

CHLORIDE PROFILES

Analysis and Interpretation of Observations

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ABSTRACT

When unprotected concrete is exposed to aggressive substances containing chloride, the chloride will penetrate the concrete. The natural content of chloride in the pore liquid and the binder of the near-to-surface layer of concrete will rise. It is possible to describe the chloride exposure and the ingress by the content and distribution of chloride in the near-to-surface layer of concrete. The distribution of chloride of the near-to-surface layer of concrete is named the chloride profile of the concrete.

The paper describes how a chloride profile can be determined, i.e. the grinding techniques of producing the powder samples, the analyses of their chloride contents and the interpretation of these observations. Furthermore, it is described how the chloride profile can be reduced to three parameters when the chloride ingress is caused by chloride diffusion. Finally, it is discussed how these parameters are estimated from a given chloride profile.

Keywords. Chloride profile, grinding techniques, chloride analysis, diffusion, curve-fitting.

INTRODUCTION

When concrete is exposed to chloride it has become normal practice to describe the concrete's response to the chloride exposure by its chloride profile, i.e. the distribution of the chloride content of the concrete in its near-to-surface layer or the concentration-distance curve. The techniques of how to determine a chloride profile have developed through the years, but a standard technique for the procedure has not yet been established. There are various grinding and drilling techniques, but there are neither standard requirements to the grinding and drilling techniques nor recommendations as to interpretation of the observations found using these techniques.

Sources of chlorides

There are several sources of chlorides. Traditionally, the origins of chlorides in concrete are divided into

- *Chlorides incorporated* in the concrete when it was mixed, e.g. from salty aggregates, salty mixing water and admixtures containing chloride.
- *Chlorides penetrating* into the concrete from the environment, e.g. from seawater, salty pool-water, salty groundwater, sea spray, de-icing salts, from processing or storage of halites, and from other industries like the food-industries (slaughterhouses, osterias etc.).

Only a decade ago it was believed that the chlorides incorporated in the concrete when it was mixed were bound (insoluble) chlorides and should therefore not be risky as long as the content of chloride was kept at a maximum of 2 per cent by mass binder. Now several cases have shown that bound chlorides will be released by carbonation and leaching leading to corrosion.

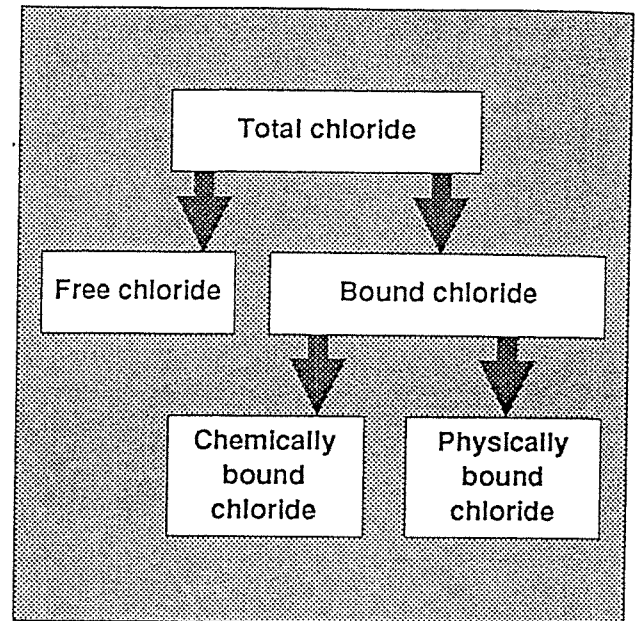
Types of chloride ingress

Chloride can penetrate into the hardened concrete from its environment applying various mechanisms of transport

- *Absorption* of salty water by capillary suction, i.e. the water moves towards the driest part.
- *Permeation* of salty water caused by hydrostatic pressure, i.e. the water moves towards part of the concrete with less pressure.
- *Diffusion* of chlorides caused by differences in chloride concentration, i.e. the chloride moves towards part of the concrete with less chloride concentration.

Figure 1. The chlorides of concrete are bound to the cementing matrix in various degrees. Some chlorides are free and found in the pore liquid as a solution. Some chlorides are bound to the cement gel, i.e. the C-S-H particles of the binder. Physical binding (adsorption) as well as chemical binding exist.

The relationship between the free and the bound chlorides will vary with the type of binder and has to be determined experimentally.



- *Electro-migration* of chlorides caused by differences in electrical potential, i.e. the chloride moves towards part of the concrete with higher electrical potential.

In general chloride ingress into concrete is a combination of several transport mechanisms but with one mechanism as the predominant. A special case is »wetting and drying« of concrete in the splash-zone where the cycling effect will increase the absorption of chloride.

The dominant transport mechanism of uncracked high performance concrete is diffusion, while permeation is the dominant transport mechanism of any cracked concrete.

Types of chloride profiles

Concrete contains »free« chloride in its pore liquid and chloride »bound« to its cementing matrix. The bound chlorides are chemically as well as physically bound (adsorption). The »total« chloride is defined as the content of free and bound chloride. The various types of chlorides in concrete call for four different chloride profiles.

The gradation of the coarse aggregates changes with the distance from the concrete surface, cf. [Suenson, 1942, p.228] and [Frederiksen 1993, p.90]. The content of cement matrix is higher in the near-to-surface layer. For concrete cast in a mould this layer will be of the order of half the maximum grain size of the aggregates. At horizontal concrete surfaces where separation of the coarse aggregates has taken place the layer of concrete being rich in cement matrix will often be significantly thicker.

The chlorides of concrete are present in the cement matrix, either as free chlorides in the pore liquid or bound to the binder, e.g. the cement and flyash. Thus, when relating the chloride to the binder of the concrete the concrete's »binder profile« must be known. When the aggregate does not contain calcite the distribution of binder through the near-to-surface layer of the concrete is determined by means of the calcium profile of the concrete.

Measurements of chlorides

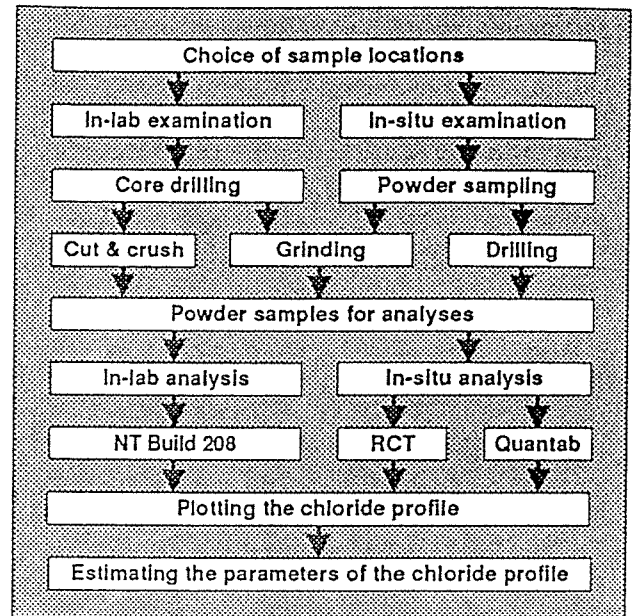
The various types of chlorides in concrete are determined by measurements in different ways. The total amount of chloride is found as acid-soluble chloride while the free chloride is found as water-soluble chloride. Thus the bound chloride is the difference between the total and the free chloride.

It is the free chlorides that are able to cause corrosion of embedded reinforcement and inserts of corrosive metals. Therefore, it is of interest to measure the free chlorides of concrete, especially, since the ratio bound to free chlorides varies with the types of binders. E.g. concrete

Figure 2. Flow-diagram of the possible ways for the determination of a chloride profile. It can either be determined in-situ by grinding or drilling techniques and obtain enough (7-10 nos.) powder samples to determine a chloride profile, cf. Figure 4, by the test method RCT or by Quantab in order to determine the chloride content of each powder sample.

It can also be done by drilling a core from the concrete structure and produce enough powder samples in the laboratory by cutting or grinding techniques, cf. Figure 3, so that the chloride profile can be determined by the test method NT Build 208 in order to determine the chloride content of each powder sample.

Each of the operations of this flow-diagram will add uncertainties to the determination of the chloride profile. This has to be studied in detail before the application of the chloride profile, e.g. for the determination of the structure's service lifetime.



made with flyash and slag as part of the binder has a high binding capacity. Even concretes made with the various types of cement have different binding capacities. Concrete made with sulphate resisting cement for example has a lower binding capacity than concrete made with other Portland cements, other parameters made equal.

When in the USA the chloride content of concrete became an important parameter to control ACI required in 1977 that the free (water soluble) chloride of the concrete was kept at a low level. Later this was changed to a requirement to the total (acid soluble) chloride content of concrete, determined by the test method ASTM C 114, due to lack of reproducibility of the content of the free chlorides.

Sources of uncertainties

There are several sources of uncertainties and even mistakes can take place as shown by several round robin tests. There are four main sources of uncertainties

- *Exposure conditions*, in field as well as in laboratory.
- *Preparing samples for analyses*, in-situ as well as in laboratory.
- *Analysis of chloride content*, the test methods chosen in-situ as well as in the laboratory.
- *Interpretation of observations*, when rejecting or accepting observations for curve-fitting.

A few comments on these main sources are given as follows.

Exposure conditions in field

The local environment plays an important role for the chloride ingress, cf. [Sand 1993, p.113]. A predominant direction for strong winds leads to difference in chloride ingress at windward and leeward parts of a structure exposed to airborne chloride, e.g. in coastal regions. Generally speaking the concrete at the leeward part of the structure will contain more chloride than the concrete at the windward side, other parameters being equal. The concrete at the leeward side is often sheltered from the heavy rains which at the windward side tend to wash down most of the chlorides deposited at the concrete surface by sea spray, salty fogs etc.

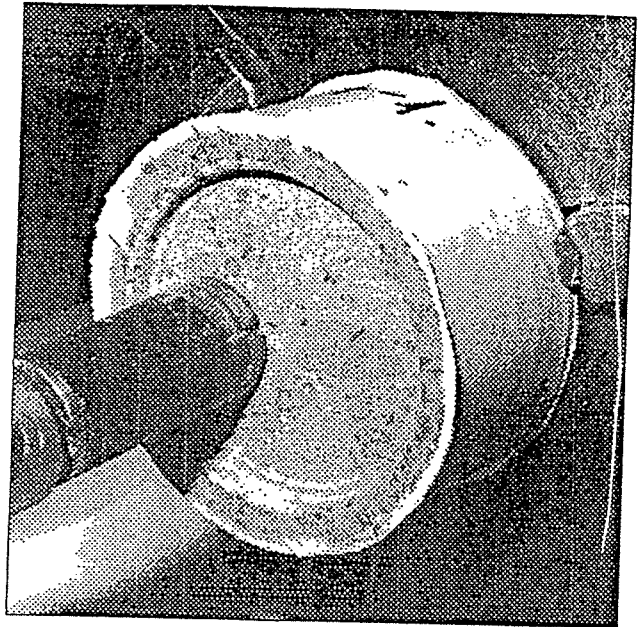
Besides the influence from this shelter effect the concentration of the airborne chloride is not constant but varies with the level above sea-level and the distance from the beach.

When sampling concrete in order to determine its chloride content one has to take the above mentioned influences into account. No guidance, recommendation or standard exist for the sampling of concrete for this purpose.

Figure 3. Equipment for the grinding and collecting of concrete powder from thin layers, each from 0.7 mm to 2 mm. The photograph shows a technique used for the grinding process when applying a turning lathe. The concrete core is fixed into the lathe and rotates simultaneously while very thin layers of concrete powder are milled away by a rotating diamond tool which moves horizontally.

The concrete powder is collected and analysed by a chemical test method, e.g. NT Build 208, in order to determine the chloride content of the powder.

The diameter of the core and the thickness of the layers milled away should be chosen such that the cement content of a powder sample for an analysis fulfil the requirement given by NT Build 208 or similar test method used for the analysis of the chloride content.



Laboratory exposure conditions

In order to characterise the intrinsic chloride diffusivity of concrete, samples of concrete are exposed to a standard solution of chloride as for the test method APM 302, cf. [AEC 1991] and [Frederiksen 1992], or a similar test method. By keeping important parameters like temperature, chloride concentration and exposure period constant and by cutting off a 10 mm thick slice of the concrete from the exposed surface, the deviation of the observation is kept at a minimum.

However, the deviations found by round robin test are not negligible and the sources of the uncertainties may be found in minor differences in test conditions, the microstructure of the concrete (degree of compaction and intensity of defects), and the processing of the powder samples for analyses more than the application of titration procedures.

Preparation of powder samples for analyses

As explained later several techniques are used in order to prepare samples of the exposed concrete. The various sampling methods involve different types of deviation and it is important for the application of the found chloride profiles that this is taken into account. Furthermore, the choice of the numbers of observations to determine one chloride profile is also important, cf. [Pedersen 1993, p.81].

There is a need for several techniques for the preparation of the powder samples for analyses. However, one should realize the difference in the accuracy when applying a chloride profile determined by analyses of three powder samples prepared by hammer drilling compared with a chloride profile determined by a dozen observations found by powder grinding. Both test methods are needed but the accuracy should be taken into account when applying the profiles.

Analysis of chloride content

Several test methods exist suitable for measurements in-situ as well as for laboratory purposes, cf. [Gran 1992], [Gran 1993, p.71] and [Reknes 1994]. Applied test methods in the Nordic countries are

- RCT-method*, the Rapid Chloride Test method.
- Quantab-method*.
- Volhard-titration*, e.g. NT Build 208, cf. [NT Build 208 1984].
- Potentiometric titration*.

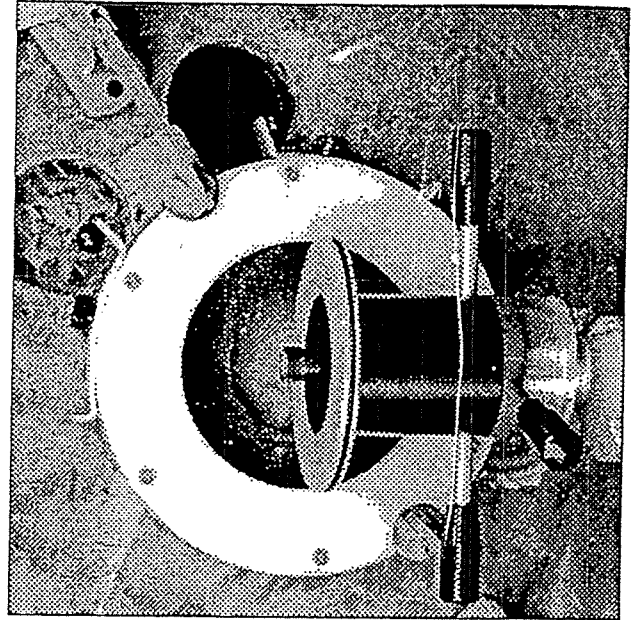
The conclusion from the round robin test reported by [Reknes 1994] is that sufficient accuracy is obtained if

Figure 4. In-situ equipment for the grinding and collecting of concrete powder from thin layers, each by depth increment of 0.5 mm and upwards.

The Profile Grinding Kit is fixed to a concrete surface and the principle of milling correspond to that of Figure 3. On horizontal surfaces the powder is collected with a dustbuster with re-usable filter. On a vertical surface the collection of powder is made automatically in a plastic bag attached to the grinding plate.

The grinding area is circular with a diameter of 73 mm. The maximum depth of grinding is 50 mm. One powder sample from a 2 mm thick layer of concrete may be collected in appx. 5 minutes.

When a chloride profile has to be determined e.g. in the tensile zone of a beam it is not possible to use grinding of the concrete from a circular area with a diameter of 73 mm. Thus an oblong grinding area is used in order to avoid harming the rebars.



- Skilled personal should have fixed routines for the test method applied.
- The test equipment should be calibrated and well-kept.
- In-situ methods should not be applied in laboratory testing.
- Blind test samples should be incorporated to reveal any mistakes during the analysis.

Interpretation of observations

Based upon the theory of the assumed transport mechanism the observations are fitted to an analytic equation. This is discussed in details in the following section of the present paper.

PARAMETERS OF THE CHLORIDE PROFILE

Chloride ingress into the surface of a concrete structure can be determined and described by the achieved chloride profile. The total information about the environment, the exposure time and the achieved chloride profile will give a clear but also an inconvenient picture of the chloride exposure and the response of the concrete.

The information given by the exposure time and the achieved chloride profile of the concrete may be simplified by a few parameters, sufficient to determine the shape of the chloride profile from a mathematical point of view. The values of these parameters, their stochastic distributions and their development with time will give a convenient way of handling the chloride ingress into concrete.

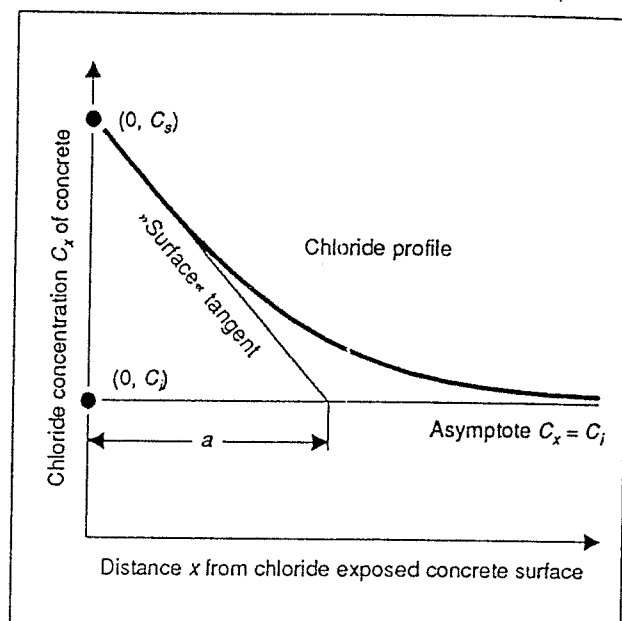
As previously said the transport mechanism may vary with the composition, the compaction and the intensity and widths of the cracks of the concrete. Here, it is assumed that *diffusion is the predominant mechanism* of the chloride ingress and that the concrete is a quasi homogeneous material. These assumptions have proved to be valid for test specimens of uncracked high performance concrete having water/binder-ratios from 0.35 to 0.7 and tested by field exposure at Träslövsläge Harbour in Sweden. Similar agreement is found by the Great Belt Link Ltd. for a test specimen placed at the beach of Nyborg in Denmark.

Chloride profiles for diffusion

It is convenient to speak about two different chloride profiles, the *achieved chloride profile* and the *potential chloride profile*. These chloride profiles may determine bound chlorides as well as free chlorides according to the purpose of testing.

The achieved chloride profile is found in a concrete structure or a concrete specimen when

Figure 5. The definition of the line segment a as the distance along the asymptote $C = C_i$ from the ordinate axis to the intersection between the asymptote and the »surface« tangent.



field exposed to chloride. It could be said that the achieved chloride profile is the concrete's response to the chloride exposure from a given environment.

The potential chloride profile is found in a concrete specimen when exposed to a standard solution of chloride at a standard temperature and during a standard length of time. It could be said that the potential chloride profile is the concrete's intrinsic parameter, i.e. a materials constant.

For comparison it could be said that the achieved parameters and potential parameters are to be compared with the mechanical stresses in a loaded concrete structural member and the strength parameters of the concrete respectively – measured in a standard manner.

Achieved chloride profile

According to the assumptions given above the achieved chloride profile for chloride diffusion will be unambiguously determined by the following three parameters

- The initial chloride content C_{ia} of the concrete.
- The ordinate C_{sa} of the chloride profile at the surface of the concrete.
- The chloride diffusion coefficient D_a of the concrete.

As said these three parameters are not materials constants but they refer to the exposure load, including the exposure time and the age of the concrete. The achieved chloride profiles are determined by the test method APM 207, cf. [AEC 1989], or a similar test method.

Potential chloride profile

According to the assumptions given above the potential chloride profile for chloride diffusion will be unambiguously determined by the following three parameters

- The initial chloride content C_{ip} of the concrete.
- The ordinate C_{sp} of the chloride profile at the surface of the concrete.
- The chloride diffusion coefficient D_p of the concrete.

These three parameters are materials constants, but they refer to the test method. Potential chloride profiles are determined by the test method APM 302, cf. [AEC 1991], or any similar test method.

Equation of a chloride profile

The equation of a chloride profile created by chloride diffusion in concrete, the achieved as well as the potential chloride profile, is found by solving Fick's second law of diffusion for a semi-infinite medium, cf. [Crank 1973] and [Poulsen 1993]. When the chloride exposure

Figure 6. Observations for a potential chloride profile found by means of the test method APM 302, cf. [AEC 1991]. The chloride profile is determined by the chloride contents C_x of 11 nos. of powder samples, each given by its distance x from the chloride exposed concrete surface.

These observations are the basis for the examples covered by this paper. Various methods of estimation of the parameters of the chloride profile of the concrete are illustrated by the examples given, cf. examples 1-5.

Observation no.	Distance x mm	Chloride C_x % by mass concrete
1	0.40	0.440
2	1.30	0.306
3	2.25	0.227
4	3.00	0.145
5	3.80	0.094
6	4.80	0.051
7	6.15	0.025
8	7.90	0.011
9	9.35	0.005
10	48.25	0.001
11	53.20	0.001

remains constant the analytical expression of the chloride profile may be written as

$$C_x = C_i + (C_s - C_i) \operatorname{erfc}\left(\frac{x}{\sqrt{4tD}}\right)$$

Here and in the following the index a and p for achieved and potential properties respectively are left out. How to estimate the three parameters D , C_s and C_i from a given set of observations is dealt with later.

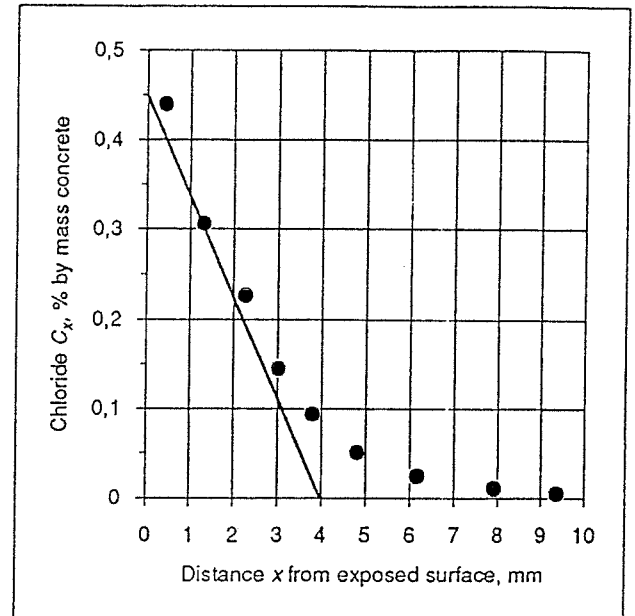
Deviations from the ideal shape

It is common knowledge that sometimes the above given mathematical equation will deviate from the shape of a determined chloride profile. Several possible reasons for such deviations could be mentioned. However, in each case the concrete should be investigated (e.g. by microstructural examination) before jumping to conclusions.

Two main deviations are observed, namely at the exposed concrete surface and at a small distance from the surface. The observed types of deviations are not the same for achieved and potential chloride profiles. Some reasons are listed below.

- A carbonated surface layer of chloride exposed concrete will have a much smaller binding effect than the non-carbonated concrete. This means that the concrete cannot be considered as a quasi homogeneous material but rather as two layers of different materials. This will not be relevant to the potential chloride profile since the concrete is not exposed to carbonation, cf. [AEC 1991].
- A leached surface layer of chloride exposed concrete will have a much smaller binding effect than the non-leached concrete. This means that the concrete cannot be considered as a quasi homogeneous material but rather as two layers of different materials. This will not be relevant to the potential chloride profile since the concrete normally is only exposed for a short period (35 days) to a chloride solution and care is taken to minimize any leaching effect, cf. [AEC 1991].
- A significant part of the penetrating chloride is bound to the C-S-H particles in the cement matrix of the concrete. Since the cement matrix is not uniformly distributed through the concrete (highest content at surface) the concrete is not a quasi homogeneous material. This phenomenon could be taken into account by another mathematical solution than given above. However, it is also a possible way to neglect the observations of chloride content in the outermost layer corresponding to appx. half the size of the coarse aggregate, i.e. appx. 10 mm. When determining a concrete's potential chloride profile this is done physically by cutting away the outermost layer of a thickness of 10 mm, cf. [AEC 1991].
- The exposure of concrete specimens to a concentrated solution of chlorides, as applied by

Figure 7. The observations (x, C_x) given in the Table of figure 6 plotted and the best estimate of the »surface« tangent drawn, i.e. the tangent of the chloride profile at $x = 0$, cf. example 1.



the test method APM 302 or similar methods, often results in a higher chloride concentration at the concrete surface ($x = 0$) than appears from the mathematical solution given above, cf. [Frederiksen 1993]. It is generally believed that chloride concentrates in cavities and voids of the exposed surface and this phenomenon has nothing to do with the diffusion mechanism.

Approximative methods of graphical estimations

It is a typical engineering method to plot the chloride profile and to estimate the parameters from the shape of the graph.

There are several such engineering methods the use of which mainly is for a first estimate of the parameters of chloride profiles, e.g. for a more accurate estimation by one of the iterative methods.

Method of »surface tangent«

From the graph of a chloride profile it is possible to give fairly accurate estimates of C_i and C_s while the estimate of D is not possible without a geometrical estimate of the position of the tangent of the chloride profile at the exposed concrete surface.

The slope of the chloride profile at the point (x, C_x) is the partial derivative of the function modeling the chloride profile

$$\frac{\partial C_x}{\partial x} = - \frac{C_s - C_i}{\sqrt{\pi t D}} \exp\left(- \frac{x^2}{4 t D}\right)$$

Thus the tangent of the chloride profile at the point $(0, C_s)$ determines a line segment a of the asymptote from the ordinate axis to the intersection between the tangent and the asymptote. The length of a is

$$a = \sqrt{\pi t D}$$

From this equation it is seen that the chloride diffusion coefficient D could be expressed as

$$D = \frac{a^2}{\pi t}$$

Figure 8. Observations for a potential chloride profile found by means of the test method APM 302, cf. [AEC 1991]. The chloride profile is determined by the chloride content C_x of 11 nos. of powder samples, each given by its distance x from the chloride exposed concrete surface.

For the purpose of approximative determination of the diffusion coefficient D by linear curve-fitting a new ordinate y is calculated, where

$$y = \operatorname{erfc}^{-1}\left(\frac{C_x - C_i}{C_s - C_i}\right)$$

Observation no.	Distance x , mm	Chlorid C_x , % by mass concr.	Transformed y no unit
1	0.40	0.440	—
2	1.30	0.306	0.292
3	2.25	0.227	0.473
4	3.00	0.145	0.702
5	3.80	0.094	0.892
6	4.80	0.051	1.127
7	6.15	0.025	1.369
8	7.90	0.011	1.620
9	9.35	0.005	1.798
10	48.25	0.001	—
11	53.20	0.001	—

This equation leads to a simple rule: from the graph of the chloride profile the asymptote C_i is estimated. The line segment $b = C_s - C_i$ of the ordinate axis cut off by the chloride profile and the asymptote is estimated and the parameter yields $C_s = b + C_i$. Finally the line segment a of the asymptote from the ordinate axis to the intersection between the tangent and the asymptote is estimated and the chloride diffusion coefficient is calculated from the above found formula where t is the exposure time.

Example 1. A chloride profile has been determined by measuring the simultaneous values of x and C_x as shown in the table of Figure 6. The observations were obtained by means of the test method APM 302, cf. [AEC 1991], and the exposure period was $t = 0.18$ year.

The initial chloride content of the concrete C_i was measured on samples of virgin concrete at a distance of appx. 50 mm from the exposed concrete surface, cf. samples nos. 10 and 11 in the Table of Figure 6. This yields the initial chloride content as

$$C_i = 0.001 \text{ per cent by mass concrete}$$

The chloride profile is drawn, cf. Figure 7. From this graph it yields that the ordinate of the chloride profile at the surface of the concrete is

$$C_s = 0.45 \text{ per cent by mass concrete}$$

The tangent of the chloride profile at the point $(0, C_s)$ is drawn and the the segment line a is estimated to be $a = 4$ mm, cf. Figure 7. Thus the chloride diffusion coefficient yields

$$D = \frac{a^2}{\pi t} = \frac{4^2}{\pi \times 0.18} = 28 \text{ mm}^2/\text{year}$$

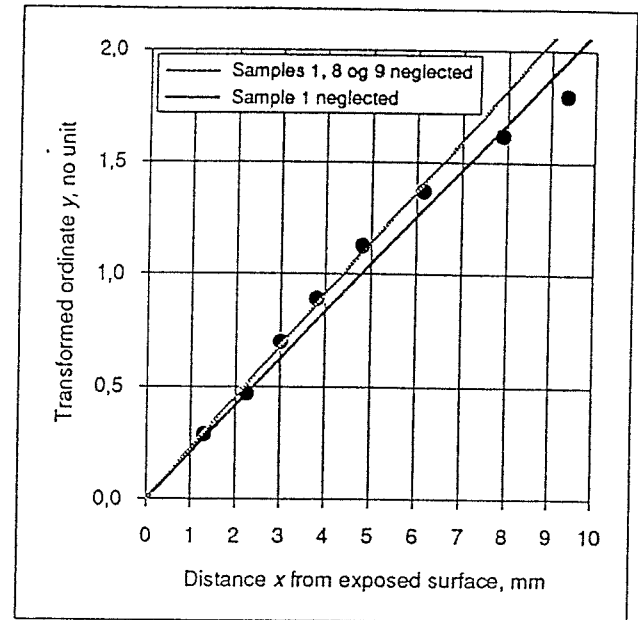
Estimation by means of three sets of observation

Estimation of the parameters of a chloride profile by the above mentioned method requires that the chloride profile is undisturbed at the surface. However, an achieved chloride profile will often be influenced by side effects as described above. This means that it may be difficult to estimate the position of the tangent of the chloride profile at the concrete surface.

From the shape of a given chloride profile it is possible to estimate C_i and C_s with a suitable accuracy even if the chloride profile is disturbed at the surface ($x = 0$). In order to estimate the diffusion coefficient D a suitable point (x_m, C_m) of the chloride profile can be estimated. The parameter D is then determined in such a way that the chloride profile

- Starts at $(x, C_x) = (0, C_s)$.
- Passes through $(x, C_x) = (x_m, C_m)$.
- For $x \rightarrow \infty$ yields the asymptote $C_x = C_i$.

Figure 9. The transformed ordinate y plotted versus the distance x from the chloride exposed concrete surface. Two lines found by curve-fitting are shown – one taking samples nos. 2-9 into account and one taking samples nos. 2-7 into account, cf. example 3.



These conditions will give a convenient determination of D . However, the result depends on the choice of the point (x_m, C_m) and the determination of D is not unambiguous.

Thus, it is required that (x_m, C_m) is a point of the chloride profile

$$C_x = C_i + (C_s - C_i) \operatorname{erfc}\left(\frac{x}{\sqrt{4tD}}\right)$$

This means that D can be determined by the following equation

$$C_m = C_i + (C_s - C_i) \operatorname{erfc}\left(\frac{x_m}{\sqrt{4tD}}\right)$$

By introducing a new parameter y_m defined by the expression

$$y_m = \operatorname{erfc}^{-1}\left(\frac{C_m - C_i}{C_s - C_i}\right)$$

the diffusion coefficient is found by the following solution

$$D = \left(\frac{x_m}{y_m \sqrt{4t}}\right)^2$$

Values of the functions erfc and erfc^{-1} are tabled in suitable handbooks of mathematics, cf. [Spiegel 1968], and in textbooks on diffusion theory, cf. [Crank 1973].

Example 2. For the same chloride profile as dealt with in Example 1 it is estimated that it should pass through a point with abscisse $x_m = 3.0$ mm and ordinate $C_m = 0.145$ per cent by mass concrete, corresponding to the observation no. 4 in the Table of Figure 6.

As in Example 1 the values of the parameters $C_i = 0.001$ per cent by mass cement and $C_s = 0.45$ per cent by mass cement are estimated. Thus the parameter y_m is

$$y_m = \operatorname{erfc}^{-1}\left(\frac{0.145 - 0.001}{0.45 - 0.001}\right) = \operatorname{erfc}^{-1}(0.321) = 0.702$$

By applying $x_m = 3.0$ mm, $y_m = 0.702$ and taking that the chloride exposure period was $t = 0.18$ year the

Figure 10. Observations for a potential chloride profile found by means of the test method APM 302, cf. [AEC 1991]. The chloride profile is determined by the chloride contents C_x of 11 nos. of powder samples, each given by its distance x from the chloride exposed concrete surface.

For the purpose of approximative determination of D and C_s by linear curve-fitting a new ordinate y is calculated, cf. example 4, where

$$y = \sqrt{C_x - C_i}$$

Observation no.	Distance x , mm	Chloride C_x , % by mass concrete	$\sqrt{C_x - C_i}$
1	0.40	0.440	0.663
2	1.30	0.306	0.552
3	2.25	0.227	0.475
4	3.00	0.145	0.379
5	3.80	0.094	0.305
6	4.80	0.051	0.224
7	6.15	0.025	0.155
8	7.90	0.011	—
9	9.35	0.005	—
10	48.25	0.001	—
11	53.20	0.001	—

chloride diffusion coefficient D is determined by the formula given above and yields

$$D = \left(\frac{3.0}{0.702 \times \sqrt{4 \times 0.18}} \right)^2 = 25 \text{ mm}^2/\text{year}$$

Approximative methods of linear curve-fitting

The semi-grafical methods as explained above are just suitable for rough estimates of the parameters of a chloride profile. There is a certain need for approximative methods of estimation which apply to all observations. This can be done at two levels as described in the following.

Estimation of D by linear curve-fitting

It is possible to rewrite the mathematical equation of the chloride profile

$$C_x = C_i + (C_s - C_i) \operatorname{erfc} \left(\frac{x}{\sqrt{4 t D}} \right)$$

into a simpler form

$$y = \frac{x}{\sqrt{4 t D}}$$

Here y is defined as

$$y = \operatorname{erfc}^{-1} \left(\frac{C_x - C_i}{C_s - C_i} \right)$$

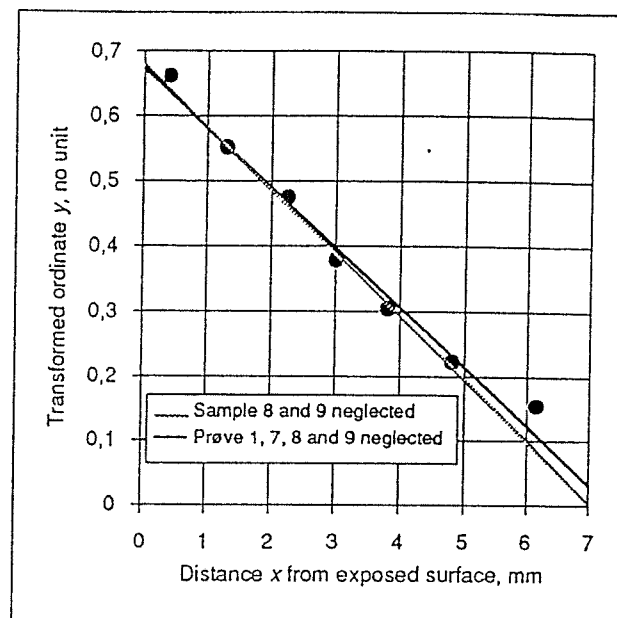
By plotting the observations as x and y in a cartesian coordinate system the observations will be represented by a straight line plot. By a linear curve-fitting the straight line best fitting the observations and also passing through origo is determined. From the slope of this straight line the chloride diffusion coefficient D is determined when the exposure period t is known.

Example 3. The chloride diffusion coefficient D should be estimated from all observations in the Table of figure 6, assuming that $C_i = 0.001$ per cent by mass concrete and $C_s = 0.45$ per cent by mass concrete. The necessary and sufficient calculations are shown in the Table of Figure 8.

By a linear curve-fitting of the transformed observations (x , y) the following straight line is found

$$y = 0.209 x$$

Figure 11. The transformed ordinate y plotted versus the distance x from the chloride exposed concrete surface. Two lines are shown found by means of curve-fitting – one taking samples nos. 1-7 into account and one taking samples nos. 2-6 into account, cf. example 4 and the Table of Figure 10.



where $R^2 = 0.994$. The plot of the transformed observations are shown in the Diagram of Figure 9. Thus the chloride diffusion coefficient is determined by solving the following equation

$$\frac{1}{\sqrt{4 t D}} = 0.209$$

Since the exposure time is $t = 0.18$ year the chloride diffusion coefficient yields

$$D = \frac{0.25}{0.18 \times 0.209^2} = 32 \text{ mm}^2/\text{year}$$

By neglecting the observations nos. 8 and 9, cf. the Table in Figur 8, the following straight line $y = 0.228 x$ is found with $R^2 = 0.999$. Thus the following value of D is obtained

$$D = \frac{0.25}{0.18 \times 0.228^2} = 27 \text{ mm}^2/\text{year}$$

This difference may be caused by a non-homogeneous microstructure of the concrete. However it may also be caused by inaccuracy in the analyses if the samples nos. 8 and 9. Only further examination of the concrete can tell about the reason for the deviation found.

Estimating C_x and D by linear curve-fitting

It is possible to estimate not only D but also C_s by linear curve-fitting. An approximation is introduced for the error function complement

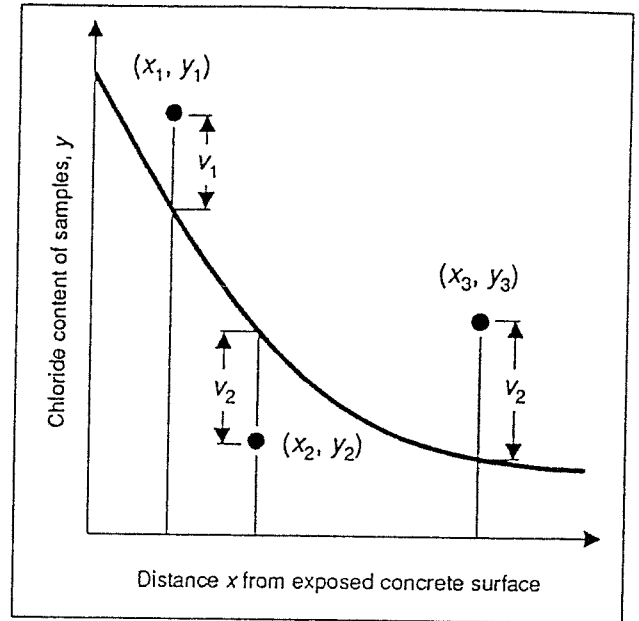
$$\text{erfc}(z) \approx \left(1 - \frac{z}{\sqrt{3}}\right)^2$$

This approximation is valid in practice in the interval $0 \leq z < \sqrt{3}$. By using this approximation the mathematical expression of the chloride profile yields

$$C_x = C_i + (C_s - C_i) \left(1 - \frac{x}{\sqrt{12 t D}}\right)^2$$

This approximation is not, as said above, valid for all values of x . However, by following the rule of thumb, cf. [Pedersen 1993], that the major part of the observations made for the determination of a chloride profile should fulfil the requirement $x < 5 \times \sqrt{t D}$, the following

Figure 12. Under the conditions that the graph shown should pass the observations (x_1, y_1) , (x_2, y_2) and (x_3, y_3) the parameters of the graph should be determined in such a way that the sum of the squares of the deviations $v_1^2 + v_2^2 + v_3^2$ will obtain a minimum. This is the principle of curve-fitting by the method of least squares.



limit of the approximation will often leave a sufficient number of observations for the analysis

$$0 \leq x < \sqrt{12 t D}$$

Thus, the limit is generally not a hindrance. By rewriting the mathematical expression of the chloride profile in the following way

$$\sqrt{C_x - C_i} = \sqrt{C_s - C_i} - x \sqrt{\frac{C_s - C_i}{12 t D}}$$

it is seen that it obeys the well-known expression of a straight line $y = \alpha x + q$, if the following substitutions are introduced

$$y = \sqrt{C_x - C_i}$$

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

$$\alpha = -\sqrt{\frac{C_s - C_i}{12 t D}} = -\frac{q}{\sqrt{12 t D}}$$

When α and q are found by linear curve-fitting the parameters of the chloride profile yield

$$C_s = q^2 + C_i$$

$$D = \frac{(q/\alpha)^2}{12 t}$$

The initial chloride content C_i of the concrete is determined by analysis of virgin concrete.

Example 4. The chloride diffusion coefficient D and the ordinate C_s of the chloride profile at surface ($x = 0$) should be estimated by linear curve-fitting applying the above given approximation and the observations in the Table of Figure 6.

In the Table of Figure 10 the observations (x, C_x) are repeated and the transformation y shown. The initial chloride content is found by the observations nos. 10 and 11, i.e. $C_i = 0.001$ per cent by mass concrete. From a linear curve-fitting of the observations nos. 1 to 7 (see later about x_{max}) the following straight line is found

$$y = 0.673 - 0.0902 x$$

with $R^2 = 0.982$. By applying $\alpha = -0.0902$ and $q = 0.673$ the parameters of the chloride profile yield

Figure 13. Chloride content in powder samples versus their distance from the chloride exposed concrete surface. The parameters of the chloride profile are determined by non-linear curve-fitting taking all observations into account (second column) and only a part of the observations (third column), cf. example 5.

Distance x , mm	Chloride C_x % by mass concrete	Chloride C_x % by mass concrete
0.40	0.440	—
1.30	0.306	0.306
2.25	0.227	0.227
3.00	0.145	0.145
3.80	0.094	0.094
4.80	0.051	0.051
6.15	0.025	0.025
7.90	0.011	—
9.35	0.005	—
C_s	0.486 % mass concrete	0.466 % mass concrete
D	23.9 mm ² /year	25.4 mm ² /year
C_i	0.001 % mass concrete	0.001 % mass concrete

$$C_s = 0.673^2 + 0.001 = 0.454 \text{ per cent by mass concrete}$$

$$D = \frac{(0.673 / 0.0902)^2}{12 \times 0.18} = 26 \text{ mm}^2/\text{year}$$

cf. the diagram of Figure 11. The limit of x for the application of the approximation is

$$x_{max} = \sqrt{12 \times 0.18 \times 26} = 7.5 \text{ mm}$$

Methods of non-linear curve-fitting

For any final estimation of the parameters of a chloride profile a non-linear curve-fitting should be applied. Here it is the choice if the parameter C_i should be estimated by the curve-fitting (i.e. three parameters to estimate) or the observations should be planned in such way that the observations are divided into two groups – one for the estimation of D and C_s and another for the estimation of C_i . It has become general practice to use the last choice and only this is described in detail in the following.

Assumptions

It is supposed that a chloride profile has been determined by the following observations

$$(x_1, C_1), (x_2, C_2), (x_3, C_3), \dots, (x_n, C_n)$$

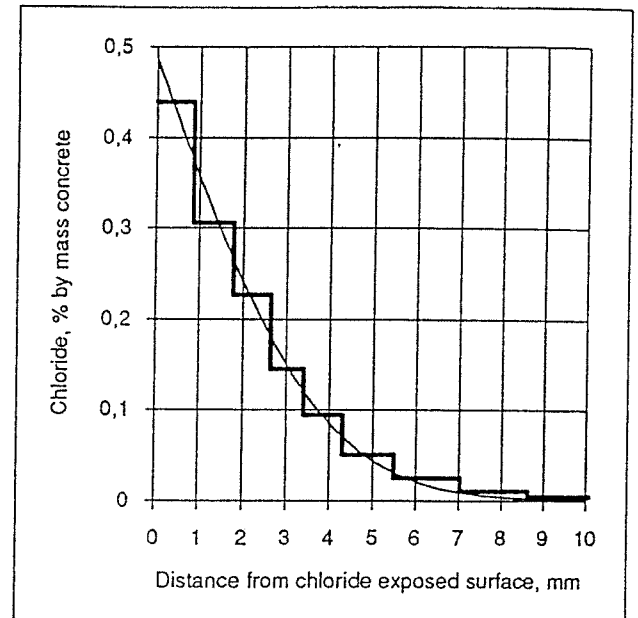
From these observations C_s and D in the the following equation should be determined

$$C = C_i + (C_s - C_i) \operatorname{erfc}\left(\frac{x}{\sqrt{4tD}}\right)$$

assuming that the values of C_i and t are known. This will give n equations and two unknowns. Thus, the determination of C_s and D is not unambiguous unless further assumptions are made. If the observations are plotted into a Cartesian coordinate system it is unlikely that a chloride profile described by the equation given above for any chosen values of C_s and D will pass through all the observations.

However, if it is required that a measure of the deviations between the chloride profile and the observations is at the minimum the determination of C_s and D will become unambiguous. The accuracy by which x is determined when using a grinding technique is far better than the accuracy of C . However, this is not the case when a hammer-drill technique is applied but

Figure 14. Observations of the chloride content of concrete versus the distance from the chloride exposed concrete surface. In the same diagram is also shown the chloride profile found by the non-linear curve-fitting, cf. example 5. The deviations between the observed and the estimated chloride profile are shown in Figure 15.



documentation has not been reported. Here the use of the grinding technique is assumed.

Assuming that the inaccuracy of C plays the predominant role and x should be considered deterministic the method of least squares will lead to an unambiguous determination of C_s and D , i.e. it is required that

$$v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2 = \text{minimum}$$

cf. Figure 12. Here v_1 is the deviation between the observation C_1 and the ordinates for x_1 of the equation in question, i.e.

$$v_1 = C_i + (C_s - C_i) \operatorname{erfc}\left(\frac{x_1}{\sqrt{4tD}}\right) - C_1$$

and so on for the deviations $v_2, v_3, v_4, \dots, v_n$.

Example 5. The observations given in the Table of Figure 6 are finally used in order to determine C_s and D by application of a non-linear curve-fitting. Observations nos. 10 and 11 determine $C_i = 0.001$ per cent by mass concrete. The found values of the parameters are shown in Figure 13. In Figure 14 the determined values of the mathematical chloride profile are shown together with the observed. The Table of Figure 15 illustrates these findings.

Deviations between mathematical and observed chloride profiles

No curve fitting, linear or non-linear, is able to determine the mathematical model of a chloride profile. Only the knowledge of the transport mechanism and the influences from the concrete and its environment will be able to determine the mathematical model of a chloride profile.

In this paper the mathematical model of diffusion into a quasi homogeneous semi-infinite medium is supposed. However, the medium may not be quasi homogeneous. It is well-known that D is a function of the distance from the exposed concrete surface, and open cracks will disturb the flow of chloride in concrete, while a time dependent medium does not change the shape of the chloride profile, cf. [Poulsen 1993].

By plotting the determined and observed chloride profiles into one Cartesian coordinate system it can be seen if the observations have a systematic deviation from the determined chloride profile. If so, it is advisable that the reason for this deviation is examined depending on the future application of the determined chloride profile.

Figure 15. Table of the observed chloride content, $obs\{C_x\}$, in the powder samples and the estimated chloride content, $est\{C_x\}$, found by means of the non-linear curve-fitting applied in example 5, which determined the parameters equal to $C_s = 0.486$ per cent by mass concrete and $D = 23.9 \text{ mm}^2/\text{year}$. The initial chloride content of the concrete was estimated to $C_i = 0.001$ per cent by mass concrete from samples nos. 10 and 11 (not shown here). The deviations $v(x)$ are also shown versus the distance x from the chloride exposed concrete surface.

Distance x , mm	$obs\{C_x\}$, % by mass concrete	$est\{C_x\}$, % by mass concrete	$v(x)$, % by mass concrete
0.40	0.440	0.431	-0.009
1.30	0.306	0.322	+0.016
2.25	0.227	0.217	-0.010
3.00	0.145	0.151	+0.006
3.80	0.094	0.095	+0.001
4.80	0.051	0.050	-0.001
6.15	0.025	0.019	-0.006
7.90	0.011	0.004	-0.007
9.35	0.005	0.002	-0.003

As mentioned before carbonation or leaching of the outermost concrete surface will change the chloride binding effect of the cement matrix. Since it is the change of the chloride profile around the rebars in concrete which is important for the service lifetime of the reinforced concrete, the observations (x, C_x) in the carbonated or leached surface layer could be omitted instead of trying to formulate a mathematical model for this special case.

However, neither recommendations nor standards deal with this problem. Thus, the determination of parameters C_s and D of a chloride profile from observations are in fact not unambiguous – *but it ought to be!*

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LIST OF NOTATIONS

α	Slope of a straight line in Cartesian coordinates.
a	The line segment of the asymptote from the ordinate axis to the intersection between the »surface tangent« of the chloride profile and the asymptote.
b	$= C_s - C_i$.
C	General notation for chloride content (contraction) of concrete.
C_1, C_2, C_3, \dots	Chloride content of concrete at the distances $x_1, x_2, x_3, \dots, x_n$ from the chloride exposed concrete surface.
C_i	Initial chloride content of concrete
C_{ia}	Initial chloride content of concrete referring to achieved chloride diffusivity.
C_{ip}	Initial chloride content of concrete referring to potential chloride diffusivity.
C_m	Chloride content of concrete at the distance x_m from the chloride exposed surface.
C_s	Ordinate of a concrete's chloride profile at the chloride exposed concrete surface, i.e. at $x = 0$.
C_{sa}	Ordinate of a concrete's achieved chloride profile at the chloride exposed concrete surface, i.e. at $x = 0$.
C_{sp}	Ordinate of a concrete's potential chloride profile at the chloride exposed concrete surface, i.e. at $x = 0$.
C_x	Chloride content of concrete at the distance x from the exposed surface.
C-S-H	Calcium silicate hydrate gel formed by the hydration of silicates in Portland cement.
D	General notation for the chloride diffusion coefficient of concrete.
D_a	Chloride diffusion coefficient referring to achieved chloride diffusivity.
D_p	Chloride diffusion coefficient referring to achieved potential diffusivity.
erfc	The error-function complement.
erfc ⁻¹	The inverse error-function complement.
est{ C_x }	Estimated chloride content of concrete at the distance x from the chloride exposed concrete surface.
obs{ C_x }	Observed chloride content of concrete at the distance x from the chloride exposed concrete surface.
q	The line segment of the ordinate axis between the origin and the intersection of a straight line.
R^2	Squared sample correlation coefficient.
t	Time period of chloride exposure.
$v(x)$	Deviation versus x of an observation from the corresponding ordinate of the fitted curve.
v_1, v_2, v_3, \dots	Deviations of observations from the corresponding ordinates of a fitted curve at the points 1, 2, 3, \dots, n .
x	Distance from a chloride exposed concrete surface.
x_m	Distance from a chloride exposed concrete surface to a point near the centre of the samples determining the chloride profile.
x_1, x_2, x_3, \dots	Distances from a chloride exposed concrete surface to the points 1, 2, 3, \dots, n .
y	General notation of an ordinate which is transformed by a function of chloride content of the concrete.
y_m	Ordinate with special reference to x_m transformed by a function of chloride content of the concrete.
y_1, y_2, y_3, \dots	Ordinates of the points 1, 2, 3, \dots, n .
z	General notation of an independent variable.