* C_i *is estimated as the chloride concentration deep into the concrete. Thus, the achieved diffusion characteristics are* $C_s = 0.424$ *% of mass concrete and* $D_o = 27$ *mm*^{2}*/yr.*

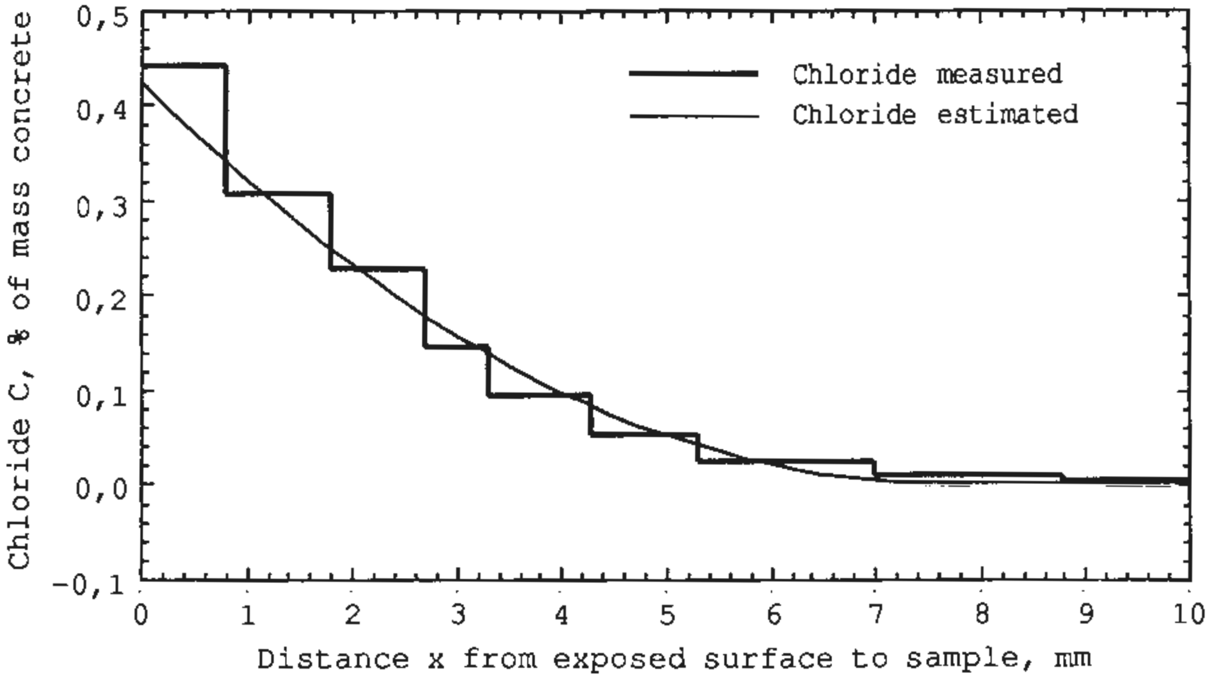

Figure 3. Comparison between the measured chloride profile (shown as a step-graph) and the estimated chloride profile on the basis of the approximation, cf. (9), and the linear regression analysis, cf. figure 2, of the data given in table 1. As seen the chloride diffusion characteristics found by this linear curve-fitting are excellent estimates for a non-linear curve-fitting.

Thus, the limits are fulfilled. Figure 3 shows the test values and the chloride profile, calculated as the approximation (5) on the basis of the chloride diffusion characteristics determined.

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