Chiselling

The chiselling technique mainly resembles traditional repair by removing and replacing damaged concrete. The technique was used in early investigations and is only suitable for measurements of the mean chloride content in large samples. The sample must be crushed and homogenized before chloride analysis, cf. Nordtest [1984b].

Dry drilling

Dry drilling is probably the most commonly used sampling technique due to low costs and simplicity. Unfortunately this method is associated with a significant amount of uncertainty. Farstad et al. [1993] have shown that the bore size is a critical parameter. A bore diameter above maximum aggregate size is essential in order to obtain sufficient accuracy and precision in chloride measurements.

Carlsen [1995] has developed a method to collect the concrete dust by using a vacuum attachment to a hand held drill with a bore diameter of 24 mm. As this bore size is considered to be close to an upper practical limit for hand held operation, dry drilling is only recommended for concretes with maximum aggregate size smaller than 16-20 mm. And in this case only when concrete dust from five or more holes is combined into one sample.

In all circumstances the dry drilling sampling technique shows poorer accuracy and precision than core drilling or grinding techniques.

One problem in using this technique for measuring chloride profiles is that it is difficult to prevent dust from the side of the hole in outer layers from mixing with dust from inner layers. Another problem arises when the hardness of the cement paste and the aggregate differs. In these cases which are very normal the bore will tend to avoid the harder parts in the concrete when using the hand held hammer drill. In these cases, the accuracy will probably improve if the chloride content is related to the amount of binder in the concrete sample.

Core drilling

This sampling technique gives very good accuracy and precision, provided that the maximum aggregate size is not too large compared with the core diameter. A ratio not less than 1:3, as recommended in standards for sampling of cores for strength tests, cf. Nordtest [1984a], will normally be adequate.

Core drilling requires heavier equipment on the sampling site and additional cutting and crushing before chemical analysis. It is therefore more costly in use.

The drilled concrete core is mostly used for determination of chloride profiles. Profiles can be made by cutting the core into thin slices down to approx. 5 mm thickness. Profile grinding, cf. Figure 4-20, must be applied if a fine graduation of the profile is wanted. It is possible to remove layers of approx. 0.5 mm by this technique, cf. AEClaboratory [1992b].

In-situ profile grinding

Recently in-situ profile grinding equipment, cf. Petersen [1995], was developed from the experiences of profile grinding in the laboratory. In-situ profile grinding is a very accurate and promising sampling technique, but there are still some initial complications. The most important complications are that the grinding diameter is limited to 73 mm and the collection of concrete dust can be somewhat troublesome.

4.7.2 Chloride analysis techniques

The chloride analysis techniques used for field exposure tests are the same as those used for tests in the laboratory.

In most cases the concrete samples are brought to the laboratory for chloride analyses. Then the highly reliable methods can be used, such as Volhard titration or potentiometric titration, cf. Sections 4.1.1 and 4.1.2.

If an immediate result is needed on site, only one technique with a reasonable accuracy is applicable so far. This is the commercially available RCT method, based on a chloride selective electrode, cf. Section 4.1.3. It is possible to produce reliable results on site using this method, but the accuracy is not the same as that of the better lab methods.

If the penetration depth of chloride is the only interest, the colorimetric spray indicators can be used, cf. Section 4.1.6.

4.7.3 In-situ test methods

To our knowledge no standardized specifications exist for field tests of chloride penetration into concrete. Field tests are usually performed on either specially manufactured test specimens or existing structures by measurement of the chloride profiles after a certain exposure period using one of the above mentioned sampling techniques, cf. e.g. Maage et al. [1993], Sandberg [1993], Steen [1995] and Stoltzner [1995].

There is a need for a standard specification which describes how reliable field tests and examination of existing structures are to be performed, including design of test specimens, registration of environmental load, sampling technique, sampling frequency, analysis and evaluation of measurements. This need is urgent because the exposure time in field tests is a period of years and decades before sufficient data is collected for evaluation. Today test results from different research groups are very difficult - if not impossible - to compare, due to the varying test conditions and missing registrations. This could be changed if an international standard were accepted world wide.

4.7.4 Petrographic examination of concrete

A petrographic examination cannot reveal the chloride distribution in concrete. However, it is a very relevant test method when chloride contents and chloride profiles in concrete are evaluated. It can give much valuable information, which facilitates the interpretation of the measured chloride distribution in the concrete. This paragraph describes the petrographic examination and the information which can be obtained using this technique.

The properties of concrete revealed by petrographic examination are primarily described in view of the compressive strength, although the greatest advantage of thin section analyses is in the field of concrete quality with respect to durability.

Strictly speaking “Petrography” is a science in the field of geology. It deals with descriptions of naturally occurring rocks and relationships between minerals that constitute rocks. But petrography has also been used successfully in the study of artificial products e.g. concrete and ceramics.

Important publications on the use of petrography for studying concrete (and concrete aggregates) are those by Mather [1966], Mielenz [1966], Christensen et al. [1981] and Jensen [1986].

Guidelines for the petrographic method are given in the ASTM standard: Practice for Petrographic Examination of Hardened Concrete, cf. ASTM [1990], the British Concrete Society Report No. 32: Analysis of Hardened Concrete - 9. Microscopic Methods, cf. Concrete Society [1989] and the Danish test method TI-B 5(87): Petrographic examination of hardened concrete, cf. Danish Technological Institute [1987].

Petrographic examination of rocks and concrete is often considered as an optical microscopy method. Traditionally, optical microscopy has been the principal petrographic method with the petrographic microscope and the thin section technique as the main tools. In its broadest aspects, petrographic examination may also include x-ray diffractometry and electron microscopy.

Petrographic microscope

The petrographic microscope is a polarizing microscope, where plane-polarized light is sent successively through a thin section, an objective, an analyzer (that is a polarizing filter) to the oculars where the concrete is examined by using different magnifications, typically from around 20x to 500x.

The thin section

A thin section is a small plate of concrete that has been vacuum-impregnated with epoxy containing a yellow fluorescent dye. The thin section normally covers an area of 30 x 45 mm and has a thickness of around 20 μm.

Evaluation of features related to the initial quality of concrete

The petrographic examination can give information about the initial quality, the normal evolution and eventually an abnormal deterioration of the concrete. A petrographic examination can give the following information related to the initial quality of concrete:

Aggregates

- Type (proper petrographic term) and quality of the coarse aggregates.
- Type, quality, quantity and grading of the fine aggregate.

Cement paste

- Cement type and degree of hydration.
- Content of pulverized fuel ash (PFA).
- Presence of condensed silica fume (CSF).
- Capillary porosity expressed as an equivalent water/cement ratio (eq. *w/c* ratio).
- Paste homogeneity, which depends on mixing efficiency and stability of the components which form the fresh cement paste.
- Morphological characteristics of the portlandite ($Ca(OH)_2$) formation.

Air voids

- Content, distribution, size and shape of air voids.
- Precipitates in air voids (particularly portlandite).

Cracks

- Presence of micro cracks with crack widths below 0,005 mm, that occur in the cement paste and around aggregate particles. These cracks are associated with the normal hydration of the cement.
- Fine and coarse cracks with crack widths over 0,005 mm that are not related to the normal hydration of the cement.

Exposed surface

- Texture and defects related to the surface treatment - particularly defects caused by evaporation of water from the young concrete (curing defects).

Concrete

- Mix proportions
- Internal structure.

Pozzolans

Pozzolans such as condensed silica fume (CSF) and pulverized fuel ash (PFA) are used in the production of concrete. These constituents can either directly or indirectly be detected by a petrographic examination.

Condensed Silica Fume (CSF)

The particle size distribution of CSF shows most particles to be smaller than 1 µm, with an average diameter of about 0.1 µm, which is approximately 100 times smaller than the average cement particle, cf. ACI [1987]. Due to its small particle size, CSF cannot be seen directly in the thin section if it is properly dispersed. Nevertheless it is often possible to see the influence of CSF on the cement paste, in the form of reduced content of portlandite (mineralogical name of $Ca(OH)_2$ crystals) and a special diagnostic opalescence or rather milky appearance of the paste. However, the occurrence of lumps of CSF is easily recognized in thin section analyses.

Pulverized Fuel Ash (PFA)

PFA can occur in concrete both as a primary component of the Danish portland cement and as additive to the concrete mix. If the fuel ash is a primary component of the cement, it is ground together with the cement clinker and thereby possesses a particle size distribution equal to that of the cement clinker. During the grinding process the PFA particles, originally spherical in shape, are more or less crushed. This enables a distinction to be made in the petrographical examination between primary PFA and PFA added to the concrete mix.

Characteristics of the cement paste

In a thin section the hardened cement paste is observed to consist of unhydrated and partly hydrated cement minerals (clinkers) in a matrix of hydration products.

Clinker

In young concrete, and especially in high performance concrete with low *w/c* ratio, the content of unhydrated clinker minerals is high and the proportions between C_3S, C_2S and C_4AF can be deduced. The clinker mineral C_3A cannot be detected in the polarisation microscope due to its isotropic and colourless appearance. The hydration products in the paste form a porous mass, whose solid matrix is a mixture of amorphous C-S-H-gels and crystalline CH (portlandite - $Ca(OH)_2$), AFt-phase minerals and AFm-phase minerals.

C-S-H-gel
In the polarisation (N-mode) microscope the C-S-H-gel is observed as a brownish felted mass between still unhydrated clinker minerals. In concrete with *w/c* ratio of 0.5 the C-S-H-gel constitutes approximately 50 % by volume of the cement paste.

Portlandite
The amount and morphological characteristics of the portlandite present in concrete can be observed in a thin section. These observations give valuable information of possible degradation effects, such as carbonation, leaching and moisture actions.

AFt- and Afm-phases
These constituents are normally present in the cement paste only in a low concentration. The AFt and AFm-phase minerals cannot under normal conditions be seen in the petrographic microscope.

Capillary porosity
The capillary porosity of the cement paste can be evaluated by fluorescent microscopy in a thin section of the concrete. The method utilizes the impregnation of the capillary pores with fluorescent epoxy, which in fluorescent light (F-mode of the petrographic microscope) makes the paste light up. The higher the capillary porosity, the more it lights up. The capillary porosity is depends on the *w/c* ratio. This is used for an indirect determination of the *w/c* ratio for a given sample by comparison with standard thin sections of known *w/c* ratios. This method is first described by Thaulow et al. [1982]. Furthermore the homogeneity, and hence mixing efficiency and stability, of the cement paste can be evaluated.

Cracks
The micro-scale crack types and crack patterns in concrete can be evaluated by fluorescent microscopy in a thin section of the concrete. Supplementary investigations of plane sections must be applied if the macro-scale cracks are of interest.

Classification of cracks
It is customary to use the crack width as a purely descriptive class reference. This is specified in the Danish test method for petrographic examination of hardened concrete as follows, cf. Danish Technological Institute [1987]:

- *Coarse cracks* Crack width over 0.1 mm
- *Fine cracks*. Crack width between 0.01 and 0.1 mm
- *Micro cracks*. Crack width below 0.01 mm

Coarse and fine cracks may together be called macro cracks.

It is further found useful to make a distinction of micro cracks based on their location in the concrete:

- *Adhesion cracks.* Cracks which run along aggregate particles
- *Cracks in paste.* Cracks which run in the paste
- *Cracks in aggregate.* Cracks within aggregate particles

It is often more convenient to place the distinction between cracks in the paste and fine cracks at a crack width of 0.005 mm, due to a more naturally distinction between cracks related to the normal hydration of the cement (cracks in paste) and cracks related to defects or deterioration of the concrete. This distinction is among others used by Christensen et al. [1981].

A further classification of cracks can be based on the morphology of the cracks i.e. the form and structure of the individual crack or system of cracks:

- *Discordant cracks* with sharp edges that may pass through aggregate particles. Such cracks are assumed to have formed in a relatively hardened and strong concrete.
- *Concordant cracks* of irregular shape that are often deflected around aggregate particles. Such cracks are assumed to have formed in a relatively young, plastic and weak concrete.

Important observations for chloride penetration

Some of the observations obtained from a petrographic examination are of special interest when evaluating chloride distribution in concrete. Some of these observations are set out below:

- *Carbonation* will change the capillary porosity of the cement paste and often create cracks due to the shrinkage related to the carbonation process, thereby changing the chloride transport rate. Another very important property of carbonated cement paste is that the chloride binding capacity is very low.
- *Densified surface skin* is often observed in old concrete. In underwater structures the surface can be densified due to chemical reactions between ions in the pore water and ions in the marine environment. The formation of brucite and aragonite has been reported, cf. Section 5.5.1. The skin effect can have a significant effect on the transport of chloride ions into the concrete.
- *Inhomogeneous capillary porosity* is often observed in concrete. Many factors have an influence on the homogeneity of the cement paste. The use of form work types and textiles is one important factor for chloride transport properties. Use of form textiles drains the concrete closest to the form work, thereby reducing the *w/c* ratio and the capillary porosity near the concrete surface, cf. Sandberg et al. [1993b].
- *Crack intensity* in the concrete has an influence on the chloride transport properties, cf. Sandberg [1995]. In the petrographic analysis it is often possible to detect the cause for the formation of cracks.
- *Determination of concrete mix design* is important when old structures of unknown concrete composition are examined.

4.8 Binding test methods

Since chloride binding is a vital part of the chloride penetration properties of a concrete, and chloride binding properties determine the division of

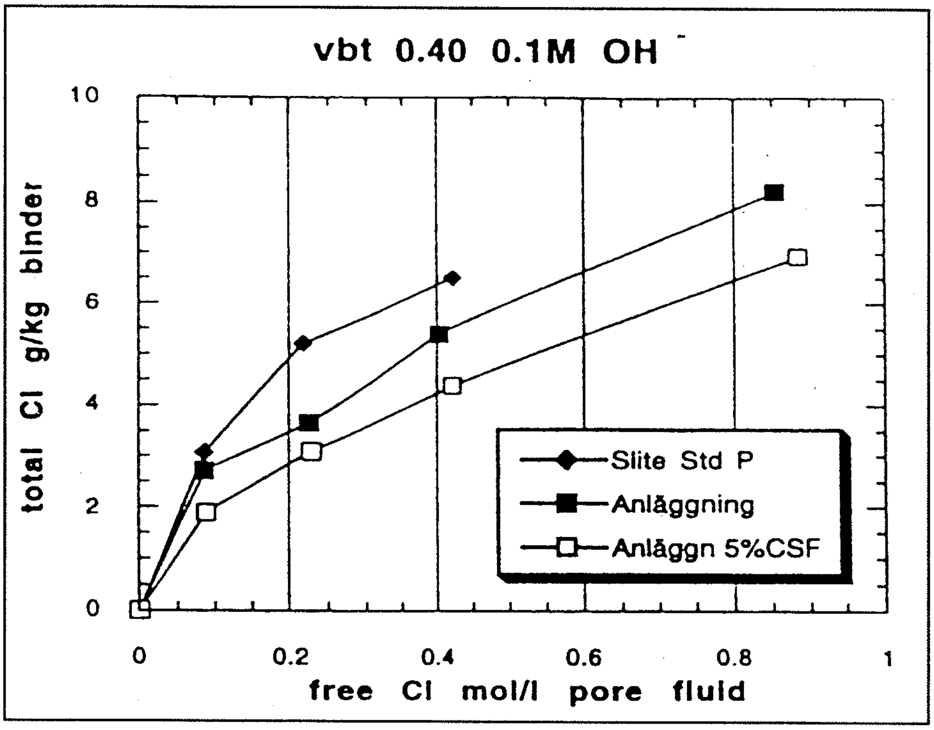


Figure 4-21. Chloride binding isotherms from an equilibrium concentration test method. Larsson & Sandberg [1993].

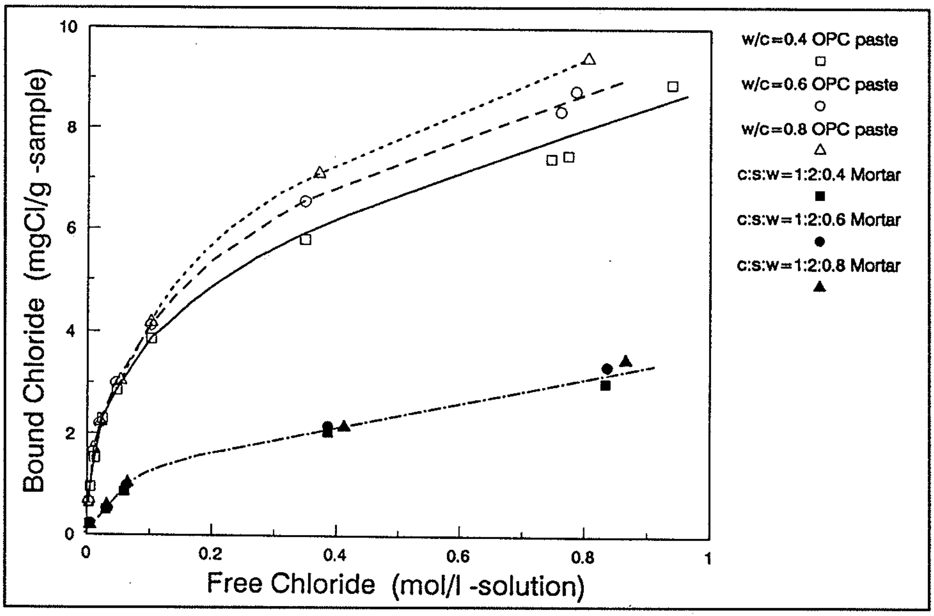


Figure 4-22. Example of chloride binding isotherms. Tang & Nilsson [1993a].

the chlorides in a concrete into free and bound chlorides, these properties are essential when evaluating the corrosion threshold values and when predicting the surface concentrations in a particular chloride environment.

Standardised binding test methods are lacking

In this section a number of binding test methods are reviewed and discussed. None of them, however, is standardised and most of them are scarcely used as test methods.

4.8.1 Immersion binding test methods

The most straightforward methods to determine chloride binding properties are to simply put samples in a known chloride solution and wait for equilibrium to be reached. The choice of the composition of the solution is important since leaching of alkalis and hydroxides will influence the binding properties.

Equilibrium concentration method

Samples in a solution with a known concentration

A crushed or sliced sample of a paste, mortar or concrete, is immersed in a solution with a known chloride concentration. The concentration is maintained constant until equilibrium is reached. The total concentration of chlorides in the sample is then measured, valid for the concentration of the solution. One point on the binding isotherm is obtained in this way.

This method has been frequently used, cf. eg. Byfors [1990], Frederiksen [1993] and Larsson & Sandberg [1993]. An example of test results is shown in Figure 4-21.

Concentration drop methods

Immerse a sample and measure the drop in concentration

By immersing a crushed or sliced sample of a paste, mortar or concrete, which contains no chlorides originally, in a solution with a known chloride concentration and measuring the drop in concentration of chlorides in the solution, the binding properties of the sample may be tested.

The method has been used eg. by Tang & Nilsson [1993a] and Glass & Buenfeld [1995a]. An example of test results is shown in Figure 4-22.

Because of the hysteresis in chloride binding, the volume of the solution should be designed in such a way that the drop in concentration will be small. This is somewhat in contradiction to achieving high accuracy in measuring the size of the drop in concentration.

The time required to reach equilibrium is long; several weeks also for crushed samples, cf. Figure 4-23.

Glass & Buenfeld [1995a] studied the effect of ultrasonic treatment and managed to reduce the required time to equilibrium from some ten weeks to less than two weeks. The final binding was, however, not identical.

Immersion penetration test methods

Immersion tests give binding data

In immersion tests for measuring apparent transport coefficients, curve-fitting a chloride profile to the error-function solution to Fick's 2nd law gives the concrete surface content C_s as a second regression parameter. With the particular concentration c of the salt solution used in the immersion test, one point (c, C_s) on the binding isotherm is determined.

Short term tests, however, are usually made with a very high concentration of chlorides. In such a case the point on the binding isotherm is far away from the conditions in practice. The surface chloride content is more relevant for applications when found in a long term test.

Figure 4-23. The equilibrium process in the concentration drop method.
Tang & Nilsson [1993a].

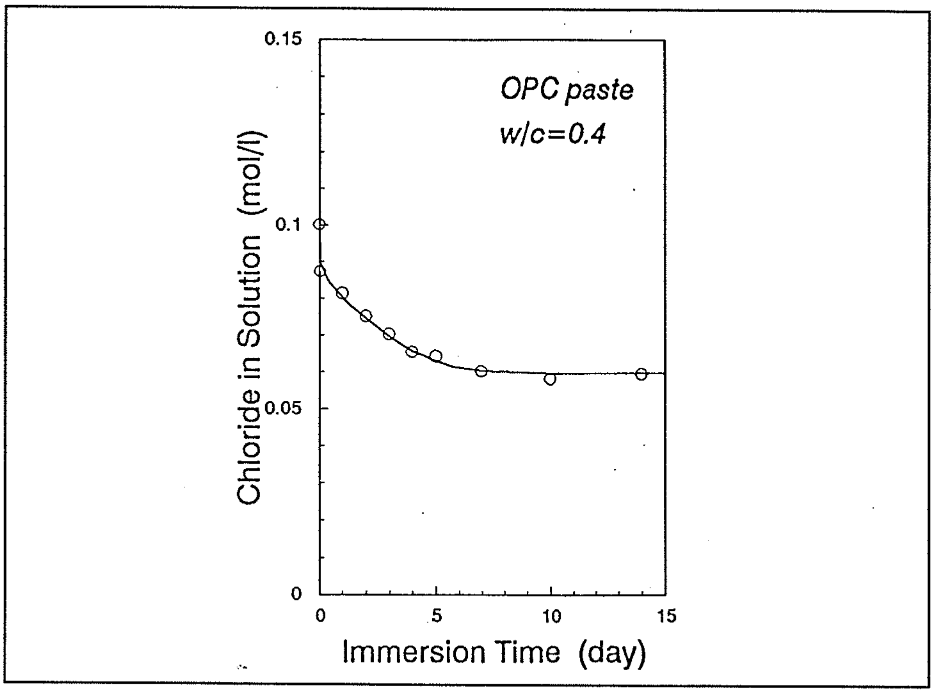
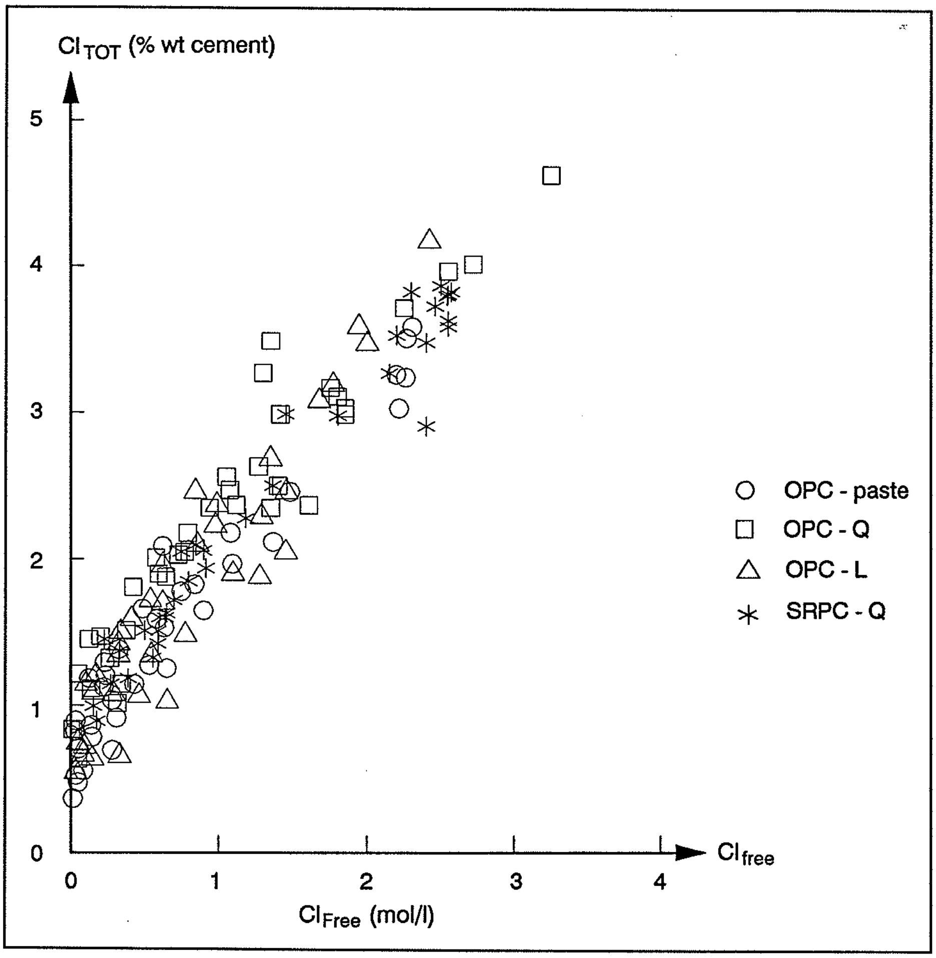


Figure 4-24. An example of chloride binding data from pore solution extraction measurements, *w/c* = 0.5, paste and concretes. Page et al [1991].



4.8.2 Free chlorides on samples

By measuring both the total amount of chlorides and the concentration of free chlorides in the pore water of a sample, one point on the chloride binding isotherm is directly determined. Two methods are used to measure the free chlorides.

Pore solution extraction

Squeeze a sample and analyse the drops of solution

By subjecting a small sample of paste, mortar or concrete, from an experiment or from a concrete structure, to a high pressure in a special device in a testing machine a part of the pore solution may be extracted. The composition of this solution can then be analyzed for its content of ions, including the chlorides. An example is shown in Figure 4-24.

Difficult for high quality concrete

Only a small part, some 10-20 %, of the pore solution will be squeezed out of the sample. For high quality concrete, with a *w/b* ratio below 0.50, with significant self-desiccation, it is very difficult if possible at all to obtain any pore solution.

Strange results due to temperature effects

The pore solution extraction method has been used for decades and the method is widely used today, also for measuring chlorides. However, in a number of cases, strange results have been found where the concentration of chlorides in a sample was very much higher than the concentration in the surrounding solution or sea water. In extreme cases a factor of 2.0 was found between the two concentrations, Nagataki et al. [1993]. Mangat & Molloy [1995] found more chlorides in the pore solution than totally present in the samples! Most of these differences, when measurements are made on field samples, are probably temperature effects when the temperature conditions for the sample are changed by moving it from a colder structure to a laboratory. As mentioned in Section 3.1, chloride binding will decrease when temperature increases, liberating bound chlorides into the pore solution.

A 30% error possible

Similar, but smaller, discrepancies have been found by a number of researchers, cf. Glass & Buenfeld [1995a], who found an error of some 30 % higher concentration in the pore solution. These findings cast a shadow of doubt on results from the pore solution extraction method used in different laboratories. Further clarification is needed.

Leaching techniques

With leaching methods, a sample is crushed to powder and mixed with a solvent. The concentration of chlorides in the solution is then measured. Arya & Newman [1990] reviewed a number of techniques and made comparisons between a few of these and other methods.

Not sufficiently accurate

None of the leaching techniques were "found to be sufficiently accurate" in their tests over the range of mixes they used. Several techniques, each with a limited range of application, were suggested.

4.8.3 Diffusion and migration cell methods

The experiments used for determining diffusion coefficients could be utilized for measuring the binding properties in various ways. A suggested test method is the Bigas′ method, but specimen in ordinary cell methods could be analysed for chloride contents after the experiment is terminated.

Bigas' method

By using a series of diffusion cell tests for concrete slices with different chloride concentration in the upstream cells, the chloride binding isotherm may be determined, Bigas [1994]

A series of diffusion cell tests

In the diffusion cell tests, the flow $F(t)$ through each test sample is measured regularly by measuring the concentration of chlorides in the upstream cell. From that information the steady-state flow and the time lag is evaluated for each sample. Because of the non-linear chloride binding, the time lag will be different for each diffusion cell test, Nilsson [1992], Bigas [1994]. From the measured time lags as a function of chloride concentration in the upstream cells, the full non-linear chloride binding isotherm can be measured.

Non-destructive

The advantage of this method is the possibility of measuring on mortar or concrete samples; the method is non-destructive. The disadvantage, of course, is the very long test periods required; months for mortars and years for concrete!

Common diffusion and migration cell methods

Analyse the specimen after a diffusion cell test

By analysing the total content of chlorides in the specimen after a diffusion cell test has been terminated, an estimate of the chloride binding properties of the test sample may be made.

In its simplest form, the "average" total concentration of chlorides in the interval between the concentrations in the two cells will be determined

$$c_{tot}(0,\ c_{f,1})$$

The concentration in cell 1, $c_{f,1}$, is maintained throughout the whole experiment. The concentration in cell 2, $c_{f,2}$, is measured regularly in a diffusion cell test and replaced by a new solution having a zero concentration of chlorides.

Depending on the intervals of replacement and the chloride flow through the test sample during the intervals, the concentration $c_{f,2}$ will reach a level at the end of each interval that depends on the length of the replacement intervals, the diffusion coefficient of the sample, the volume of cell 2 and the time from the start of the test.

The flow through the sample usually starts from zero and increases up to a maximum steady-state flow. The concentrations in cell 2 will then depend very much on the length of each interval between replacing the solution. The whole idea of a diffusion cell test is to maintain a concentration in cell 2 as close to zero as possible, but of course a small increase $\Delta c_{f,2}$, is to be measured at the end of the intervals. Since the chloride binding capacity is very high at low concentrations, the level of this increase will significantly increase the total content of chlorides in the test sample. Because of the hysteresis between increase and decrease of chlorides, the content of chlorides in the surface region close to the upstream cell will not drop to zero after each replacement of the solution in that cell. The chloride content in the upstream side of the sample will instead adjust to the top values of the concentration in cell 2, Massat [1993]. The chloride content of the sample will consequently be closer to the "average" total chloride content in the interval between the concentration in cell 1 and the maximum concentration in cell 2

$$c_{tot}(\Delta c_{f,2})$$

By measuring the porosity of the test sample after the test has been terminated, the content of free chlorides in the sample can be determined. Since the total amount of chlorides was measured, the content of bound chlorides will finally be determined.

Has not been used very much

This method has not been used to a large extent for chloride binding tests because of the long test period. However, it may be used on thin slices of paste to reduce the time and it may give more useful information than a simple immersion of a similar disc at one concentration that gives only one point on the chloride binding isotherm. This method gives an average binding capacity in an interval.

Migration tests may the future binding test methods

In recent years steady-state migration test methods have been suggested for determining chloride binding isotherms, e.g. Arsenault et al. [1995]. Electrical migration will help in reaching equilibrium conditions in a short time. After a migration test the chloride distribution is almost constant throughout the specimen, cf. Section 3.3. From one experiment one point on the binding isotherm is measured. With a series of migration tests with different upstream concentrations a full binding isotherm could be determined.

Glass & Buenfeld [1995a] report preliminary results from migration tests showing lower chloride concentration inside the specimen than in the surrounding solution. Further studies must clarify and verify the applicability of migration experiments as rapid binding test methods. Because of their simplicity and the short test periods, these methods are promising and should be fully developed.

4.8.4 Other methods

Quantitative X-ray diffraction analysis (QXDA) was used by Arya & Newman [1990] to measure the amount of bound chlorides as calcium chloroaluminate. By measuring the total amount of chlorides in the same sample, the free chlorides may be found by simple subtraction. The free chloride content was overestimated compared with results from the pore solution extraction method.

5 Effects of decisive parameters

5.1 Concrete composition and constituent materials

The chloride diffusivity of concrete, the potential as well as achieved diffusivity, depends on the composition of the concrete and the types of some of the concrete's constituent materials. The decisive parameters are those which determine the porosity of the cement matrix and have an influence on binding the chloride, physically as well as chemically. Sørensen [1995, p.12] has summarised the decisive parameters, i.e. the types of constituent materials and the composition of concrete which influence the chloride diffusivity (rate of chloride ingress):

Cement
- Composition
- Alkali content
- Fineness

Pozzolan
- Fly ash
- Silica fume
- Slag

Admixture
- Plasticiser
- Air-entraining agent
- Polymer

Aggregate
- Porosity
- Transition zone

Composition of concrete
- Water/cement ratio
- Binder content
- Grading curve

It should be noticed that the parameters do not act separately but in combination and interaction between the influences can be expected. One main influence is not taken into account here – namely the influence on chloride diffusivity when the concrete suffers from lack of durability, e.g. disintegration as a result of alkali aggregate reaction, or freezing and thawing, cf. Sandberg [1995, p.62]. However, this topic is not dealt with here. This does not mean that interaction between reinforcement corrosion due to chloride ingress and lack of durability for some other reason are not important – they are, but they have not been studied to the extent that it is possible to draw a practical conclusion.

The chloride diffusivity of concrete is described by the parameters of chloride profiles, cf. Section 2.4. These parameters are:

- The chloride diffusion coefficient D_a or D_p.
- The surface chloride content C_{sa} or C_{sp} of an exposed concrete surface, i.e. the ordinate of the chloride profile at the exposed concrete surface.
- The initial chloride content of the concrete C_i, i.e. the chloride concentration of the virgin concrete.

The influence on the chloride diffusivity of concrete, i.e. the parameters of the chloride profiles, is studied by laboratory experiments and by tests carried out in field exposure stations. The test methods used are explained in Chapter 4. It is assumed that the chloride profiles refer to a determination of the total amount of chloride, i.e. the free and bound chlorides.

5.1.1 Cement

Since the beginning of this century the cement industries have tried to develop portland cement of such properties and characteristics that concrete cast with this cement will be durable and resistant to sea water attack. The research and development were based upon plain concrete and mortar specimens, mainly exposed to sea water and solutions of sulphate. This may be one of the reasons why corrosion of reinforcement induced by chloride ingress was not a part of this research and development.

In the 1980s Ben Gerwick Jr. postulated that concrete made with a typical sulphate resistant portland cement was not as good at resisting chloride ingress as a concrete made with an ordinary portland cement non-resistant to sulphate, all other parameters being kept constant. This postulate inspired many researchers to look more critically upon portland cement as the binder of marine concrete.

Chloride diffusion coefficient and surface chloride concentration

The influence of the type of cement on the chloride diffusivity of concrete has been studied at an increasing rate during the last decade. The chloride diffusion coefficient D_a and the surface chloride content C_s are correlated variables and they are not discussed separately in the following.

Cement composition. It has been a general practice for marine RC structures in Denmark, cf. Efsen [1948], as well as abroad, cf. e.g. ACI, ASTM and BS, to specify a portland cement with a low content of C_3A, i.e. a sulphate resistant cement. Tests carried out by Page [1986] showed that cement paste made from an ASTM Type V portland cement with 1.9 % C_3A by mass showed a significantly higher chloride diffusion rate than other types of portland cement with a higher content of C_3A.

These findings were confirmed by other tests, cf. Rasheeduzzafar [1987]. Hjort [1984] concludes that the higher chloride diffusion coefficient of concrete made from the Danish sulphate resistant portland cement could be neglected by decreasing the *w/c* ratio by 0.05.

An interesting test was carried out by Gjørv [1979] when mortar bars made with five types of cement were exposed to sea water during a period of 54 months. The chloride profiles clearly showed that the surface chloride content and the chloride diffusion coefficient were correlated. The following was observed:

- The Norwegian sulphate resistant cement had the lowest surface chloride content but showed the deepest chloride ingress of all the cements tested.
- A slag cement with 80 % of slag by mass had the highest surface chloride content but showed the smallest chloride ingress of all the cements tested.

Bijen [1985, p.221] concludes: "Although sulphate resistant portland cement is behaving relatively badly regarding chloride ion penetration it is unfortunately often used in coastal areas and offshore in the Middle East".

However, today when marine RC structures contain pozzolan, this is no longer a relevant question, at least in Denmark. Other properties of the cement are important when selecting the cement for a marine concrete mixture design such as low heat generation, early strength etc.

Alkali content of cement. The porosity of the cement matrix depends on the hydration process. A high alkali cement has been preferred for Norwegian offshore RC structures while in Denmark a low alkali cement is preferred for concrete bridges. Various reasons are given for these choices, but the chloride diffusivity of the concrete does not play any role. When concrete is mixed with cement and pozzolan a high alkali cement could create a less porous cement matrix than a low alkali cement. However, the type of cement will often be chosen from other points of view.

Fineness of the cement. The general impression is that the fineness of the cement is of importance for the chloride diffusivity. This was earlier demonstrated by concretes made from Danish ordinary portland cement and Danish rapid hardening portland cement. The fineness was the only difference between the two cements.

Today the Danish ordinary portland cement is no longer produced. The Danish super white portland cement has a very high fineness. However, the type of cement will often be chosen from other points of view.

5.1.2 Pozzolan

ASTM C 318-84 describes a pozzolan as a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with lime (liberated by hydrating portland cement) at ordinary temperatures to form compounds possessing cementitious properties.

It should be noticed that a pozzolanic activity index, cf. ASTM C 618-84 and BS 3892: Part 1:1982, is specified for an assessment of pozzolanic activity with cement. This activity index is based upon compressive strength and has nothing to do with the properties of pozzolan concerning chloride diffusivity.

Chloride diffusion coefficient and chloride surface content

Pozzolan has a good effect on the chloride diffusivity of concrete.

Fly ash. The effect of fly ash on the chloride diffusivity of concrete is generally speaking very positive. When the concrete contains fly ash chloride binding by the cement matrix increases significantly involving an increase in the surface chloride content of the exposed concrete surface as compared with concrete with plain portland cement as binder. Since the binding effect is so high the ingress of chloride is retarded. This means that the chloride diffusion coefficient of concrete containing fly ash is much smaller than that of concrete containing plain portland cement, all other parameters being equal.

The attractive effect of fly ash on chloride diffusivity takes time. On the other hand the good influence of concrete containing fly ash on the chloride diffusivity seems to continue for a long period of time. This makes the use of fly ash very attractive.

Byfors [1987] carried out laboratory tests with fly ash showing that fly ash improves the chloride diffusivity of concrete. This has been supported by others and by the field exposure test in Träslövsläge carried out by the BMB group, Sandberg [1995].

Thus, addition of fly ash to concrete has a great influence on the development of other properties of the concrete. However, by a supplementary addition of silica fume it is possible to adjust these properties. This is one of the reasons why the concrete of the second tube of the Guldborgsund Tunnel was made with a combination of fly ash and silica fume (to gain compressive strength, and to improve air buble distribution in order to ensure the freeze/thaw resistance). The concrete for the structures of the Great Belt Link was from the start planned to contain fly ash as well as silica fume in order to minimise the intensity of micro-cracks, to gain compressive strength, and to improve the freeze/thaw resistance.

The use of fly ash as well as of silica fume has improved the chloride diffusivity of concrete to a great extent, and concrete for future marine RC structures will no doubt contain fly ash (and silica fume).

Silica fume. The effect of silica fume on chloride diffusivity is very positive. In concrete containing cement with silica fume as binder there is not much change in chloride binding by the cement matrix compared with concrete containing only ordinary portland cement. The big difference is that the addition of silica fume results in a cement matrix having a very high concentration of solids leading to a very low porosity, i.e. the ingress of chloride is retarded significantly by an addition of silica fume. This means that the chloride diffusion coefficient of chloride containing silica fume is much smaller than that of concrete containing plain portland cement, all other parameters being equal.

Tests carried out by Byfors [1987], the BMB group, cf. Sandberg [1995], and The Danish Road Directorate, cf. Larsen [1995], showed that silica fume is a type of binder which in a most promising way can decrease chloride ingress into concrete without any critical side effects, especially when combined with the use of fly ash.

Blast furnace slag. Today marine RC structures are made with concrete in which the binder consists of portland cement and blast furnace slag or more simply just portland blast furnace slag cement. The blast furnace slag is a waste product in the manufacture of pig iron.

Typical uses are in mass concrete because of a lower heat of hydration, and in marine RC structures because of a better resistance to sulphate attack and chloride ingress than ordinary portland cement. Portland blast furnace slag cement is in common use in countries where slag is easily available. A variant is part replacement at the mixer of portland cement by dry-ground granulated slag of the same fineness.

The use of blast furnace slag has never become popular in Denmark. The side effects, like the lack of durability to freezing and thawing, a sensitivity to plastic shrinkage etc., and lack of availability on the Danish market have failed to motivate the designer and the contractors of marine RC structures to prefer concrete made with blast furnace slag cements. Several attempts have been made in order to introduce blast furnace slag on the Danish market, cf. the Vejlefjord Bridge and some experimental RC structures for The Great Belt Link.

Efficiency factor. Pozzolan reacts in the concrete in a different way than portland cement, and the hydration products are different, physically and chemically. The *w/c* ratio is the main parameter for many properties of one-binder concrete. A similar main parameter for a two- or a three-binder concrete must include the proportions of binders and water per m^3 of concrete. Since the effects of various types of Holl pozzolan (e.g. silica fume and fly ash) on the properties of concrete are different from the effect of portland cement, e.g. the chloride diffusivity, it will not be possible to use the water/binder ratio (*w/b* ratio) as a reliable parameter:

$$w/b = \frac{W}{C+S+F} \tag{5.1.2:1}$$

Here W is the mixing water, C the cement content, S the content of silica fume and F the content of fly ash, all by mass per volume of concrete, e.g. kg/m^3 of concrete.

The term equivalent *w/c* ratio for a given concrete refers to the value of the *w/c* ratio for a corresponding concrete, where the pozzolan is replaced by such an amount of portland cement that this concrete, with otherwise identical constituent materials, has the same properties (here chloride diffusivity) as the given concrete.

The equivalent *w/c* ratio is not a simple function of W, C, S and F. Furthermore, the function is dependent on the temperature, time and mix proportions. Very little is known about this function from laboratory tests, from experiments carried out in field exposure stations and from examination of marine structures. Therefore, the equivalent *w/c* ratio is defined by the following formula:

$$\text{eqv } w/c = \frac{W}{C+k_sS+k_fF} \tag{5.1.2:2}$$

Here k_s and k_f are the efficiency factors for silica fume and fly ash respectively. In practice, however, the problem is that an efficiency factor depends on both the property in question and on the maturity at which this property is measured – the efficiency factors are not material constants.

The values of the efficiency factors given by the Danish Code of Practice DS 411, i.e. $k_s = 2.0$ and $k_f = 0.5$, are not relevant for the prediction of chloride ingress into concrete.

Maage [1989] found that the efficiency factor of silica fume for chloride ingress into cement paste which was cured for more than six months depends on the water/binder ratio, and the amount of silica fume added. Values of the efficiency factor were found to vary from 5 to 20, and e.g.

five per cent of silica fume was found more efficient than an addition to the cement paste of 10 per cent of silica fume. It was observed that the efficiency factor increased with increasing value of the water/binder ratio. This means that the efficiency of the silica fume is highest in the most porous cement paste.

The question is if these results are relevant for concrete in marine structures. However, there is no doubt that the values given for the efficiency factors by the Danish Code of Practice are too low with respect to chloride diffusivity. Evaluation of the measurement of chloride ingress into various marine RC structures containing pozzolan shows clearly that addition of pozzolan to concrete is a good way to retard chloride ingress and that the efficiency factor is high – but there is a long way to go before the values of efficiency factors are determined, tabulated and accepted.

5.1.3 Admixture

Modern concrete for marine RC structures could not be made without the use of admixtures. Most of the commonly used admixtures have no direct effect on ingress of chloride into concrete. However, the admixtures have an indirect effect, e.g. by producing concrete of better workability and compactibility, i.e. a less porous concrete. Some admixtures especially suited for making the concrete less porous have a direct and good influence on the chloride diffusivity of concrete.

Chloride diffusion coefficient and surface chloride content

Since most of the admixtures act indirectly by making the fresh concrete more workable and compactable, they have no direct influence on the parameters of the chloride profile except what is usual when the concrete becomes more compact.

Plasticiser. It has been proved by laboratory tests that superplasticisers will be able to reduce permeability and chloride diffusivityof concrete, cf. McCurrich [1986]. The effect is believed to be a simple effect of a better compactibility even if the concretes tested achieved a constant workability.

Where the plasticisers are used as water reducing admixtures, the chloride diffusivity is improved by a reduction of the *w/c* ratio – and that is the main effect of plasticisers on the improvement of the chloride diffusivity of concrete.

Air-entraining agent. The air-entraining admixtures have a direct influence on the amount of entrained air bubbles per volume of the cement matrix. Besides this air entrainment has an indirect effect on improving the workability of the concrete. This also improves the chloride diffusivity, but this effect is of minor importance compared with a reduction of the *w/c* ratio which is also possible.

Polymer. A special admixture has been developed for repair mortars. It is the various admixtures of polymers for polymer modified repair mortars. These admixtures, such as styrene-butadiene rubber latex, ethylene-vinyl acetate and polyacrylic ester emulsions have shown good performance in laboratory tests and in practice as admixtures for repair mortars, cf. Ohama [1985, 1986] and Øye [1989].

Polymeric admixtures are still so expensive that they are not used in concrete technology except for admixtures for repair mortars.

5.1.4 Aggregate

The aggregates are a predominant part of concrete. Therefore, aggregate has a large effect on the properties of concrete, including chloride diffusivity. This is not generally recognised.

E.g. the porosity of aggregates has an effect on the chloride permeability of concrete. However, it is very important how connective the porosity is. Zhang et al. [1991] has tested some high-strength lightweight aggregate concretes. They observed that the permeability was more dependent on the porosity of the cement matrix than the porosity of rather porous lightweight aggregate. But they did also observe that the use of natural sand instead of lightweight sand reduced the permeability.

5.1.5 Concrete composition

For given types of constituent materials the chloride diffusivity of concrete is mainly influenced by the capillary porosity of the cement matrix, compaction of the concrete and the ability of the cement matrix to bind the chloride.

This means that for given types of constituent materials the chloride diffusivity is mainly influenced by the *w/c* ratio, the concrete's content of binder and the properties which influence the workability of fresh concrete, e.g. the grading of aggregates and the slump of the concrete.

Chloride diffusion coefficient

The chloride diffusion coefficient of concrete depends on the maturity of the concrete. The rate of change of the chloride diffusion coefficient versus time depends on several parameters, one of which is the *w/c* ratio of the concrete. However, here it is assumed that the chloride diffusion coefficient of a concrete refers to a specified maturity, e.g. a maturity age of 28 days.

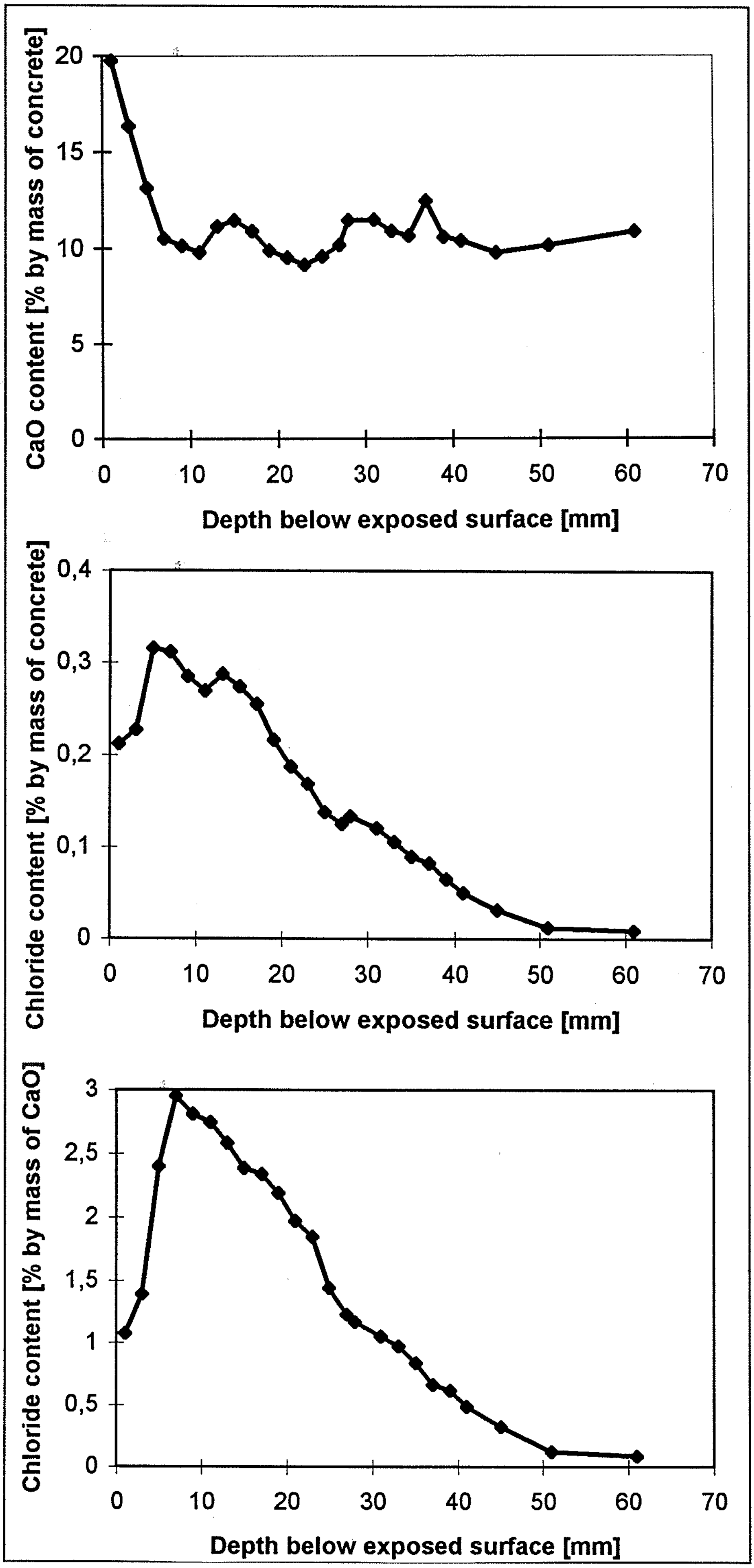
Water/cement ratio. The capillary porosity of the cement matrix is a function of the *w/c* ratio for specified curing conditions of the concrete. Several test series have been carried out in order to study the effect of the *w/c* ratio on the chloride diffusion coefficient of concrete.

Byfors [1987] carried out laboratory test series in order to study the influence of the *w/c* ratio (and other parameters) on the chloride diffusion coefficient.

Binder content of concrete. Concrete for marine RC structures and other RC structures exposed to a chloride containing environment is generally made of non-porous aggregates. This means that the cement matrix of the concrete constitutes the path for ingress of chloride into the concrete. However, the aggregates are not equally distributed in concrete, especially not close to its surface.

Grading of aggregates. The grading curve of the aggregates has little direct influence on the chloride diffusivity of the concrete when the *w/c* ratio is kept constant. But as the water requirement must be varied or the workability adjusted by a change of the added plastisicers, a change of the

Figure 5-1. An example of the variation of binder content, and chloride content, with depth, Andersen [1996].



chloride diffusion coefficient with the grading of the aggregate can be expected.

However, when grading of aggregates results in a harsh concrete impossible or difficult to compact, the grading of aggregate has a predominant influence on the chloride diffusion coefficient.

Surface chloride content

The surface chloride content C_s of the exposed concrete varies with the length of the period of exposure, cf. Uji [1990], and the chloride concentration of the environment. Therefore, for practical purposes C_s should be determined either from examination of older marine RC structures and highway structures or from studies of concrete specimens placed in a field exposure station.

Water/cement ratio. From inspection of marine RC structures, cf. Sørensen [1995] and highway RC structures, cf. Larsen [1995], there has not so far been found a clear picture of a systematic influence of the *w/c* ratio on the surface chloride content of exposed concrete surfaces.

Binder content of concrete. The surface chloride content C_s depends among other characteristics on the binding capacity of the binder. This means that C_s when measured as % by mass of concrete increases with increasing binder content of the concrete, cf. Bamforth [1993a], Browne [1980], Thomas [1990], Gjørv [1979], Mausin [1986] and Makita [1980]. However, when C_s is measured as % by mass of binder C_s seems to be independent of the binder content of the concrete, cf. Bamforth [1993a]. However, since C_s depends on the exposure period the test data collected from several authors show a rather large scatter.

Grading of aggregates. There has not so far been found an influence of the aggregate grading on the surface chloride content of exposed concrete surfaces.

5.2 Heterogeneity

The more or less "normal" heterogeneity of a concrete due to "wall effects", or other surface effects, at the formwork cannot usually be avoided. However, with the use of special formwork material these effects may be intentionally reduced and even "inverted" by producing a surface layer that has a better quality than the rest of the (homogeneous) concrete.

A cast surface gives a "wall effect" with a higher binder content

Close to a cast surface the amount of larger aggregates is reduced due to the wall effect. Similarly, depending on the particle size, the local composition of the concrete is strongly depth dependent and heterogeneous. The amount of binder varies with the depth from the surface, cf. Figure 5-1.

The differences in binder content naturally cause differences in chloride content since chloride binding is a function of the amount of binder, cf. Figure 5-1. Obvious effects of this kind of heterogeneity are increased chloride contents close to the surface when relating the amount of chlorides to the weight of concrete or weight of sample. For short exposure times this effect could cause tremendous changes in the chloride profiles.

Fibrous formwork densifies the surface

Basheer et al (1995) report a study on the effect of a polypropylene fibre "controlled permeability formwork" (CPF). By "draining away the surplus mixing water and entrapped air from the surface of the wet con-

Figure 5-2. Chloride profiles after a salt water suction test of concrete surface layers produced with CPF or timber form work.
Basheer et al. [1995].

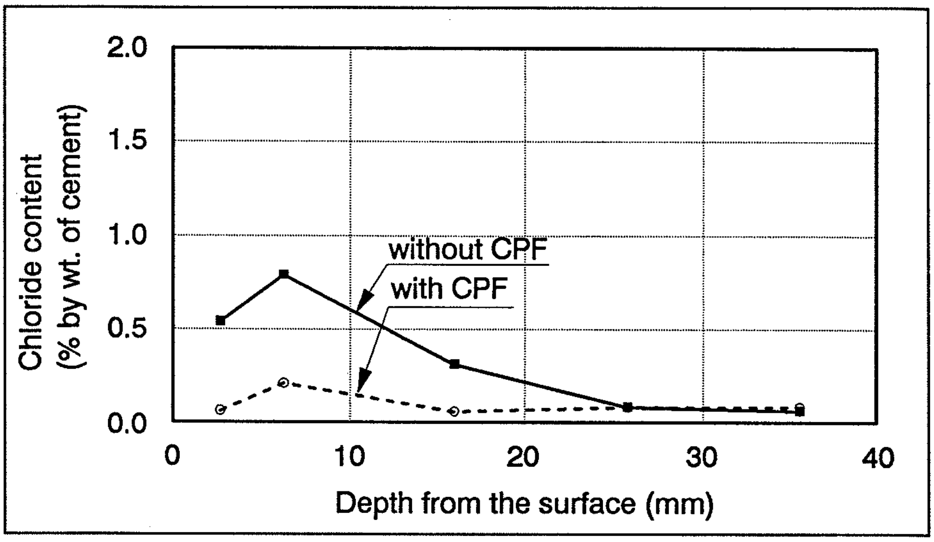
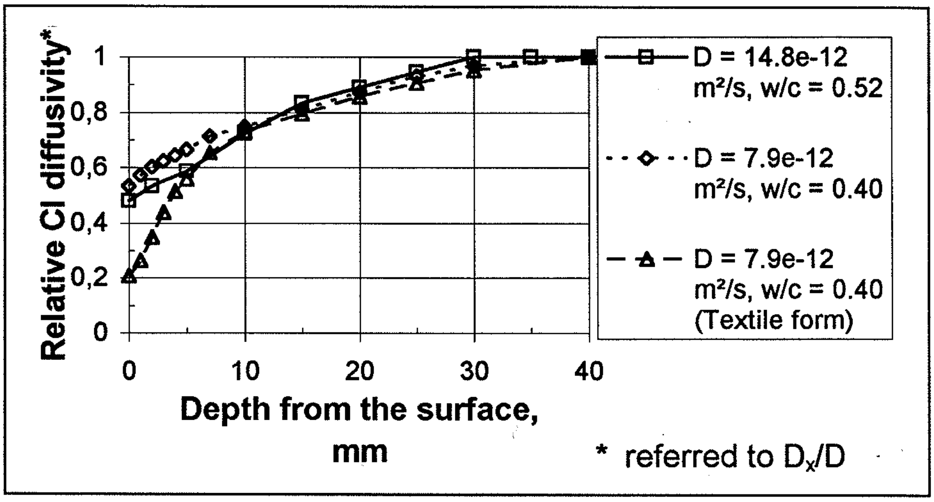


Figure 5-3. Diffusion coefficients at different depths from surfaces cast with textile formwork and timber formwork respectively.
Sandberg & Tang [1993].



crete" a lower permeability surface layer is supposed to be produced. The procedure gives a significant reduction, compared with conventional timber formwork, in the chloride penetration tests that they report. Both w/c=0.45 and w/c= 0.65 were tested, cf. Figure 5-2.

The tests were a kind of a salt water capillary suction test for 24 days, after no curing and 75 days of drying. The difference in densification of the surface layers with the two types of formwork obviously changes the permeability to (salt) water in a very significant way.

Similar formwork was used in the repair of the Öland Bridge on the east coast of Sweden. Cores from the bridge were tested after four years, cf. Figure 5-3.

The findings from the field concrete in Figure 5-3 cannot explain the extreme effects found by Basheer et al. The concretes and the formwork are not identical. In spite of this, it may be concluded that further experience must be gained to get a proper quantification of the effects of fibrous formwork on the heterogeneity, chloride binding and chloride transport properties of the surface layer.

5.3 Curing

The microstructure which concrete develops depends on the curing and the development of the concrete's maturity with time. Especially the concrete of the near-to-surface layer is sensitive to its curing conditions.

The permeability of concrete with regard to environmental exposure to harmful substances such as chloride is determined by the capillary porosity and microstructural defects, cracks and gross porosities of the cement matrix. It must be borne in mind that porosity and permeability are not synonymous. A porous material can quite well be impervious if defects, voids and cracks do not form an interconnected system.

The dimension of a chloride ion is in the order of 2 Å. The capillary pores commonly have a diameter in the order of 0.02-50 Å. Thus they can provide access for ionic transportation when the capillary pores are filled or partially filled with pore liquid, and for transportation of gases when the capillary pores are filled with air.

Concrete generally has a certain intensity of defects, i.e. microcracks, fine and coarse (non-structural) cracks, paste separation and voids. It must be borne in mind that not all these defects have free access to the surroundings. Therefore, it can not be expected that defects will increase the permeability and diffusivity of the cement matrix and the concrete.

The conclusion is that concrete for marine structures should be designed, cast, compacted and cured in such a way that the effect of the capillary porosity and micro- and macrodefects on chloride diffusivity is a minimum. The experience so far of the influence of the microstructural defects is minimal so that until further knowledge is available one must aim at producing a concrete with as few microstructural defects as possible. There is, however, sufficient experience to point out that the cement matrix must have as low a capillary porosity as possible, and be without continuous cracks, macro cracks and micro cracks.

5.3.1 Optimising the capillary porosity

Concrete should be cured so that the cement during the hydration process develops a cement matrix with as little capillary porosity as possible at the time when the concrete is exposed to chloride for the first time.

Curing time

The capillary porosity of the cement matrix decreases with increasing maturity of the concrete. This means that concrete should be exposed to chloride as late as possible. This is an old requirement, e.g. specified by the Danish Code of Practice for marine RC structures from 1926 where Section 8 specifies:

"Concrete made with portland cement should not be exposed to sea water before the curing time of the concrete has achieved a minimum of six weeks. If the concrete has a surface protection of tar or is protected in another similar way, only the strength requirement determines the time of sea water exposure".

This good old rule seems to be completely forgotten today.

Surface protection

Today surface protection of concrete by applying tar could easily be replaced by more modern coatings suitable for application on wet concrete surfaces. Application of such coatings will form a counterpart to the curing compound by which concrete is sealed in order to prevent evaporation of water and formation of shrinkage cracks.

The coatings need not be very durable since the purpose is just to protect the young concrete from chloride ingress until the concrete has achieved such a maturity that its capillary porosity is suitable to withstand the chloride exposure without too high a penetration rate.

The application of silanes as a coating in particular can potentially reduce chloride levels significantly, cf. Pfeifer [1987]. Thus the UK Department of Transport now specifies a surface treatment of this type for bridges which are exposed to de-icing salts. Results from field exposure at the South Coast of England indicate significant benefits of the use of silanes with C_s being reduced by 60 %, cf. Bamforth [1993a]. It must howevr be born in mind that such results are only valid for that particular concrete and cannot be generally adopted.

Curing temperature

It is well-known that the capillary porosity of a cement matrix can be damaged by allowing the concrete to develop too high a temperature during the curing process. The effect of too high a temperature is that the capillary pores become somewhat coarser than if a lower temperature had been applied until the same maturity was reached. This could affect the rate of carbonation and chloride ingress when the concrete is exposed to these aggressive substances. Thus, specifications for large RC marine structures such as the Great Belt Link prescribe an upper limit for the temperature of the concrete when the hydration process takes place.

The limitation of the curing temperature during the hydration process is especially important for the production of precast elements. There are no tests dealing with the chloride diffusivity of precast concrete elements versus various temperature levels.

5.3.2 Precaution against defects

Defects such as cracks, especially the macro cracks, have a tendency to form an interconnected system. If these cracks pass through the reinforcement cover the defects will have a significant influence on the chloride diffusivity of the concrete.

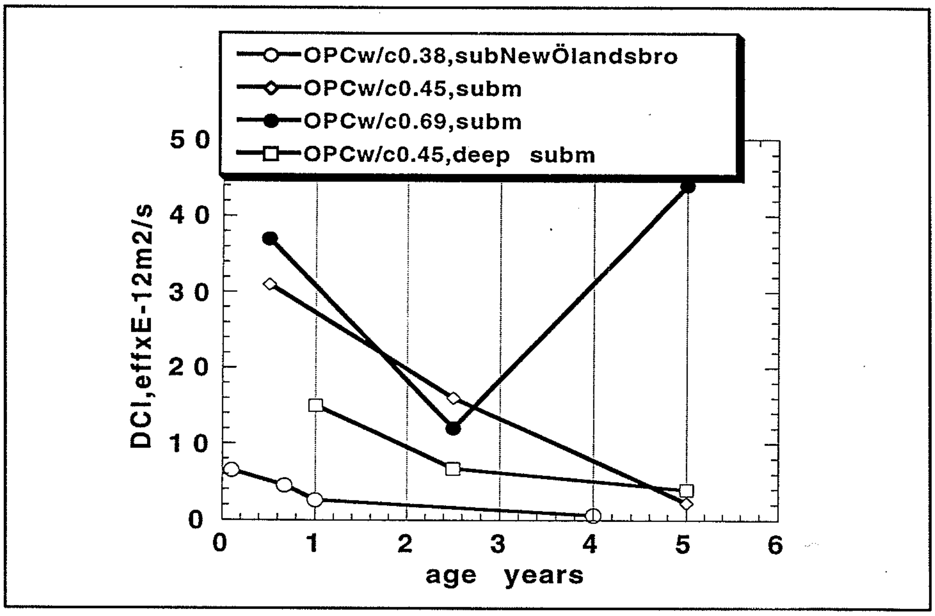


Figure 5-4. "Effective chloride diffusivities" from repeated measurements on Portland cement concrete, submerged marine exposure. Stillwell [1988], Sandberg and Tang [1993].

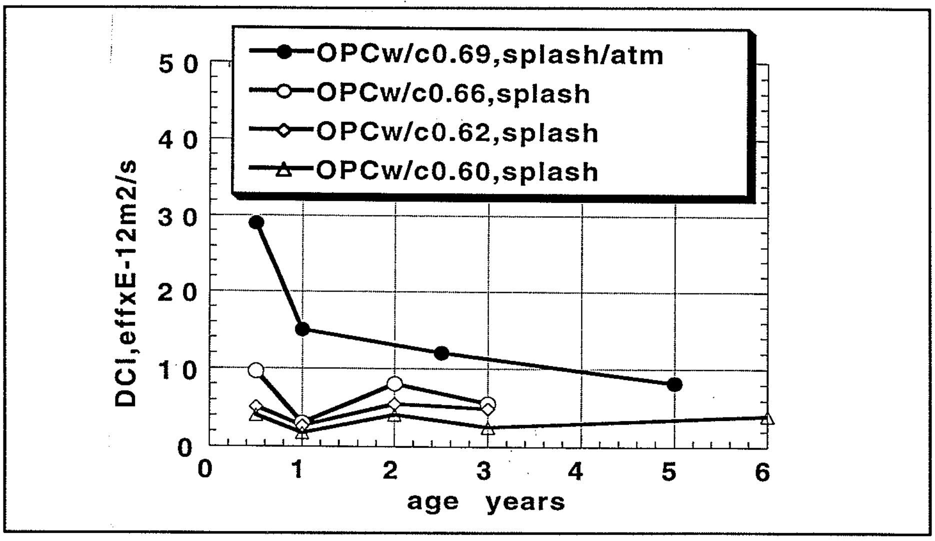


Figure 5-5. "Effective chloride diffusivities" from repeated measurements on Portland cement concrete exposed in the splash- or tidal zone. Stilwell [1988], Bamforth [1993, 1995].

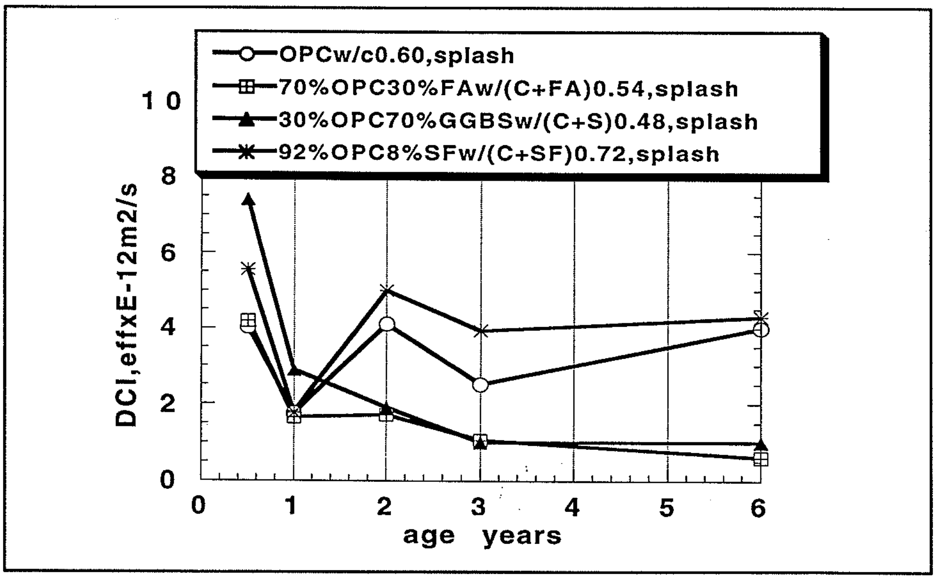


Figure 5-6. "Effective chloride diffusivities" from repeated measurements on concrete with various mineral admixtures, splash zone exposure. Bamforth [1995].

Thermocracks

Thermocracks in a concrete surface will pass perpendicular to the surface and pass through the reinforcement cover. Concrete specimens with thermo-cracks have been exposed for nine years to sea water at a beach near Halsskov. Tests have shown that the chloride ingress was higher than expected according to the type of cement used and the *w/c* ratio applied, cf. Poulsen [1990].

Cracks will increase the chloride diffusivity, especially when the crack intensity is high. The influence of cracks on the risk of corrosion is dealt with in detail in Section 6.1.

Controlled permeability formwork

The method of controlled permeability formwork (CPF) or the Textile Form Method was first developed 10 years ago on the Aseishi-Gawa Dam Project in Japan in order to reduce air bubbles or blow holes generated on sloping concrete surfaces. cf. Takayoshi [1986]. The textile form method employs conventional plywood panels that have been perforated with small holes (3-5 mm in diameter) spaced approx. 100 mm apart. The panels are covered with a alkaline resistant ductile synthetic textile. The method allows air and water to permeate through the holes in the panels while preventing the loss of cement particles. This produces a lower *w/c* ratio in the near-to-surface-layer of the concrete as well as a bubble-free surface.

Tests have shown an improvement of the near-to-surface layer of the concrete surface, e.g. the depth of chloride penetration is reduced significantly (by a factor of up to 5), cf. Machida [1986] and Marosszeky [1987,1990].

Tests carried out by the AEClaboratory and Chalmers University of Technology have shown similar results, cf. Sandberg & Tang [1993b].

5.4 Exposure time

The chloride transport rate expressed as an achieved chloride diffusion coefficient decreases over time.

Only limited data have been obtained by repeated measurements at various exposure times on the same concrete. In Figure 5-4 the calculated diffusion coefficients at various exposure times are shown for portland cement concrete submerged in sea water, data from Atlantic exposure, Stillwell [1988] and Baltic Sea exposure, Sandberg and Tang [1993a]. Note that the chloride concentration in the Baltic Sea at New Öland Bridge is only 20-25% of that in the Atlantic. Furthermore, a special textile formwork was applied at the New Öland Bridge, allowing a reduction of the *w/c* ratio in the concrete surface from *w/c*=0.38 in the bulk to *w/c* around 0.35 close to the cast surface. The 5-year data for submerged concrete with *w/c*=0.69 does not follow the general trend. This is difficult to explain, since no freezing and thawing or other degradation processes would be expected to significantly affect the microstructure of submerged concrete already after 5 years of exposure.

Data from concrete with w/b ratio > 0.60 are more conflicting, especially in the splash or tidal zone

The data from repeated measurements in the splash or tidal zone are more conflicting, although the general decrease in chloride transport rate is observed in most cases. As illustrated for Atlantic exposure in Figure 5-5, Stillwell [1988] found a decreasing chloride transport rate over time for portland cement concrete (*w/c* = 0.69), as opposed to the results for portland cement concrete (*w/c* = 0.60-0.66) reported by Bamforth [1993, 1995]. As indicated in Figure 5-6, Bamforth [1995] found a decrease in chloride transport rate over time for concrete containing fly ash or slag,

Figure 5-7. "Effective chloride diffusivities" from repeated measurements on concrete with various additions of silica fume, tidal zone exposure. Hammer et al. [1991], Gautefall [1993].

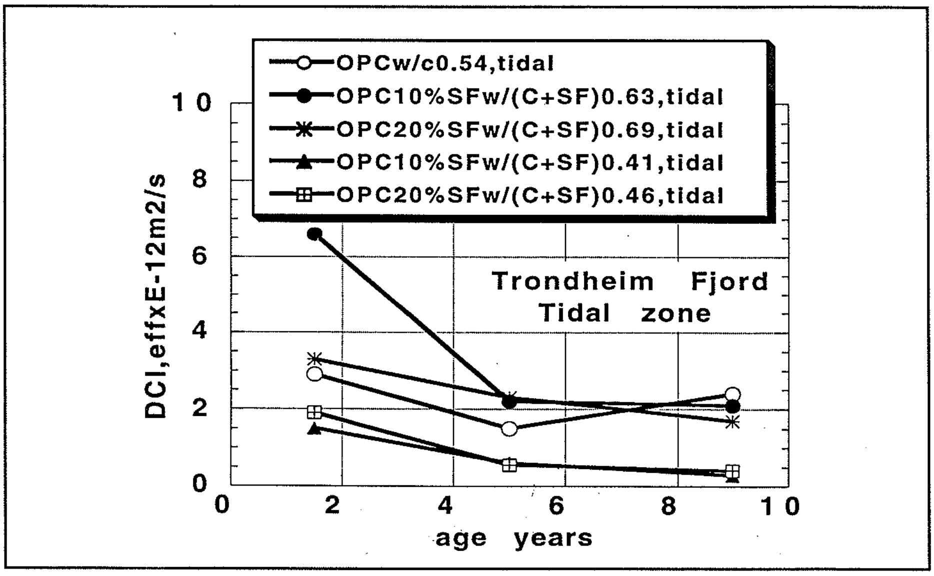


Figure 5-8. "Effective chloride diffusivities" from repeated measurements on high performance concrete exposed in the splash zone.
Sandberg [1995].

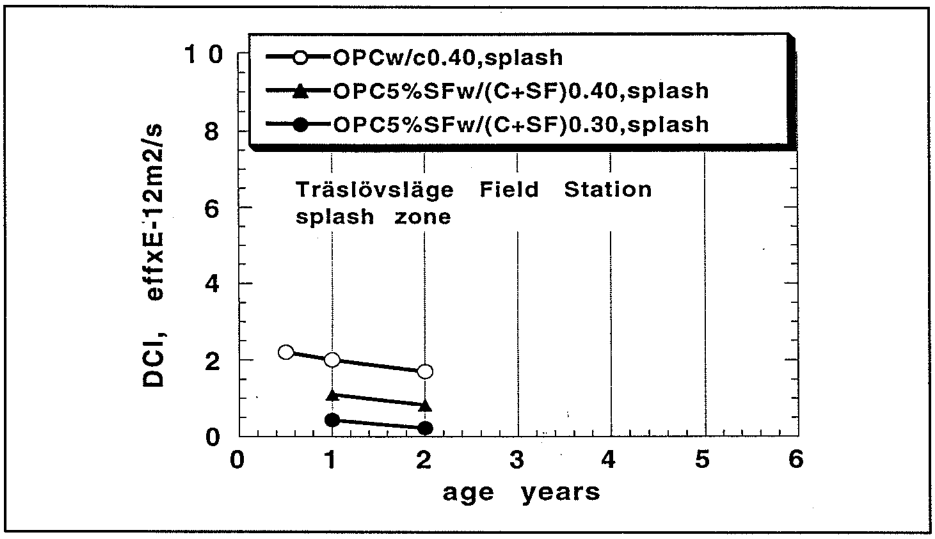
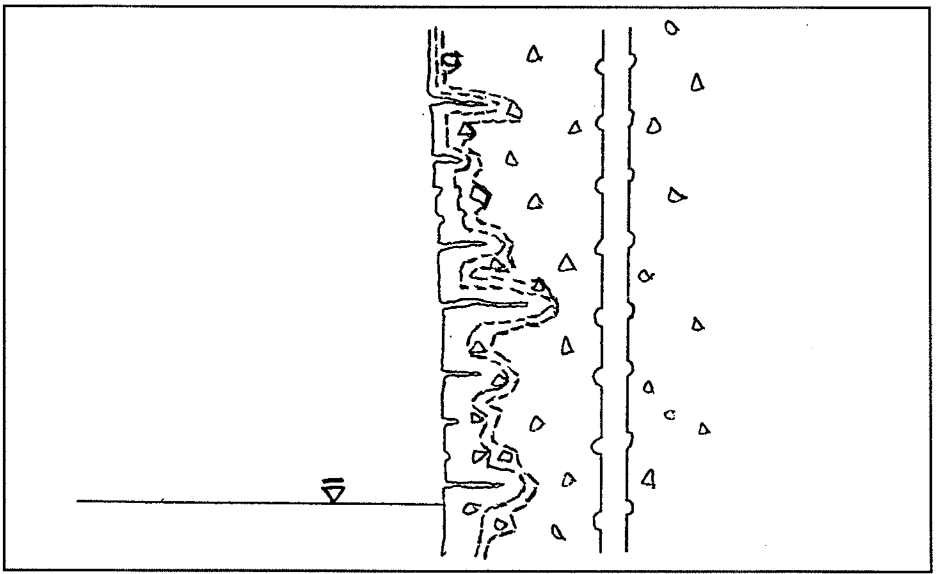


Figure 5-9. Schematically illustration of the chloride penetration front following the crack surfaces.



but an increase over time for concrete containing silica fume and for plain portland cement concrete. Note that the *w/b* ratios vary over a wide range in the data used by Bamforth.

Data from Atlantic exposure sites in Norway and Sweden have supported the tendency for a decrease in chloride transport rate over time as reported by Stillwell [1988], also for plain portland cement concrete and for concrete with silica fume as illustrated in Figure 5-7, Hammer et al. [1991], Gautefall [1993] and in Figure 5-8, Sandberg [1995]. Vennesland and Gautefall [1995] found that the chloride transport rate did not decrease in the Ekofisk Storage Tank from 5 years to 9 years of splash and tidal zone exposure.

The decrease in the achieved chloride diffusion coefficient over time is most pronounced during the first 5 years of exposure

Looking at all the data in Figures 5-4 to 5-8, one may conclude that the tendency for a decrease in chloride transport rate over time was valid for all concrete mixes with a *w/b* ratio < 0.60. The effect is most pronounced in the first years of exposure. The picture is less clear for lower grade concrete, possibly because other degradation mechanisms may become relatively faster and therefore affect the concrete permeability. Furthermore, the well known positive effect of a decrease in the *w/b* ratio was confirmed as illustrated in Figures 5-4, 5-7 and 5-8.

5.5 Cracks and cavities

The presence of macrocracks and cavities in the exposed surface of a concrete structure will of course increase chloride penetration into the concrete, no matter whether the structure is submerged, in the splash zone or exposed to deicing salts. The chloride penetration front then follows the crack surfaces as schematically presented in Figure 5-9.

If macro cracks or cavities are not in contact with the concrete surface, the situation can be quite different. Chlorides need water to be able to move within the concrete. Macrocracks and cavities without surface contact are often not filled with water. In these situations the defects will act as a barrier against chloride ingress.

5.5.1 Macrocracks in submerged concrete

In submerged structures macrocracks are permanently filled with water, thereby acting as a high velocity diffusion path for chlorides. However, cracks in submerged concrete tend to be sealed (blocked) by reaction products between compounds in the concrete and compounds in the seawater. Formation of brucite (manganese hydroxide) and aragonite (calcium carbonate) has been reported by several authors, cf. Somerville [1978], Conjeaud [1980], Stillwell [1983] and Sandberg et al. [1993a].

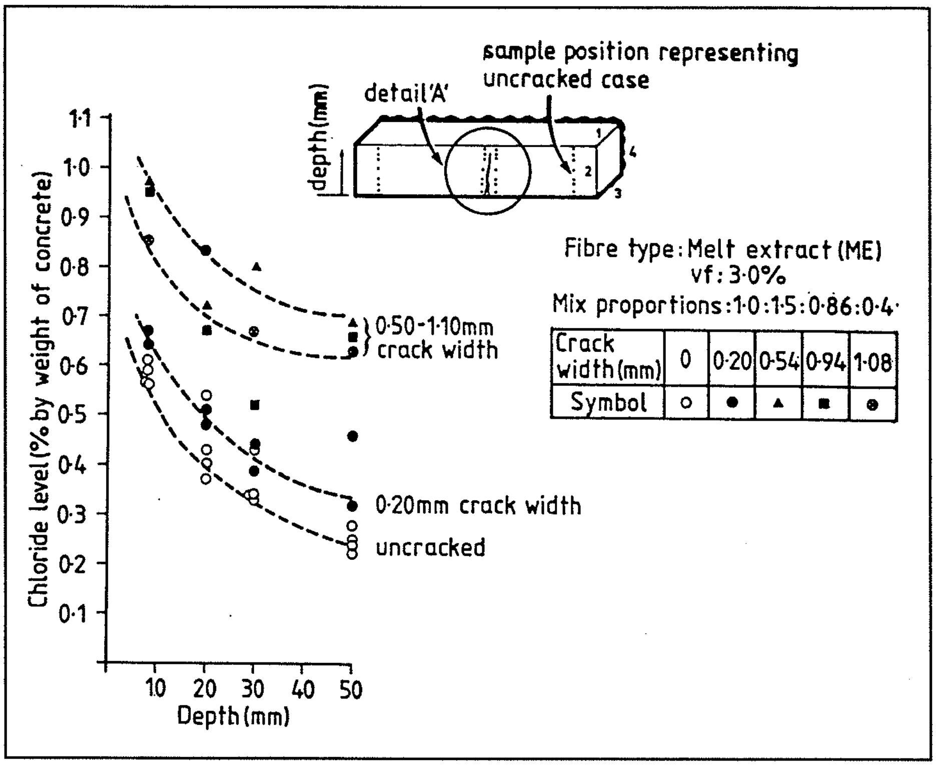
5.5.2 Macrocracks in atmospheric zone concrete

Wetting and drying is generally the most aggressive exposure condition for cracked concrete. The cracks will occasionally be filled with water. Smaller cracks can even have capillary suction of saline water. Further more the chloride content will be concentrated during drying periods.

Mangat et al. [1987] show data on the Cl^--concentrations close to cracks. They conclude that the concentration in the vicinity of cracks increases with increasing crack width, cf. Figure 5-10.

A self healing effect has been reported for deicers containing CMA (calcium magnesium acetate), cf. Page et al. [1982], but less is known about the effect of NaCl and $CaCl_2$ based deicing salts.

Figure 5-10. Effect of crack width on chloride penetration after exposeure to 1450 marine spray cycles.
Mangat et al. [1987].



5.5.3 Fine cracks (less than 0.1 mm)

Permeability depends on crack intensity

The significance of fine cracks (width less than 0.1 mm) in concrete for permeability is highly dependent on the crack intensity. Samaha et al. [1992] found that load-induced fine cracks will not increase the permeability until the load exceeds about 75 % of maximum strength. This implies that the crack intensity must exceed a certain level before the crack system becomes connective and thereby influences the permeability. This is confirmed by Fagerlund [1993], who modelled chloride penetration into concrete with and without such cracking. Fagerlund's calculations showed that isolated fine cracks have only a marginal effect on the diffusivity of concrete unless the frequency and crack width are exceptionally large, whereas continuous cracks have a large effect for dense concretes with low *w/c* ratios. Investigations of Ölandsbron in Sweden showed that concrete with a connective system of fine cracks can increase the rate of chloride penetration by a factor of 3-5 compared with uncracked concrete, cf. Sandberg et al. [1993a].

Isolated microcracks have only marginal effect

5.5.4 Cavities

The effect of cavities are similar to those of macrocracks. They act conductive to chloride penetration if filled with water, and if not they act resistive.

5.6 Environmental Conditions

The rate of chloride ingress into concrete exposed to marine environment and de-icing salts depends on the concrete itself (the potential properties) as well as the chloride aggressiveness of the environment. In fact, the chloride diffusivity of the concrete differs. Ingress of chloride into concrete in the splash zone could be smaller than ingress of chloride into concrete in the marine atmospheric zone during the time of exposure.

The various environmental parameters have a predominant influence on the chloride ingress into chloride exposed structures, marine RC structures as well as inland structures. Thus, the various environments are studied by many laboratories and institutions, but so far this has not yet resulted in a standard for the description of a chloride laden environment, e.g. similar to the standard for the wind actions on buildings. However, it has generally been agreed that certain parameters of a chloride laden environment are dominant regarding the ingress of chloride into concrete structures.

The ingress of chloride into concrete structures at a specified position of a chloride exposed concrete surface is described by the achieved chloride profile as a function of the exposure period. A chloride profile is determined by several parameters, and the parameters of the environment may also have various or even opposite influence on the parameters of the chloride profile, and some of the profile parameters may be invariant to the environmental conditions.

A chloride profile is described by the following four parameters:

- The achieved chloride concentration at the concrete surface C_{sa}.
- The initial chloride content of the concrete C_i.
- The achieved chloride diffusion coefficient D_a.
- The exposure period $\Delta t = t - t_{ex}$, where t_{ex} is the time when the concrete is exposed to chloride for the first time and t is the age of the concrete.

Naturally, the initial chloride content of the concrete is invariant to the environmental conditions.

It is possible to combine the effect of these parameters by introducing the ingress x_r of a reference chloride concentration C_r, often taken as 0.1 % by mass of the concrete. However, the nuances would easily disappear in this way. Thus, it is preferred to give a brief summary of the influences of the basic parameters of the chloride profile.

The parameters of a chloride laden environment which influence the achieved chloride profile are as follows:

- The temperature of the concrete.
- The chloride concentration of the liquids in the environments (e.g. sea water and melting water containing de-icings salts).
- The moisture saturation of the concrete.
- The chloride exposure zones of marine RC structures: The wet zones (submerged, splash, tidal and wave zones) and the semi-wet zones (marine atmospheric zone, leeward and windward sides).
- The de-icing salt exposure of RC structures: The horizontal upward concrete surfaces (e.g. parking deck, bridge deck) and the traffic splash zones (e.g. bridge pillars, tunnel walls, edge beams).

5.6.1 Temperature

Chloride ingress by diffusion depends on the temperature of the concrete, cf. Sørensen [1990, p.4], and is claimed to obey the Arrhenius equation.

Application of the Arrhenius equation forms one of the assumptions of the method by Saetta et al. [1993] for the analysis of chloride diffusion into partly saturated concrete.

Chloride diffusion coefficient of concrete

However, only few tests series have been carried out in order to determine the influence of the temperature on the chloride diffusion coefficient, cf. Sørensen [1990]. Many test series show a gross deviation compared with the numbers of test samples. This may be due to the fact that the diffusion coefficient D_a and the surface chloride content C_{sa} of the concrete are correlated, and the temperature does not have the same influence on C_{sa} and D_a as seen later.

The influence of temperature on the diffusion process is mainly studied by laboratory tests. However, by examination of chloride profiles from concrete in hot and cold countries it should be possible to study the influence of temperature on the chloride diffusion process in realistic environmental conditions. International cooperation is thus necessary, and an increasing understanding of the problems is on the way. As a result of this, observations and test data from experimental field stations around the world could be compared and a better understanding achieved.

Chloride content of the exposed concrete surface

Laboratory tests have shown that the chloride levels in extracted pore fluid from chloride exposed cement paste were lower at low temperatures than at higher temperatures, cf. Larsson [1995]. In this case samples of cement paste were made from low alkali sulphate resistant portland cement, the *w/c* ratio ranging from 0.40 to 0.75 by mass. Specimens, each 3 mm thick, were placed in liquids with varying OH^- and Cl^-

concentrations at temperatures of 5 °C and 20 °C for more than 22 months after which the pore fluid was extracted and analysed.

Examination of concrete exposed to sea water in Greenland shows a very high chloride content at the concrete surface and this agrees with the above mentioned laboratory tests. Otherwise, chloride profiles from sea water exposed concrete structures in hot countries like the Middle East show significantly lower chloride content at the concrete surface, cf. Weir [1985] and Pollock [1985]. However, parameters other than the concrete temperature have an influence on the chloride content of an exposed concrete surface, such as e.g. the porosity or the diffusivity of the concrete, cf. Walter [1985].

5.6.2 Degree of moisture saturation

The ingress of chloride into concrete, by diffusion, permeation etc. takes place through the pore liquid in the capillary pores, cracks and defects of the concrete and even its aggregates. Thus, it is easier for the chloride to penetrate a moisture saturated concrete than a dry or semi-dry concrete.

This is clearly illustrated by Buenfeld [1995], who carried out tests to study and model chloride transport due to wick action in connection with chloride ingress through thin concrete slices. Wick action is the transport of water (and chloride in this case) through a concrete wall specimen which has one face in contact with water and the other face exposed to air and drying out. One part of the wall will be saturated with water while the other part will be only partly saturated. The measured chloride profiles clearly show that the chloride quickly penetrates the saturated concrete, but the rate of ingress is much slower in the non-saturated part of the concrete.

It is observed that the ingress of chloride into concrete pillars of concrete bridges crossing sea water decreases with the height above sea level, cf. Sørensen [1982, p.12] and Sandberg [1995, p.43]. However, this might be a combination of the decreasing humidity of the concrete and the decrease in chloride aggressiveness with the height above sea level.

Achieved chloride diffusion coefficient of concrete

Examination and evaluation of observations from chloride profiles obtained from Danish marine RC structures show that the achieved chloride diffusion coefficient of the concrete decreases with increasing height above sea level, cf. Sørensen [1995, p.24]. A similar effect was also found by Wood [1995], Sørensen [1982] and others.

The effect of the height above sea level on the chloride diffusion coefficient could be due to the degree of saturation of the concrete, but could also be due to a decrease in the aggressiveness of the chloride in the marine atmospheric zone. However, it is believed that the degree of saturation of the concrete has a predominant role.

On the basis of the work by Bazant [1972] the method of Saetta [1993] assumes that the influence of the humidity of concrete on the chloride diffusion coefficient is proportional to the following factor:

$$f(RH) = \left(1 + \frac{(1-RH)^4}{(1-RH_c)^4}\right)^{-1} \qquad (5.6.1{:}1)$$

Here RH_c is the humidity of the concrete at which the chloride diffusion coefficient drops halfway between its maximum and minimum values. This has been inspired by the work of Bazant [1972].

Chloride content of the exposed concrete surface

Examinations of chloride profiles of concrete samples from pillars of Danish concrete bridges exposed to marine environment show that the chloride content C_{sa} of an exposed concrete surface decreases with the height above sea level. cf. Sørensen [1995, 1982]. It seems to be the general picture that C_{sa} is almost constant from 2.5 m above sea level and up to 15 m above. Below 2.5 m C_{sa} increases and seems to reach its maximum value at sea level. The same effect is observed by Sandberg [1995], Wood [1995], Bamforth [1993, p.1107] and Fluge [1995].

It could be discussed whether the effect of the height above sea level is influenced by the humidity of the concrete. For onshore structures the distance from the seaward face has a similar effect on C_{sa}, cf. Bamforth [1993] and Roper [1988], and it is not believed that the humidity changes significantly with the distance from the seaward face. Thus, the effect of the aggressiveness of the chloride is a better explanation, but more observations and further studies are needed.

5.6.3 Chloride exposure of marine structures

The ingress of chloride into the concrete of structures in a marine environment depends on the aggressiveness of the chloride. In order to simplify the complicated behaviour of several ingress mechanisms, the chloride aggressiveness is illustrated by a concrete bridge pillar in an offshore position. The pillar is divided into various zones, each representing an exposure zone significantly different from its neighbour zones. These exposure zones are from top to bottom:

Semi-dry zones:

- The atmospheric marine zone windward side.
- The atmospheric marine zone leeward side.

Wet zones:

- The splash zone.
- The wave zone.
- The tidal zone.
- The submerged zone.

Each of these zones has its characteristics and influences on the ingress of chloride into the concrete of the pillar.

Wet zones of marine RC structures

Ingress of chloride into high quality concrete in the wet zones of marine structures is significantly greater than into the concrete in the atmospheric marine zone. This is not necessarily the case for lower grade concrete.

The submerged zone. Concrete submerged in sea water has a well defined exposure condition, being constantly exposed to sea water. Diffusion is the predominant mechanism of chloride ingress into submerged concrete.

The tidal zone. At any coastal location the tide comprises a rise and fall twice a day, i.e. over a period of 12 hours and 25 minutes. As a result of this tidal action the concrete of structures is exposed to wetting and drying, heating and cooling, and freezing and thawing in two cycles daily. This kind of exposure is among the severest to which concrete can be exposed. The risk of deterioration of the concrete in the tidal zone is not limited to the corrosion of reinforcement by chloride ingress, but the concrete also risks crumbling by freezing and thawing attack, thermocracking and leaching.

The tidal range varies from a small tidal action in Denmark (0-1 m) to 3,5 m in Nuuk in Greenland. However, in some coastal areas the tidal action can be very high, e.g. more than 15 m in the Bay of Fundy on the east coast of Canada, cf. Mehta [1991].

The ingress of chloride into the concrete of the tidal zone is dominated by convection and diffusion.

The wave zone. The exposure of concrete in the wave zone does not in principle differ from the exposure of concrete in the tidal zone. Waves are caused mainly by wind action on water, but ships also cause waves. The main difference between the exposure of concrete in the tidal zone and the wave zone is that the concrete in the wave zone is exposed to the impact of waves breaking against the concrete. The pressure on the concrete in wave zones may reach a level up to 0.3 MPa, cf. Gerwick [1986].

The chloride ingress into the concrete exposed to the wave zone is dominated by convection, permeation and diffusion.

The splash zone. The part of a marine structure exposed to both waves and spray of sea water is defined as the splash zone. By experience concrete in the splash zone needs the heaviest and most careful protection against lack of durability. The concrete in the splash zone suffers from attacks of chloride ingress, freezing and thawing, leaching, ice impact and ice abrasion.

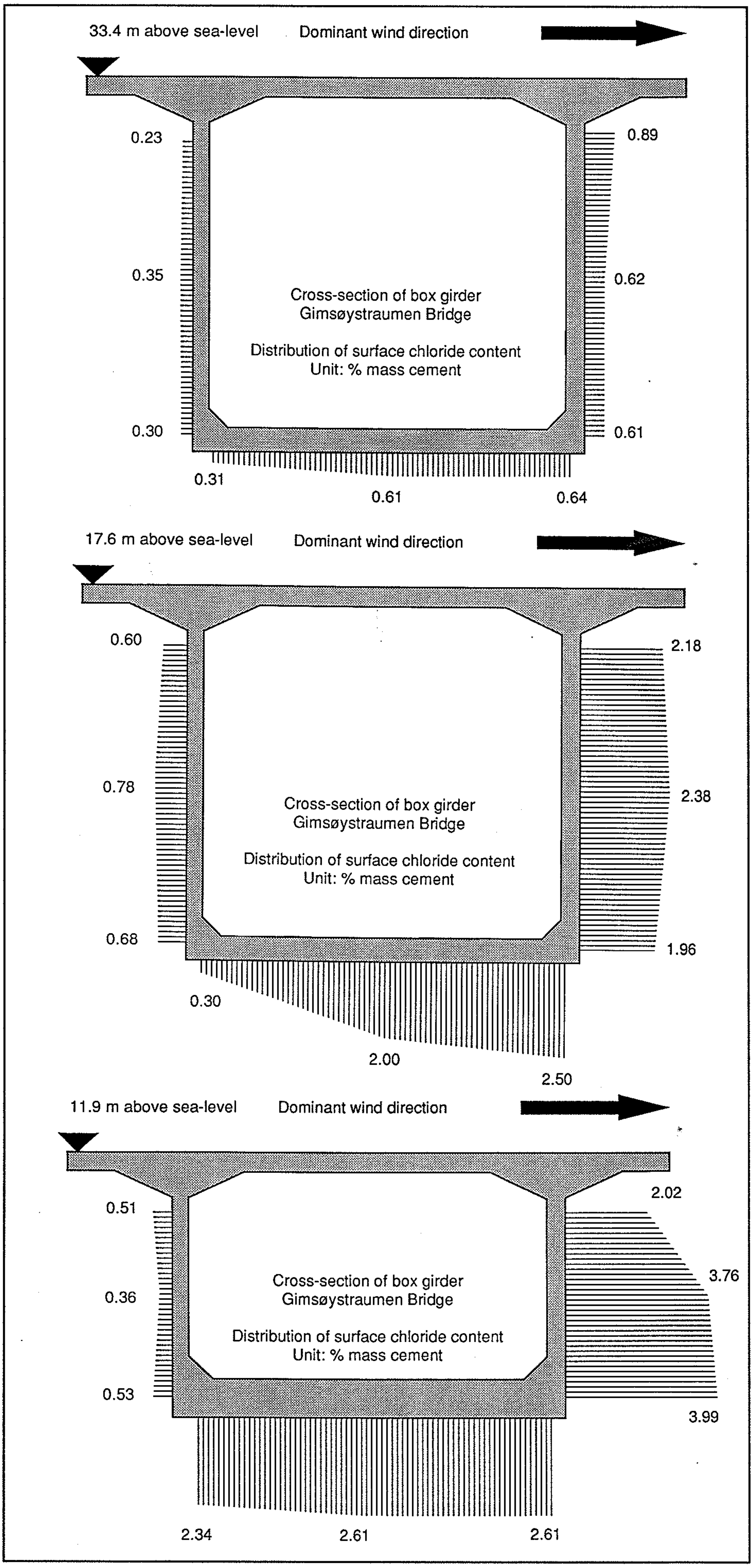
Ingress of chloride into concrete exposed to the splash zone is dominated by convection and diffusion.

Chloride diffusion coefficient of concrete in wet zones. During the last decade many marine RC structures have been examined for their chloride ingress, especially the concrete of the splash zone. Besides, the behaviour of chloride penetration into concrete specimens exposed to sea water has been studied in special field stations, cf. Sandberg [1993] and Malmström [1992]. However, at present the number of observations are not yet sufficient to allow a destinction to be made between the various wet zones of marine RC structures. The topics is dealt with in Chapter 7.

Semi-dry zones of marine RC structures

Atmospheric marine zones. The atmospheric marine zone is a semi-wet zone where the airborne chloride is the predominant source of chloride exposure. Coastal fogs are frequently the carrier of small drops of sea water originating in spray due to wind action on the waves. Strong wind in stormy weather is able to carry sea water over long distances inland. It is not unusual to observe white coatings of salt (chloride etc.) far away from the seafront in Jutland after heavy storms during the autumn.

Figure 5-11. Surface chloride concentration, C_{sa}, on a superstructure cross section at three different heights above sea level.
Data from Fluge et al. [1995].



Since the chloride is transported mainly by the wind, the geometry of the structure has an influence creating windward and leeward sides. This was pointed out by Sand [1993]. When the wind action is not so strong the influence of windward and leeward sides may not be so dominant. Sørensen [1995] points out about observations concerning the larger marine concrete bridges in Denmark that "The chloride ingress and development of corrosion do not show a systematic pattern" except that "The Langeland Bridge shows a clear tendency to a severer development of corrosion at the east side of the bridge pillars".

Marine RC structures at positions dominated by a strong wind from one direction, e.g. the Norwegian coastal bridges, will receive chloride on all their surfaces during heavy wind and storm. However, during heavy rain showers the concrete surfaces on the windward sides are rinsed and cleaned, and in this way these concrete surfaces are only exposed to chloride during a short period of time. However, the concrete surfaces on the leeward sides are not rinsed by rain showers in the same way. Therefore, the chloride coating established by strong wind to some extend remains at the concrete surface, and the chloride will penetrate into the concrete.

Examination of the Gimsøystraumen Bridge in Norway, cf. Fluge [1995], has given an excellent documentation of the chloride aggressiveness of a typical marine atmospheric zone. The superstructure of Gimsøystraumen Bridge is a box girder and the conclusions drawn may not be valid for superstructures of another geometrical shape. Furthermore, it should be noticed that the chloride penetration into the concrete has been determined at three sections. These sections have various heights above sea level, but they also have various distances from the seaward face. In order to separate these two variables, the chloride penetration into the concrete on the windward and the leeward sides of a (high) bridge pillar ought to be studied. This is done for the Hadsel Bridge, cf. Sand [1993]. Furthermore, the chloride ingress into the concrete at the windward and the leeward sides of a (horizontal) superstructure of a (long) bridge across sea water should be studied. However, no published data are available at present.

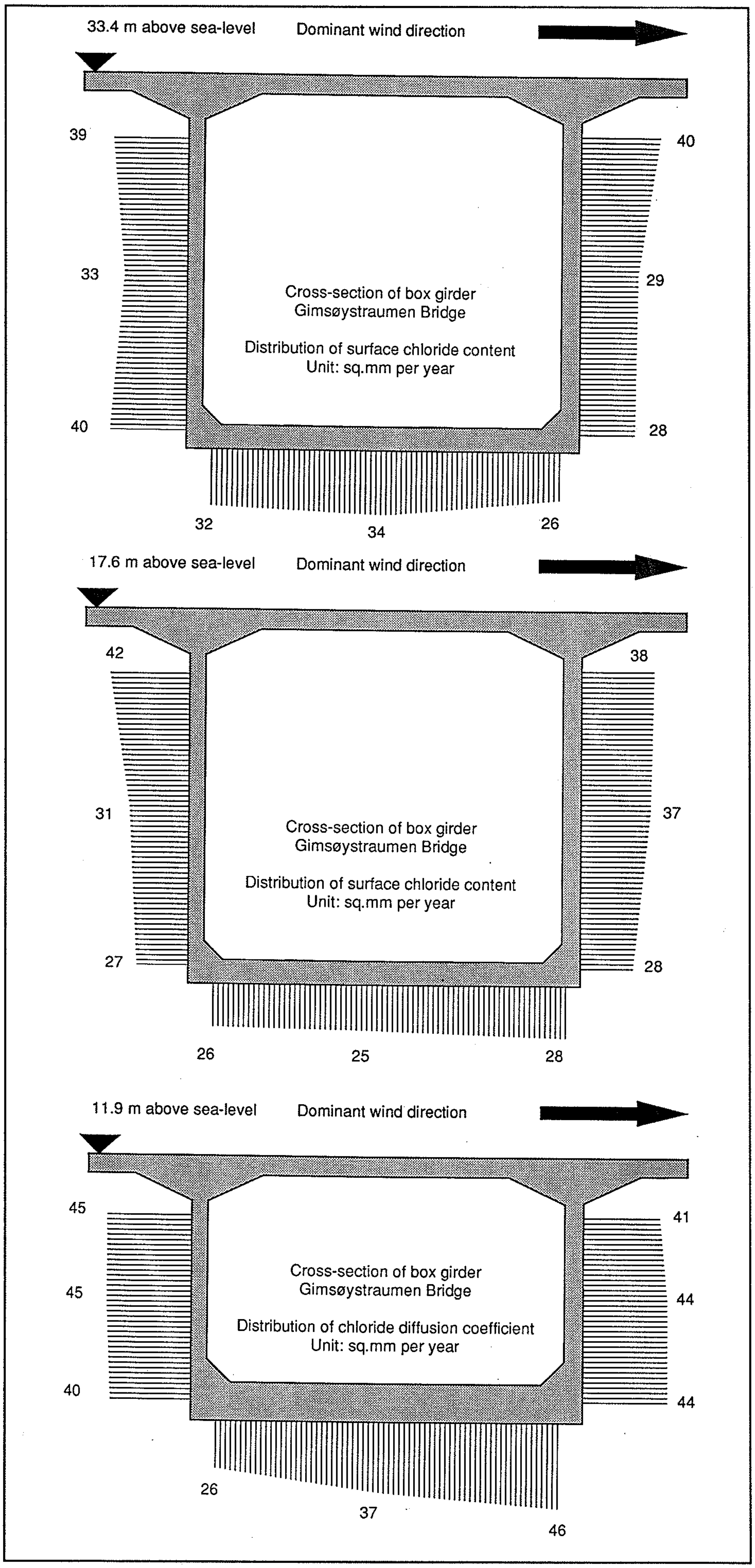
From the examination of Gimsøystraumen Bridge the following conclusions are drawn:

Surface chloride content of concrete in semi-wet zones. The determination of the surface chloride content of the superstructure shows a very clear picture of the actions on the windward and the leeward sides, cf. Figure 5-11. Cross sections at heights above sea level of 11.9 m, 17.6 m and 33.4 m respectively.

As seen the measured maximum difference of the surface chloride content is found at the cross section 11.9 m above sea level. Here, the ratio between the highest and lowest value of C_{sa} is approx. 11:1. For the cross sections at the positions 17.6 m and 33.4 m above sea level these ratios have decreased to approx. 8:1 and 3:1 respectively. This clearly shows that there is a significant influence of the height above sea level.

Chloride diffusion coefficient of concrete in semi-wet zones. The significant difference between the surface chloride content of the concrete on the windward and the leeward sides is not found for the chloride diffusion coefficient, cf. Figure 5-12. There is no significant difference between the

Figure 5-12. Achieved transport coefficient, D_a, on a superstructure cross section at three different heights above sea level.
Data from Fluge et al. [1995].



chloride diffusion coefficients determined at the three cross sections from a statistical point of view.

5.6.4 Structures of RC concrete exposed to de-icing salt

Chloride penetration into RC concrete structures due to the application of roadway de-icing salts depends on the aggressiveness of the chloride. There are two main exposure zones:

- Exposure of concrete directly by the melted water contaminated by de-icing salts (chloride), i.e. horizontal concrete surfaces.
- Exposure of concrete by traffic splash containing chloride from the roadway de-icing salts, i.e. bridge pillars for highway bridges.

The ingress of chloride into concrete from the meltwater is similar (convection and diffusion) to the ingress of chloride in marine RC structures in wet zones, but the chloride concentration of the melted water is generally much higher than that of the sea water. Chloride penetration into concrete from the traffic splash is similar to the ingress of chloride in the marine RC structures in the marine atmospheric zones. However, the main difference between marine exposure and the exposure from roadway de-icing salts is that while the marine exposure is quasi-homogeneous in time, the exposure to the de-icing salts is concentrated in the winter period, i.e. a discontinuous exposure.

The amount of de-icing salts applied to a typical bridge deck in the snow belt states of the USA is about 1.2 kg/m^2 each winter season, but some bridges will receive as much as 4.9 kg/m^2, cf. Steere [1980]. The amount of roadway de-icing salts applied in Denmark is much less, cf. Henriksen [1991, p.20 and 45].

Investigation and research on chloride ingress into concrete have so far mainly dealt with marine RC structures. Compared to this only little has been done in the field of structures exposed to roadway de-icing salts.

Parameters of chloride profiles

The ingress of chloride into the concrete of inland structures is described by parameters of the achieved chloride profiles in the same way as in the case of marine RC structures. However, since the chloride exposure from roadway de-icing salts takes place during the wintertime only, the chloride exposure is discontinuous, i.e. the concrete receives chloride during a few months per year and no chloride during the rest of the year.

The penetration of chloride into concrete exposed to roadway de-icing salts is also carried out by the same transport mechanisms as in the case of chloride penetration into the concrete of marine RC structures, i.e. convection and diffusion of chloride.

Surface chloride content of concrete. At the surface of the concrete itself and for some shallow depth the chloride concentration will vary with the season, being higher in the winter than in the summer, cf. Cady [1983]. The surface chloride content of the concrete C_{sa} will increase with time during the winter. However, during the summer period C_{sa} will decrease or keep constant. Very little is known about the changes of C_{sa} with time and very few test data are available.

Only few bridges in Denmark are constructed without insulation or protection of the bridge decks against chloride attack from roadway de-icing salts, e.g. the Ryå Bridge and Madumå Bridge, cf. Larsen [1993ab]. During an exposure period of approx. 10 years the chloride ingress x_r of the reference chloride concentration $C_r = 0.1$ % by mass of concrete has penetrated into the concrete to a depth of less than 8 mm.

Roadway de-icing salts are not applied directly to e.g. pillars of highway structures, but the chloride exposure due to traffic splash has a major impact on the durability of these structural components. This type of chloride exposure is similar to the chloride exposure of concrete to the marine atmospheric zone. The Danish Road Directorate has carried out an examination of about 20 concrete bridges, cf. Henriksen [1991]. The chloride profiles of concrete pillars have been determined at ground level and one metre above this. From this examination it is seen that:

- The surface chloride content of exposed RC pillars is higher at ground level than at one metre above ground level.
- The surface chloride content in general is significantly higher inside than outside the greater Copenhagen area.
- The surface chloride content depends on the amount of roadway de-icing salts applied, the traffic intensity and the distance between the pillars and the road.

Chloride diffusion coefficient. While the surface chloride content of concrete mainly depends on the chloride intensity of the environment and the type of binder in the concrete, the chloride diffusion coefficient of concrete mainly depends on the porosity (*w/c* ratio, cracks and compaction). Thus, one should not expect to find great differences between D_a of the concrete in various zones of structures exposed to roadway de-icing salts and marine RC structures.

The examination of concrete of highway structures in Denmark carried out by the Danish Road Directorate, cf. Henriksen [1991], supports this expectation. From the examination of the determined chloride profiles, it is seen that:

- The chloride diffusion coefficient of concrete in RC pillars at ground level has a value not significantly different from that one metre above ground level.
- The chloride diffusion coefficient of concrete in RC pillars of bridges in the greater Copenhagen area has a value significantly different from that outside (approx. 60 mm^2/year versus 25 mm^2/year).

Some interesting observations are obtained from an experimental application of traffic barriers made from concrete containing silica fume in excess of the amount specified as a maximum according to the Danish Code of Practice.

The Danish Road Directorate has carried out some interesting applications of concrete with an excess of silica fume (from 10 % by mass of cement to 50 % by mass of cement) compared to the Danish Code of Practice, i.e. maximum 10 % by mass of binder. With an effective coefficient of 2.0 for the silica fume (according to the Danish Code of Practice) the equivalent *w/c* ratio varies from 0.16 to 0.36. The traffic barriers of concrete containing silica fume were compared with concrete having a *w/c* ratio of 0.38-0.42 by mass and no addition of silica fume, cf. Larsen [1995].

Figure 5-13. Diffusion coefficients, D as a function of the microcracking density, S. Massat [1991]. The diffusivity is increasing with increasing crack density.

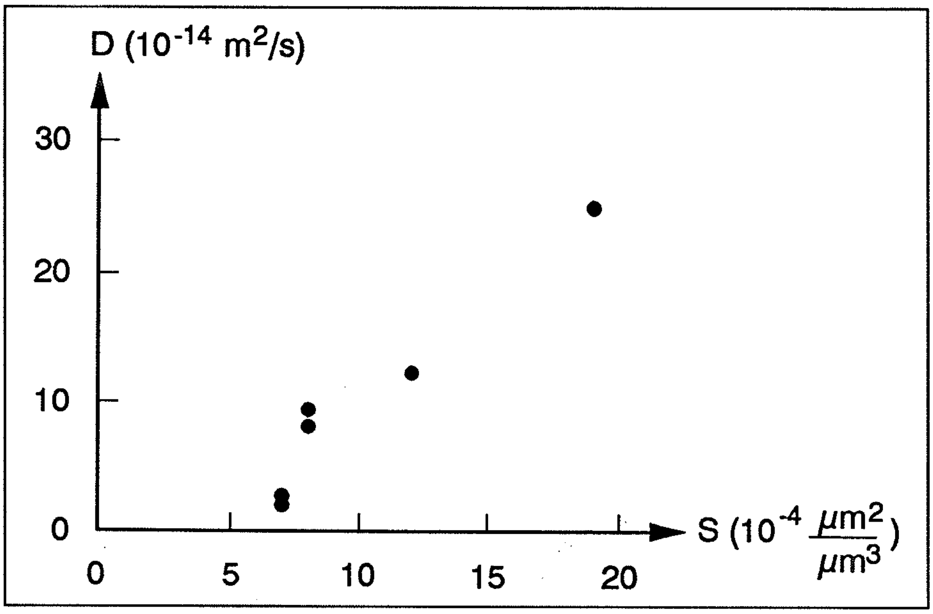
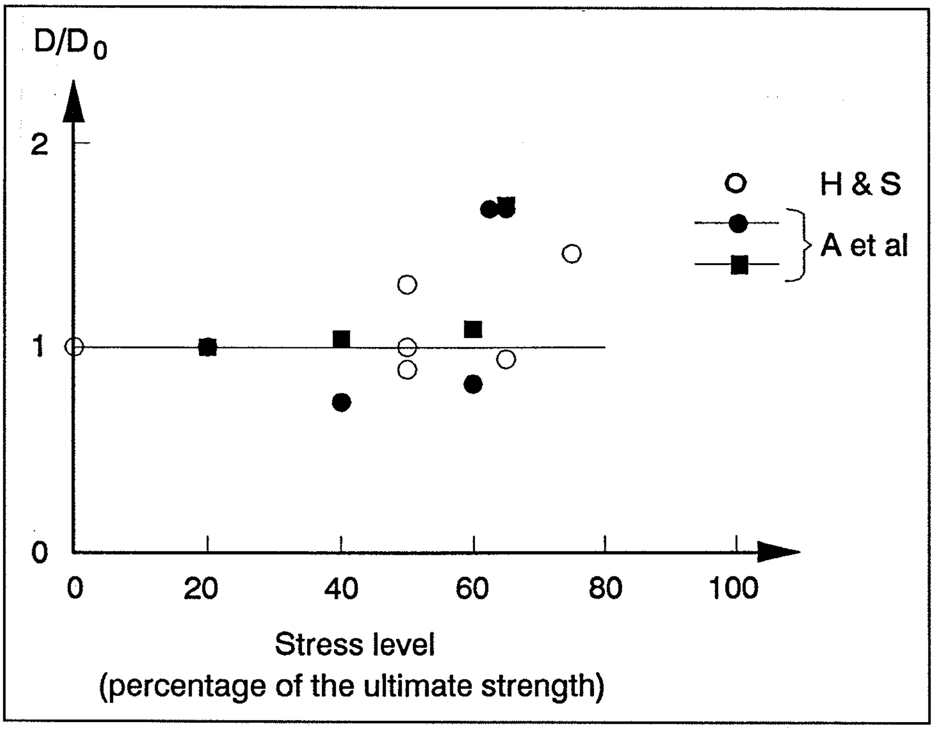


Figure 5-14. Normalised chloride diffusion coefficients at different levels of compressive loading for concretes with *w/b* ratios between 0.35 and 0.65. Sugiyama et al. [1995], Heideman & Sundström [1994, 1995].



During approx. 15 years in use, i.e. exposed to traffic splash, the concrete of the traffic barriers has shown good durability. The following is observed about the chloride ingress:

- The ingress x_r of the reference chloride content $C_r = 0.1$ % by mass of concrete is approx. 12 to 24 mm in concrete containing no silica fume, while the ingress is significantly smaller for concrete containing a high proportion of silica fume.
- The chloride profiles show a maximum value at a shallow depth corresponding to the carbonation depth which has been measured, to a surface carbonation depth of up to 3 mm with isolated pockets of deeper carbonation up to 30 mm around surface cracks. This observation agrees with the experiments of Tuutti [1982, p.70] and the underlying theory.
- The values of the chloride diffusion coefficients D_a depend on the concrete composition, mainly through the equivalent w/c ratio.
- The values of the surface chloride content C_{sa} do not seem to be dependent on the concrete composition.

5.7 Loading

Structures are stresses, most specimen are not

Most laboratory chloride tests are performed on unloaded specimens but concrete in structures is loaded. In predicting the chloride conditions in real structures, the possible effect of stress and strain on chloride penetration should be quantified.

Chloride penetration is a function of microcrack density

Massat [1991] and Locoge et al. [1992] studied the effect of different micro crack densities produced by multiaxial loading at various levels. The chloride diffusion coefficients from diffusion cell experiments were shown to depend on the micro cracking level to a great extent, cf. Figure 5-13. Strangely enough the diffusion of other substances was not affected, or affected to a much smaller degree, by micro cracking.

The effect of loading was recently studied by Sugiyama et al. [1993, 1995] and Heideman & Sundström [1994, 1995]. Their results coincide to a great extent for compressive stress, cf. Figure 5-14.

Stress levels below 65 % of the ultimate short term strength have negligible effect

It seems as if a sustained compressive load causing a theoretical stress level up to some 65-75 % of the ultimate short term strength has no significant effect in increasing chloride penetration. On the contrary, the results indicate a small increase in the resistance to chloride penetration when specimens are loaded.

For flexural tension stresses in stage I, without any macro-cracking, Heideman & Sundström [1994, 1995] found no significant effect of stress level on the penetration of chlorides.

For macro-cracked concrete, see Chapter 5.5.

5.8 Variability

The chloride penetration rate into a given concrete structure may vary with the sampling position due to at least the following reasons:

Figure 5-15. The effect of the micro environment on chloride penetration in a high performance concrete at various heights from the mean sea level. The chloride profiles were analyzed on concrete cores drilled after 4 years of exposure. Sandberg [1995].

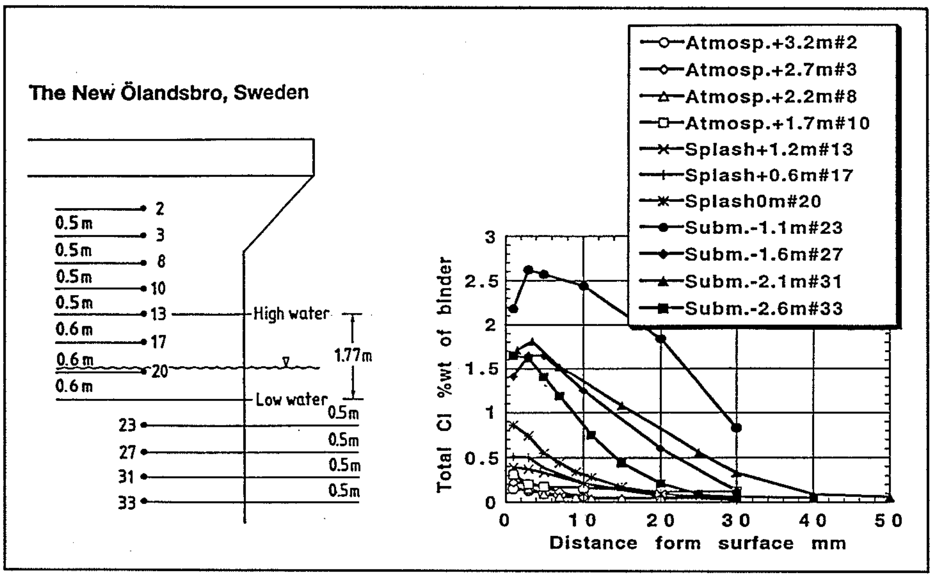
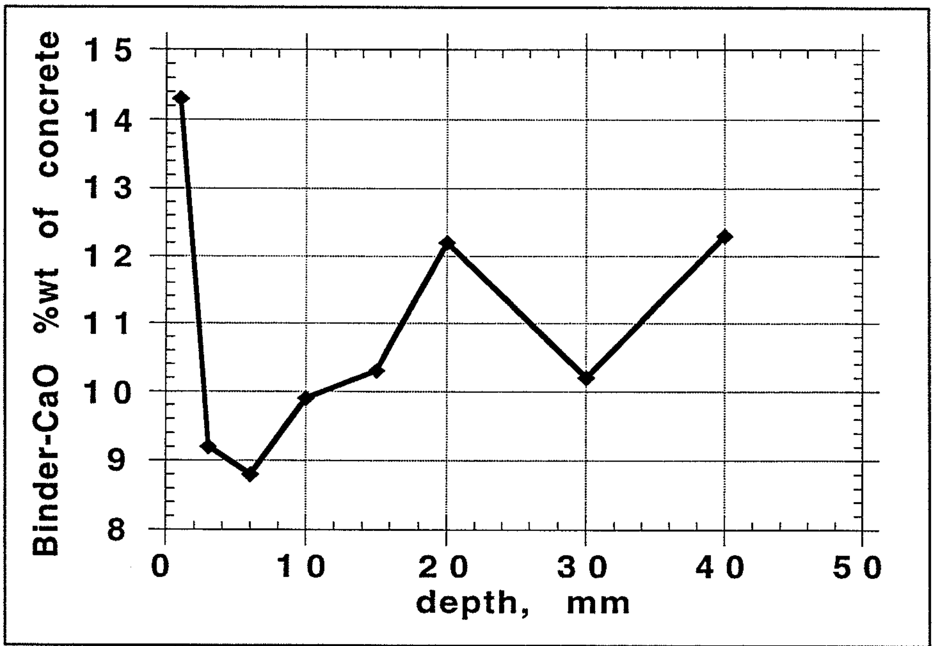


Figure 5-16. The distribution of binder measured in a Ø100 mm concrete core.



Macroscopic reasons

The microstructure of concrete varies

- The microstructure of a concrete structure is not uniform. Modern structures are often slender with a large amount of reinforcement, utilising concrete of low *w/b* ratio in order to save material and to optimise the relationship between strength and weight. The narrow space available and the stickiness of concrete with low *w/b* ratio (especially if large amounts of super-plasticisers are used!) may lead to segregation of the concrete due to local over-compaction as well as insufficient compaction in other parts of the structure. Joints may be extra sensitive to voids and cracks caused by improper compaction, thermal contraction, drying, etc. A schematic illustration of the chloride penetration front in concrete is shown in Figure 5-9.

The environmental load on the concrete surface varies

- The salt and moisture load on the concrete surface is not uniform. The effect of the distance from the water level on the chloride profiles measured in a marine concrete is shown for the New Öland Bridge after 4 years exposure in Figure 5-15, Sandberg [1995]. The effect of wind direction on the measured chloride content at the concrete surface is shown for Gimsøystraumen Bridge after 12 years exposure in Figure 5-11, Fluge and Blankvoll [1995].

Microscopic reasons

The binder content varies with the distance from the cast surface

- The distribution of aggregate relative to binder may vary extensively within a concrete sample, especially if the concrete is analysed by means of collecting concrete powder from a small drill hole. Figure 5-16 shows a typical graph of the binder content measured in a Ø 100 mm core (aggregate d_{max} =16 mm) as a function of the distance from the surface.

The properties of the concrete surface are important in controlling the chloride penetration

- The properties of the concrete surface vary with the curing and the exposure conditions, and the binder type. The use of a draining formwork for reducing the *w/c* ratio in the concrete surface apparently has a significant positive effect on surface permeability, cf. Sandberg et al. [1993b]. The presence of magnesium and carbonate ions in sea water leads to clogging of open pores and the formation of a surface layer of brucite and aragonite on the concrete surface, Buenfeld and Newman [1984]. The capillary porosity of concrete with slag cement has sometimes been found to increase with time in the splash zone, probably due to carbonation, Hansen [1995]. For portland cement concrete the capillary porosity usually decreases with time as a result of carbonation.

A statistical approach is necessary to handle the large deviations in concrete

The inherent variability in the exposure conditions and in the concrete microstructure makes it necessary for several chloride profiles to be measured at several different locations of a single structural part in order to describe the chloride penetration accurately.

6 Chloride threshold levels

Steel is passive in sound concrete.

Normally, steel in concrete is passivated in a moist, alkaline environment which is free of chlorides and other aggressive ions. The term passivity denotes that although ordinary steel reinforcement in concrete is thermodynamically not stable, the corrosion rate is depressed to an insignificantly low level by the formation of a barrier of iron oxides on the steel surface. The state of passivation is maintained until the concrete in contact with the reinforcement becomes carbonated, or until a sufficient concentration the "threshold level" of *water soluble* aggressive ions (normally chlorides) has reached the steel surface. The aggressive ions (e.g. chlorides) then locally penetrate the iron oxide layer and later on trigger the dissolution of the iron oxide layer and later on the dissolution of steel.

Chlorides accelerate the corrosion rate

The chloride threshold level

The importance of chloride ions for reinforcement corrosion in concrete has lead to the concept of the chloride threshold level, which may be defined as the minimum chloride level at the depth of the reinforcement which results in active pitting corrosion of the reinforcement.

Another possible definition of the chloride threshold level in concrete is the critical chloride content at the steel surface at a specific time, when deterioration or damage to the concrete structure starts, cf. Schiessl et al. [1990].

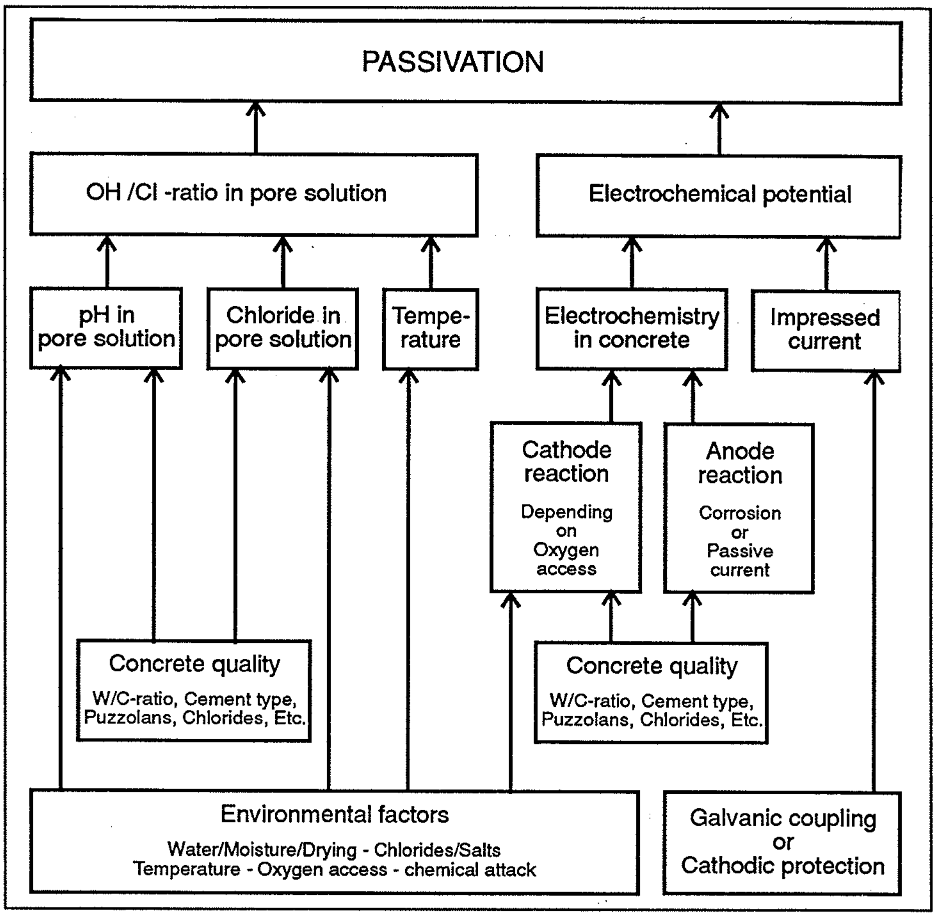
The first definition, which is adapted in this project, corresponds to the point in Tuutti's model where the initiation period stops and the propagation period starts, cf. Figure 2-1 in Chapter 2. The second definition corresponds to a less well-defined point in the propagation period.

The chloride threshold level, as defined in this project, may be easy to detect in well defined laboratory experiments, since the corrosion rate increases by orders of magnitude after the initiation of corrosion. In the field however, the threshold level is often not so clear due to several reasons:

The chloride threshold level is not easy to measure in-situ

- The passivity of steel in sound concrete is not perfect. The passive oxide layer protecting the steel is non-uniform and so is the concrete. As water, oxygen and ions move across the concrete to steel interface, several small and very localised corrosion pits develop, and repassivate, on the steel surface. This "electrochemical noise" is visualised by a fluctuating "passive" corrosion rate. Sound concrete has a strong ability to restore passivity due to its buffer of calcium and alkali hydroxides.
- Both the "passive" and the "active" corrosion rate may vary due to the changing local exposure conditions (temperature, RH, etc.)
- The corrosion rate is often difficult to measure accurately in field structures (the area of the corroding steel is not easy to define). Chloride induced corrosion mainly develops in localised corrosion pits, with a very small area as compared with the surrounding "passive" area. The measured rate is usually the average of the "electrochemical noise" from "passive" regions and the corrosion concentrated to localised corrosion pits.

Figure 6-1. Important factors for the passivity of reinforcement in concrete. Arup [1993].



The chloride threshold level can be presented in several ways:

Presentation of the chloride threshold level

- A total chloride content by weight of concrete
- A total chloride content by weight of binder
- A free (water soluble) chloride concentration in the pore solution
- A ratio between the free chloride and the free hydroxide concentration

The free concentrations are difficult to determine. The total chloride content measured parallel to the binder content is easy to measure, and reflects the ratio of aggressive substance relative to the protective binder. This approach also gives the least spread in the results, Glass and Buenfeld [1995b]. For practical reasons the chloride content of concrete is often defined as the total amount of acid soluble chloride (Cl) in per cent by mass of the dry concrete, because this is normally measured when performing chloride analyses on concrete samples. However, this means that the chloride threshold level will be strongly related to the cement content of the concrete. This relation will of course decrease if the chloride content is related to the cement or binder content.

Prestressed structures are sensitive to depassivation

In the case of prestressed structures the depassivation of the steel surface must be prevented, because very low corrosion rates can cause stress corrosion cracking of the prestressed steel. But with ordinary reinforced concrete structures the depassivation of the reinforcement may not always lead to any deterioration. E.g. if the environment is extremely dry, the corrosion rates after depassivation of the steel are very small due to the high electrolytic resistance of the concrete. On the other hand, if a concrete structure is totally water saturated, depassivation of the reinforcement will not cause high corrosion rates, because oxygen cannot reach the steel surface. Therefore the chloride content of the concrete which leads to depassivation is not the only decisive parameter governing the durability of concrete structures or the subsequent corrosion rate of the steel.

Important factors for corrosion

Arup [1993] has reported a figure showing possible important factors for the onset of reinforcement corrosion, cf. Figure 6-1. The figure illustrates that the passivation of the reinforcement depends on two main factors - the chemical composition of the concrete, approximately described as the relation between the hydroxyl and chloride ions in the pore solution - and the electrochemical potential of the embedded, so far non-corroding reinforcement.

It is known from tests on stainless steels that it is possible to determine a critical (temperature dependent) potential for each combination of chemical composition characterised by pH-value and chloride content. This potential cannot be exceeded without a risk of pitting corrosion. Conversely, a critical chloride content will exist for each combination of electrochemical potential, pH-value and temperature. This critical chloride content cannot be exceeded without risk of corrosion. So far, the relationship between electrochemical potential and chloride threshold level is unknown for steel in concrete.

6.1 Effect of decisive parameters

Reported chloride threshold levels vary extensively

The literature on chloride threshold levels for the initiation of reinforcement corrosion in concrete is very conflicting. If the most practical representation of the threshold level is used, e.g. total chloride by weight of binder, threshold levels have been reported in an interval of 0.17 to 2.5 %

Figure 6-2. Potential - pH diagram illustrating the corrosion behaviour of iron in solutions with chloride, as illustrated by Moskvin et al. [1980]. Critical chloride concentrations for the development of pitting corrosion are indicated. Pitting corrosion is impossible in and below the area marked “total passivation”.

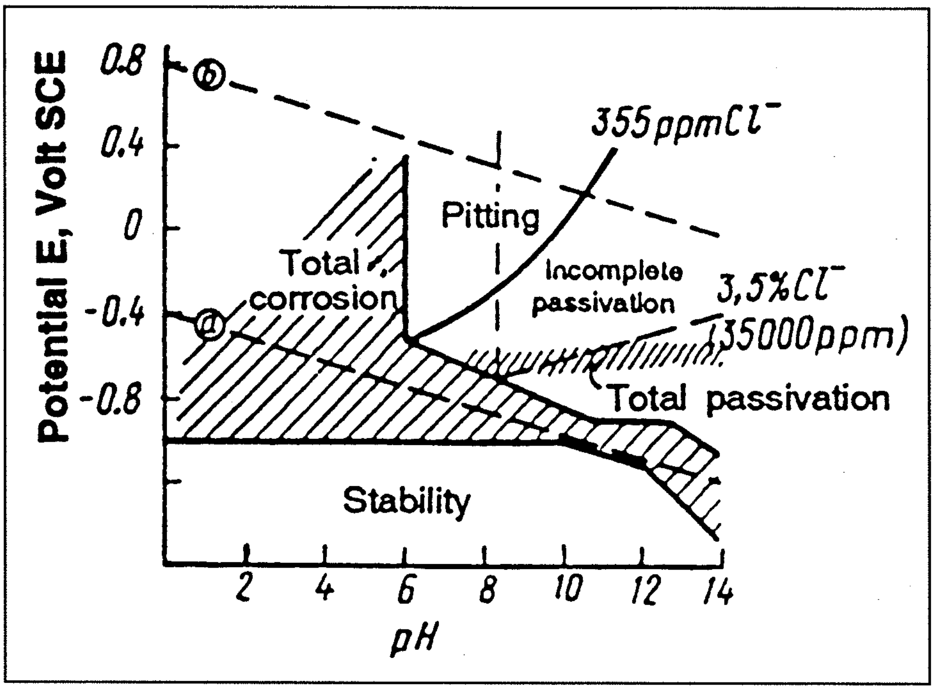
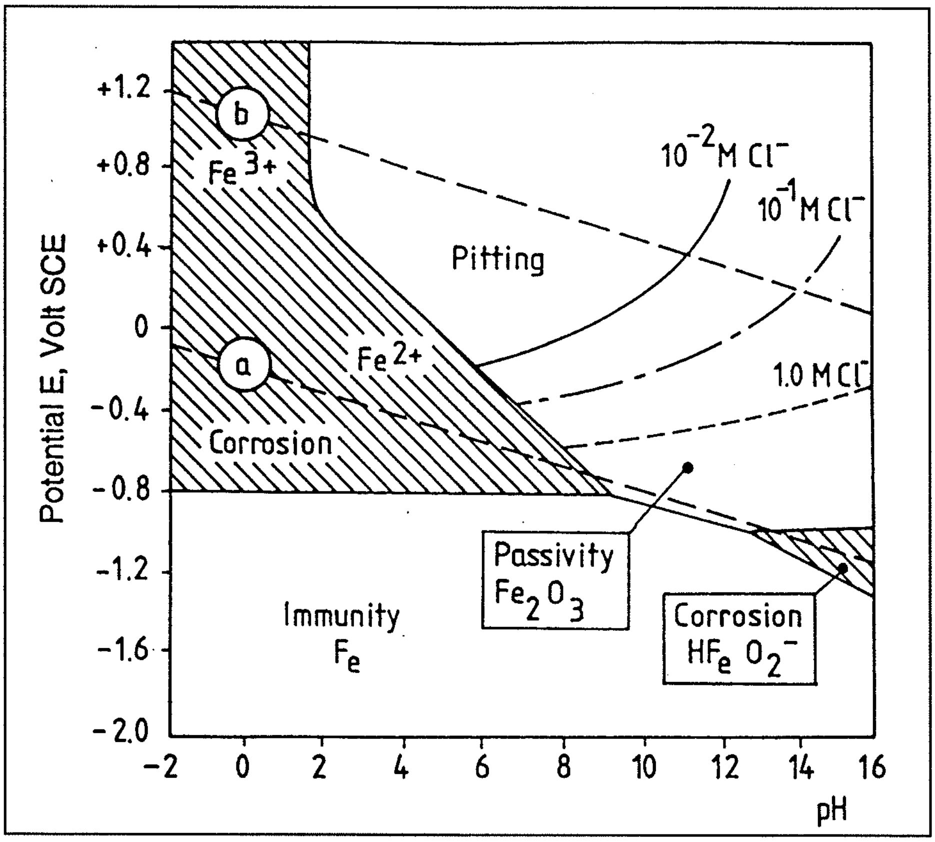


Figure 6-3. Threshold levels for reinforcement steel exposed to solutions of various alkalinity.



chloride by weight of binder, Pettersson [1992], Glass and Buenfeld [1995b].

National codes are conservative

Because of the uncertainties connected with the threshold level, national codes and recommendations, if they recognise the threshold level at all, tend to be conservative. They do not recognise the effect of exposure conditions, cover size and water to binder ratio. In Great Britain, BS 8110 and in Norway, NS 3420, a maximum of 0.4 % total chloride by weight of cement is allowed in normal concrete. In America the ACI recommends a maximum of 0.2% total chloride by weight of cement, Glass and Buenfeld [1995b].

A wide range of parameters is likely to affect the chloride threshold level in concrete. Only very recently systematic approaches have been adopted in order to identify their relative importance. The following is a review of parameters which have some evidence of being important in controlling the threshold level. More extensive information can be found in an excellent review of the literature on chloride thresholds by Glass and Buenfeld [1995b].

6.1.1 Passive steel potential and concrete alkalinity

The passive steel potential reveals the corrosion probability

By analogy with stainless steel, a critical pitting potential is believed to exist for passivated ordinary steel in alkaline concrete. The critical pitting potential depends on the alkalinity of the pore solution in contact with the steel, as indicated in Figure 6-2. Below the critical pitting potential pitting corrosion cannot be established, since the steel potential would be too low for becoming anodic, Arup [1983]. In the absence of pitting corrosion, low potential conditions in high quality concrete are usually harmless because of insignificant corrosion rates, provided that the reinforcement is properly embedded in concrete.

A potential - pH diagram for iron in aqueous solutions may serve as a schematic representation of the passivity regions for steel in concrete. Threshold levels for reinforcement steel exposed to *solutions* of various alkalinity and chloride concentrations are indicated in Figure 6-3. So far very few systematic investigations have been reported on threshold levels for reinforcement embedded in concrete as a function of passive steel potential and concrete alkalinity.

6.1.2 Carbonation

Carbonation at steel interface reduces threshold level to zero

Carbonation of concrete to the depth of the reinforcement reduces the chloride threshold level to zero, due to the following reasons:

- The carbonation of the binder leads to a drop in pH from pH > 12.5 in uncarbonated concrete to pH < 8 in carbonated concrete. As indicated in Figure 6-2 and Figure 6-3, the steel is not passive at such low pH, and pitting corrosion is easily promoted when chloride is present.
- The binder loses most of its chloride binding capacity when carbonated, resulting in an increase in the concentration of free chlorides in the pore solution.

6.1.3 Moisture and oxygen state at the reinforcement

Passivation and corrosion depends on moisture and oxygen

Both the passivating formation of an oxide barrier on the steel surface and the chloride initiated reinforcement corrosion process in concrete can be divided into two sub-processes:

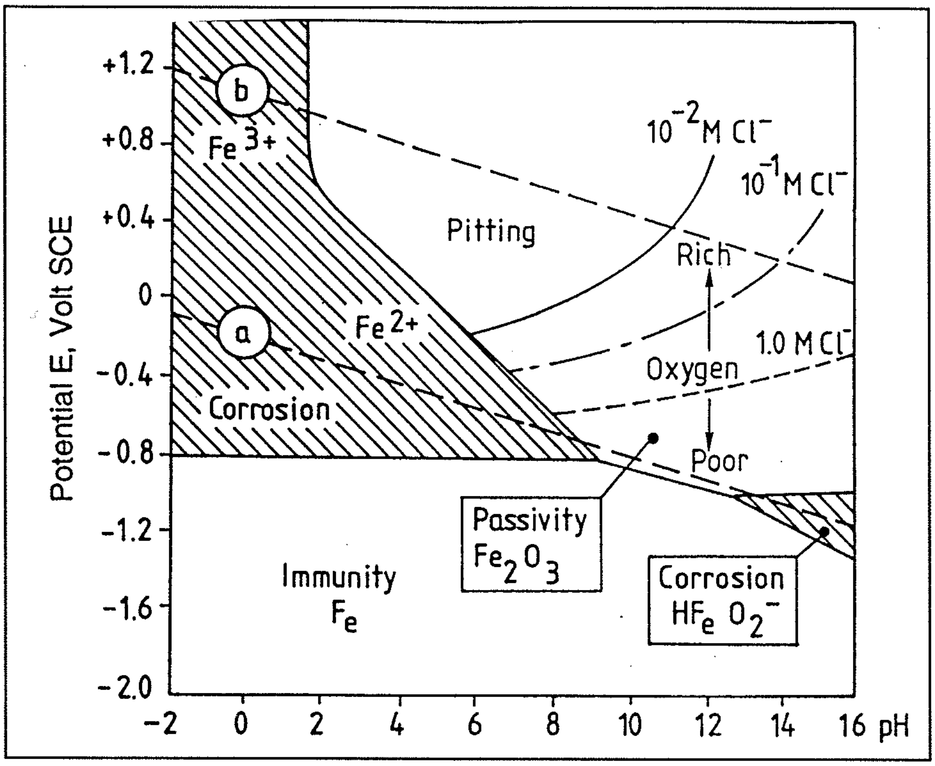


Figure 6-4. The relationship between oxygen availability at the steel surface and the passive steel potential.

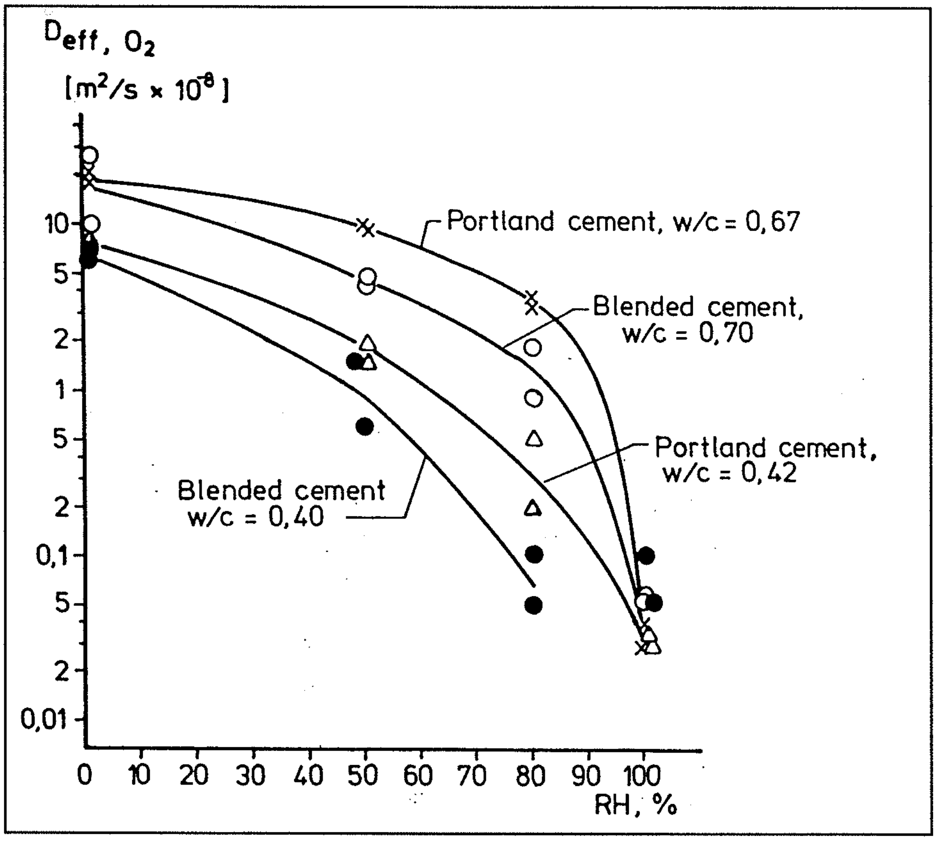


Figure 6-5. The relationship between relative humidity oxygen diffusivity in concrete.

- The anodic dissolution of steel. (In presence of chloride ions the process is boosted by the formation of soluble corrosion products).
- The cathodic reduction of oxygen.

The anodic reaction tends to decrease the steel potential and the cathodic reaction tends to increase it. This implies that the steel potential goes down as the availability of oxygen is restricted. As a result, the steel potential in concrete is closely related to the availability of free oxygen in the concrete, as illustrated in Figure 6-4.

The transport of oxygen through concrete is in turn dependent on the relative humidity of the concrete, as illustrated by Tuutti [1982] in Figure 6-5. Oxygen diffusion in gas (air) is orders of magnitude faster than diffusion in water filled pores. The oxygen transport rate in concrete therefore drops dramatically when the pores become water saturated at high relative humidity. In consequence, the steel potential in concrete is also closely related to the moisture state, as indicated in Figure 6-6. In Figure 6-7, the steep oxygen gradient in concrete submerged in seawater is schematically illustrated by Fidjestøl and Nilsen [1980].

Moisture and oxygen affect the chloride threshold level and the active corrosion rate

The practical implication of Figure 6-6 would be that the chloride threshold level is higher in water saturated concrete than in concrete which is subjected to wetting and drying. Indeed most corrosion damage in reinforced concrete is found in concrete subjected to wetting and drying, although the total chloride contents at the reinforcement may be relatively higher in submerged, water saturated concrete. Experimental results reported by Pettersson [1996] have confirmed that the chloride threshold level is substantially higher in water saturated concrete than in concrete subjected to wetting and drying.

However, some special types of corrosion may develop also in water saturated, oxygen poor concrete:

Macrocell corrosion in oxygen poor concrete

Macrocell corrosion may develop in concrete

Corrosion macrocells in concrete may develop if the cathodic reaction takes place in oxygen rich, non-water saturated concrete, and the anodic dissolution of the reinforcement takes place in water saturated and chloride rich concrete. For a concrete macrocell to develop, the resistivity of the concrete matrix surrounding the reinforcement must be low. In a moist environment a low resistivity may be the result of the following factors:

- The reinforcement is not properly embedded in concrete.
- The concrete is substantially cracked.
- A very permeable, low grade concrete is used.

Corrosion macrocells can be avoided provided that the resistivity of the concrete matrix surrounding the reinforcement is high enough. Macrocell corrosion has frequently been found in low grade concrete and in tremie concrete, probably due to the factors mentioned above.

Low potential active corrosion in oxygen poor concrete

Active corrosion in oxygen poor concrete is seldom dangerous

It is impossible to get pitting corrosion at very low passive potentials as previously shown in Figure 6-2. However, it is still possible to develop a state of low potential active corrosion, which proceeds at a very low corrosion rate, Arup [1983]. The anodic and the cathodic sub-processes must proceed simultaneously at the same rate, in order to maintain electroneu-

Figure 6-6. The relationship between the moisture state in the concrete and the passive steel potential.

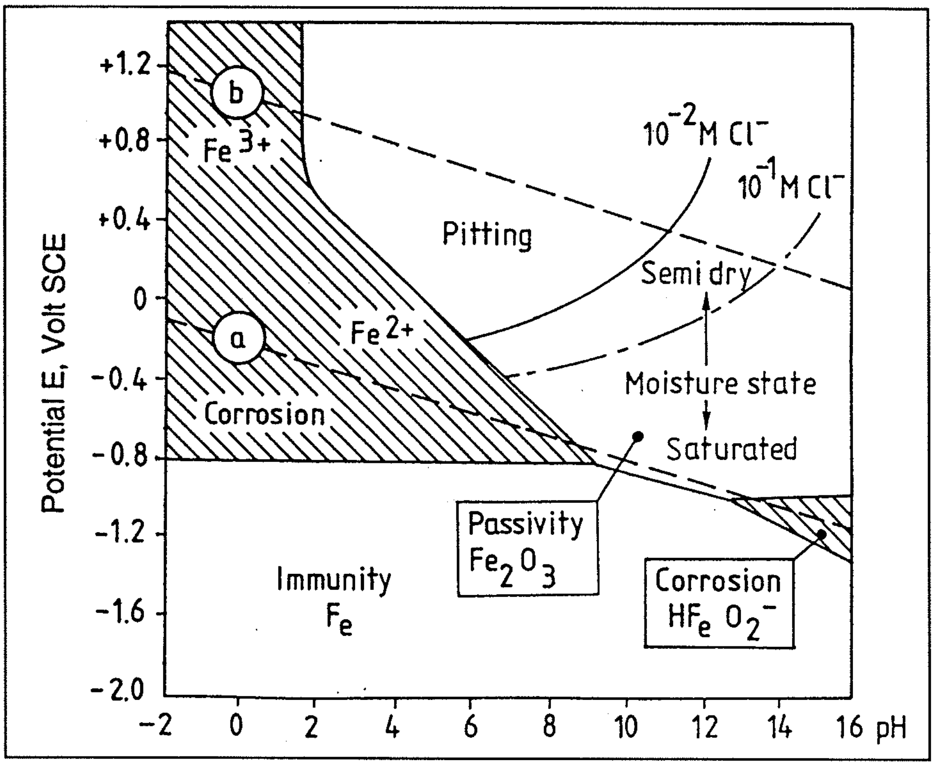
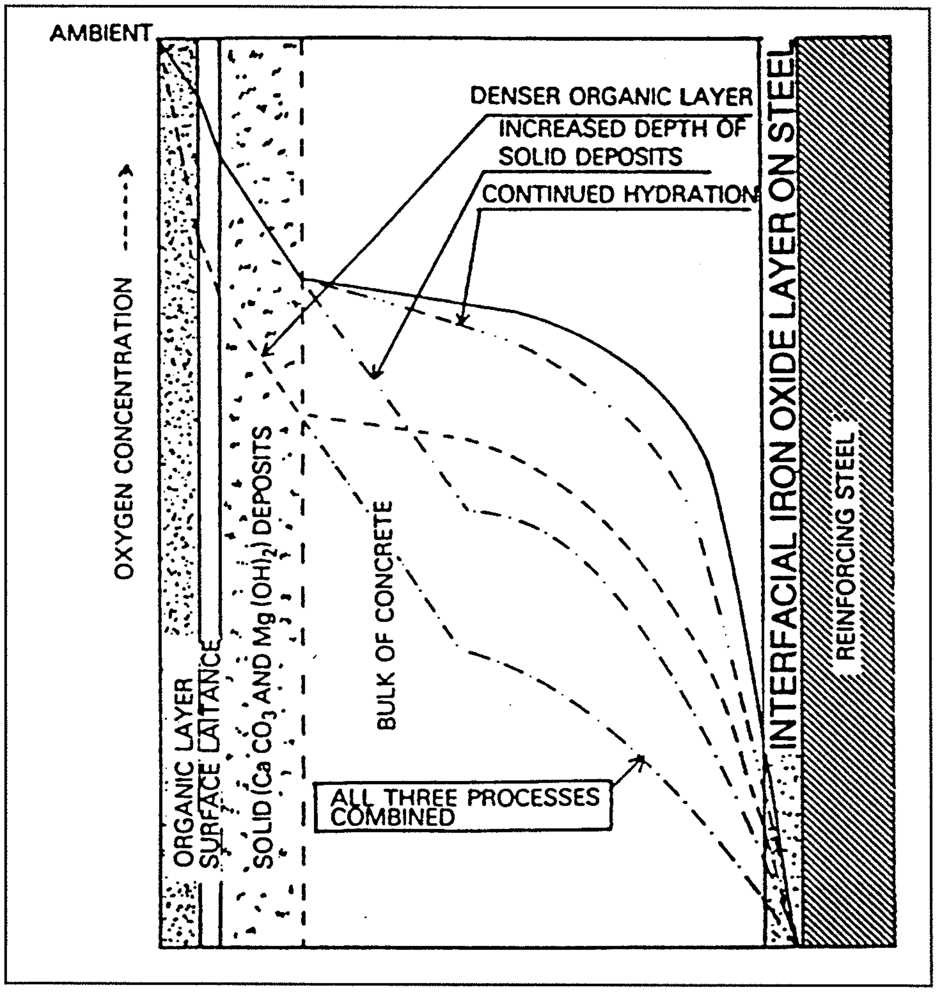


Figure 6-7. Schematic illustration of oxygen gradients in concrete submerged in sea water. Fidjestøl and Nilsen [1980].



trality. Therefore in an oxygen poor environment, the rate of anodic dissolution of the steel will be slowed down to almost zero, because of the lack of oxygen for the cathodic sub-process.

Note that the use of a chloride threshold level for pitting corrosion in oxygen rich concrete is not applicable for this type of corrosion.

6.1.4 Bonding at the steel-concrete interface

Steel in concrete normally has much higher chloride resistance than when the same steel is exposed to a solution of the same composition as the concrete pore solution. This is true also when the comparison is made at similar steel potentials. The difference in chloride threshold levels can be orders of magnitude, Page and Treadaway [1982].

Physical adhesion between cement hydrates and iron oxides improves chloride resistance

The reasons for the improved chloride resistance of steel in concrete as compared with steel in alkaline solutions, at similar steel potentials, are not fully understood. Experimental work by Yonezawa et al. [1988], including variations in the bonding between the steel and the cement matrix, have indicated that the effect of physical adhesion between cement hydrates and iron oxides formed on the steel surface is most important. It was concluded that the formation of voids at the steel-mortar interface is a necessary condition for active corrosion to start in concrete of moderate chloride content. Furthermore, observations of the protective effect of calcium hydroxide precipitated at the steel surface were reported. The protective effect of calcium hydroxide was attributed to the dissolution of calcium hydroxide crystals close to emerging pits, which thereby prevent a drop in pH in the pit.

Field investigations in Sweden and Denmark revealed the existence of an up to 200 μm thick iron oxide layer on long term exposed reinforcement in concrete, Sandberg [1995]. No "rust" or corrosion pits were found on the steel surface, which appeared to be uncorroded by a visual judgement. The corrosion rate was practically zero, and the steel potential below - 250 mV relative to the Standard Calomel Electrode (SCE). Although more than 1% chloride by weight of cement was found at the concrete - steel interface, the chloride front had not penetrated the iron oxide layer. These field results highlight the importance of proper bonding, and the expected relationship between chloride threshold levels and steel potentials.

6.1.5 Cracks

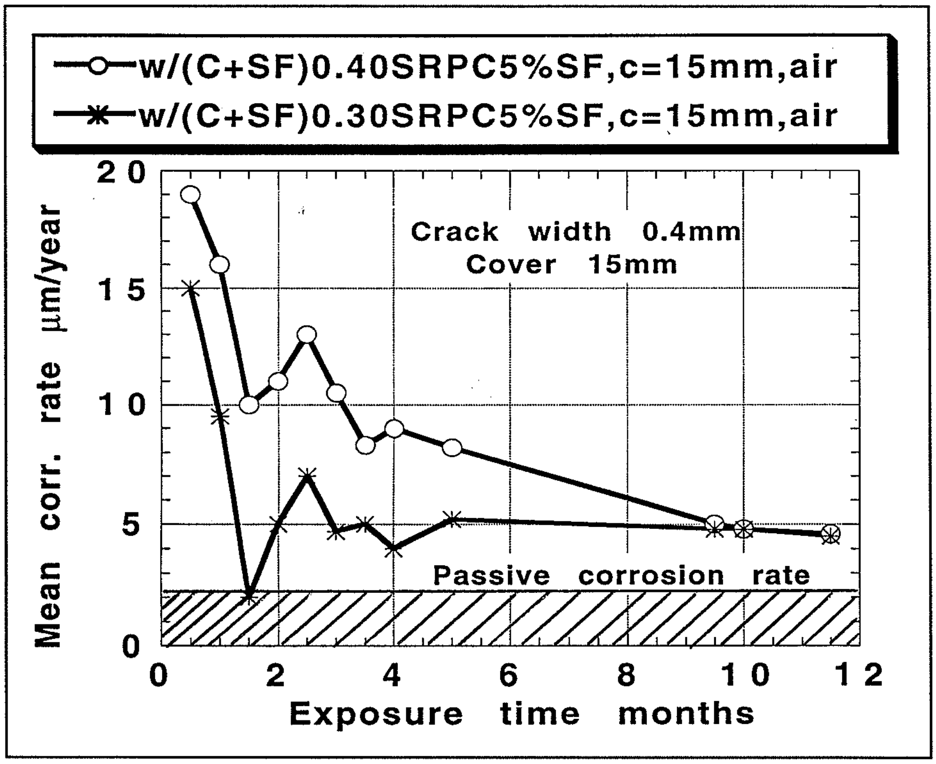
Important factors for the effect of cracks on corrosion

Macrocracks (0.1-0.8 mm wide at surface) in concrete generally accelerate the chloride transport rate and depress the chloride threshold level. The effect of macrocracks on the chloride threshold level depends on the crack size, the exposure conditions and the cover thickness, Pettersson [1996]. For submerged high performance concrete, 30 mm cover, *w/b*-ratio 0.30 and 0.4 mm crack width, Pettersson found a marginal reduction in the chloride threshold level as compared with submerged uncracked concrete. On the other hand, for the same concrete exposed to air, the chloride threshold value was reduced to almost zero.

Cracks may reduce the threshold level to zero

Extensive field and laboratory studies on cracked normal grade concrete (water to binder ratio 0.50-0.70) in Russia, Moskvin [1980], and in Germany, Schiessl [1986] have indicated that cracks up to 0.3 mm wide in concrete exposed to air had little negative effect on the long term corrosion depth. Verbetskii (reported by Alekseev et al. [1993]), found that the main effect of macrocracks in submerged concrete is a reduction of the

Figure 6-8. Corrosion rates measured by polarisation resistance on field exposed concrete, splash zone, crack width 0.4 mm, 15 mm cover, *w/(C+SF)* = 0.30 and 0.40. Pettersson [1996].



initiation time. Once active reinforcement corrosion was initiated, the corrosion rate was initially high, but rapidly decreased and soon approached the active corrosion rate found in uncracked concrete. The critical crack width for a given depth of pitting corrosion apparently depends on the exposure conditions, the cover thickness, and the *w/b*-ratio.

Influence of cracks on threshold level and corrosion rate

The influence of cracks on corrosion activity has been rewieved by Frederiksen et al. [1992]. The main conclusions were:

Influence of cross sectional cracks in the splash zone

- *Cross sectional cracks in the splash zone*
  Only a low corrosion activity can be observed in cracks with crack widths up to 0.4 mm, if the concrete cover thickness and/or permeability is sufficient to protect the corresponding non-cracked structure against chloride initiated corrosion during a long period of time.
  On the contrary, if the cover do not have a sufficient thicknes and/or permeability, damage due to corrosion will be inevitable in the short or long term, even for the non-cracked structure. Cracks in the concrete leads to an earlier initiation of corrosion, but not to a higher corrosion intensity in the long term.

Influence of longitudinally cracks in the splash zone

- *Longitudinally cracks in the splash zone*
  The conditions for longitudinally cracks are basically the same as for cross sectional cracks. However, the maximum crack width, under which one would not expect pitting corrosion is somewhat lower, than in the case of cross sectional cracks.

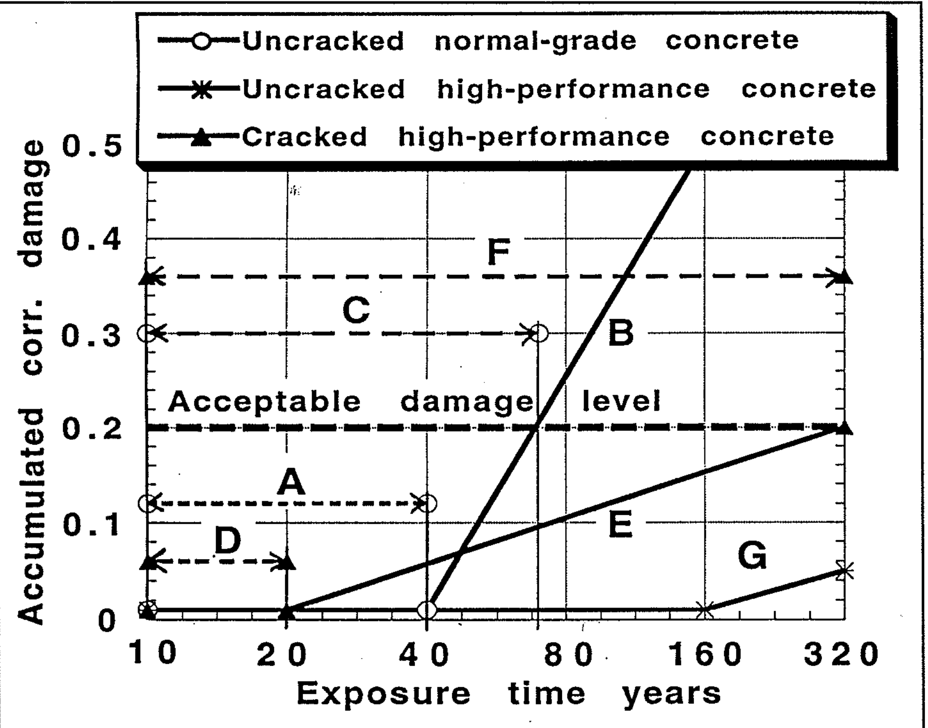
Influence of cracks in the submerged zone

- *Cracks in the submerged zone*
  It is a fact, that cracks from the surface to the reinforcement in submerged marine concrete very fast will lead the chlorides into the reinforcement. But other conditions can prevent corrosion from taking place at a significant rate, e.g. self-healing.
  Observations in the research programme "Concrete in the Oceans" has shown, that even cross sectional static cracks up to 1 mm crack width will not introduce corrosion at a significant level in submerged concrete, cf. Wilkins et al. [1980], [1988]. However, corrsion can occur even in thin cracks, if they are oriented along the reinforcement. Wilkins et al. [1986] have concluded, that corrosion in these cases hardly will be significant, if the crack widths are less than 0.6 mm. For dynamic cracks it has been reported, that corrosion has taken place in cracks with crack widths down to 0.1 mm, cf. Hodgkiess et al. [1984]. It is important to notice, that passive reinforcement in the non-cracked part of the structure and bare steel can act as effective cathodes, if there is a galvanic contact to the reinforcement at the cracks. It requires, however, that these cathodic areas do have sufficient oxygen access. This means, that they must be located in the splash zone or permanently above the water level. If this is the case, the corrosion around cracks can accelerate by the so-called macro cell corrosion.

Cracks in high performance concrete with sufficient cover is harmless

Petterson's results for partly submerged high performance concrete [1996] indicate that although the chloride threshold level and the initiation time may be close to zero for crack widths up to 0.8 mm and a concrete cover of 30 mm, the active corrosion rate will become so small that it may be considered as practically harmless, as illustrated in Figure 6-8.

In consequence, the propagation of active corrosion may proceed for a very long time before any critical damage has occurred to the structure.



Uncracked normal grade concrete	A Initiation time B Corrosion propagation C Service life
Cracked high performance concrete	D Initiation time E Corrosion propagation F Service life
Uncracked high performance concr.	G Corrosion Propagation

Figure 6-9. Schematic illustration of the initiation time and the service life for an uncracked normal grade concrete and a cracked high performance concrete. The model imply that a certain degree of reinforcement corrosion can be accepted.

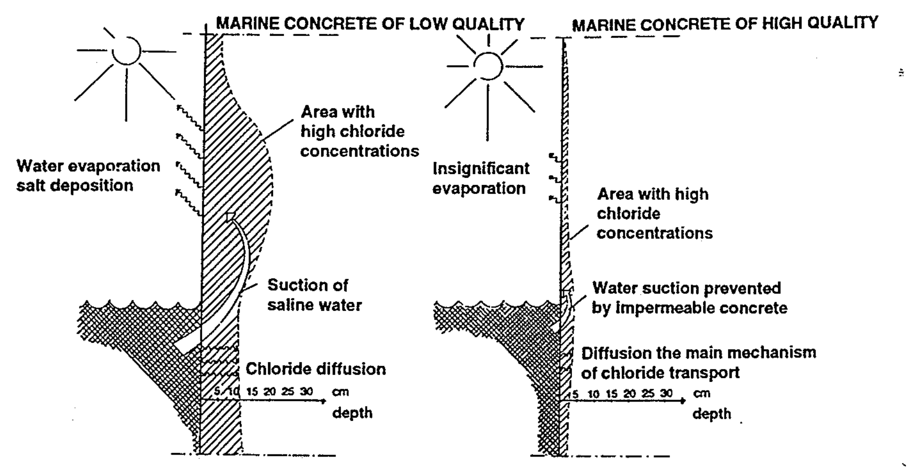


Figure 6-10. The effect of low permeability of the concrete on the micro climate affecting the reinforcement. A concrete with a low permeability will develop a constant and passivating environment at the reinforcement, whereas a concrete with high permeability will have a highly varying inner moisture level. Tuutti [1993].

Therefore, it does not seem appropriate to discuss chloride threshold levels and initiation times for cracked high performance concrete, as schematically illustrated in Figure 6-9.

6.1.6 Cast-in chlorides

Cast-in chlorides affect microstructure and chloride binding

The hydration process for portland cement with cast-in chlorides is different from that when portland cement is hydrated in chloride free water. Besides the increased chloride binding whick takes place when the aluminate phase is hydrated in the presence of chlorides, the pore size distribution is altered, which may lead to an altered permeability. On the other hand, cast-in sodium chloride causes an increase in the pH of the pore solution due to the formation of sodium hydroxide. Furthermore, the formation of passivating oxides on the steel surface is less efficient at higher chloride concentrations, Yonezawa et al. [1988]. In consequence, the chloride threshold levels which can be expected in concrete with cast-in chlorides are different from those in originally chloride free concrete. In fact most reported chloride threshold levels are derived from short term experiments with cast-in chlorides. But apparently there are too few data to evaluate whether experiments with cast-in chlorides tend to underestimate or overestimate the chloride threshold level for originally chloride free concrete.

Once initiated, however, the corrosion rate would be expected to be accelerated by cast in chlorides, due to a release of loosely bound chlorides close to acid corrosion pits.

6.1.7 Cover thickness

Concrete cover stabilises micro environment at steel interface

Besides acting as a physical barrier preventing external chlorides from reaching the reinforcement, the cover also stabilises the micro environment at the depth of the reinforcement. In other fields it is well known that changes in moisture, temperature, oxygen, salinity, etc. often promote corrosion as compared with a stable, unchanging exposure condition, Mattsson [1992]. By analogy, it is assumed that a thicker cover helps to increase the threshold level by reducing moisture and oxygen variations at the dept of the reinforcement. Proper experimental verification of the influence of the cover thickness on the threshold level is lacking. However it is well known in practice that most corrosion damage occurs in concrete exposed to cyclic wetting and drying in a saline environment and where the cover is small.

A thicker cover naturally also helps to prevent carbonation and leaching of alkali hydroxides at the depth of the reinforcement, thereby preserving the highly alkaline environment at the reinforcement.

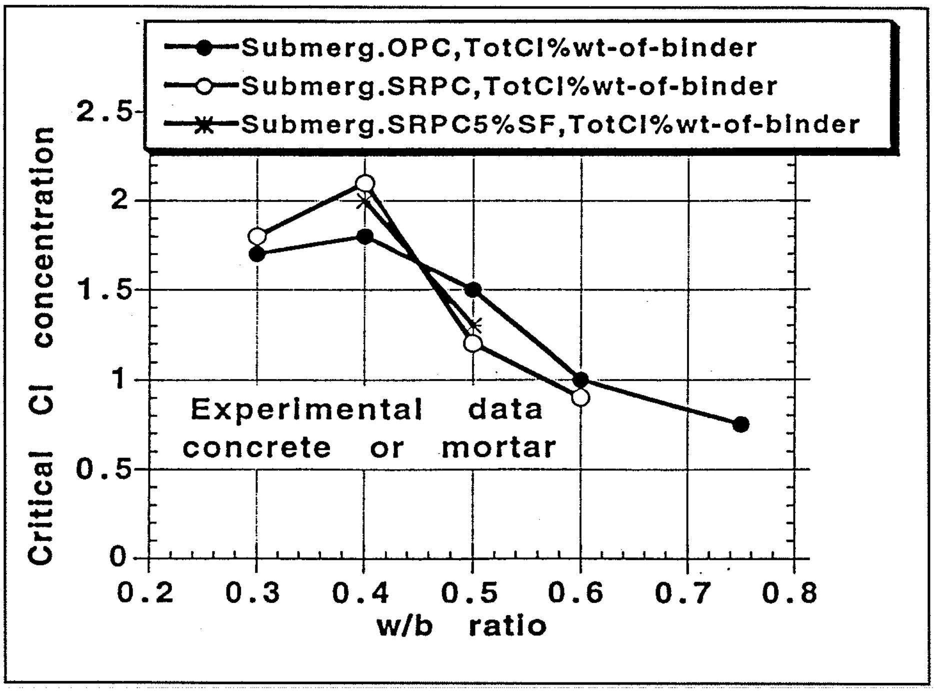
6.1.8 Water to binder ratio

Low w/b ratio stabilises micro environment at steel interface

A lower water to binder ratio helps to stabilize the micro environment at the depth of the reinforcement in a similar way as a thicker cover, as illustrated by Tuutti [1993] in Figure 6-10. In addition, a lower water to binder ratio may also have the following positive effects on the threshold level:

- A higher concrete resistivity and denser steel-concrete interface, both factors reducing the area available for corrosion cells to develop.

Figure 6-11. Experimental data for the chloride threshold levels for corrosion initiation in submerged concrete or mortar. Pettersson [1992, 1993, 1994].



- Lower chloride mobility, thereby preventing chloride accumulation in corrosion pits, with a potentially decreasing catalytic effect of chloride ions.
- A reduced leaching rate for alkalis and a buffer of unreacted cement help to maintain a high concrete alkalinity.
- A higher cement content, thereby increasing the amount of "inhibitor".

Indeed experimental results indicate a higher chloride threshold level for concrete with a lower water to binder ratio, as illustrated by data from Pettersson [1992, 1993a, 1994] in Figure 6-11. Similar results have been presented by Schiessl and Breit [1995].

6.1.9 Binder type

Observations on the effect of binder type differs

Reported results on the effect of pozzolanic and cementitious by-products (ground granulated blast furnace slag, fly ash or silica fume) on the chloride threshold level are somewhat conflicting. Bamforth & Chapman-Andrews [1994] and Thomas, Matthews & Haynes [1990] reported for ground granulated blast furnace slag (GGBS) and for fly ash (FA) that these cement replacement materials have no effect on the chloride threshold level. On the other hand Thomas [1995] later reported from an extensive field study that a cement replacement for fly ash does affect the chloride threshold level negatively. MacPhee & Cao [1993] found a negative effect of GGBS on the chloride threshold level. Hansson & Sørensen [1990] and Pettersson [1993b] found a negative effect of silica fume (SF) on the chloride threshold level.

Several factors may affect the influence of pozzolanic by-products on the chloride threshold level:

Positive effects

Pozzolans increase concrete resistivity

- The use of pozzolans in concrete results in a higher concrete resistivity and denser steel-concrete interface, factors which both make less area available for corrosion cells to develop.
- Lower chloride mobility.

Negative effects

Pozzolans increase variations in fresh concrete properties

- GGBS usually contains sulphide ions, which are known to exhibit corrosive properties similar to chloride ions, MacPhee & Cao [1993].
- Fly ash composition and properties usually vary extensively from one delivery to another. Fly ash may contain chlorides.Therefore the use of fly ash in concrete must be regulated by proper specifications of the pozzolan.
- Pozzolans, especially silica fume, consume calcium hydroxide and alkali hydroxide during hydration. Excess pozzolan may remove calcium hydroxide from the steel-concrete interface, thereby reducing some of the repassivating ability of the concrete. Pozzolans also reduce the alkalinity of concrete due to consumption of alkali hydroxides in the hydration process.

Chloride binding

Chloride binding seems to have little effect on the chloride threshold level

Contrary to their expectations Glass and Buenfeld [1995b] found in their literature survey that chloride binding has little effect on the chloride threshold level. The weak influence of reported chloride binding supports the view that most bound chlorides are so loosely bound that they may make a significant contribution to the available "chloride reservoir". Once an acid corrosion pit has developed, loosely bound chlorides would be released to boost the corrosion rate, and thereby hinder the repassivation otherwise caused by dissolving calcium hydroxide, Yonezawa et al. [1988].

Effect of type of portland cement

The portland cement type has little effect on the chloride threshold level

It is well known that the chloride binding capacity of a portland cement increases with the amount of aluminate phase (C_3A), Schiessl and Raupach [1990]. The lower chloride binding capacity of some sulphate resisting portland cements (which are low in C_3A) has been shown to shorten the initiation time and increase the active corrosion rate when compared with portland cements high in C_3A, Rasheeduzzafar, Hussain & Al-Saadoun [1992]. However, the opposite effects have also been found for a sulphate resisting portland cement high in ferrite phase (C_4AF), Byfors [1990].

Important factors with respect to concrete uniformity

In view of the weak influence of chloride binding on the chloride threshold level indicated previously, the choice of portland cement seems to be less important with respect to the chloride threshold level. The uniformity and microstructure of the cast concrete seems far more important, with respect to both concrete impermeability and bonding at the steel-concrete interface. These properties are in turn controlled by the design of the reinforcement, the mixture proportions, the choice of aggregates, and the influence of the cement on concrete workability and resistance to degradation by freezing and thawing, etc., Moskvin et al. [1980], Mehta [1989]. A concrete made with a portland cement high in C_3A usually requires a higher water to binder ratio, or a higher level of plasticizers, thereby resulting in a less uniform concrete microstructure when compared with the same concrete made with a portland cement low in C_3A.

6.1.10 Exposure time

Effect of exposure time on the threshold level is not clear

An apparent time dependence of the chloride threshold level has been reported by Yonezawa et al. [1988], for concrete with cast-in chlorides, and by Schiessl and Breit [1995], for concrete cast free of chlorides. Glass and Buenfeld [1995b] suggested that the slow redistribution of chloride ions in concrete as well as the stochastic nature of passive film breakdown may explain the reported decrease in chloride threshold over time. A reduction in the pH of the concrete pore solution at the steel surface as a result of hydroxide leaching is another possible explanation, Sandberg [1995].

6.1.11 Temperature

Effect of temperature on the chloride threshold level

The effect of temperature on the corrosion resistance of stainless steels in chloride solutions is well known, Mattsson [1992]. By analogy, the chloride threshold level would be expected to decrease as the temperature increases, but direct experimental evidence is lacking.

6.2 Threshold level test methods

Test methods is based on measurement of corrosion activity

Test methods for determination of chloride threshold levels for concrete are generally based on a measurement of corrosion activity combined with chloride analysis of the concrete at the time of corrosion initiation.

The difference between the test methods normally lies in the method applied to monitor the corrosion activity. Reported techniques to measure

Figure 6-12. Schematic diagram of the test specimen used for the mortar bar method. Hansson [1987].

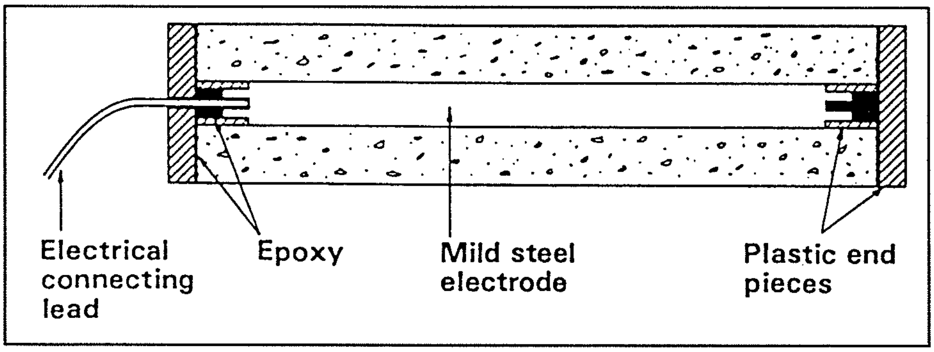
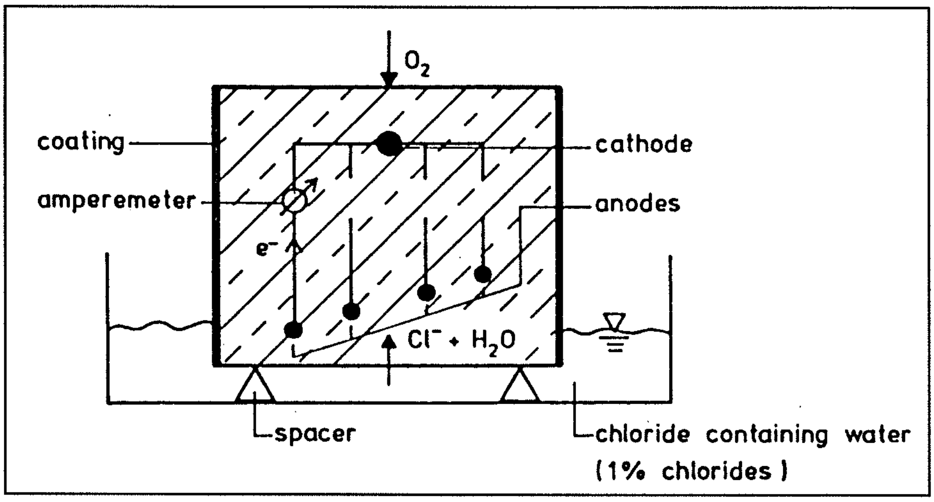


Figure 6-13..Schematic illustration of concrete corrosion cell as used by Schiessl and others. Schiessl et al. [1990].



the corrosion activity span from measurement of current in a galvanic cell, cf. Schiessl et al. [1990], current required to apply anodic polarisation, cf. Hansson et al. [1990] and Arup et al. [1995], potential measurements, cf. Bamforth et al. [1994], electrochemical impedance, cf. Elsener et al. [1986], to polarisation resistance, cf. Lambert et al. [1991].

No standard specifications are accepted

To our knowledge no standard specifications for measurement of chloride threshold levels are accepted worldwide so far. A summary of the most reliable test methods recently used by different research groups is given below.

6.2.1 Mortar bar method

Mortar bar method is based on constant anodic polarisation

Several research groups have used a mortar bar test method to measure chloride threshold levels for a range of different mortars, cf. Hansson et al. [1990]. This method uses measurement of the current required to apply a constant anodic polarisation to a centrally placed steel rod in a mortar bar sample, cf. Figure 6-12.

The applied potential is normally 0 mV SCE. The mortar bars (40×40×160 mm) are cured for about 28 days according to the specification and then immersed in aqueous 1 N NaCl solution. The potential is kept constant and the current from the embedded steel rod to an external stainless steel counter electrode is monitored daily. The initial current densities are of the order of 10^{-4} A/m^2. The current increases by approx. three orders of magnitude in the course of a few days when depassivation of the embedded steel rod occurs. At this time the chloride content at the steel surface is measured on small samples removed from the distance 0-3 mm from the steel surface.

6.3.2 Galvanic cell method

Galvanic cell method is based on measurement of macrocell current

Schiessl et al. [1990] uses a so-called macrocell. The test unit is a corrosion cell with two cast-in steel electrodes. The electrodes are connected with an electrical wire through an ammeter, cf. Figure 6-13. The concrete surface near one electrode is exposed to chloride. When a sufficient chloride concentration has built up around the surface of this electrode, it will act as an anode and the other electrode as a cathode. The corrosion activity can be followed by measuring the macrocell current flowing between them. The onset of corrosion is seen by an abrupt rise in macrocell current.

6.3.3 APM 303 - Chloride threshold levels for reinforcement corrosion

APM 303 is based on constant anodic polarisation

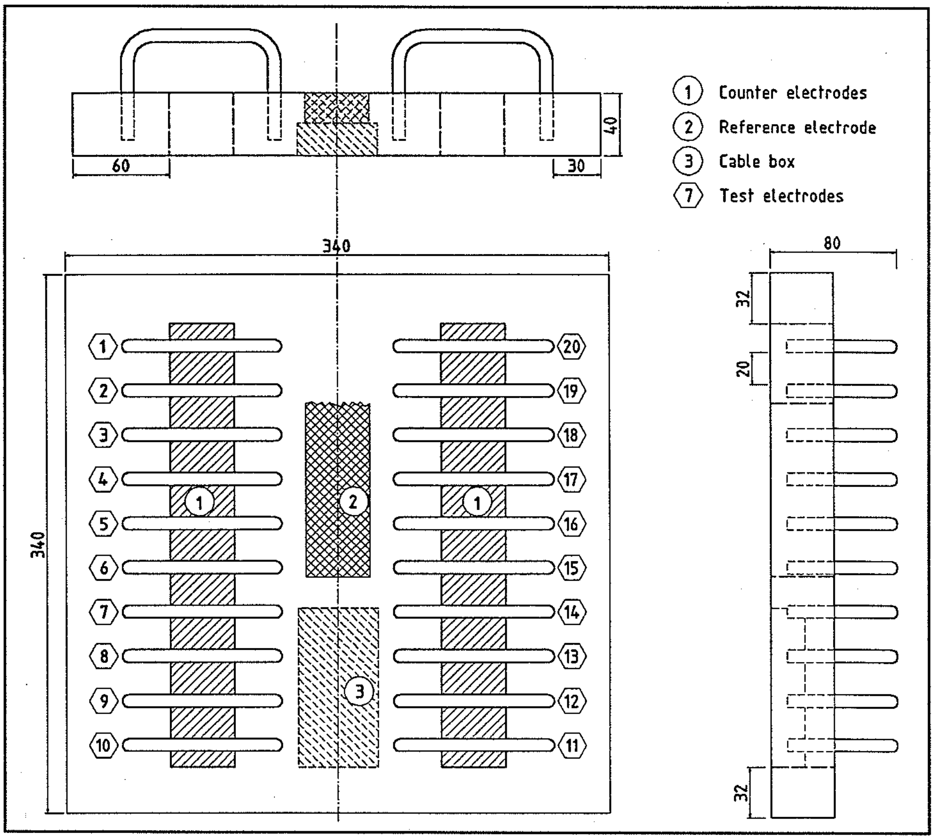
This recently developed standard specification, cf. AEClaboratory [1993], is used in the Swedish research programme Durability of Marine Concrete Structures, cf. Arup et al. [1995]. This specification describes a test method where it is possible to determine threshold levels at different electrochemical potentials.

Multiprobe test unit

A multiprobe is developed based on 20 years experience

The test method is based on a specially developed multiprobe test unit for corrosion tests in concrete, cf. Figure 6-14. The design of the multiprobe test unit is based on 20 years experience with electrochemical tests in concrete and represents a solution to a number of problems which have been encountered in earlier work. The test unit has the following characteristics:

Figure 6-14..Schematic illustration of precast multiprobe test unit. All measures are given in millimeters.



- In each test a considerable number of specimens are used so statistical methods can be used in order to consider experimental scatter.
- One potentiostat controls 20 test electrodes at different individual potentials. Electrical, non-destructive methods are used to detect onset of corrosion on each test electrode.
- The 20 test electrodes with associated counter electrodes and a reference electrode are placed in a precast unit. This ensures a very precise geometry and great freedom in exposure conditions. As an example it is possible to have electrochemical control of specimens in atmospheric exposure, and electrochemical monitoring is possible from the moment of casting the test concrete.

Test specimen

The test specimen is made with accurate cover thickness

A test specimen is produced by casting the concrete type of interest on top of the standard test unit with test electrodes made of the steel type of interest. The maximum recommended aggregate size in the concrete is 8 mm. After demoulding and curing for 14 days the test specimen is cut using a large water-cooled diamond saw to obtain a cover to the test electrodes of nominally 10 mm. A chloride proof coating is applied to the test specimen on all faces except the saw-cut face to be exposed.

Nine small specimens (approx. 70×100×100 mm) are made from the cut off concrete plate. These specimens are made and cured exactly in the same manner as the test specimen. All faces are coated on the small specimens except the faces opposite to the exposed face on the test specimen.

The test specimen and the small specimens are then cured in a saturated calcium hydroxide solution at room temperature to an age of at least 28 days or until water saturation is obtained.

Exposure

Exposure conditions are similar to those of APM 302

The water saturated test specimen and small specimens are immersed in a sodium chloride solution at 23°C. The sodium chloride content of the solution is kept at 165 g ± 3 g NaCl per litre solution.

Potentials of test electrodes

Test electrodes are kept at different constant potentials

All test electrodes except two are potentiostatically controlled during the exposure. The two free test electrodes are allowed to build up their natural free potential. Nine different potentials from -450 mV to +50 mV vs. MnO_2 are applied to the test electrodes.

Registration of corrosion activity

Corrosion activity is registrated by electrical current measurements

The corrosion activity is followed by daily measurements of the electrical current needed to maintain the test electrodes at their controlled potential. The current is normally in the range of 1-5 μA when the test electrodes are passive. At the time of corrosion start the current to the test electrode will suddenly rise above 30-50 μA. Then the test electrode is disconnected from the potentiostatic control by removing a "jumper" in the control box to avoid excess current drain from the voltage divider. From this point the free potential of that test electrode is monitored.

Determination of chloride profiles

Chloride profiles is measured according to APM 302

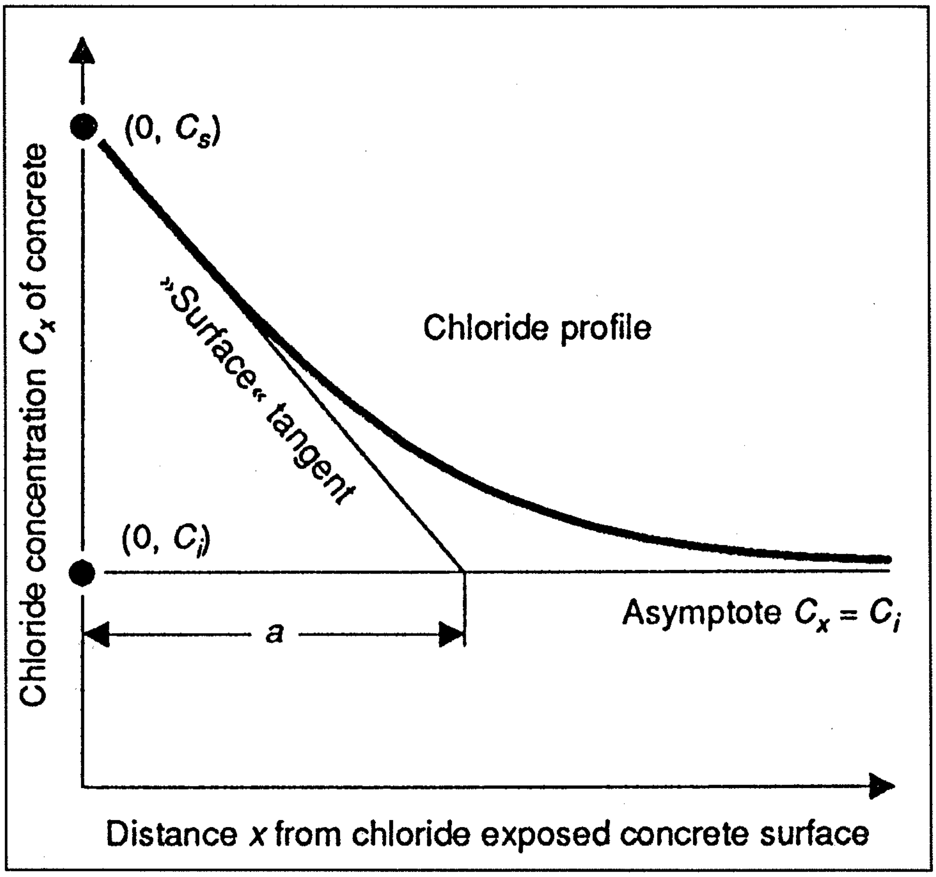
When the number of test electrodes with corrosion is 1, 5 and 20, respectively, the chloride profile is measured by profile grinding according to the principles in the test method APM 302, cf. AEClaboratory [1991a]. The chloride threshold concentration is calculated for each test electrode by interpolation between the measured chloride profiles.

The small specimens are used to measure additional chloride profiles, which makes is simple to follow the progress of chloride penetration into the concrete without disturbing the test specimen.

Presentation of results

The test results are reported as the chloride threshold values measured for each test electrode and the corresponding potential. Other results of interest are cover to test electrode, time to corrosion and chloride penetration parameters calculated according to the principles given in APM 302.

Figure 7-1. The definition of the line segment *a* as the distance along the asymptote $C=C_i$ form the ordinate axis to the intersection between the asymptote and the "surface" tangent.



7 Prediction Models

Pre-collepardian and post-collepardian periods

Until Collepardi et al. [1970, 1972] published his model of diffusion of chloride into concrete, no mathematical model of chloride ingress into concrete was available. Therefore, during the "Precollepardian Period" the prediction of e.g. the cover to reinforcement and the concrete composition necessary for the maintenance of a required service lifetime were mainly based upon experience and rules of thumb. Several topics came up for discussion among engineers and concrete technologists, cf. Poulsen [1926]. In this particular case the question was whether the cover to reinforcement should be greater or smaller than 50 mm for a marine concrete structure.

7.1 Chloride penetration

Introduction of a mathematical model of chloride diffusion

By means of Fick's laws of diffusion, introduced by Collepardi as a suitable mathematical model of chloride ingress, cf. [1970 and 1972], it became possible to predict chloride penetration. Then it was necessary to define the chloride diffusivity of the concrete as new properties and parameters. These parameters were difficult to determine and no test methods existed at that time.

7.1.1 Chloride diffusivity of concrete

Definition of a chloride profile

By solving Fick's 2nd law of diffusion:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D(x,t,C)\frac{\partial C}{\partial x}\right) \qquad (7.1.1{:}1)$$

cf. Crank [1986] the relation between the chloride concentration $C(x,t)$ of concrete and the distance x from the surface of the chloride exposed concrete is found under the conditions assumed, i.e. the boundary conditions and the dependence of $D(x,t,C)$. The graphs of this relationship are called the "concentration distribution curves", cf. Crank [1986], or the "chloride profiles" of the near-to-surface layer of concrete.

Change in chloride profile with exposure period

Chloride profile

A chloride profile changes with time, the composition and maturity of the concrete and the exposure condition. In order to simplify the description of a chloride profile it is convenient to describe a chloride profile from a naturally exposed structure by the following parameters:

Parameters of a chloride profile

- C_{sa} i.e. the profile ordinate at the exposed concrete surface.
- C_i i.e. the chloride concentration of the virgin concrete.
- Δt i.e. the exposure period, which is $\Delta t = t_{in} - t_{ex}$, where t_{in} is the time of inspection and t_{ex} is the time of exposure. When $t_{in} >> t_{ex}$ a good approximation is $\Delta t \approx t_{ex}$.
- D_a i.e. the chloride diffusion coefficient of the concrete.

The meaning of these parameters in relation to the chloride profile are illustrated in Figure 7-1.

7.1.2 Chloride diffusivity: constant in time

The solution to Ficks 2nd law is generally applied

The solution to Fick's 2nd law of diffusion described by Collepardi, cf. [1972], was applied by several authors on condition that $D(x,t,C)$ and C_s remain constant. Collepardi as well as Sørensen [1978], Tuutti [1982], Browne [1980] and Poulsen [1990] have applied the analytical solution, when $D(x,t,C) = D_a$ and C_{sa} are constants in order to predict the future penetration of the chloride, i.e.:

$$C(x,t) = C_i + (C_{sa} - C_i)\,\mathrm{erfc}\,\frac{x}{\sqrt{4(t - t_{ex})\,D_a}} \qquad (7.1.2{:}1)$$

Achieved parameters

The index a indicates that C_{sa} and D_a are determined as "achieved" parameters, i.e. determined from in-situ concrete exposed to the environment in question.

At the beginning a constant chloride diffusivity was assumed

The parameters were assumed to remain constant, i.e. that C_{sa} and D_a remain constant. When applied to old marine concrete structures this assumption is acceptable, but for younger structures and for newly cast structures this assumption would lead to gross deviation from what is now found in practice

The "error function solution"

Chloride ingress into concrete

When the chloride diffusion parameters C_{sa} and D_a are assumed to remain constant the ingress x_r of a given (reference) chloride concentration C_r can be estimated by solving the following equation (the "error function solution"), cf. Poulsen [1990]:

$$C_r = C_i + (C_{sa} - C_i)\,\mathrm{erfc}\frac{x_r}{\sqrt{4\,(t - t_{ex})\,D_a}} \qquad (7.1.2{:}1')$$

The solution yields:

$$x_r = \sqrt{4\,(t - t_{ex})\,D_a}\;\mathrm{erfc}^{-1}\left(\frac{C_r - C_i}{C_{sa} - C_i}\right) \qquad (7.1.2{:}1'')$$

The square root formula

and can be abbrevated as the following square root formula:

$$x_r = \xi_r\sqrt{(t - t_{ex})\,D_a} \qquad (7.1.2{:}1''')$$

ξ_r is an important parameter

where ξ_r stands for the following mix of parameters:

$$\xi_r = 2\,\mathrm{erfc}^{-1}\left(\frac{C_r - C_i}{C_{sa} - C_i}\right) \qquad (7.1.2{:}2)$$

The ingress x_r of the reference chloride content C_r can also be written in the following way:

$$x_r = x_0\sqrt{\frac{t}{t_{ex}} - 1} \qquad (7.1.2{:}3)$$

Here x_0 is defined by:

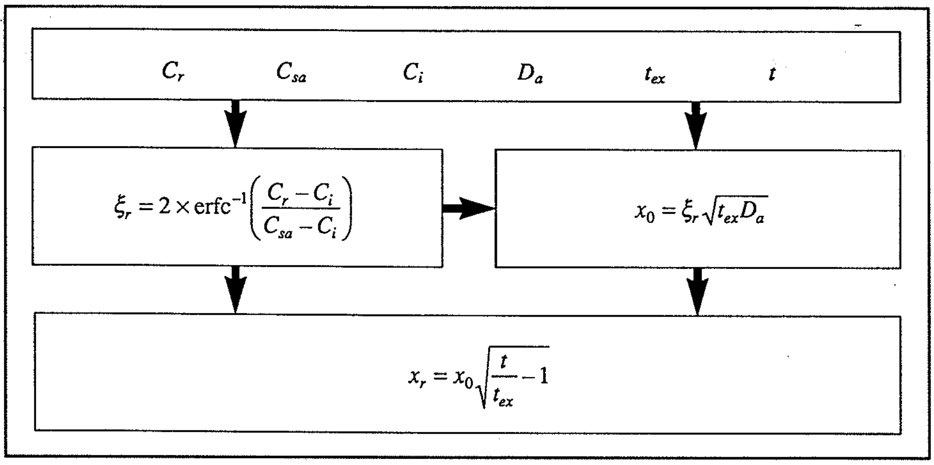


Figure 7-2. Flow chart for the calculation of the chloride ingress x_r into concrete of a reference chloride concentration C_r. Here the assumption is that C_{sa} and D_a remain constant and that C_i is uniformly distributed throughout the concrete.

$$x_0 = \xi_r \sqrt{t_{ex} D_a} \qquad (7.1.2:4)$$

K_1 is a convenient parameter

First year ingress

It is convenient to define another parameter, the first year ingress, cf. Poulsen [1985 p.86]:

$$K_1 = \xi_{cr} \sqrt{D_a} \qquad (7.1.2:5)$$

The "square root formula"

By means of the first year ingress the ingress x_{cr} of the threshold value of the chloride concentration C_{cr} yields the "square root formula":

$$x_{cr} = K_1 \sqrt{t - t_{ex}} \qquad (7.1.2:6)$$

Reference chloride concentration

Normally, the reference chloride concentration C_r is taken as the threshold value of the chloride concentration $C_r = C_{cr}$, i.e. the lowest concentration of chloride around a steel reinforcement in concrete which causes initiation of corrosion. In the splash zone the threshold value is often taken as $C_{cr} = 0.1$ % by mass concrete, corresponding to approx $C_{cr} = 0.8$ % by mass of binder. However the threshold value varies with many parameters of the concrete and its environment, cf. Chapter 6.

Flow chart for chloride ingress

Flow chart for calculation of chloride ingress

Figure 7-2 presents a flow chart for the calculation of the chloride ingress x_r into concrete of a reference chloride concentration C_r. Here the assumption is that C_{sa} and D_a remain constant and that C_i is uniformly distributed throughout the concrete.

7.1.3 Chloride diffusivity: time dependence

The parameters of chloride ingress are time-dependent

The estimation of chloride ingress into concrete based upon a time-independent chloride diffusivity of the concrete has shown gross errors. However, the inspection of marine concrete structures which include determination of the achieved chloride profiles started late in the 1970s. The first realization of the influence of time on the chloride diffusivity of marine concrete therefore appears about a decade later, cf. Morinaga [1988] and Takewaka [1988].

Field studies of the chloride ingress

In order to find the details of the time dependency for concrete in marine structures many field studies have been carried out. However, only little is known so far, but many reports and papers in the 1990s show progress, cf. Morinaga [1990a], Bamforth [1993a], Bjergovic [1994], Mangat [1994], Maage [1995] and Poulsen [1994 and 1995b].

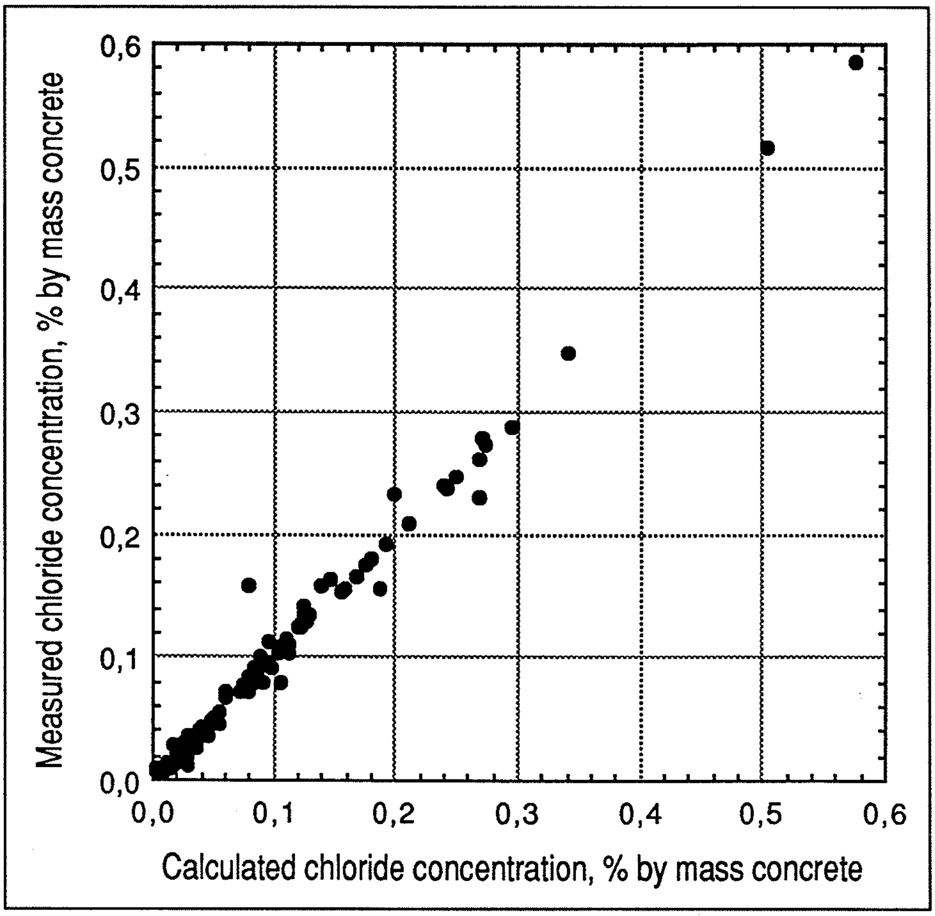
The general form of Fick's 2^{nd} law of diffusion

Fick's 2^{nd} law of diffusion

The general form of Fick's 2^{nd} law of diffusion, cf. (7.1.1:1) can be solved, cf. (7.1.2:1), when the chloride diffusion coefficient D_a is a known function of time t. The boundary conditions shall remain constant, cf. Poulsen [1993a] and Mejlbro [1995], i.e.:

- Concrete surface $x = 0$ and all time $t > 0 \Rightarrow C(x,t) = C_{sa}$.
- Time $t = 0$ and all $x > 0 \Rightarrow C(x,t) = C_i$.
- $x \rightarrow \infty$ for all $t \geq 0 \Rightarrow C(x,t) \rightarrow C_i$.

Figure 7-3. A plot of 129 Nos of measured chloride concentrations in concrete as a function of the calculated concentrations in the same depth according to Fick's 2nd law. Sørensen [1979].



Definition of D_a

The parameter D_a is now defined as:

$$D_a = \bar{D} = \frac{1}{t}\int_0^t D(\tau)\,\mathrm{d}\tau \qquad (7.1.3{:}1)$$

Various types of chloride diffusion coefficients

cf. Poulsen [1993a]. This means that it is necessary to distinguish between various types of chloride diffusion coefficients:

The real D

The achieved D_a

The potential D_p

- The real (but unknown) chloride diffusion coefficient D_{F2}.
- The achieved (measured) chloride diffusion coefficient $D_a(t_{in})$ obtained by curvefitting (7.1.2:1) to a profile measured by means of the test method APM 207, cf. AEClaboratory [1992b], or similar test methods, at the time of inspection $t = t_{in}$.
- The potential chloride diffusion coefficient D_P as measured by means of the test method APM 302, cf. AEClaboratory [1991a], or the CTH test method, cf. Tang [1993], normally at a maturity age of 28 days.

It is seen that the graph of a chloride profile has the shape of the "error function complement", when C_{sa} is constant, C_i is uniformly distributed and the real D_{F2} is time-dependent, as theoretically proved by Poulsen [1993a]. This has also been shown by Sørensen [1979] when the chloride ingress into concrete structures in the Great Belt area was measured, cf. Figure 7-3.

Achieved chloride diffusion coefficient

During the late 1980s it was recognized that:

- The achieved chloride diffusion coefficient D_a (measured on concrete samples from exposed structures) was significantly smaller than found from concrete specimens exposed and tested in the laboratory, cf. Poulsen [1990].
- When measuring the achieved chloride diffusion coefficient D_a versus time it is noticed that D_a is time dependent. For concrete in a "constant" environment D_a is generally found to be a non-increasing function of time, cf. Takewaka [1988].

The difference in laboratory exposure and field exposure (e.g. chloride concentration and temperature of the environment), is mainly taken as the explanation of the phenomenon that the chloride diffusion coefficient in laboratory exposed specimens and the field exposed concrete (in structures) are different, cf. Poulsen [1990].

The time-dependency of the chloride diffusion coefficient is considered as a combination of the complexity of the physical phemenon taking place during the chloride ingress, cf. Chapter 3 and the variation of intensity of the chloride exposure, i.e. submerged zone, tidal zone, splash zone, and atmospheric zone of the marine environment and even the effect of windward and leeward sides in the atmospheric zone, cf. Sand [1993], Swamy [1994], and Fluge [1995].

Long-term field studies of chloride ingress in marine RC structures are costly and time consuming. However, it is the only way to study the influence of time on the chloride diffusivity of marine concrete.

At the end of the 1980s and the beginning of the 1990s the first suggestions appear of a mathematical description of the (achieved) chloride diffusion coefficient. Among the most interesting contributions are Takawaka [1988], Maage [1993], Mangat [1994], and Bjergovic [1994].

Takawake [1988] states that the chloride diffusion coefficient depends on the w/c ratio of the concrete and the exposure period $\Delta t = t - t_{ex}$ according to the following expression:

$$D_{Cl} = D_{w/c} D_1 \Delta t^{-0.1} \qquad (7.1.3{:}2)$$

Here the parameter $D_{w/c}$ describes the influence of the w/c ratio and the parameter D_1 describes the influence of the cement type. Takewaka [1988] presents tables for the determination of the values of these parameters. The paper does not give the experimental background for this statement. It is noticed that the dimension of D_{cl} is [m^4/s]!

However, it inspired Bjergovic [1994] to apply this proposal for the development of a computer programme CHLODIF applied for the construction of the new Maslenia Bridge in Croatia.

A similar relationship for the achieved chloride diffusion coefficient versus time was found by Mangat [1994] by studying concrete in seawater:

$$D_{ac} = D_i t^{-m} \qquad (7.1.3{:}3)$$

Here the factor D_i denotes the effective chloride diffusion coefficient at the time $t = 1$ s (since SI-units are applied). The exponent m is found empirically to obey the relation:

$$m = 2.5\ w/c - 0.6 \qquad (7.1.3{:}4)$$

This mathematical model has been found from experimental data from field exposure of concrete specimens to seawater during a period of five years.

Maage [1993 and 1995a] has taken another approach to the problem, by an examination of older marine concrete structures, mainly costal bridges in Norway. In order to take into account the variation in chloride aggressivness of the marine environment as well as the properties of the concrete, e.g. the w/c ratio, the chloride diffusivity of concrete in marine structures has been derived in two ways from a concrete core, drilled from the structure:

- The parameters of the achieved chloride profile (D_a, C_{sa} and C_i) are determined from the exposed end of the core by means of APM 207 or a similar test method.
- The parameters of the potential chloride profile (D_p, C_{sp} and C_i) are determined from the virgin concrete, i.e. from the non-exposed end of the core by means of APM 302 or the CTH test method.

Maage [1993] defines a new parameter:

$$\delta = \frac{D_a}{D_p} \qquad (7.1.3{:}5)$$

and shows that $\delta = 1$ when $t = t_{ex}$ and that δ versus time t approximately obeys a power function, i.e.:

$$\delta \approx \left(\frac{t_{ex}}{t}\right)^{\gamma} \qquad (7.1.3{:}6)$$

In addition Tang & Nilsson [1992b] has shown that the potential chloride diffusion coefficient also obeys a power function:

$$D_p = D_{pex}\left(\frac{t_{ex}}{t}\right)^{\beta} \qquad (7.1.3{:}7)$$

It should be noted that the sign of β may change cf. Sandberg [1995 p.94].

Takawake [1988], Maage [1993], Mangat [1994] and Bjergovic [1994] have shown that also the achieved chloride diffusion coefficient versus time t obeys a power function:

$$D_a = D_{aex}\left(\frac{t_{ex}}{t}\right)^{a} \qquad (7.1.3{:}8)$$

Thus, the achieved chloride diffusion coefficient yields:

$$D_a = \delta D_p \approx \left(\frac{t_{ex}}{t}\right)^{\gamma} \times D_{pex} \times \left(\frac{t_{ex}}{t}\right)^{\beta} = D_{aex}\left(\frac{t_{ex}}{t}\right)^{\alpha} \qquad (7.1.3{:}9)$$

From this it is seen that

$$D_{aex}=D_{pex} \qquad (7.1.3{:}10)$$

and that

$$\alpha=\beta+\gamma. \qquad (7.1.3.11)$$

α depends on chloride intensity and w/c ratio of concrete

Furthermore, Maage [1995b] has shown that α depends on the chloride exposure intensity of the local environment and the *w/c* ratio of the exposed concrete. Thus Mangat [1994] and Maage [1993, 1994 and 1995ab] agree on the form of time dependence and the influence of the composition of the concrete, especially the *w/c* ratio. Maage [1995b] does not give an analytical expression of α versus the *w/c* ratio.

High performance concrete yields simple formula for α

Poulsen [1995c] has proposed the following expression, valid for high performance concrete, i.e. $0.25 \le w/c \le 0.45$:

$$\alpha = 3 \times (0.55 - w/c) \qquad (7.1.3{:}12)$$

- and more complicated formula for ordinary concrete

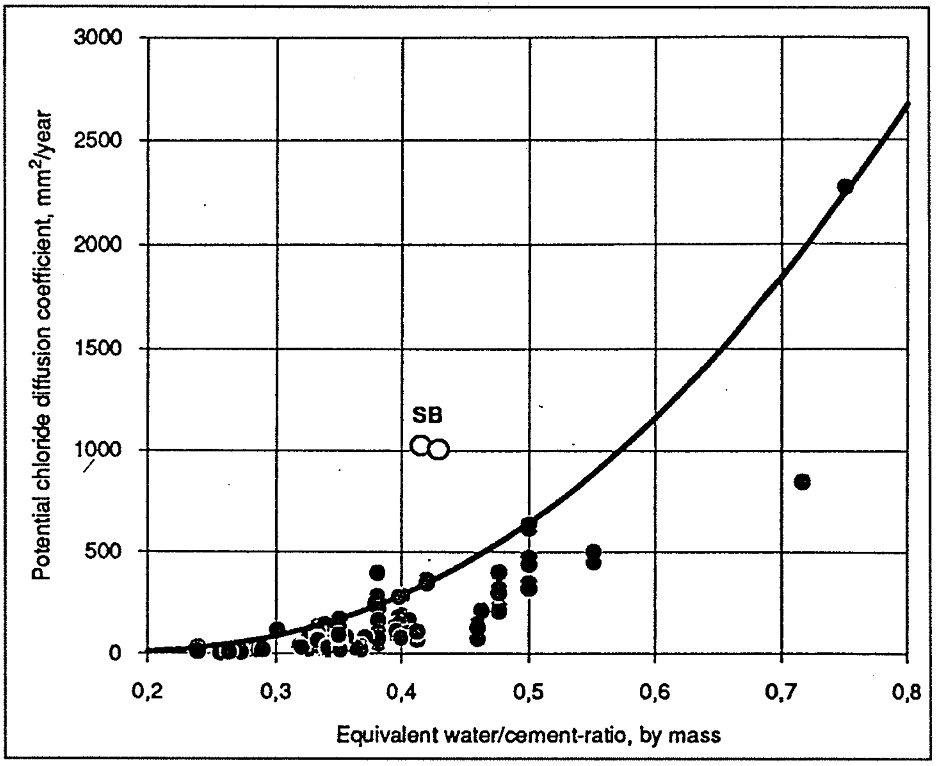
For ordinary concrete, i.e. $0.25 \le w/c \le 0.60$, Poulsen [1995c] has proposed the following expression:

$$\alpha = \exp\left(-\frac{(w/c)^2}{0.19}\right) + 0.1 \times \exp\left[-\left(\frac{0.1}{w/c}\right)^{2.5}\right] \qquad (7.1.3{:}13)$$

Proposed standard for the description of the exposure to marine concrete

Based upon the concept of Maage [1995] Poulsen [1995a] has proposed a standard of how to describe the exposure to chloride of marine concrete structures, i.e. marine environment.

Figure 7-4. Values of the potential chloride diffusion coefficient (acc. to APM 302 or the CTH method) of concrete versus the *w/c* ratio applying efficiency factors of 2.0 for silica fume and 0.5 for fly ash. The age of the concretes varies from 90 days to 1387 days except for observations marked SB. They were 9 years old and had thermocracks. Maage [1995, p. 18].



Potential chloride diffusion coefficient

As seen above the potential chloride diffusion coefficient plays an important role for the concept of Maage [1993 and 1994].

CTH test method and APM 302 agree very well

Tang [1993 p.34] has shown that the CTH test method and the APM 302 test method agree very well. Furthermore, Tang & Nilsson [1992b] has shown that the potential chloride diffusion coefficient develops (decreases) with time. In Figure 7-4, Maage [1995, p.18] the observations were *not* made at the same maturity age. This means that the test data will lie below the mean curve corresponding to a maturity age of 28 days. It is seen that the curve shown in Figure 7-4 corresponds to the formula:

$$D_{pex} = 570{,}000 \times \exp\left(-\sqrt{\frac{23}{w/c}}\right) \tag{7.1.3:14}$$

Surface chloride concentration

It is not only the achieved chloride diffusion coefficient, $D_a = D_a(t)$ which is time-dependent, but also the concrete's surface chloride concentration, $C_{sa} = C_{sa}(t)$, cf. Uji [1990], Purvis et al. [1994] and Gautefall [1994]. For the prediction of the time dependence of $C_{sa}(t)$ it has been suggested that it is proportional to the square root of the time, i.e.

$$C_{sa}(t) = S_1\sqrt{t} \tag{7.1.3:15}$$

cf. Uji [1990], Purvis et al. [1994] and Gautefall [1994]. Here, the coefficient S_1 is the value of the concrete's surface chloride concentration after one year of exposure (the first-year uptake) and t is the time of exposure. The unit of the time t and the exposure time t_{ex} is years.

However, in order to satisfy the boundary conditions at $(x,t) = (0,0)$, the time dependence $(t \geq t_{ex})$ ought to be written as:

$$C_{sa}(t) = \begin{cases} C_i & for \quad 0 \leq t \leq t_{ex} \\ C_i + S_1\sqrt{t - t_{ex}} & for \quad t \geq t_{ex} \end{cases} \tag{7.1.3:16}$$

Here, C_i is the equally distributed, initial chloride concentration of the concrete. S_1 is a parameter to be determined after about one year of exposure or more. If the concrete is inspected at time t_{in} and the surface chloride content is $C_{sa}(t_{in})$, S_1 thus yields the following value:

$$S_1 = \frac{C_{sa}(t_{in}) - C_i}{\sqrt{t_{in} - t_{ex}}} \tag{7.1.3:17}$$

The variation of $C_{sa} = C_{sa}(t)$ with time mainly takes place during the first period of a structure's lifetime.

It should be noticed that in cases where C_{sa} is time-dependent the "error function solution" (7.1.2:1) is *not* the solution to Fick's 2nd law of diffusion. This is easily proved by differentiation. In spite of this (7.1.2:1) is convenient to use and is widely used in practice to find C_{sa} and D_a from the achieved chloride profiles by regression analyses.

The solution of Fick's 2nd law of diffusion given the conditions that $C_{sa}(t)$ and $D_a(t)$ are time-dependent is not presented in text books on diffusion theory, except for some special cases. The solution for a given case might be found as a numerical solution, cf. Smith [1965]. However, in the important case:

$$C_{sa}(t) = S_1 \, t^{\,p} \qquad (7.1.3{:}18)$$

where

$$p = 0.0,\ \ 0.5,\ \ 1.0,\ \ 1.5,\ \ 2.0,\ \ 2.5,\ \ 3.0, \ldots$$

there are simple solutions to Fick's 2nd law of diffusion (7.1.1:1) where D is a constant, cf. Crank [1986, pp.33-34].

In cases where the diffusion coefficient is a function of time $D(t)$, (7.1.1:1) is solved by introducing the substitution $dT = D(t)\ \mathrm{d}t$, i.e.:

$$T = \int_0^t D(\tau)\ \mathrm{d}\,\tau \qquad (7.1.3{:}19)$$

and (7.1.1:1) is reduced to the following form:

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial x^2} \qquad (7.1.3{:}20)$$

where the well known solutions can be applied, cf. Poulsen [1993a].

In cases where the chloride surface concentration is given as:

$$C_{sa}(t) = C_i + S_1 \, t^p \qquad (7.1.3{:}21)$$

use can be made of the fact that for a linear differential equation the sum of two solutions is itself a solution.

In cases where the chloride surface concentration is given as:

$$C_{sa}(t) = C_i + S_1 \, (t - t_{ex})^p \qquad (7.1.3{:}22)$$

the solution is simply found by a simple translation of the axes as shown later.

The general solution where D_{a0} is a constant and $C_{sa}(t) = S_1 \, t^{\,p}$ is written as follows, cf. Mejlbro [1996]:

$$C(x,t) = S_1 t^p \Psi_p(z) \qquad (7.1.3{:}23)$$

where

$$z = \frac{x}{\sqrt{4 t D_{a0}}} \qquad (7.1.3{:}24)$$

For all $p \geq 0$ and where p is a constant $\Psi_p(z)$ is given by the following expression, cf. Mejlbro [1996]:

$$\Psi_p(z) = \sum_{n=0}^{+\infty} \frac{4^n}{(2n)!} p^{(n)} z^{2n} - 2\frac{\Gamma(p+1)}{\Gamma(p+0.5)} \sum_{n=0}^{+\infty} \frac{4^n}{(2n+1)!} (p-0.5)^{(n)} z^{2n+1} \qquad (7.1.3{:}25)$$

where Γ is the Gamma function. The following notation is used:

$$q^{(0)} = 1,\ q^{(1)} = q,\ q^{(2)} = q(q-1),\ q^{(n)} = q\,(q-1)\,(q-2)\ldots(q-n+1)$$

where $n \geq 1$. The notation is valid for $q = p$ and $q = p - 0.5$.

Especially for $p = 0$ the above solution yields the well-known "error-function solution", i.e.:

$$C(x,t) = S_1 t^0 \Psi_0\left(\frac{x}{\sqrt{4tD_{a0}}}\right) = S_1\,\text{erfc}\left(\frac{x}{\sqrt{4tD_{a0}}}\right) \tag{7.1.3:26}$$

Especially for $p = 0.5$ the solution given by Crank [1986, p.34] and applied by Uji [1990], Purvis et al. [1994] and Gautefall [1994] yields:

$$C(x,t) = S_1 t^{0.5} \Psi_{0.5}\left(\frac{x}{\sqrt{4tD_{a0}}}\right) \tag{7.1.3:27}$$

or by the usual notation for the analytical functions:

$$C(x,t) = S_1\sqrt{t}\left[\exp\left(-\frac{x^2}{4tD_{a0}}\right) - \frac{x\sqrt{\pi}}{\sqrt{4tD_{a0}}}\,\text{erfc}\left(\frac{x}{\sqrt{4tD_{a0}}}\right)\right] \tag{7.1.3:28}$$

Thus, in a more general case where the diffusion coefficient is time-dependent $D_a(t)$ and $t>0$ the surface chloride content is as given in (7.1.3:16) the general solution yields:

$$C(x,t) = C_i + S_1\sqrt{t - t_{ex}}\left(\exp(-z^2) - z\sqrt{\pi}\,\text{erfc}(z)\right) \tag{7.1.3:29}$$

where:

$$z = \frac{x}{\sqrt{4(t - t_{ex})D_a(t)}} \tag{7.1.3:30}$$

Chloride ingress into concrete

The formula of chloride ingress applied by Uji [1990], Purvis et al. [1994] and Gautefall [1994] assumes that the chloride surface concentration obeys (7.1.3:15). It is seen that it is assumed that the initial chloride concentration of the concrete C_i is neglected and that $t_{ex} = 0$.

Now, to be more general, it is assumed that the surface chloride concentration obeys (7.1.3:16) and that the achieved chloride diffusion coefficient of the concrete obeys (7.1.3:8). Thus the ingress x_r of a given (reference) chloride concentration C_r can be estimated by solving the following equation:

$$C_r = C_i + S_1\sqrt{t - t_{ex}}\,\Psi_{0.5}\left(\frac{x_r}{\sqrt{4(t - t_{ex})D_a(t)}}\right) \tag{7.1.3:31}$$

The solution yields:

$$x_r = \sqrt{4(t - t_{ex})D_a(t)}\;\Psi_{0.5}^{-1}\left(\frac{C_r - C_i}{S_1\sqrt{t - t_{ex}}}\right) \tag{7.1.3:31'}$$

where Ψ^{-1} stands for the inverse function of Ψ. The solution can be abbreviated as:

$$x_r = \xi_{0.5r}\sqrt{(t - t_{ex})D_a(t)} \qquad (7.1.3{:}31'')$$

where $\xi_{0.5r}$ stands for the following mixture of parameters and time dependence:

$$\xi_{0.5r} = 2\,\Psi_{0.5}^{-1}\left(\frac{C_r - C_i}{S_1\sqrt{t - t_{ex}}}\right) \qquad (7.1.3{:}32)$$

In case the time-dependent chloride diffusion coefficient has the form in (7.1.3:8) the ingress x_r of the reference chloride concentration C_r yields:

$$x_r = \xi_{0.5r}\sqrt{t_{ex}D_{aex}\left(\frac{t}{t_{ex}} - 1\right)\left(\frac{t_{ex}}{t}\right)^{\alpha}} \qquad (7.1.3{:}33)$$

In case $t >> t_{ex}$, this formula yields the simpler expression:

$$x_r \cong \xi_{0.5r}\sqrt{t_{ex}D_{aex}\left(\frac{t}{t_{ex}}\right)^{1-\alpha}} \qquad (7.1.3{:}34)$$

7.1.4 Probabilistic model of chloride ingress into concrete

The use of the probabilistic concept in making service life predictions for construction materials has been explored by several researchers, cf. Sentler [1984 and 1985], and Martin [1985]. However, so far only little has been done in the field of chloride ingress into concrete by applying probabilistic methods.

A group of researchers at the University of Aalborg is working on a computer programme for the estimation of chloride ingress and reinforcement corrosion applying the probabilistic concept.

Karlsson [1995] has published a probabilistic method by which the cover to reinforcement is designed. This method also includes estimation of chloride ingress into concrete determined by the probabilistic concept.

There is no doubt that the probabilistic concept will be widely used in time in view of the increasing numbers of observations of chloride ingress from the inspection of marine concrete structures.

7.1.5 Prediction of service lifetime

The ingress of chloride into concrete will, sooner or later, cause a risk of corrosion. Other "concrete deceases" may also reduce the structural durability, and phenomena like alkali aggregate reaction, carbonation and freeze/thaw attack may interact with the chloride initiated corrosion and shorten the lifetime of a RC structure. However, in this report it is assumed that precaution is taken against such "concrete deceases" and that the chloride initiated corrosion is the only phenomenon to deal with.

About the term "service lifetime"

In this section the term service lifetime equals the initiation period

The term "service lifetime" is defined in Chapter 2. Here the term is simplified to be equal to the initiation time.

Prediction of lifetime

In Section 7.1.2 the chloride ingress x_r of a reference chloride concentration C_r is determined under various assumptions. Since the lifetime here is taken to be equal to the initiation period the lifetime is easily determined as the time for the threshold value $C_r = C_{\text{cr}}$ of the chloride concentration to penetrate through the cover and reach the reinforcement, cf. Maage [1995].

It is a problem that the prediction of the service lifetime goes far beyond the period of time in which it has been possible to check any of the current lifetime models – and therefore it is also impossible to say from experience which model is the best. It is belived that the more closely the assumptions agree with the short term observations, the better the model.

This also means that there will be a certain risk in applying the prediction models to marine RC structures made from concrete containing new types of cementing matrix (binders). Therefore, such structures should always be inspected regularly – particularly in the first period of time.

Prediction of lifetime is mainly of interest in connection with inspection of marine RC structures. The task is: to predict the lifetime from a determination of the chloride diffusivity of the concrete in the structure. Then the question is: what type of sample to take, which test method to use, and how to evaluate the observations, i.e. the application of formulae?

Constant chloride diffusivity

As said earlier the chloride diffusivity of concrete develops with time, cf. Takawake [1988], Maage [1993], and Mangat [1994]. However, the change of the chloride diffusion coefficient with time obeys a power function and therefore the major change will occur during the first approx 10 years after casting (depending on the *w/c* ratio). When the inspection of RC marine structures takes place at a late stage it is convenient to assume a constant chloride diffusivity (D_a and C_{sa}) of the concrete for the prediction of the residual lifetime of the structure, but this is not necessary as shown later.

When D_a and C_{sa} are constant a simple formula can be developed for the lifetime, cf. Poulsen [1994]. According to these assumptions it has been shown that the ingress x_r of the threshold value C_{cr} versus time t obeys (7.1.2:6). It is now assumed that the structure is inspected at time $t=t_{in}>10$ years and it is observed that the ingress of C_{cr} is $x_{\text{cr}} = x_{in}$. Thus, from (7.1.2:6) it is found that:

$$x_{in} = K_1\sqrt{t_{in}} \;\Rightarrow\; K_1 = \frac{x_{in}}{\sqrt{t_{in}}} \qquad (7.1.5:1)$$

Thus the further ingress during the residual lifetime:

$$x_{\text{cr}} = x_{in}\sqrt{\frac{t}{t_{in}}} \qquad (7.1.5:2)$$

The definition of the service lifetime t_{LT} yields:

$$x_{\text{cr}} = c_{\min} \;\Rightarrow\; t = t_{LT} \qquad (7.1.5:3)$$

where $c_{\min}$ is the minimum thickness of the cover to reinforcement. Thus, the lifetime can be found as the solution to the following equation:

$$c_{\min} = x_{in}\sqrt{\frac{t_{LT}}{t_{in}}} \qquad (7.1.5:4)$$

Figure 7-5. Example of a graphical estimation of t_{LT}.

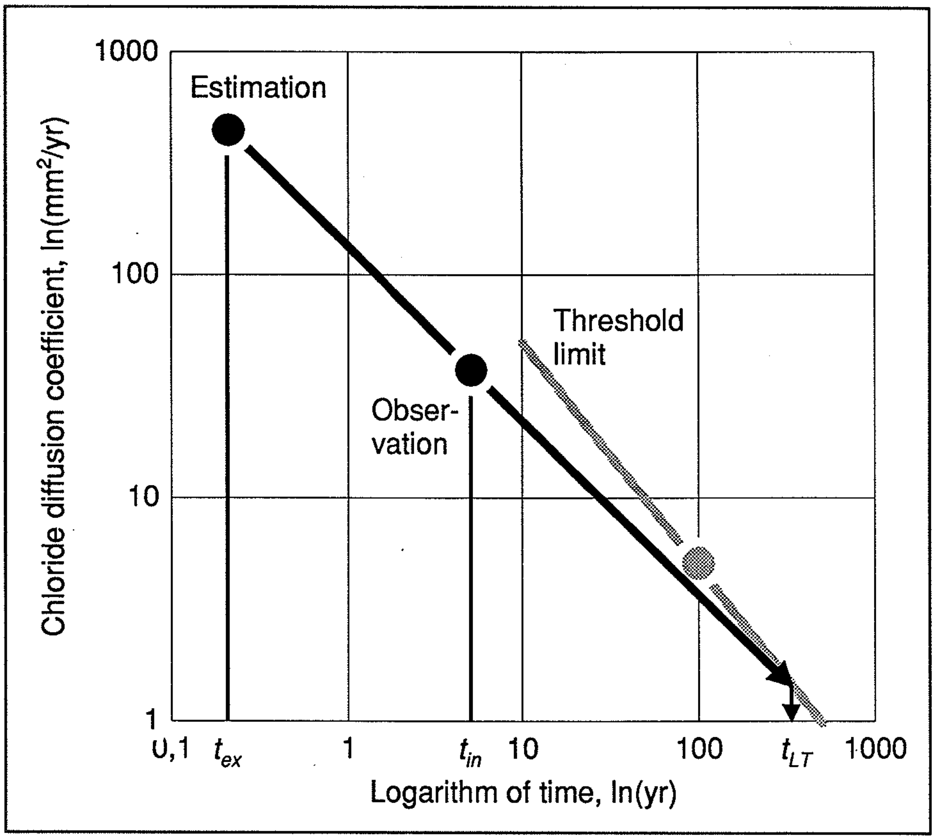
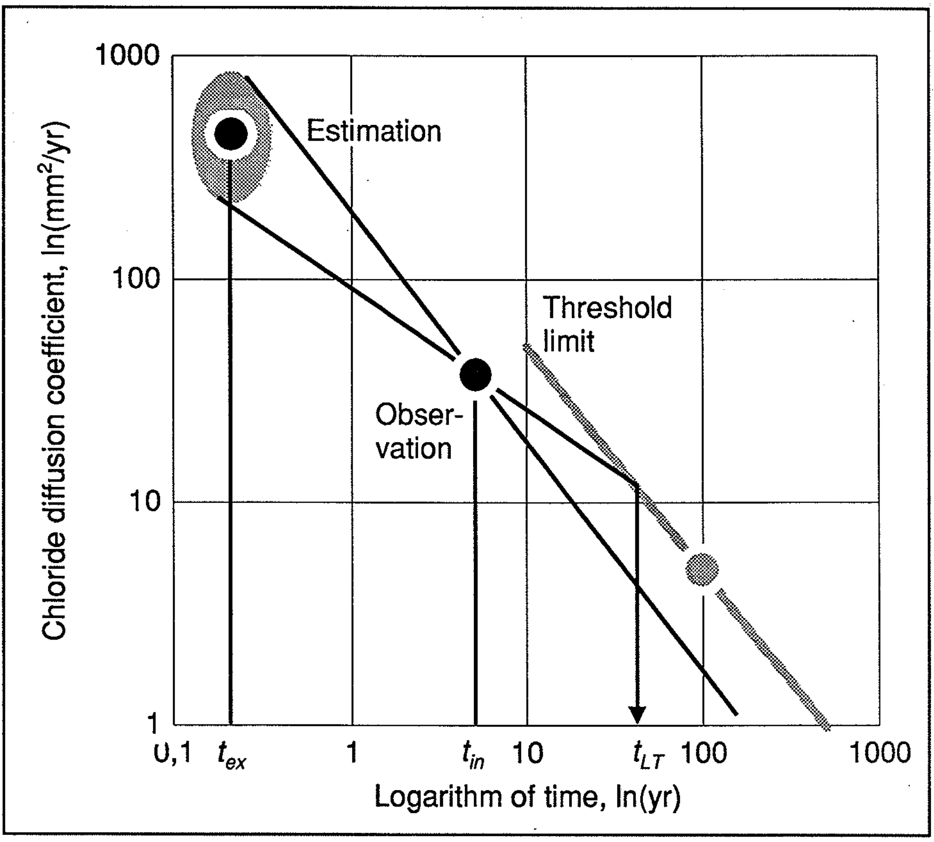


Figure 7-6. Example of a graphical estimation of t_{LT}.



which yields:

$$t_{LT} = t_{in}\left(\frac{c_{\min}}{x_{in}}\right)^2 \tag{7.1.5:4'}$$

Therefore, it follows that the residual lifetime res$\{t_{LT}\}$ is:

$$\text{res}\{t_{LT}\} = t_{LT} - t_{in} = t_{in}\left[\left(\frac{c_{\min}}{x_{in}}\right)^2 - 1\right] \tag{7.1.5:5}$$

It should be pointed out that this formula has its limits – but when the assumptions are satisfied it is a convenient formula.

The residual service lifetime may also be found graphically. From the relation (7.1.2:6) it follows that:

$$\ln x_{\text{cr}} = \ln K_1 + 0.5 \times \ln t \tag{7.1.5:6}$$

Thus, a diagram from which the lifetime may be determined is easily constructed.

Constant C_{sa} and time-dependent D_a

The LIGHTCON service life model, cf. Maage [1995], covers the case where it is assumed that $D_a(t)$ versus time t is described by a power function and that C_{sa} remains constant. C_{sa} has to be estimated from experience with similar types of concrete in the same environment or from the measurement of C_{sa} at the time of inspection t_{in} combined with the proposal of Gautefall [1994]. C_{sa} should be estimated as an average value for the residual lifetime, cf. Mangat [1993].

The ingress x_{cr} into concrete of the threshold value C_{cr} obeys the following relation as explained earlier:

$$x_{\text{cr}} = \xi_{\text{cr}}\sqrt{t_{ex}D_{ex}}\sqrt{(t - t_{ex})\left(\frac{t_{ex}}{t}\right)^{\alpha}} \tag{7.1.5:7}$$

During an inspection at time $t = t_{in}$ of a marine RC structure the following data are normally assumed to be obtained:

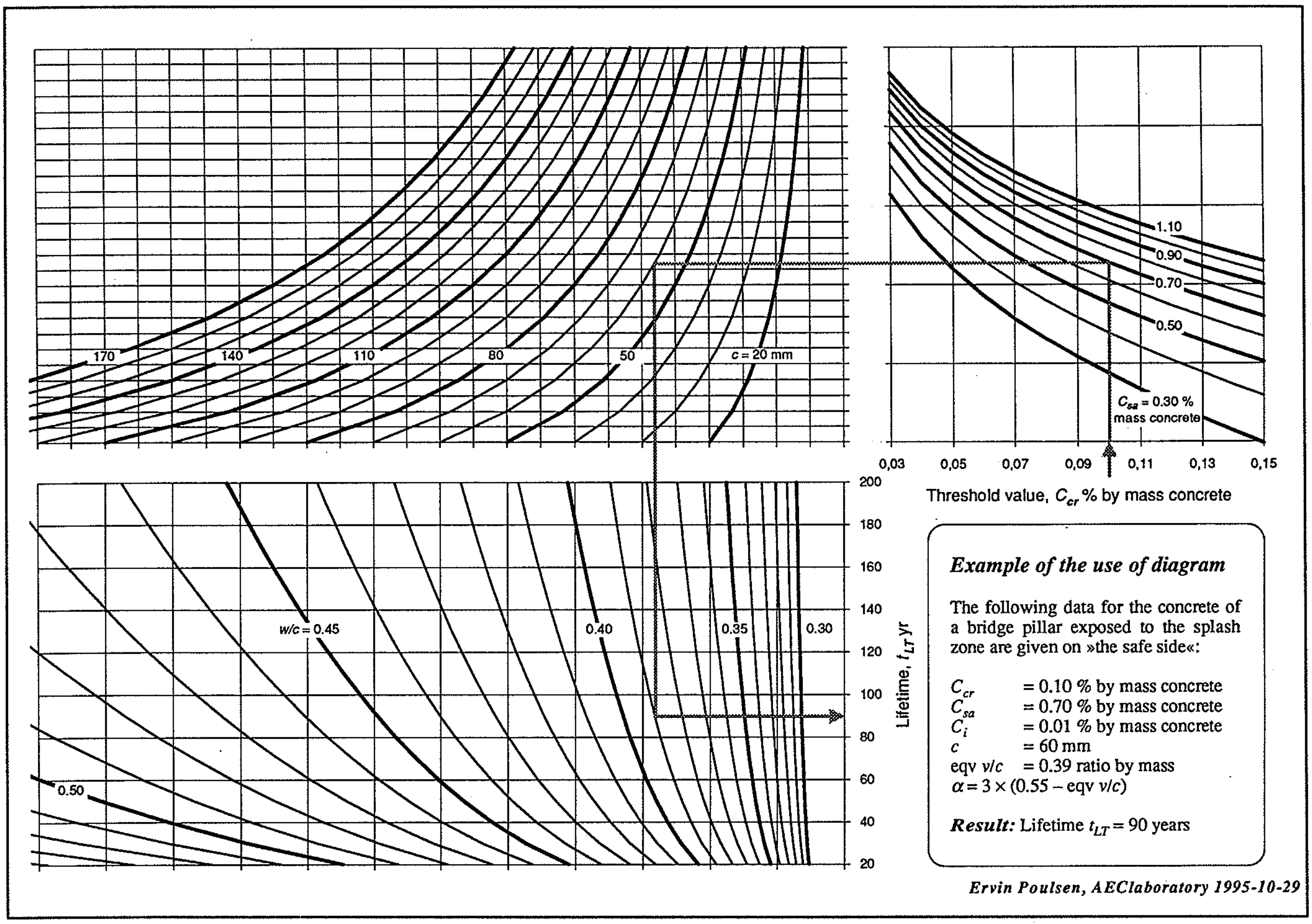
- The ingress x_{in} of the threshold value C_{cr} of the chloride concentration in the concrete, normally $C_{\text{cr}} = 0.10$ % by mass of concrete.
- The achieved chloride diffusion coefficient D_{ain}.
- The achieved chloride concentration C_{sa} at the concrete surface.
- The *w/c* ratio of the concrete.
- The minimum reinforcement cover $c_{\min}$.

From these observations the following parameters are determined: D_{aex} from (7.1.3:14) and ξ_{cr} from (7.1.2:2) and α from:

$$\alpha = \frac{\ln(D_{ain} / D_{aex})}{\ln(t_{ex} / t_{in})} \tag{7.1.5:8}$$

Now, it is possible to draw the graph showing the ingress x_{cr} of the chloride concentration (the threshold value) C_{cr} into the concrete versus time in a Cartesian coordinate system (t, x_{cr}) in such way that the curve will

Figure 7-7. By introducing the relation between α and the *w/c* ratio Poulsen [1995b] made it simple to estimate the service lifetime graphically.



Example of the use of diagram

The following data for the concrete of a bridge pillar exposed to the splash zone are given on »the safe side«:

C_{cr} = 0.10 % by mass concrete
C_{sa} = 0.70 % by mass concrete
C_i = 0.01 % by mass concrete
c = 60 mm
eqv v/c = 0.39 ratio by mass
$\alpha = 3 \times (0.55 - \text{eqv } v/c)$

Result: Lifetime t_{LT} = 90 years

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pass through the points (t_{ex}, 0) and (t_{in}, x_{in}). Here it should be noticed that a regression analysis could be needed since the inspection gives an excess of observations. In regression analysis the determination of the *w/c* ratio or x_{in} be omitted. However, in this way solving the problem does not become easier.

By drawing the best fitted curve for the ingress x_{cr} of the threshold value C_{cr} into the concrete the time t_{LT} when the minimum reinforcement cover c_{min} is exceeded can be estimated.

It is convenient to solve the above equations graphically. In this way it is also easier to overlook the influence of the deviation of the various parameters involved, cf. Poulsen [1995b]. In brief this procedure has the following steps:

Step 1. In a double logarithmic coordinate system $D(t)$ is shown as a straight line, since it is assumed that $D(t)$ versus time is described as a power function. If $D_{aex} = D_{pex}$ has been determined at time $t = t_{ex}$ in connection with pre testing, trial mixes or trial castings this value should be used. Otherwise from the inspection the *w/c* ratio of the concrete is determined. Thus, the achieved diffusion coefficient at time $t = t_{ex}$ is estimated, e.g. by (7.1.3:14), cf. Maage [1995] or a similar formula.

- ***Step 2***. From the inspection at $t = t_{in}$ the achieved chloride diffusion coefficient $D_a(t_{in})$ has been determined from the achieved chloride profile by the test method APM 207 or a similar test method.
- ***Step 3***. In a double logarithmic coordinate system a straight line is drawn between the points representing (t_{ex}, D_{aex}) and (t_{in}, D_a).
- ***Step 4***. At time $t > t_{in} > t_{ex}$ the chloride ingress x_{cr} is:

$$x_{cr} = \xi_r \sqrt{(t - t_{ex})\, D_a(t)} \qquad (7.1.5:9)$$

Thus the value of $D_a(t)$ which leads to $x_{cr} = c_{min}$ becomes:

$$D_{acr}(t) = \frac{(c_{\min} / \xi_{cr})^2}{t - t_{ex}} \qquad (7.1.5:10)$$

The curve $D_{acr}(t)$ versus t is plotted in the double logarithmic coordinate system (use a spread sheet).

- ***Step 5***. The lifetime $t = t_{LT}$ is determined as the intersection points between the lines determined in step 3 and step 4, cf. Figures 7-5 and 7-6.

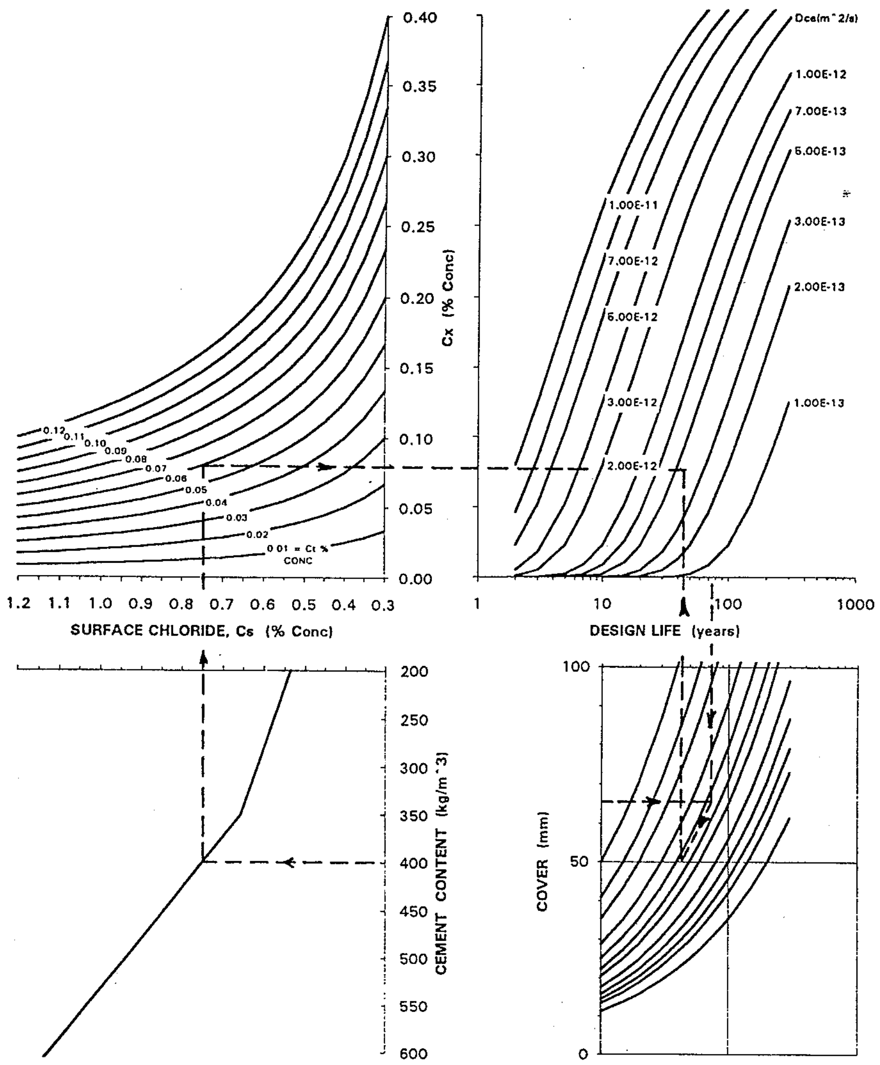
Other easy-to-apply diagrams can also be designed. Maage [1995] and Mangat [1993] have shown that for the splashzone α depends on the *w/c* ratio of the concrete. By introducing the relation between α and the *w/c* ratio, e.g. as in (7.1.3:12) Poulsen [1995b] has made it simple to estimate the service lifetime graphically, cf. Figure 7-7.

Bamforth [1994] has made a similar diagram for the prediction of the service lifetime, cf. Figure 7-8.

Time-dependent C_{sa} and D_a

The LIGHTCON service model, cf. Maage [1995], can be easily extended to cover the case where $C_{sa}(t)$ as well as $D_a(t)$ are time-depentent. The time-dependence of $C_{sa}(t)$ can be taken as proposed by Uji [1990] and applied by Gautefall [1994] and Purvis et al. [1994], or similar relations

Figure 7-8. Diagram for the prediction of the service lifetime from Bamforth [1994]. Compare with Figure 7-7.



1. Select design life (75 years) and drop a vertical line
2. Select cover (65mm) and project a horizontal line
3. At the intersect from 1 and 2 project a curve, parallel to the nearest curve, to 50mm cover
4. At the intersect of 3 with 50mm cover, project a vertical line
5. Select C_s based on cement content (400kg/m^3) or from local knowledge
6. Project vertical line from selected C_s to threshold level (0.06% of concrete)
7. At intercept with appropriate threshold level curve, project a horizontal line
8. At intercept of vertical line from 4 and horizontal line from 7 determine max, D_{ce}

found by observation of RC marine structures or specimens in field test stations, cf. Malmström [1992] and Sandberg [1993].

When $t_{LT} >> t_{ex}$ the general equation for determination of the service lifetime t_{LT} can be written as:

$$C_{\mathrm{cr}} \cong C_i + S_1 t_{LT}^p \,\Psi_p\left(\frac{c}{\sqrt{4\,t_{ex} D_{aex}\left(t_{LT}/t_{ex}\right)^{\alpha}}}\right) \tag{7.1.5:11}$$

In this way it is *not* possible to develop a simple formula for the estimation of the service lifetime since the problem involves the solution of a transcendental equation. However, recent work by Mejlbro [1996] has proved it possible to define a set of functions:

$$\Lambda_p(z) = \frac{\Psi_p(z)}{z^{2p}} \tag{7.1.5:12}$$

by which Poulsen [1996] has shown that the service lifetime, defined as the initiation period, $t_{LT} = t_{\mathrm{cr}}$, yields:

$$t_{LT} = t_{ex} \times \left(\frac{0.5c}{\sqrt{t_{ex} D_{aex}} \times \mathrm{inv}\,\Lambda_p(y_{\mathrm{cr}})}\right)^{\frac{2}{1-\alpha}} \tag{7.1.5:13}$$

where:

$$y_{\mathrm{cr}} = \frac{C_{\mathrm{cr}} - C_i}{S \times (0.5c)^{2p}} \tag{7.1.5:14}$$

and invΛ_p is the inverse function of Λ_p.

Earlier, the easiest way to estimate the service lifetime (period of initation) was to determine the curve of chloride ingress into the concrete versus time in such a way that the curve passes through the point determined by inspection $(t, x_{\mathrm{cr}}) = (t_{in}, x_{\mathrm{cr}.in})$. The service lifetime is determined graphically from the point where $(t, x_{\mathrm{cr}}) = (t_{LT}, c_{\min})$.

Due to leaching and other influences the threshold value C_{cr} may change with time, cf. Sandberg [1995]. When it is possible to estimate this change the lifetime can be estimated by any of the above methods, cf. Sandberg [1995].

Purvis et al. [1994] has derived a formula for the determination of the lifetime, the "SPHR lifetime model", which deviates basically from the concepts of Maage [1995], Bamforth [1994] and Poulsen [1995b].

The SPHR lifetime model is based upon work by Clear [1976], and has the following form:

$$t_{LT} = \left(\frac{2.695 \times c_k^{1.22} \times t_{\mathrm{in}}^{0.21}}{C_{sa}^{0.42} \times w/c}\right)^{0.8265} \tag{7.1.5:15}$$

Here, referring to the inspection section in question,

- t_{LT} is the time for the first sign of deterioration (service lifetime).
- c_k is the characteristic reinforcement cover, defined as the 10 %-fractile.
- t_{in} is the time of inspection.
- C_{sa} is the surface chloride concentration.
- w/c is the water/binder ratio.

7.1.6 Long term inspection of marine RC structures

Many marine RC structures represent an important investment. Therefore, maintenance is important in order to preserve the structures. Thus an inspection plan for the estimation of the service lifetime or the residual lifetime is an important task. Maage [1995] propose three possible inspection plans:

- *Planned inspection* includes the determination of the potential chloride diffusivity (APM 302) at the time of chloride exposure $t = t_{ex}$ combined with the determination of the achieved chloride diffusivity (APM 207) at the time of inspection $t = t_{in}$.
- *Inspection during service life* includes the determination of the achieved chloride diffusivity (APM 207) at the time of inspection $t = t_{in}$ but no initial information on the chloride diffusivity of the concrete exists, i.e. at the time $t = t_{ex}$.
- *Periodical inspection* includes a running verification of the service lifetime as an integral part of the planning and design of RC marine structures, i.e. periodical inspection of the achieved and potential chloride diffusivity of the concrete in the structures.

At present "during service life" is the common procedure, if any. However, in future "planned inspection" and even "periodical inspection" may be adopted.

Since the inspection is carried out by an examination of drilled cores from inspection sections of the structure Sandberg [1995] has proposed that special specimens are prepared for core drilling and placed upon the structures in the relevant local environment. The specimens should be cast of the same concrete as the RC marine structure itself and not be so small that a scale effect will occur.

When a periodical inspection is applied it will be convenient to plot the observation obtained in a diagram supplied with an upper boundary line. In this way it is easy to determine whether the observations move towards the borderline or away from it. In this way the technique of sequential analysis is applied, cf. Mohr [1980], and early action in the form of preventive maintenance is possible.

7.1.7 Necessary cover to reinforcement

The structural designer follows a set of standard reinforced concrete details depending on the aggressiveness of the environment. These details include tables in the Code of Practice of the necessary reinforcement cover corresponding to the various environments, e.g. as given by Eurocode and ENV 206. The routines applied by the structural designer are rather stable. Thus, it will only have little effect if a lifetime concept such as lifetime models is introduced in the structural design. However, it is possible to introduce the lifetime concept by supplying the Code of Practice with tables of the reinforcement cover necessary to ensure a specified service lifetime.

It is possible to arrange the formulae of the service lifetime with respect to the reinforcement cover. Such tables should include parameters of the environment as well as the composition of the concrete.

Such tables have been determined, e.g. by Takawaka [1988], Morinaga [1990a], Karlsson [1995] and Poulsen [1995b].

Formulae for the necessary cover to reinforcement

The formulae for the ingress x_r of the threshold value C_{cr} of the chloride concentration are all included in the general form:

$$x_{cr} = x_{cr0} \sqrt{\left(\frac{t_{ex}}{t}\right)^{\alpha}} \qquad (7.1.7{:}1)$$

where x_{cr0} is the ingress of C_{cr} in case $\alpha = 0$, i.e.:

$$x_{cr0} = \xi_{cr} \sqrt{t_{ex} D_{aex}} \sqrt{\frac{t}{t_{ex}} - 1} \qquad (7.1.7{:}2)$$

To ensure a service lifetime of t_{LT} the minimum reinforcement cover c_{min} shall obey the following condition:

$$c_{min} \geq \xi_{cr} \sqrt{t_{ex} D_{aex}} \sqrt{\frac{t_{LT}}{t_{ex}} - 1} \sqrt{\left(\frac{t_{ex}}{t_{LT}}\right)^{\alpha}} \qquad (7.1.7{:}3)$$

It should be noticed that the determined c_{min} does not include any safety margin. The concept of the safety margin is explained below.

Safety margin

A reinforcement cover determined as the expectation value will not be suitable as a design value. Only about 50 % of the results will be safe in the long run. In design it is required that there is an appropriate safety against reinforcement corrosion when the structure reaches an age of t_{LT} years. It is not possible to achieve a safety level of the same order of magnitude as applied in structural design. However, this is not necessary if the concrete is controlled in a proper way, i.e. by testing the chloride diffusivity when the concrete is exposed to chloride for the first time, and if the structure has periodical inspection including determination of the achieved chloride diffusivity versus time.

It is not a purely technical question to decide upon the level of the safety against corrosion – it is also a political question involving the building owner as well as Society. However, finding the optimum in a given situation is a technical question but there seem to be different opinions about the level of safety against corrosion, cf. Karlsson [1995] and Poulsen [1995].

The methods developed enable us to design reinforcement covers as soon as it has been decided how thick the cover to reinforcement should be for a specified concrete in a given environment, cf. Karlsson [1995] and Poulsen [1995b].

As in structural design there are two methods of obtaining an appropriate level of safety:

- To determine the necessary cover to reinforcement on the basis of design values according to the same principle as found in the Code of Practice for the structural design of RC structures, cf. Poulsen [1995b].
- To determine the necessary cover to reinforcement by probabilistic methods where the statistical distribution is decided from observation of RC structures and where the level of safety is decided from an acceptable reinforcement cover proved in practice to be satisfactory, cf. Karlsson [1995].

Denmark has good experience of being a pioneer for the determination of partial safety factors in soil mechanics and design of RC structures, cf. Brinch Hansen [1956] and Moe [1970].

There have been no basic differences between the way in which the Code of Practice has determined the reinforcement covers at the beginning and end of this century – this important durability requirement cannot be decided by "show of hands". The 1930 edition of the Danish Code of Practice introduced the well-known 1-2-3 cm rule for reinforcement covers. With some interpretation revisions this simple rule is still valid. It is notable, because the Code of Practice in the UK and the USA introduced a corresponding 1-2-3 inches rule for the reinforcement cover at the same time.

The thickness of the cover to reinforcement must at least depend on the environment, the intended lifetime, the consequences and types of corrosion, and the quality and workmanship of concrete and reinforcement. Probability analysis is advisable, cf. Karlsson [1991] and Poulsen [1993a].

7.2 RC structures exposed to de-icing salts

RC structures exposed to de-icing salts differ from marine RC structures in the following ways:

- The exposure to de-icing salts only takes place during the winter, i.e. the exposure is not quasi-continuous as in the case of a marine RC structure. There is an active and a passive (dormant) period of exposure.
- When exposed to de-icing salts the horizontal concrete surfaces are generally exposed to meltwater of a higher chloride concentration than that of seawater.
- The traffic splash during the wintertime is to a certain extent similar to the exposure of marine RC structures to airborne chloride, but the traffic splash is not quasi-continuous like the exposure of marine RC structures.

During the wintertime there is an uptake of chloride by the exposed concrete surfaces, and during the summertime there is no exposure to chloride, but in some cases there will be a leaching of the chloride from the concrete surface exposed to rain, cf. Cady [1984]. This means that the surface chloride concentration can also have a dormant period during the summertime, and it can even decrease with time.

Figure 7-9. Predicted profiles of free chlorides by *ClinConc* the sixth year after exposure. The curves are for April (6 years), July (6.25) and October (6.5). OPC concrete with w/c=0.40 exposed to sea water with 14-18 g/l of Cl.

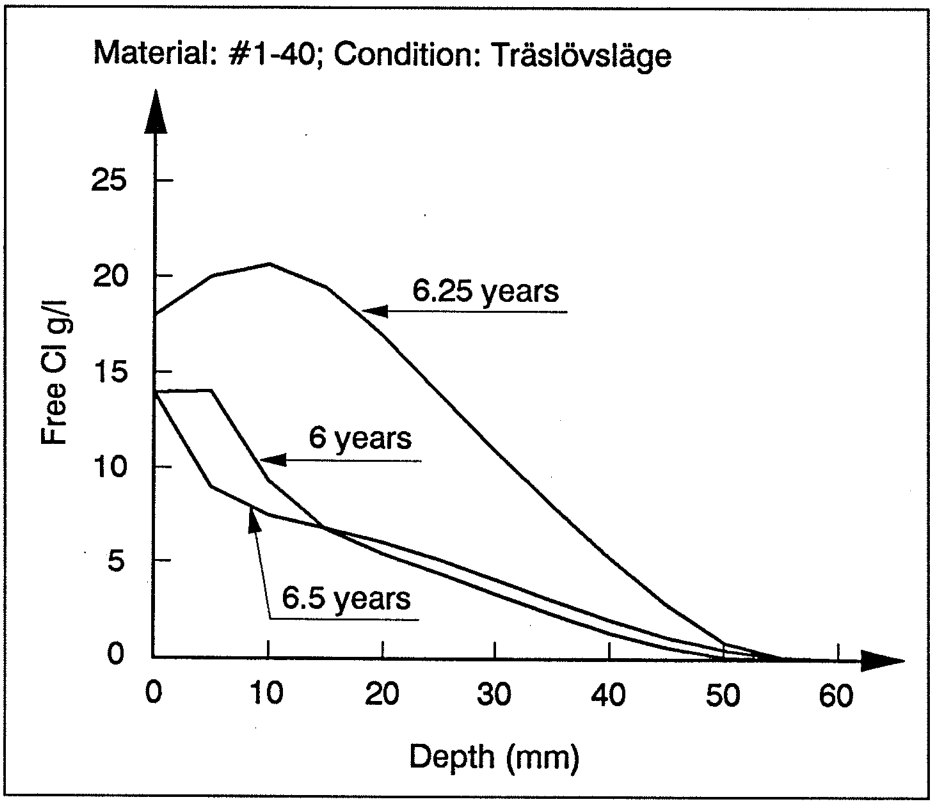
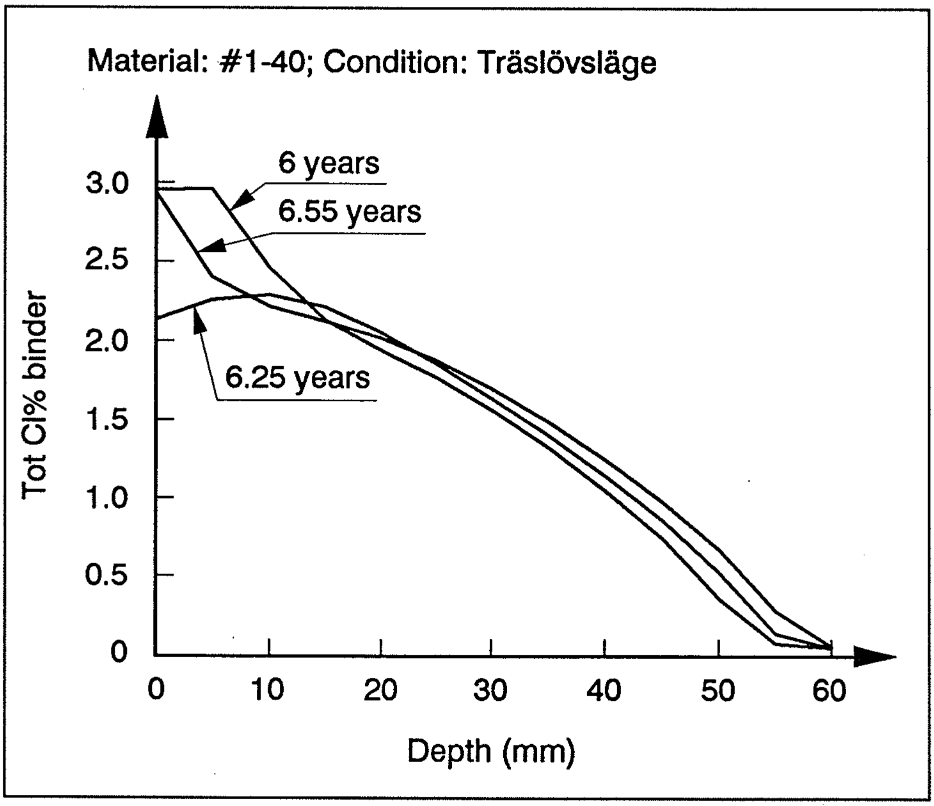


Figure 7-10. Predicted profiles of total chlorides by *ClinConc* the sixth year after exposure. The curves are for April (6 years), July (6.25) and October (6.5). OPC concrete with w/c=0.40 exposed to sea water with 14-18 g/l of Cl.



7.2.1 Chloride penetration

If a mathematical model need not go into details, it is possible to estimate the chloride surface concentration of the exposed concrete surfaces, e.g. by a power function like (7.1.3:22). In this way the mathematical models of the chloride penetration developed for marine RC structures can be applied. This is the common way of estimating chloride ingress into RC structures exposed to de-icing salts, cf. Cady [1984], Henriksen [1991] and Larsen [1993ab, 1995].

From a mathematical point of view it is possible to solve Fick's 2nd law of diffusion (7.1.1:1) in the general case where:

$$C(x,0) = C_i \tag{7.2.1:1}$$

$$C(0,t) = C_i + \sum_{j=1}^{n} S_{1j} t^{p_j} \tag{7.2.1:2}$$

By the use of tables for the functions $\Psi_p(z)$ defined in (7.1.3:25) earlier it is possible to model even complicated findings of $C_{sa}(t)$ versus time. The problem is that there is a lack of information concerning $C_{sa}(t)$ versus time. However, near Borås in Sweden the BTB group have recently established a field exposure station for RC structures exposed to de-icing salts. Thus, observation and test data are expected during the next few years.

7.2.2 Service lifetime

In the same way as inthe estimation of chloride penetration into RC structures exposed to de-icing salts, it has become a general practice to apply the methods developed for marine RC structures, cf. Henriksen [1991,1993ab] and Cady et al. [1992]. However the only reason why these methods are used is that the application of a more realistic description of chloride ingress into concrete when this is exposed to de-icing salts would involve extensive numerical calculations - and no attempt has been reported so far.

7.3 The ClinConc prediction model

The ClinConc prediction model for chloride penetration and service-life

One of the most advanced models for predicting chloride penetration into concrete, *ClinConc*, was presented by Tang & Nilsson [1994] and Tang [1995]. By using a FDM numerical approach, most of the factors involved in chloride penetration are considered in a relevant and scientific way. The ambition is to model the full chloride profile, to be able to compare predicted and measured ones. A comparison with the chloride threshold values for corrosion can be done, in terms of total chlorides, free chlorides or the Cl/OH ratio, to predict service-life of a structure.

Effect of depth and age included

The mass balance equation (3.2:11) for chlorides is solved by using separate terms for chloride diffusion and for chloride binding. The basic diffusion coefficient is the "true" chloride diffusion coefficent D_{F1}, evaluated from the D_{CTH} from the CTH migration test method. Additionally, the effect of depth from a cast surface, as shown in Figure 5-3, is taken into account. The effect of age is described as shown in Figure 3-9 and in (3.2:3).

Figure 7-11. Comparison of chloride profiles predicted with *ClinConc* and measured for concentrated NaCl in the APM302 test for 40 days. OPC concrete with w/c=0.4 and D_{F1} =7.2×10^{-12} m^2/s.

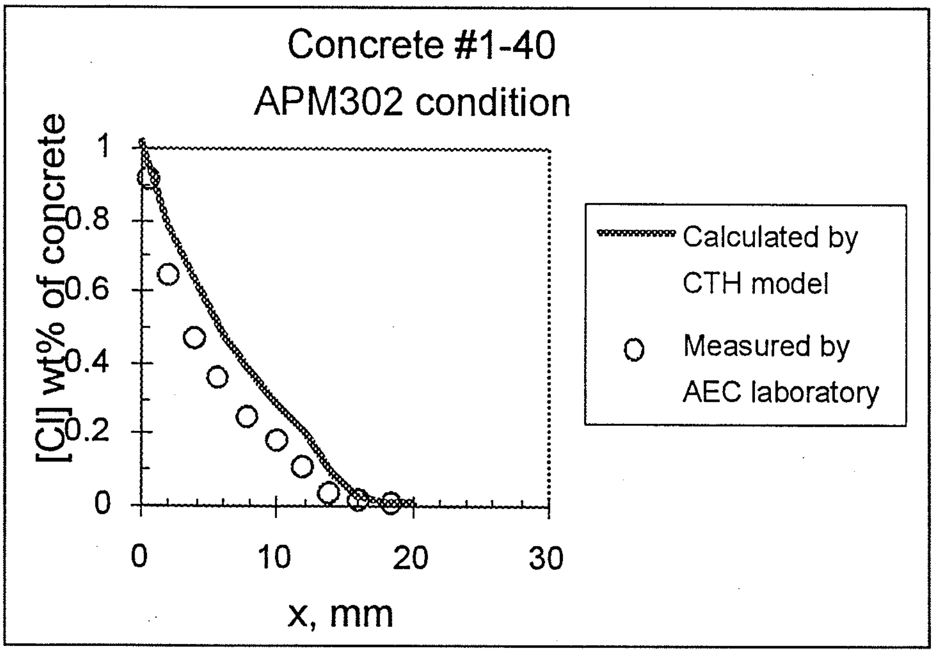
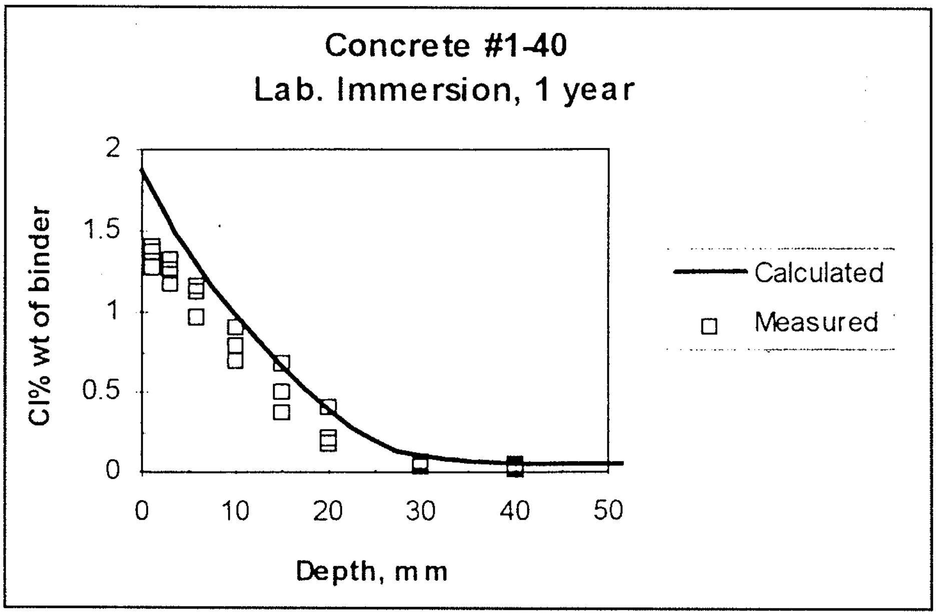


Figure 7-12. Comparison of chloride profiles predicted with *ClinConc* and measured in a laboratory immersion test with a concentration of 10.3 g/l. OPC concrete with w/c=0.4 and D_{F1}=7.2×10^{-12} m^2/s.



Non-linear chloride binding, effect of temperature and pH

The chloride binding is described with a non-linear binding isotherm as in Figure 3-6. There is no parameter involved, only the amount of gel as calculated from the concrete mix composition. The effect of temperature is considered with an Ahrrenius equation and the effect of pH as in Figure 3-6. Lack of knowledge on the temperature effect is provisionally dealt with by fitting field data from the surface near region to predictions for a number of field studies. The pH effect is based on available measurements.

Leaching of alkalis

Diffusion of alkalis is described in a similar way as diffusion of chlorides to model the leaching process. Leaching of hydroxides from $Ca(OH)_2$ and CSH is not yet included, i.e. a drop in pH from some 13.5-14 to some 12.5 is modelled to be able to properly describe the chloride binding. For long exposure times and high *w/c* concrete presumably the leaching of hydroxides to pH below 12.5 should be included. That is, however, of minor importance for high quality concrete.

Exposure conditions involve temperature variation

The exposure conditions are described as a chloride concentration in the sea water in contact with the concrete surface, with a variation between a maximum and minimum value, and a temperature variation during eg. a year cycle. Since the temperature has a tremendeous effect on chloride binding, the temperature variations will strongly affect the predicted free chloride profiles, cf. the example in Figure 7-9.

Submerged conditions only

Since the chloride transport is modelled by pure diffusion, the model so far may only predict the chloride penetration at submerged conditions with little influence of water transport. Of course it is possible to make predictions with an "equivalent" or "achieved" chloride concentration at the surface, as is done with analytical prediction models, but that is to exceed the limits of the relevance of the scientific-based model. Further development of the model to include convection of chlorides and non-saturated conditions is going on in order to be able to model the conditions in the splash zone and in structures exposed to deicing salts.

The *ClinConc* model is unique in several ways. Since it includes most relevant factors in a sophisticated way, without large simplifications, it actually predict, to a large extent, the true nature of the combined processes involved when chlorides are penetrated into concrete in a structure.

Temperature variations give a maximum in predicted profiles and a counter-diffusion of chlorides during summer periods!

An example is shown in Figures 7-9 and 7-10. The effect of temperature variations during a year cycle is shown as the predicted profiles of the free and total chlorides respectively. The strong temperature dependence of chloride binding causes some of the bound chlorides to dissolve when the temperature increases, from April to July (6 to 6.25 years of exposure), resulting in a large increase in concentration of free chlorides. The concentration at the surface, however, does not change very much during a year. Consequently, the profile of free chlorides shows a larger concentration in the concrete pores than in the surrounding sea water. This may explain some of the strange results discussed in Section 3.1 and Section 4.8.2. The predicted profiles also show a maximum of free chlorides at a certain depth, i.e. a counter-diffusion of chlorides out of the concrete, during the summer period!

The shape of chloride profiles depends on what time of the year the cores where taken!

The predicted effect of temperature variations on the profiles of total amount of chlorides are shown in Figure 7-10. The effect is mainly close to the surface, but a maximum is predicted in summertime also for the total chlorides. According to the predicted results, measured chloride profiles should depend very much on the time of the year when samples where taken.

Figure 7-13. Comparison of chloride profiles predicted with *ClinConc* and measured for the Öland Bridge after four years exposure to sea water with 4.1 g/l Cl. OPC concrete with *w/c*=0.4 and D_{F1}=7.2×10^{-12} m^2/s.

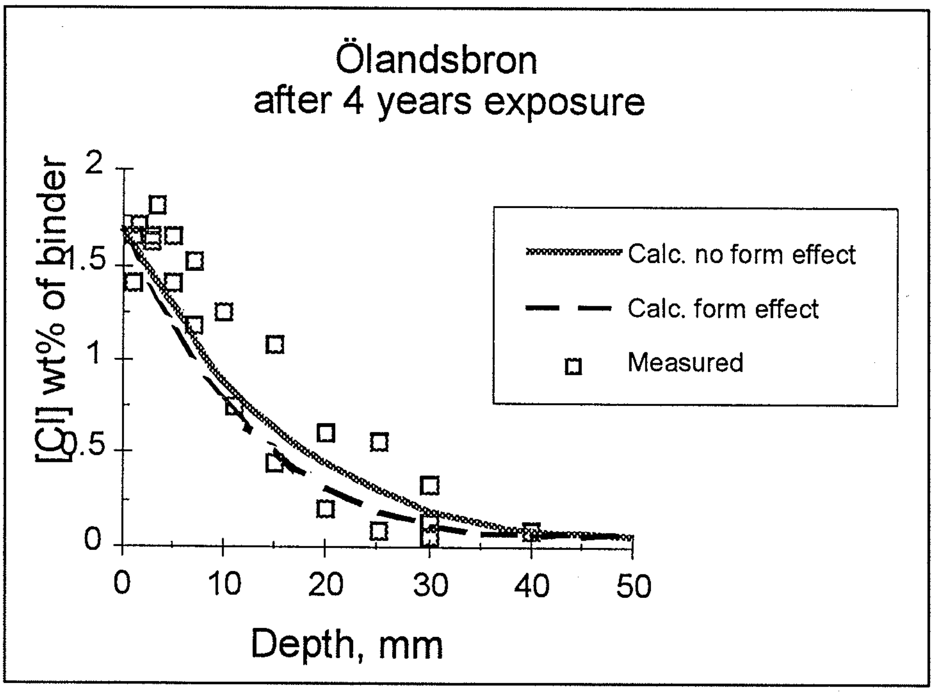
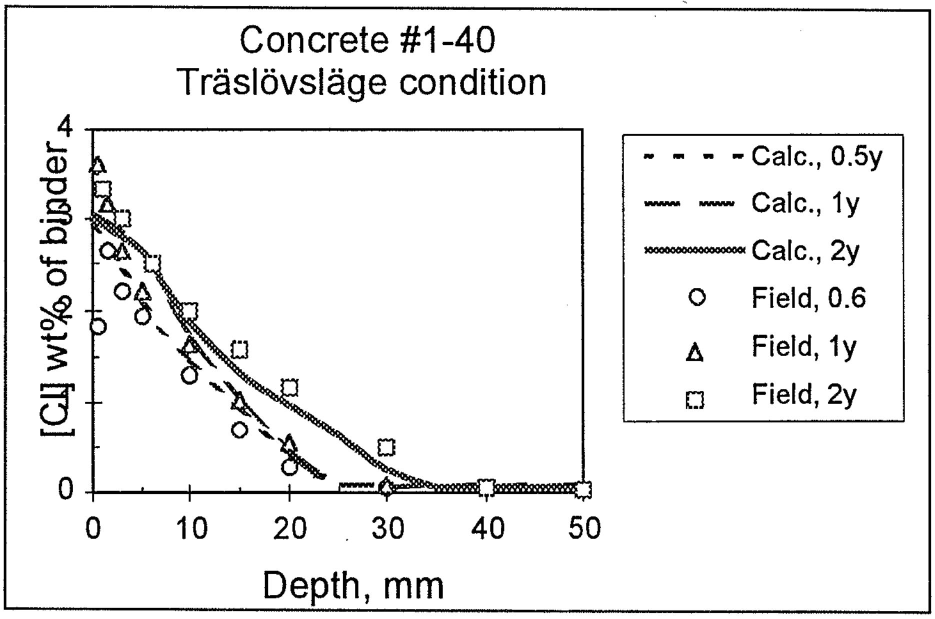


Figure 7-14. Comparison of chloride profiles predicted with *ClinConc* and measured for various times of field exposure to sea water of 14 g/l Cl at the west coast of Sweden. OPC concrete with *w/c*=0.4 and D_{F1}=7.2×10^{-12} m^2/s



Only one parameter, measured in an independent test, and no curve-fitting involved!

Another unique feature in the *ClinConc* model is the small number of parameters to be inserted into the model. Actually only one parameter has to be determined, the diffusion coefficent of the particular concrete at a certain age, and that one is determined in an independent test and no curve-fitting is involved. The other parameters in the model follow from the mix composition and the exposure conditions. At this stage the most uncertain part is the temperature effect on chloride binding, since available data is scarce.

Only a small number of comparisons have been done

So far only a small number of comparisons between predicted and measured chloride profiles have been done, since profiles for submerged concrete where the concrete is tested for D_{CTH} are few. Examples are shown in Figures 7-11 to 7-14, for one particular concrete exposed to quite different laboratory and field conditions for various exposure times. The concrete composition used for the repair of the Öland Bridge at the east coast of south Sweden was used. Note that the input data is only one parameter, the D_{CTH} for the concrete, for all four cases!

In Figure 7-11 the chloride profile in the same conditions as in the APM302 test method is predicted and compared to the measured profile for a similar concrete. The agreement is not perfect but quite good considering the extremely high concentration in the test solution.

Predicted and measured profiles in very different conditions agree quite well

In Figure 7-12 the profiles after one year of laboratory immersion in a solution with a fairly low concentration are compared. The predicted concentration at the surface does not coincide very well, but the rest of the profile and penetration depth are predicted quite well.

In Figure 7-13 the predicted and measured profiles at the Öland Bridge are compared after four years of exposure to the very low concentration in the Baltic Sea. The predicted profile falls within the scatter of the measured profiles in the submerged zone.

In the Figure 7-14 predicted and measured profiles from field exposure at the west coast of Sweden, with a higher salt concentration, are compared. Profiles were measured and predicted for three exposure times and the profiles coincide very well.

ClinConc is promising

In conclusion, the *ClinConc model* for chloride penetration is very promising for predicting actual chloride profiles in structures. The required input data is very limited and a short term test method is standardized to determine it. The predicted results are meant to be used for direct comparisons with measured profiles without involving curve-fitting. Any discrepancies found will immediately indicate where the most important lack of knowledge is to be looked for.

Direct comparison with measured profiles

The possible application is limited so far

The possible application, however, is so far limited. More binding data is needed for concretes other than OPC concrete and the effect of special formwork, special aggregates and cracks have to be studied to widen the range of possible applications. The knowledge and understanding of the processes in the non-saturated conditions in structures exposed to the splash of sea water or deicing salts must be improved before they can be added to the model.

8 Conclusions

Comparison between strength and chloride diffusivity

The properties of chloride diffusivity and concrete strength are different, but they also have something in common. These properties will develop with increasing maturity of the concrete, but the Code of Practice does not allow any increase beyond the 28 M-day strength. At the moment no Code of Practice specifies the application of the property of chloride diffusivity, but this may change, and there are two possibilities:

Two possibilities

- The development of chloride diffusivity versus the maturity of the concrete is neglected beyond 28 M-days as is the case of concrete strength in many Codes of Practice today. This means that chloride diffusivity should be kept constant at its 28 M-days property value.
- The development of chloride diffusivity versus the maturity of the concrete follows its development beyond the 28 M-day property. This means that chloride diffusivity shall obey the time dependence on the safe side found by testing.

Too little was known about the time-dependence of the concrete's chloride diffusivity

Two decades after Collepardi's suggestion in 1970 of applying Fick's diffusion theory of chloride ingress into concrete too little was known about the diffusion parameters and their dependence on time. Thus, it was obvious to follow the first assumption mentioned above, as suggested by e.g. Browne [1980] and followed in the design and construction of the marine concrete structures of the Great Belt Link, cf. Poulsen [1990].

25 years of misusing Fick's 2nd law

Fick's 2nd law has been widely used to predict chloride penetration into concrete structures. The error-function solution has been curve-fitted to chloride profiles from laboratory experiments and field structures, for determining so called diffusion coefficients. These coefficients have been regarded as material properties and used for predictions. Important structures have actually been designed with this approach.

8.1 Chloride ingress

Non-constant "apparent" diffusion coefficient

We learnt only recently, from 1992 onwards, that this approach was a tremendous underestimation of the resistance of concrete to chloride ingress. Concrete is actually much better than its reputation in this respect. Theoretical studies and field measurements showed clearly that Fick's 2nd law in its *simple form* is not valid for chloride penetration. A number of factors, if not properly included, make the "apparent" diffusion coefficient in Fick's 2nd law dependent on the exposure time. It was unclear how results from test methods and from short term field exposure were to be used.

A lot of scattered knowledge and data

A lot of knowledge and data about the processes involved in chloride penetration have been collected during these 25 years. The present state of knowledge, and the lack of knowledge, about various topics have been summarized in Chapters 2-7.

8.2 Prediction models

Two completely different prediction approaches are used

Two quite opposite approaches have been suggested for improving the utilization of prediction models in the design for service life of concrete structures. They are both based on Fick's diffusion theories:

- a scientifically based, numerical approach, describing the involved processes as correctly as possible and verifying the model by comparison with details in measured profiles.
- an empirically based, analytical approach, describing the chloride penetration process with a small number of decisive parameters and obtaining empirical constants from curve-fitting to measured profiles.

Both approaches include a short term test of material characteristics and possibly a calibration after a short exposure time.

Present limitations to be overcome

The two approaches have individual limitations. The first method needs a lot of detailed knowledge and data on transport processes and environmental conditions; to a large extent, these are not available today, especially for structural parts that are exposed to splashing of sea water and deicing salts. The second method needs a lot of relevant data from the field and the extrapolation from that data will always be uncertain.

A combination of the two methods seems to be a promising solution to the uncertainties and limitations. A theoretical description of the decisive transport properties and the environmental conditions, even though a lot of the specific data is lacking, could be a sound base for extrapolations from the more applicable, empirical method.

This is what is suggested for the further work in the project.

Expected prediction approach

The result is expected to be a system requiring only few parameters found by tests on the actual concrete type and data or experience about the aggressiveness of the environment and its fluctuations. The system will be applicable to both new and existing structures.

8.3 How to deal with defects

Reinforced concrete is neither a homogeneous no-defects material nor an inert material. It reacts to the environmental actions resulting in a complex mixture of different transport processes. On top of this, the defects of the material must also be considered.

It has been shown that the difficulties due to the transport processes can be overcome by a dual approach: the scientific and the empirical. No model can deal with all defects but defects like coarse cracks that occur as a natural part of the material when concrete is used in structural components can be assessed and handled.

The report describes the problems of cracking with regard to chloride ingress and corrosion initiation. It is concluded that in a concrete having sufficient resistance to chloride ingress, cracks of a limited width will accelerate chloride ingress and may start a corrosion process, but this will fade out and will not start again until the chlorides have reached a concentration sufficient to initiate a stable corrosion process.

Other less visible defects e.g. inhomogeneities and micro cracking are dealt with by applying realistic test methods and principles to the concrete material in question.

8.4 Test methods

Several test methods have been assessed in the report. There seems to be no urgent need for further development of the test methods regarding chloride ingress. It is however important to continue the development of test methods for reliable measurement of chloride threshold values as these measurements can help us understand why reinforcement is not corroded in concrete shown by field investigations to be chloride contaminated, and can at the same time lead to great improvements in prediction.

9 Need for further research

More data and more knowledge of rapid development and progress in recent years have brought the state of the art to a point where the first version of a complete system for a rational handling of the task “prediction of service life” can be formulated.

9.1 *In the laboratory*

Research topics for the next decade

In the previous chapters gaps of knowledge and missing data have been identified. Extensive research regarding the most important of these is recommended in general during the next few years. Knowledge, understanding and quantification must be improved, especially regarding:

- The conditions necessary to initiate chloride induced reinforcement corrosion.
- Test methods for convective chloride transport; the conditions in migration tests and the utilization of the test results from current test methods.
- Transport processes in non-saturated concrete.
- Chloride binding; test methods, the effect of different binders and the effects of temperature variations.
- Mechanical properties of reinforcement suffering from chloride attack.

Based on this improved knowledge, the present models for predicting chloride penetration can be improved to correctly predict the full chloride profiles during the service life. A scientifically based definition of the term “service life” can further be established with special regard to the problems of structural safety after initiation of corrosion.

9.2 *In the field*

In recent years it has become generally accepted to make use of selected outdoor environments in order to study concrete under conditions that are as realistic as possible for structures to be placed in such environments. The main drawback of field stations is the time needed before results are safe and prediction models can be checked for relevant “lifetimes”. The main advantage is that the work can be done under controlled and realistic conditions.

To overcome the drawback of the field stations, observations from real structures in service must be utilized as much as possible. Sampling and investigations are expensive and that is why they must be done properly.

Further research in the field should result in more information about:

- Environmental conditions for structures exposed to splashing from sea water and de-icing salts.
- True electrochemical potentials of reinforcement depending on the environmental conditions.
- The influence of the micro climate on the ingress of chloride in various positions on the structure.

- Relations between "achieved" and "potential" parameters describing chloride penetration.
- The variations of the properties with the seasons.
- The applicability of the prediction models for exposure times up to 100 years of natural exposure.

Some of the above measurements are either to be made solely on real structures or solely on specimens placed in field stations.

9.3 What is needed for HETEK

Based on the above improvements, it will be possible to develop even better methods for predicting the service life of structures.

Research needs for the HETEK project

For the HETEK project, only those parts that have the highest priority for developing an applicable prediction method can be realized in the course of the HETEK project. A selection from, and a limited study of, all the topics listed above must be made. These are:

- Testing the basic chloride diffusivity characteristics for a range of *w/c* ratios with Danish cement (low alkali sulphate resisting Portland cement), with the test method APM302, a resistivity test method, the CTH migration test method and a binding test method.
- A comparison of profiles predicted by the *ClinConc* model and profiles measured by the test method APM 302.
- A limited theoretical analysis and a first, simple modelling of the transport processes in non-saturated concrete with convection of chlorides, taking the variations in environmental conditions into account.
- Analysis of available and a few, new field measurements on Danish road bridges.
- An analysis of the environmental conditions for structures exposed to deicing salts.
- An improvement, and a theoretical verification, of the analytical prediction method and widening its field of application to structures exposed to deicing salts.

A proposal is expected to be made for a prediction model with a good scientific and empirical basis and a certain verification in experiments and field measurements. Combined with the prediction method, a few short term test methods for material characteristics will be proposed, together with a description of the way the test results are to be used in the prediction model and in production control.

10 Notation

Symbol	Unit[1]	Description and reference to definition in text
Latin Letters		
a	m	Length of the asymptote between C-axis and the point of intersection between the asymptote and the tangent to the chloride profile at the exposed surface.
A	m^2	Cross sectional area.
b	m	Breadth.
B	kg/m^3	Content of binder in concrete (powder: Portland cement, pulverized fuel ash, micro silica, and/or ground granulated blast furnace slag)
c	m	Thickness of concrete cover above reinforcement.
c_{min}	m	Minimum thickness of concrete cover above reinforcement.
c_f	kg/m^3	Concentration of free chloride ions by volume of material.
c_b	kg/m^3	Concentration of bound chloride ions by volume of material.
c_l	kg/m^3	Chloride concentration of a liquid.
c_s	kg/m^3	Surface chloride concentration of concrete.
C	kg/m^3	Cement content in concrete.
$C(x,t)$	mass%	Chloride concentration of concrete at a depth x beyond the concrete surface at the time t.
C_b	mass%	Concentration of chloride ions bound in material.
C_f	mass%	Concentration of free chloride ions in material.
C_i	mass%	Initial chloride content of concrete.
C_s	mass%	Surface chloride concentration of concrete.
C_{sa}	mass%	Surface chloride concentration of concrete, determined by regression analysis of an achieved chloride profile from natural exposure.
C_{sp}	mass%	Surface chloride concentration of concrete, determined by regression analysis of a potential chloride profile from standard exposure in laboratory.
C_x	mass%	Chloride concentration of concrete at a depth x at a non-specified time.
C_s	mass%	Surface chloride concentration of concrete.
d	m	Diameter.
d	1	Relative density (relative to water).
d_{max}	mm	Maximum grain size in material (the nearest smaller standard sieve size through which 90% by mass of the material passes).
D	m^2/s	Diffusion coefficient.
D_m	m^2/s	Molecular diffusion coefficient.
D_{F_1}	m^2/s	Diffusion coefficient in Fick's 1st law.
D_{F_2}	m^2/s	Diffusion coefficient in Fick's 2nd law.
$D_{s\text{-}s}$	m^2/s	Diffusion coefficient measured in a steady-state experiment.
$D_{n\text{-}s}$	m^2/s	Diffusion coefficient measured in a non-steady-state experiment.
D_a	m^2/s	Achieved transport coefficient characterising a chloride profile after a natural exposure for a non-specified time.
D_{aex}	m^2/s	Achieved transport coefficient characterising a chloride profile after a natural exposure at time t_{ex}.
D_p	m^2/s	Potential transport coefficient characterising a chloride profile after a standard exposure in laboratory for a non-specified time.

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[1] Unless otherwise specified in text the stated unit is used.

D_{pex}	m^2/s	Potential transport coefficient characterising a chloride profile after a standard exposure in laboratory at time t_{ex}.
E	V	Electric potential.
F		Faraday's number.
FF	1	Formation factor.
G	$1/\Omega$	Electric conductance ($G=1/R$).
h	m	Height.
i	A/m^2	Electric current density.
I	A	Electric current.
k	$kg/m^2\sqrt{s}$	Capillarity.
K	m/s	Coefficient of permeability
K	$mm/\sqrt{yr}$	Penetration parameter (the ingress after one year's exposure).
l	m	Length.
m	kg	Mass.
m	g/mol	Molecular mass.
m_{ssd}	kg	Sample mass of a porous material in saturated surface dry condition.
m_d	kg	Sample mass of a porous material in dry condition (after drying at 105°C).
m_{ions}	kg	Mass of ions.
M	mol/l	Molarity.
M_{Cl}	g/mol	Molar weight of the chloride ion.
N_A	mol^{-1}	Avogadros constant (6.023×10^{23})
N_m	1	McMullin number
p	Pa	Pressure.
p_o	m^3/m^3	Open porosity (determined after drying to constant weight at 105°C).
p_l	m^3/m^3	Porosity containing a liquid.
q	kg/m^2s	Flux.
Q	C	Electric charge.
Q	kg/m^2	Mass flow in a cross section.
r	m	Radius.
R	J/mol K	Molar gas constant (8.31441 J/mol K).
R	Ω	Electric resistance.
S	1	Degree of saturation.
S_1	mass%	Surface concentration of concrete after one year of exposure (the first year uptake).
t	s	Exposure time.
t_{ex}	s	The beginning of the exposure (to a chlorine environment).
t_j	1	Transference number.
t_{LT}	s	Life time.
T	K	Absolute temperature.
v	1	Vapour concentration.
V	m^3	Volume.
V	V	Electric potential.
w	kg/m^3	Water content.
x	m	Distance below the exposed concrete surface.
x_{cr}	m	Depth below a chloride exposed concrete surface to which the critical chloride concentration has penetrated.

Greek Letters

α	1	Degree of hydration.
α_D	1	A parameter describing the decrease with time of the achieved chloride diffusion coefficient.
α_ρ	1	Thermal coefficient for electric resistivity.
β_D	1	A parameter describing the change with time in the potential chloride diffusion coefficient.
δ	m	Thickness.

δ	1	Ratio between D_a and D_p.
φ	%RH	Relative humidity of air.
γ	1	A parameter describing the decrease with time of the ratio between D_a and D_p.
ρ	kg/m^3	Density (mass).
ρ_d	kg/m^3	Dry density.
ρ_{ssd}	kg/m^3	Density in saturated surface dry condition.
ρ_w	kg/m^3	Density of water.
ρ	Ωm	Electric resistivity.
ρ_l	Ωm	Electric resistivity of a liquid.
ρ_{Θ}	Ωm	Electric resistivity at a characteristic temperature.
σ	N/m	Surface tension.
σ	1/Ωm	Electric conductivity
θ	°C	Temperature.
τ	1	Tortuosity.

Indices

0	Reference point (e.g. time or temperature)
s	Solid, surface.
l	Liquid.
m	Material, molecular.
d	Dry.
b	Bound.
a	Achieved.
f	Free.
ex	Exposure.
LT	Life time.
F_1	Ficks 1st law.
F_2	Ficks 2nd law.
p	Potential.
x	Depth.
s-s	Steady-state.
n-s	Non steady-state.
min	Minimum.
max	Maximum.
i	Initial.
ssd	Saturated surface dry.
cr	Critical.

Mathematical functions

erf	Error function.
erf^{-1}	Inverse of the error function.
erfc	Error function complement (1−erf).
erfc^{-1}	Inverse of the error function complement $(1-\text{erf})^{-1}$.
$\exp x$	Exponential of x ($e^1 = 2.718281828...$).
Σ	Summation.
Δx	Finite increase of x.
dx	Total differential of x.
$f(x)$	Function of x.
df/dx	Derivative of f.
$\partial f/\partial x$	Partial derivative of x.
$\ln x$	Natural logarithm of x.

w/b	kg/kg	Water/binder ratio (powder: Portland cement, pulverized fuel ash, micro silica, and/or ground granulated blast furnace slag).
w/c	kg/kg	Water/cement ratio.

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