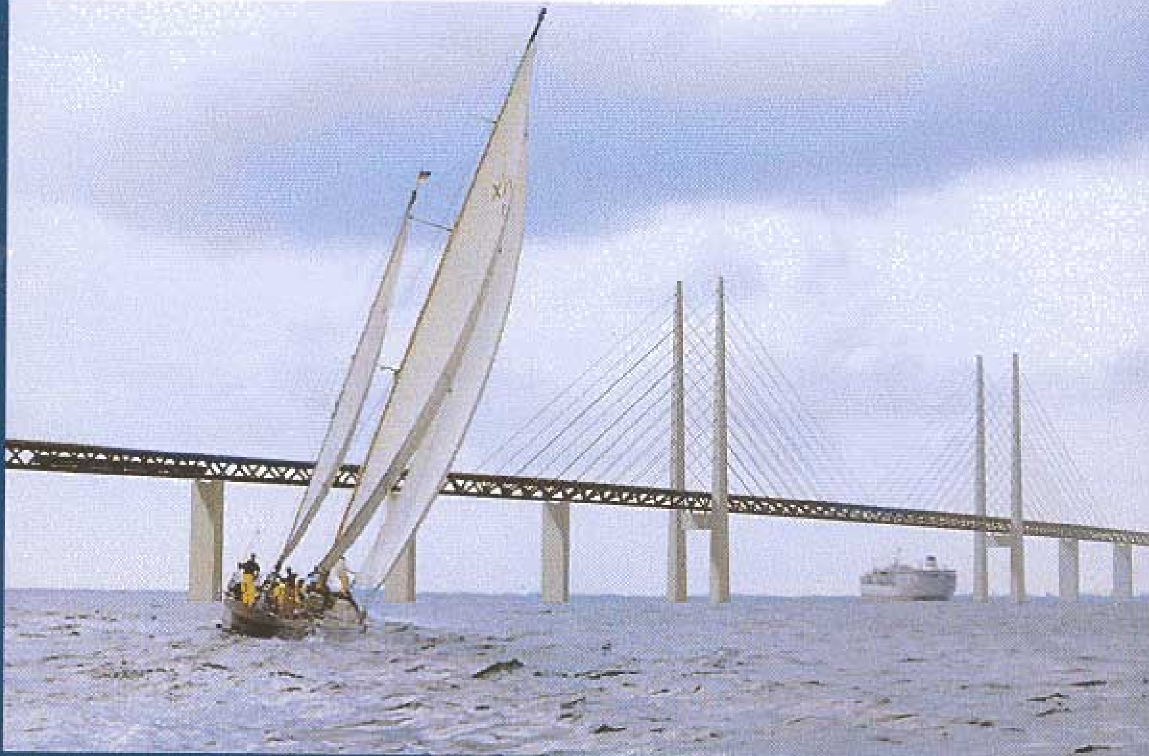
HETEK

Chloride penetration into concrete State of the Art

Transport processes, corrosion initiation, test methods and prediction models



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Abstract:

This report is part of a series of reports generated in the research project HETEK headed by the Danish Road Directorate. The present subtask is concerning chloride transport into concrete and this report presents the state of the art on that topic. The report forms the basis for the further research and developmint in the subtask.

Mathematical models for binding of chlorides in concrete and for diffusion and migration are presented and commented. Test methods for various properties of concrete related to the understanding and evaluation of chloride transport in concrete are commented. Various decisive parameters are highlighted and their effects on chloride transport are commented. The effect of various parameters on the threshold chloride concentration that can initiate corrosion is commented. All this knowledge is to be compiled into a service life system of which essential parts are presented in the chapter "Prediction models".

The report states how to apply Fick's 2nd law in a more correct way and how to overcome the empirical problem of an apparent chloride diffusion coefficient that decreases with time. The application of Fick's 2nd law when both the diffusion coefficient and the surface boundary condition are varying with time is demonstrated.

At the end is given a 21 page long list of the litterature that formed the basis for the report.

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Contents

1 Preface

1.1 Background

The Road Directorate in Denmark has launched a number of research projects in late 1995 to be performed and completed during 1996. The package of projects has been given the name "HETEK", which is short, in Danish, for "High quality concrete, the Contractors TEChnology". The projects cover eight topics.

Eight topics in HETEK

1. Test methods for chloride resistance of high quality concrete
2. Test methods for freeze/thaw durability of high quality concrete
3. Self-desiccation
4. Curing Technology
5. Casting and compaction
6. Curing treatment
7. Guidance in trial castings
8. Remedial measures during the execution phase

The projects are to give a state-of-the-art report, identify the need for further research, perform some of that research and finally give guidelines for the contractor.

The research consortium ACCE

The research consortium ACCE was given the first project HETEK-1 on chloride resistance of high quality concrete. The task for this project is to re-evaluate existing methods, and develop new ones, for determining chloride penetration in high quality concrete. The methods must consider the differences in environmental actions on the concrete structure. Quantitative criteria for approval shall be laid down to ensure compliance with the durability requirements and the economy of the methods shall be estimated.

The research consortium ACCE consists of the three partners AEC, Chalmers University of Technology and Cementa AB.

AEC

AEC Consulting Engineers (Ltd.) A/S is a private consultant company in Denmark. AEC works mainly in the field of concrete structures and topics related to the repair, durability and maintenance of those. The typical clients of AEC are other consultants, contractors, building owners, insurance companies, cement producers and suppliers and producers of materials for concrete repair and maintenance. The company has two departments: a *structural* department, which offers consultancy regarding specialized construction problems and conventional consultancy in civil engineering and a *materials* department. The materials department, the AEClaboratory, assesses deterioration of concrete structures, prescribes and develops repair methods and assesses repair materials. Research and development regarding concrete durability tasks are solved for clients and/or financed by fundings.

Chalmers

Chalmers University of Technology educate civil engineers and researchers and do research in a number of basic and applied sciences and technologies. The department of Building Materials at the School of Civil Engineering, is participating in HETEK-1. The main research area is transport processes in porous building materials, mainly cement-based and wooden-based materials and surface materials on such materials. Examples of concrete research are: *Moisture* binding and flow properties of concrete, *self-desiccation and drying* of hardening high performance concrete, *plastic shrinkage* and early age cracking, *chloride* penetration into structures exposed to sea water and de-icing salts. The relationships between mix design, micro and pore structure and properties are experimentally studied and the behaviour in different environments are modelled and verified on concrete structures.

Cementa

Cementa AB is a cement producer in Sweden. The activities of Cementa regarding concrete research are as follows: *High Performance Concrete*, i.e. high strength, low water content and low permeability. *Concrete and environment*, i.e. problems regarding moisture in concrete and emissions from concrete. *Durable Concrete*, i.e. long time experiments regarding chloride ingress, permeability, strength evolution and carbonation. *No Slump Concrete*, i.e. rheological aspects of making precast concrete products.

Recent activities of the ACCE partners

The partners within ACCE have been very active in the field of chloride resistance for a number of years. The group was main partners in a research project in Sweden 1992-1995 on "Durability of Marine Concrete Structures", "BMB" in short in Swedish. The knowledge and experience gained in this project is an important foundation for the work in HETEK.

The partners in ACCE have been arranging, and important contributors to, a number of seminars and workshops 1993-1995 within the topic for the research project.

A Nordic Mini Seminar on Chloride Penetration into Concrete Structures was arranged in Gothenburg in January 1993. Some 40 papers from Denmark, Norway and Sweden were presented and discussed. A report was published, Nilsson [1993].

Two Nordic one-day seminars were given in Stockholm and Copenhagen in 1993 on Durability of Marine Concrete Structures with a number of lectures. The lectures were published by Cementa [1993].

A second Nordic Mini Seminar on Corrosion of Reinforcement. Field and Laboratory Studies for Modelling and Service Life was arranged in Lund in February 1995. Another 40 papers from Denmark, Norway and Sweden were published, Tuutti [1995].

A RILEM International Workshop on Chloride Penetration Into Concrete was held in St Remy les Chevreuse, France, in October 1995. Some 40 papers from Europe and North America were summarised and the topic was thoroughly discussed. The papers and the conclusions will be published in 1996 as a RILEM Publication, edited by Nilsson & Ollivier [1996].

The contributions to these seminars and workshops are an important input to the state of the art of chloride resistance of concrete. Another important and recent input to the topic are the proceedings of the international conference on Concrete Under Severe Conditions, CONSEC95, in Sapporo, Japan, in August 1995. A number of papers from these proceedings are referred to in this report.

1.2 Scope

The scope of the report is to summarise and analyse the present knowledge on chloride penetration into concrete structures and the required conditions for reinforcement corrosion to occur. Identification of important areas where there is a lack of knowledge and the need for further research are also within the scope of the report.

1.3 Structure

The report first gives an introduction in Chapter 2 to the topic with a qualitative description of the decisive parts of the processes involved. Then a thorough description is given in Chapter 3 of the transport processes mechanisms and the corresponding mathematical models. The methods of testing transport properties of concrete are summarised in Chapter 4 and selected test methods that are assumed to be further used in the project are described in more detail. The present knowledge on the effect of decisive parameters is given and quantified to the extend possible in Chapter 5. Chapter 6 gives the state of the art on the chloride contents required to initiate corrosion of the reinforcement. Finally, a description is given of the present utilisation of all this knowledge in predicting chloride penetration and the service life of concrete structures with respect to reinforcement corrosion initiated by chlorides.

At the end conclusions are drawn and the need for further research is identified in Chapters 8 and 9. In Chapter 10 a list of the notation used throughout the report is given. At last the literature referred to is listed in an alphabetical order.

The main authors of the various sections were:

L-O Nilsson: 1, 2-2.1, 2.3, 3.1-3.4, 4.2, 4.4, 4.6, 4.8, 5.2, 5.7, 7.3, 8, 9
E. Poulsen: 2, 5.1, 5.3, 5.6, 7.1-7.2, 8
P. Sandberg: 2.2, 4.7, 5.4, 5.8
H. E. Sörensen: 2.4, 3.5, 4.1, 4.3, 4.7, 5.5, 6.1-6.3
J. M. Frederiksen: edited and performed the quality assurance

Section 4.5 was written by O. Klinghoffer, FORCE Institutes, as a subcontractor to the consortium.

1.4 Limitations

The report gives the state of the art, i. e. the present state of knowledge, not always the full historical background of how that knowledge was derived. The report is not a bibliography. The literature referred to has not always been published. Papers available to the authors and to be published during 1996 are included.

The report further concentrates on those aspects that are likely to be treated or utilized later in the project.

2 Introduction

Early use of plain concrete for marine structures

The potential durability of concrete led early to its application as the building material for marine structures, cf. Smeaton [1793]. Among first applications of marine structures in Denmark were the constructions in 1858 of the marine fortress Prøvestenen, cf. OL [1967], in 1870 of a pier in Esbjerg Harbour, cf. Suenson [1911 p.454] and Hansen [1889], and in 1889 of the Middelgrund fortress in Øresund, cf. Hansen [1892]. However, these marine structures were made of plain concrete.

Early use of reinforced concrete for marine structures

At the beginning of this century reinforced concrete was used as a building material for the construction of marine structures. In Denmark reinforced concrete was used in Copenhagen Harbour in 1892 as protection against shipworm attack on timber wharf structures, cf. Suenson [1931 p.9]. However, reinforced concrete was not used on a large scale for marine structures before the construction of a large number of concrete bridges across seawater and brackish water in the 1930s, e.g. Oddesund Bridge cf. Engelund [1935], Lillebælt Bridge, cf. Flensborg [1935] and Storstrøm Bridge, cf. Flensborg [1937].

Traffic concrete structures exposed to de-icing salts

De-icing salt was introduced in Denmark during the winter of 1956/57, cf. Poulsen [1989 p.130]. The traffic structures were thus exposed to a more aggressive environment than in the past. This was due to the direct spray of de-icing salt as well as airborne chloride from traffic splash. It resulted in several cases of disintegrating traffic structures.

Requirements for marine and traffic concrete structures

Much effort was made to predict the service lifetime of marine and traffic concrete structures, cf. Danø [1914], Poulsen [1923] and DBF [1973], and the requirements for concrete composition and cover to reinforcement were increased during each revision of the Code of Practice. The same trend is found in many countries, cf. Halstead [1955], Fulton [1957], Walbank [1989] and Brown [1989].

Unreinforced concrete exhibits excellent long term behaviour

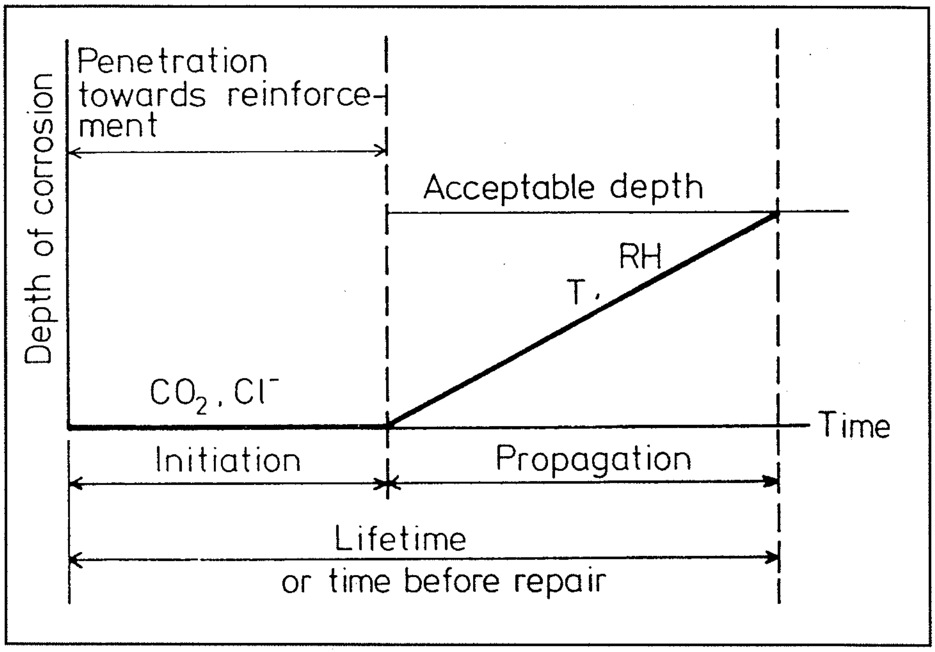
The ingress of chlorides into concrete structures in different environments is sometimes of decisive importance for the durability and service life of the structure. Long term experience, see e.g. Nagataki [1995], of unreinforced concrete structures exposed to sea water shows that they exhibit excellent behaviour and a service life of a century or so. Chloride penetration limits the service life of reinforced concrete structures because the chlorides initiate corrosion of the reinforcement.

2.1 Service life

The service life of a concrete structure with respect to corrosion is usually described in terms of initiation and propagation of corrosion, first presented by Tuutti [1982], cf. Figure 2-1.

Various opinions of the term “service lifetime” exist. Fidjestøl [1995] declares that the consideration of lifetime versus reinforcement corrosion has a strong philosophical aspect. The critical point in time can be considered to be any one of the following four:

Figure 2-1. The service-life model of Tuutti [1982], with an initiation period and a propagation period.



- Initiation of corrosion.
- Corrosion products become visible on the concrete surface.
- Cracking and/or spalling due to corrosion occurs.
- The bearing capacity of the structure is seriously reduced due to loss of steel section.

Besides these technical criteria Fidjestøl [1995] also stresses that other issues are likely to be important:

- *Aesthetics*. Rust stains of high visibility on the surface are often undesirable.
- *Public opinion*. Regardles of technical issues, people do not like to drive over a bridge which has cracks with rust showing through.
- *Public safety*. Falling pieces of concrete are hard and can damage people and property.

Two (official) definitions exist and should be mentioned:

- *Eurocare*: "The service life is the period of time after installation during which all essential properties meet or exceed minimum acceptable values, when routinely maintained".
- *ISO TC 59 / SC 3*: "The design life is the designer's intended durability for the building and its parts as specified by the client".

When the reinforcement bars of concrete marine structures starts to corrode due to attack by chloride, the form of corrosion is pitting, cf. Fontana, [1986 p. 63]. When corroding reinforcement bars becomes pitted, its properties and characteristics change. The effective cross section decreases, i.e. the ultimate tensile force of a corroding reinforcement will decrease. Pitting will also decrease the ultimate elongation outside the necking zone. Fontana [1986 p.63] states: "*Pitting is particularly vicious because it is a localized and intense form of corrosion, and failures often occur with extreme suddenness*."

Thus, two basic properties for the structural design of RC structures are changed by pitting corrosion: the bearing capacity and the ductility of the structure.

It is common practice to apply a corrosion model, where the service lifetime of a RC structure is subdivided into an initiation stage and a propagation stage as shown in Figure 2-1, cf. Tuutti [1982], Somerville [1986], Clifton [1993] and Fidjestøl [1995]. It is on the safe side to consider the service lifetime to be identical to the initiation stage, cf. Maage [1995], but many RC structures are said to have an excess of reinforcement. Thus, an acceptable degree of corrosion ought to be considered.

However, RC structures like bridges, parking structures and jetties which are exposed to dynamic loads need to be ductile. Here, the Danish Code of Practice, DS 411 Clause 3.1.1 "Reinforcement" state: "*The elongation outside the necking zone should be at least 3 %. However, for steel used for shelters it should be at least 10 %.*" Reinforcement with pits from corrosion will not be able to satisfy these requirements.

This indicates that the initiation stage is taken as the service lifetime of a chloride exposed structure. Furthermore, the cost of rehabilitation of a RC structure during its initiation stage is generally small compared with rehabilitation during its propagation stage, cf. de Sitter [1984].

All parameters concerning concrete, its reinforcement and environment are uncertain, i.e. stochastic variables. Thus, being a function of uncertain parameters the term service lifetime also becomes uncertain – or said in another way: All the reinforcement will *not* start to corrode at the same time. Hence, the most convenient way to define the term service lifetime is the time by which a certain fractile of the reinforcement, e.g. the 5 %-fractile, in an inspection zone has started to corrode. Therefore, the service lifetime ought to be determined by means of probabilistic methods, cf. Karlsson [1995].

Methods for the predition of lifetime are mainly a tool for evaluation of observations from inspection of RC structures exposed to chloride. Here, a deterministic prediction is satisfactory, e.g. one based upon mean values or characteristic values of the parameters involved.

The corrosion initiation period

Corrosion is initiated after some time, at the end of the initiation period, by carbonation or chloride ingress through the concrete cover of the reinforcement. Here it should be noted that corrosion in cracks can start very soon after the chloride exposure but the corrosion will stop again after some time, i.e. the initiation is not stable. Below *initiation* is refered to as the *stable* initiation.

Only stable initiation is considered

Once corrosion is initiated, it continues at a certain rate depending on the concrete quality and the environmental conditions of the structure. At some stage of corrosion the corrosion products may have increased in volume so much that they cause spalling of the cover. The cross sectional area of the reinforcement may be reduced to such a level that the load carrying capacity is too low for the required safety and performance of the structure.

The service life concept

As seen above the definition of the concept "service life" is not established. Sometimes the service life is defined as being equal to the initiation period. The structure may well "serve" for many more years, several decades or so, and the propagation period is sometimes included in the service life. Even after extensive spalling or heavy reduction of the cross section of the reinforcement, the load carrying capacity of the structure may well satisfy technical requirements. The "service life" may be reached anyway because of aesthetic reasons or because of public opinion regarding the expected safety of the structure.

The Owner must decide the requirements

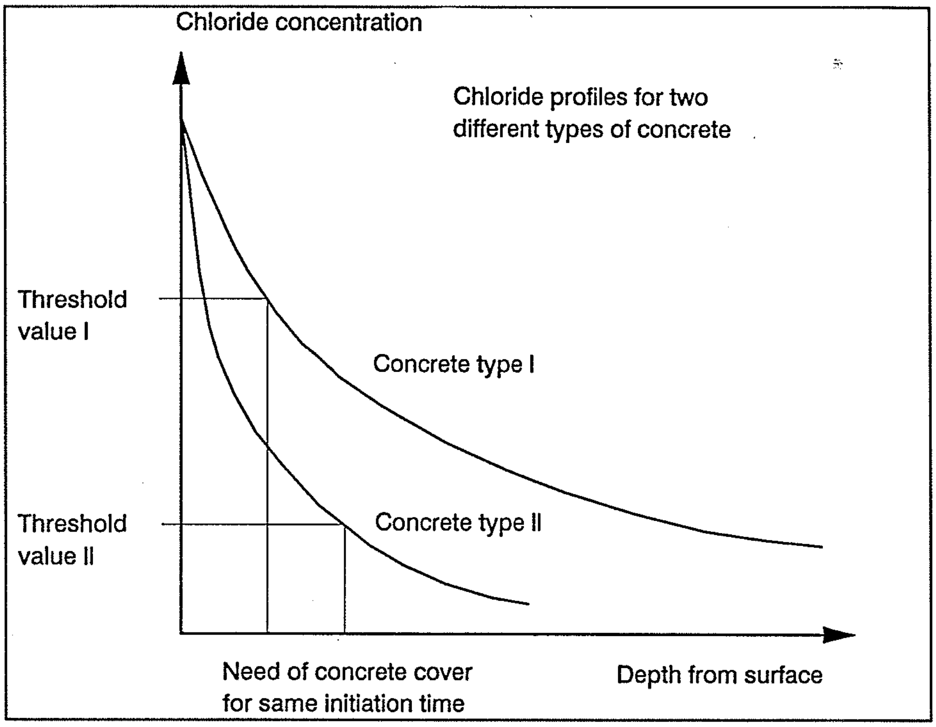
The requirements for a particular structure can only be decided by the owner. If he does not want any corrosion at all to occur in the structure, he should make the initiation period the service life requirement. His choice of remedial measures before corrosion has started may be different from the options once corrosion has reached a certain degree. This concept has been chosen in this report, i.e. the propagation period and rates of corrosion are not included at all.

For modern concrete carbonation is normally of little importance for the initiation of corrosion. Initiation by chloride ingress is the main concern.

Design by simple rules and standards

The design of the resistance to chloride penetration is still based on simple rules in codes and standards. The scientific foundations for these rules are doubtful, but a tremendous development has occurred the last few years. Very soon it should be possible to actually predict the penetration of chlorides into a concrete structure in a certain environment. Of course, such a prediction today still has some degree of uncertainty and a lot of the required data is missing.

Figure 2-2. Chloride profiles compared with the chloride threshold values for corrosion, for two concretes at the end of the initiation period, the "service-life".
Fidjestöl & Tutti [1995].



Comparing chloride profiles with corrosion threshold values

The penetration of chlorides is the result of a number of chloride transport and binding processes. The combined transport processes are quantified in terms of "chloride profiles" showing the distribution of chlorides with depth from the concrete surface at different times of exposure. The initiation time for chloride induced reinforcement corrosion is estimated by comparing the chloride concentration in such a chloride profile with the "chloride threshold value" for corrosion, at a depth corresponding to the thickness of the cover of the reinforcement, see Figure 2-2.

Chloride profiles alone do not give the service life

As seen in Figure 2-2 the threshold value for corrosion to be initiated is a parameter of the same importance as the penetration of chlorides for the estimation of the service life of a structure. Concretes cannot be compared with respect to durability and service life by comparing only chloride profiles or chloride penetration properties of the concretes. Consequently, both the chloride transport processes and the required conditions for corrosion are treated in this report.

2.2 Transport processes

The distribution of chlorides (concentrations at different depths) is a time-dependent function of the environmental conditions, the design of the structure and the material properties. The mechanisms of chloride transport and binding involved are complicated and usually combined in a complicated way. The processes are not always understood and still not easy to quantify.

A function of the environmental conditions

The transport and distribution of chlorides in a concrete structure is very much a function of the environmental conditions, mainly the concentration and duration of the solutions in contact with the concrete surface. The conditions are quite different in different exposure situations. A summary and some comments are given in this introduction.

Below the level of sea water

Below the level of sea water the concentration of chlorides is more or less constant with time. The penetration is a "pure diffusion process" at constant boundary conditions. At early ages, however, the chlorides may be sucked with the sea water by a suction process, into those parts of the pores that are empty.

Most other cases of exposure situations have boundary conditions that change according to a more or less rapid and complicated relationship with time.

The splash zone

In the splash zone above sea water level salt water is sucked into the concrete surface. Rain water washes the surface free from chlorides and may remove some of them. Evaporation increases the concentration. Chlorides move inwards and outwards due to moisture flow and ion diffusion.

The conditions are different at different heights from the average sea water level. A maximum chloride content may be found at a height where salt water is frequently supplied to the surface but where the surface intermittently dries out. Closer to the sea water level the concrete is almost continuously saturated by water and no additional salt water can be "added".

The tidal zone

In a tidal zone the conditions are somewhat similar to a splash zone. The time of wetness and the intermittent drying time, however, are different.

De-icing salt exposed structures

Bridges and road structures that are exposed to de-icing salts have boundary conditions that vary strongly. In wintertime parts of the structure are exposed to saturated salt solutions that are rapidly diluted as the ice and snow melts. This exposure can be repeated frequently, sometimes once a day.

Rain washes the surfaces and moves salt water to other parts of the structure. Evaporation increases the concentration of salts.

The effect of water penetration into a concrete structure depends on the magnitude of the flow, that is the permeability and the pressure gradient, and the possibility of evaporation at the opposite surface or inside the structure. Prediction of the location of the evaporation front is probably most decisive.

Chlorides in the concrete mix

Chlorides present in the concrete mix may originate from an admixture, the aggregate, mixing water, salt deposits at the reinforcement bars etc. Drying and wetting cycles and bleeding may concentrate the chlorides close to the surfaces. Kay et al [1981] show an example.

If the curing water contains chlorides, or if the structure is exposed to salt water very early, the salt may penetrate deep into the young concrete since its permeability is high and the contraction sucks water into the young concrete.

Cracks and defects

Salt water penetrates cracks and joints very easily. Consequently, the occurrence and effect of defects must be considered in the evaluation of the behaviour of a structure.

2.3 Binding

Chloride binding removes chloride ions from the concrete pore solution

Chloride binding in concrete is important since the bonding process removes chloride ions from the concrete pore solution into the solid hydrated binder phase. By analogy with general sorption processes in a porous solid phase - liquid phase system, equilibrium conditions are normally assumed between chlorides in the pore solution and chlorides bound to the solid hydrates. Equilibrium implies that under a given set of conditions, a certain concentration of dissolved, free chlorides corresponds to a concentration of chlorides bound to the solid phase. In practice, chloride binding may help to prevent or to delay the chloride activation of reinforcement corrosion in two different ways:

The binding of chloride ions delays chloride ingress into the concrete

- The rate of chloride ingress into concrete is decreased, since the chloride binding process reduces the concentration of chloride ions in the pore solution available for transportation. At low concentrations the binding process is very effective, removing nearly all free chlorides from the pore solution.

Bound chlorides are less effective in promoting reinforcement corrosion

- Only mobile chloride ions, i.e. ions dissolved in the pore solution, are believed to initiate reinforcement corrosion. The total amount of chlorides (free and bound) which can be tolerated in concrete at the depth of the reinforcement is therefore assumed to be a function of the chloride binding capacity. If this assumption is right, a higher chloride binding capacity implies that a higher total amount of chlorides (by weight of binder) corresponds to a given critical concentration of free chlorides in the pore solution.

The mechanisms of chloride binding are still not clear

The mechanisms of chloride binding in concrete are not yet well understood. Historically it was inorganic chemists, who specialised in crystallography and dominated the field of cement chemistry, who claimed that the formation of chloro-aluminate sulphates was the only means of chloride binding. (Crystalline compounds could be identified, and characterised, whereas amorphous compounds were left behind, since proper in-

Figure 2-3. A typical "chloride profile" in concrete.

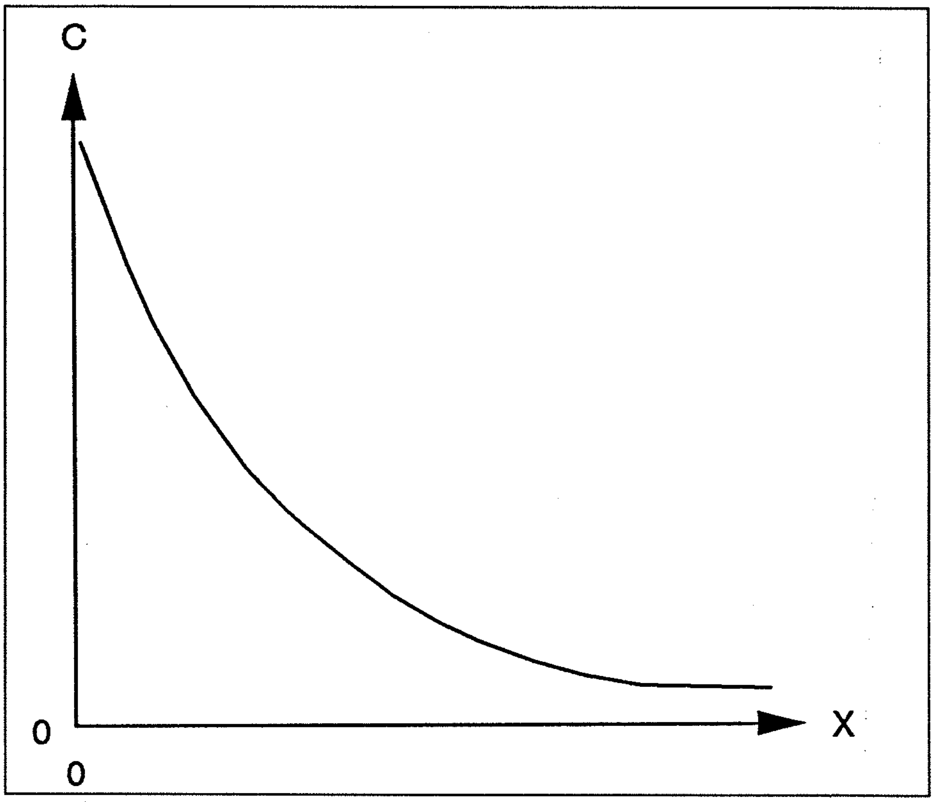
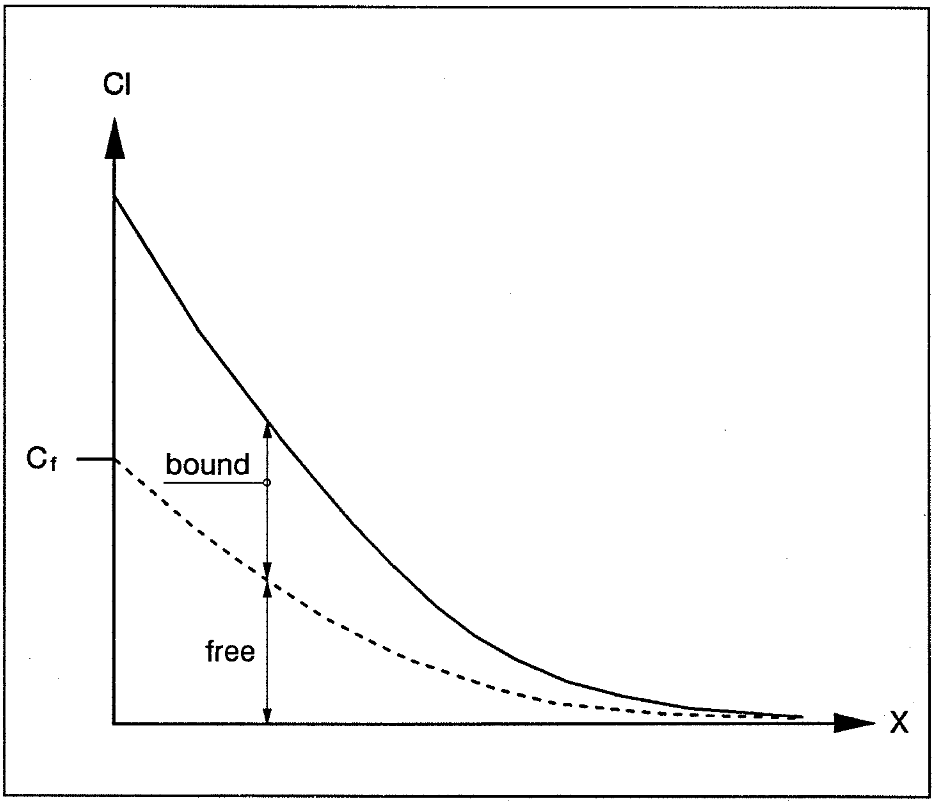


Figure 2-4. Typical profiles of free and bound chlorides.



strumentation techniques and theories were lacking. However, > 60% by mass of the hydrated binder is non crystalline!)

Today most cement chemists working with chloride binding agree that chloride binding in concrete is the result of several different mechanisms. The "pure chemical" binding by the formation of chloro-aluminate sulphates has been found to be of minor importance in field exposed concrete, if it has been cast free of chlorides. The development of chemisorption and ion exchange theories in other fields indicates that these mechanisms are more likely to describe the process of chloride binding in concrete.

The definition of bound chlorides is not clear

The definition of what are free and what are bound chlorides is not clear. Chloride binding seems to vary in strength over a wide range, from chlorides which are not even dissolvable in boiling nitric acid, to chlorides which are released by minor changes in temperature, pressure, relative humidity, pH, etc. It is not known to what extent such loosely bound chlorides actually take part in diffusion processes, thus affecting both the chloride transport rate and the chloride threshold value.

However, it is well known that in most cases corrosion initiation implies several cycles of acidification and repassivation of a local corrosion pit on the steel surface, before the corrosion process becomes accelerated. Loosely bound chlorides are likely to be released as a result of the local acidification at a very early stage in the corrosion initiation process, thus decreasing the chloride threshold value for a binder with a large capacity for loosely bound chlorides. The effect of local acidification and debonding of loosely bound chlorides counteracts the assumed effect of chloride binding stated previously.

Factors affecting chloride binding in concrete

Although proper theoretical models for the mechanisms of chloride binding are not yet fully developed to model the process of chloride binding in concrete, several factors have been found to affect the chloride binding capacity of concrete.

Without going into details, it is important to note that the chloride binding capacity is largely affected by how the chlorides enter the concrete. If chlorides are added to the fresh concrete mix, the chlorides will alter the hydration procedure as compared to a chloride free mix. The formation of chloro aluminate sulphates may become significant if chlorides are present in the early hydration of aluminate and ferrite in the cement.

Chlorides also alter the pore size distribution of the hydrated binder, which is likely to affect the absorption capacity of the hydrated binder.

2.4 *Chloride profiles*

A measured or predicted distribution of chlorides at a certain time in a part of a structure or in a specimen is usually shown as a "chloride profile", a curve showing the total amount of chlorides as a function of depth, see Figure 2-3.

The penetration of chlorides by diffusion means that the content of chlorides is largest at the exposed surface and the content decreases with increasing depth. The slope of the profile is smaller and smaller at larger depths. That explains the appearance of a hypothetical chloride profile as in Figure 2-3.

Figure 2-5. Chloride profiles for two concretes with different chloride binding properties at the same time of exposure.

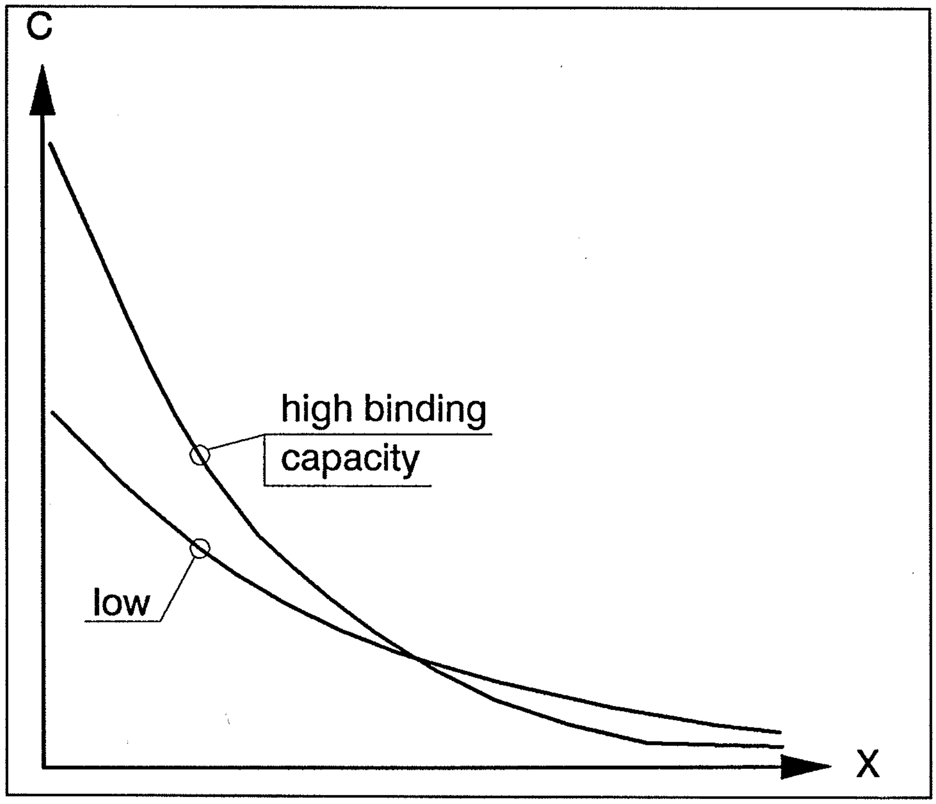


Figure 2-6. A more realistic chloride profile with a lower content at the surface and a maximum at a certain depth.

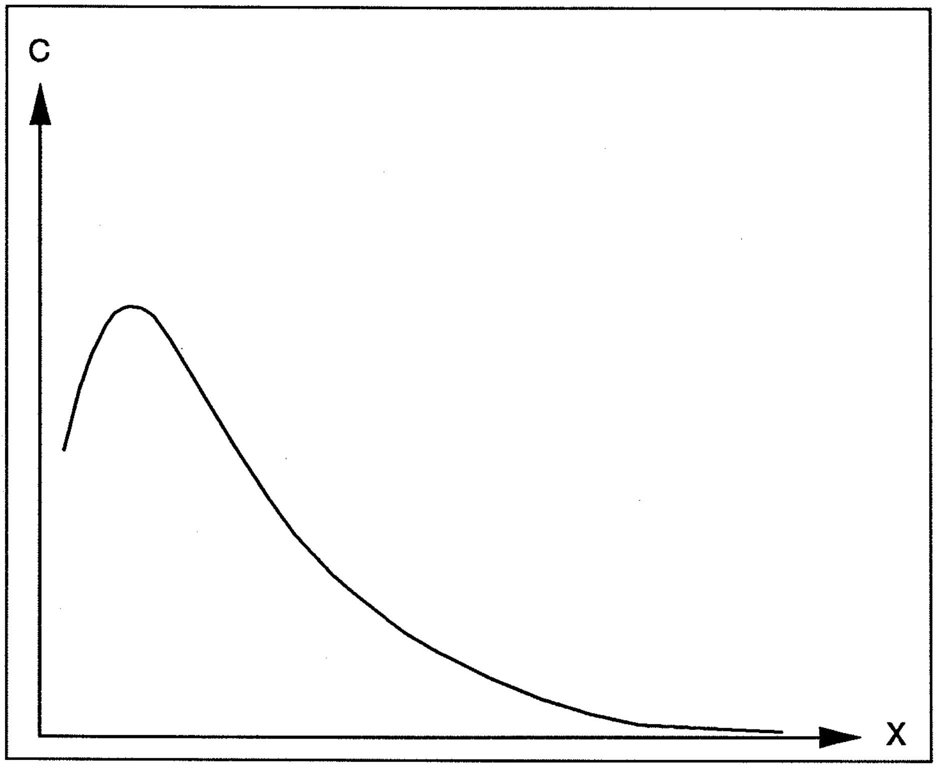


TABLE 4.8.1 “Intrinsic” migration coefficients D_0 for a series of OPC concrete, Tang [1995]

w/c	0.35	0.40	0.50	0.75
Steady-state	11.4	15.2	16.3	23.0
Non-steady state	9.4	18.1	40.8	91.8

Initial chlorides

At large depths a certain amount of chlorides may be present, cf. Figure 2-3. That is the initial chloride content in the concrete which is mixed into the concrete.

Free and bound chlorides

However, the chlorides in concrete are present in different states. Some of them are "free", dissolved in the pore liquid. The rest is more or less bound to the constituents and to the pore walls in the concrete binder. Normally, chloride profiles show the total amount of chlorides, the free plus the bound ones. In figure 2-4 typical chloride profiles are shown, separating free and bound chlorides.

The concentration of free chlorides in the pores of the concrete surface is usually assumed to be equal to the concentration of chlorides in the surrounding environment. i.e. the sea water, cf. Figure 2-4. The amount of bound chlorides is related to the concentration of free chlorides in the pore liquid. Consequently the profile of bound chlorides and the profile of the total amount of chlorides follow the profile for the free chlorides.

Effect of binding

The binding of chlorides is different for different concretes depending on the concrete composition and the type of binder. The binding properties will influence the shape of the chloride profiles. In Figure 2-5 the effect of binding is shown as a comparison of chloride profiles for two concretes which differ only with respect to chloride binding properties.

The concrete with a higher binding capacity will have a higher total chloride content at the concrete surface, since the amount of bound chlorides is larger. On the other hand, the penetration depth in that concrete will be smaller because more of the chlorides that penetrate are bound, which will delay the penetration.

However, measured chloride profiles do not always have the simple theoretical shape as expected from pure diffusion. Frequently a lower chloride content is found close to the surface and a maximum in chloride content is found at some depth, cf. Figure 2-6.

A maximum in the chloride profile

The shape of the chloride profile in Figure 2-6 may have several explanations. Variations in the environmental conditions could cause such a shape, with water movement and evaporation concentrating chlorides at some depth and washing out chlorides from the surface near region. Leaching of substances other than chlorides, or carbonation, both of which influence the binding properties, may be other explanations.

More chlorides close to the surface due to a higher binder content

Since the binding of chlorides is related to the amount of binder, the total chloride content at each point in the chloride profile will depend on the binder content in each sample taken for creating the profile. For this reason the sampling technique could cause differences in chloride profiles. The normal variation in binder content with depth will have an effect, especially close to a cast surface where the binder content is always much higher than at depths greater than the maximum size of the aggregate. For this reason cut surfaces are frequently used in short term tests to avoid the effect of binder content effect on the chloride profiles. The content of chlorides may be presented, not only as a certain percentage of the mass of the sample or the concrete, but also as a percentage of the mass of binder in the sample. If so, when a chloride profile is determined, the binder content profile is also determined.

2.5 Chloride threshold levels

The reason why chloride penetration in reinforced concrete is not only of academic interest is of course that chlorides cause corrosion of the reinforcement. A certain amount of chloride must be present near the steel surface before chloride initiated corrosion can take place in concrete. This amount is generally referred to as the chloride threshold level. Corrosion mechanisms and corrosion rates will not be discussed in this work, but chloride threshold levels are unavoidable when dealing with chloride penetration combined with service life estimation.

The chloride threshold level is not a single value valid for all types of concretes, steels and environments. On the contrary a number of different factors affects the chloride threshold level. This is described in more detail in Chapter 6.

The methods used today for predicting the service life of reinforced concrete structures exposed to chlorides requires knowledge of the chloride threshold level for the structure in question. For that reason it is of great interest to determine the chloride threshold levels for a given situation, not only characterised by the concrete mix design, but also by curing conditions, age, temperature, etc. Environmental factors determining the moisture state of the concrete and the electrochemical potential of the reinforcing bars are also very important parameters for the chloride threshold level, cf. Arup [1993].

3 Transport Processes and Models

Pure diffusion and convection processes

Ions move in a porous material, without any electrical field, in two completely different ways; as pure diffusion in non-moving water and in convection *with* the moving water. In recent years a number of accelerated test methods using an electrical field have been introduced. At such conditions chloride ions move as an electrical migration. In concrete structures a number of these transport processes are combined in different ways depending on the particular environmental conditions. In most of the processes the binding of chlorides to the concrete binder and its pores is a decisive process.

The current knowledge of the various transport mechanisms is summarised and discussed in this chapter.

A number of substances are involved

Some transport processes, especially carbonation and leaching, involve a number of substances other than chlorides and water. The combined effects of these processes and chloride transport are also reviewed here.

Chloride transport and binding are described in a number of ways. Material data are derived with various assumptions and it is very often difficult to understand and compare the results from different researchers. To overcome some of the sources of misunderstanding a few essential variables are defined.

3.1 Binding

3.1.1 Definition of chloride contents

The content of chloride ions in concrete may be expressed in a number of ways. Nilsson [1993b] gave a thorough description used here, with some further comments based on later findings.

Chloride content expressions

The most frequently used expressions are:

c_{I}	[kg Cl/m^3 of solution]	(3.1:1)
c_{II}	[kg Cl/m^3 of pore solution]	(3.1:2)
c_{III}	[kg Cl/m^3 of material]	(3.1:3)
c_{IV}	[kg Cl/m^3 of solid material]	(3.1:4)
c_{V}	[kg Cl/kg of cement or binder]	(3.1:5)
c_{VI}	[kg Cl/kg of gel] (“gel”=$aC+w_n$)	(3.1:6)
c_{VII}	[kg Cl/kg of concrete]	(3.1:7)
c_{VIII}	[kg Cl/kg of sample]	(3.1:8)

but in rare cases even

c_{IX}	[ppm]	(3.1:9)

is used. One may wonder if “parts per million” are parts by volume or parts by weight. For aqueous solutions at low concentrations, it should be weight of solute per volume of solution, and at high concentrations one has to correct for the difference between a m^3 of solution and a m^3 of solvent.

Confusion and errors if not properly defined

Consequently, giving the amount of chlorides in only [kg/m^3], [kg/kg] or [%] might cause confusion and large errors in trying to use the data.

The mass in kg is sometimes replaced by moles. It does not change the relations and the relation between kg Cl and moles Cl is obvious.

Most of the relations between the different concentrations in (3.1:1) to (3.1:8) are simple.

At the boundary with a surrounding chloride solution, e.g. sea water, one would of course expect the same concentration of chloride ions in the solution as in the pore solution of the concrete, i.e.

$$c_{\mathrm{I}} = c_{\mathrm{II}} \tag{3.1:10}$$

if the porous material is in equilibrium with the solution and only the free ions are concerned.

The relationship between the concentration in the pore solution and the surrounding sea water is being questioned

However, some doubts have been thrown on this simple and intuitive relationship, e.g. by Nagataki et al. [1993]. Similar results have been found in the BMB-project, cf. Sandberg [1995]. Nagataki et al found, by pore solution extraction from field samples, almost twice as high a concentration in the pores as in the surrounding sea water! Different numbers, but higher concentrations from pore water squeezing have been found by others. Glass & Buenfeld [1995a] found a 30 % increase, in a laboratory study, which they considered to be an indication of the error obtained in the pore solution expression technique, due to “the release of loosely bound chloride”.

The explanation may be the temperature effect on binding

The largest part of this discrepancy is believed to be caused by the effect of temperature on binding. Concrete samples from a structure or field exposure will increase in temperature when taken to the laboratory. The temperature change decreases binding and some bound chlorides are liberated and dissolved. Consequently, the concentration of free ions in the pore water increases. That pore water with a higher chloride concentration is squeezed out from the sample. The pore solution extraction technique (pore pressing) may add some minor error to the measured concentration difference. Obviously, it is still reasonable to believe that (3.1:10) is true.

The concentrations c_{III} to c_{IX} are related to each other by the dry density of the material γ, dry density of the solid material ρ, cement content C, degree of hydration α, the moisture content w and the molar weight of chloride M_{Cl}.

What part of the pore water acts as a solvent for chloride ions?

The relation between c_{II} and c_{III} to c_{VIII} is more difficult, however:

$$c_{\mathrm{II}} = c_{\mathrm{III}}/p_{sol} \tag{3.1:11}$$

where the problem is to define the porosity p_{sol}. It includes only that part of the porosity that contains a liquid which acts as a solvent. One might question whether all the pore water really acts as a solvent, i.e. p_{sol} = total porosity. Recent measurements by Mangat & Molloy [1995] give some information. They measured the concentration of free chlorides. When multiplied by the total amount of pore water, this gave more free chlorides than the total actually present in the samples! If the measured con-

Figure 3-1. Chloride binding shown as a "binding isotherm", i.e. with the bound chlorides as a function of the free chlorides. Two alternatives are shown at zero concentration: c_b=0 and c_b=0.6 % by weight of binder.

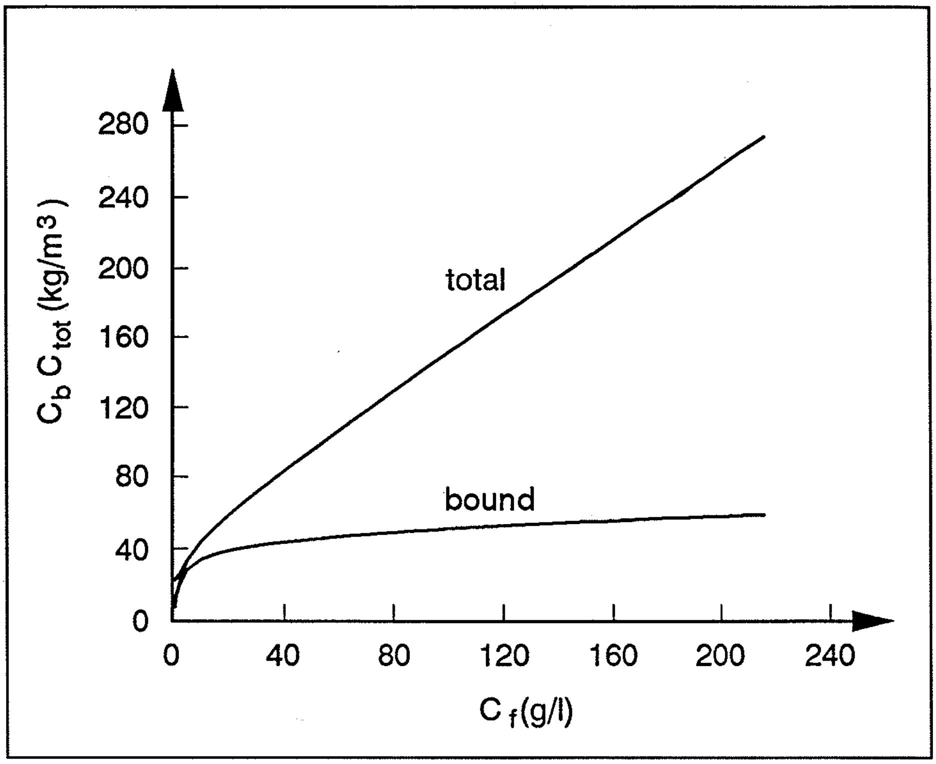
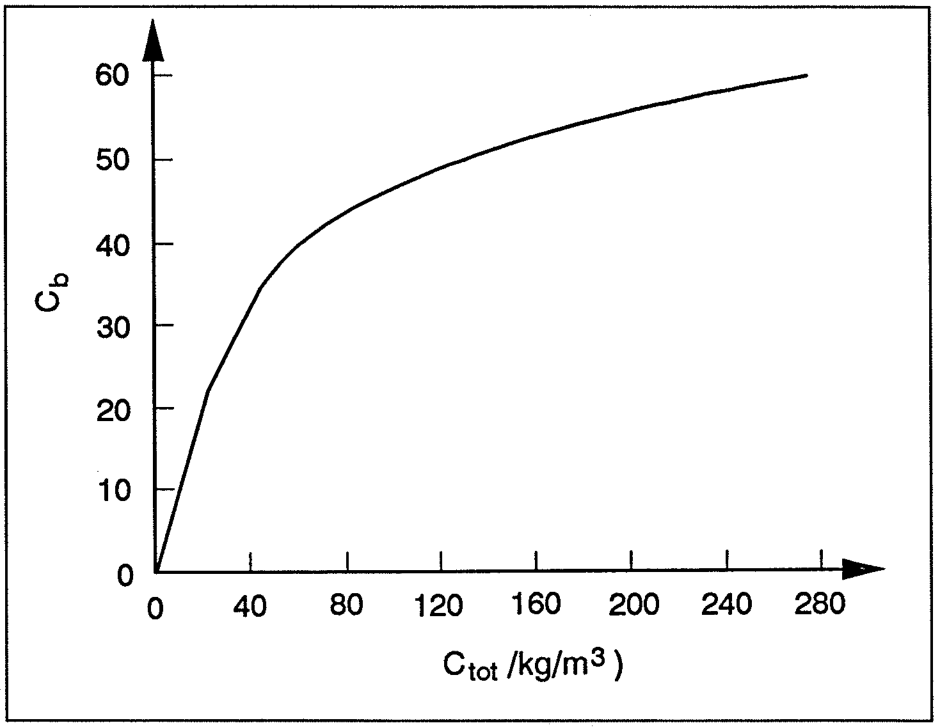


Figure 3-2. Chloride binding shown as another "binding isotherm", i.e. with the bound chlorides as a function of the total amount of chlorides.



centrations are correct, it is obvious that not all the pore water acts as a solvent. The capillary porosity or the empty porosity at 11 % RH or 45 % RH might be better alternatives until further research shows the relationship.

3.1.2 Free and bound chlorides

Chlorides occur in different forms in concrete. Some of the chlorides are free ions dissolved in the pore solution. The rest of the chlorides are chemically and physically bound to the reaction products and their surfaces

$$c_{total} = c_{free} + c_{bound} \tag{3.1:12}$$

where c is the concentration in [kg/m^3], [moles/volume] or [kg/kg]. The free chlorides are usually given per volume of solute, i.e. [kg/m^3 solution]. The bound, and total, amount of chlorides, however, are given per weight of binder or concrete. Consequently, to distinguish between free and bound chlorides as in (3.1:12) the porosity p_{sol} has to be used.

Chloride binding mechanisms are not clear

The mechanisms of chloride binding are not quite clear. Both chemical and physical binding are believed to occur. "Friedel's salt" $C_3A \bullet CaCl_2 \bullet 10H_2O$ is commonly mentioned as a major chemical binding product. Nagataki et al. [1993] even claim that Friedel's salt is all of the chloride binding! It seems, however, as if most of the bound chlorides are physically bound to a limited number of binding sites in the pore walls.

It is usual to assume equilibrium conditions between the free and bound chlorides. In accelerated tests, however, a limited binding rate may give lower amounts of bound chlorides than in long term tests and in structures. Sandberg [1995] mentions Friedel's salt as one source of a time effect on binding.

Binding in Friedel's salt

The amount of physically (and chemically) bound chlorides depends on the content of chlorides. Nagataki et al. [1993] also found a linear relationship between the amount of Friedel's salt and the total amount of bound chlorides, i.e. the chemical binding is also concentration dependent.

3.1.3 Binding isotherms

Chloride binding is not linear

The higher the total content of chlorides the more chlorides are bound, cf. e.g. Akita & Fujiwara [1995]. Some results give a linear relationship but it is more probable that the relationship between the free, bound and total amount of chlorides is non-linear, i.e. the binding capacity is concentration dependent

The effect of chloride content or chloride concentration may be shown in different ways. A "binding isotherm" gives the bound and total amount of chlorides as a function of the free chloride concentration at a constant temperature, cf. figure 3-1. Sometimes the x and y axis are reversed.

The chloride binding isotherms have been mathematically described in a number of ways:

- a straight line with an intercept on the axis for bound or total chlorides,
- a Langmuir isotherm,
- a Freundlich isotherm and
- even as a modified BET isotherm.

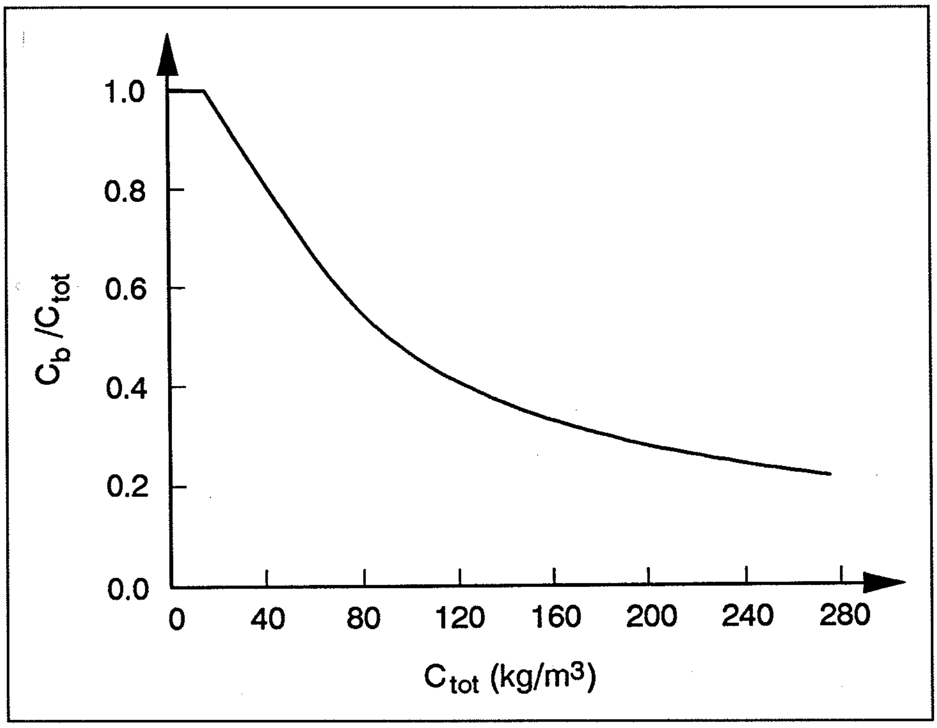


Figure 3-3. Chloride binding shown as a third "binding isotherm", i.e. with the ratio of bound and total chlorides as a function of the total amount of chlorides. The same two alternatives as in figure 3-1 are shown at low concentrations.

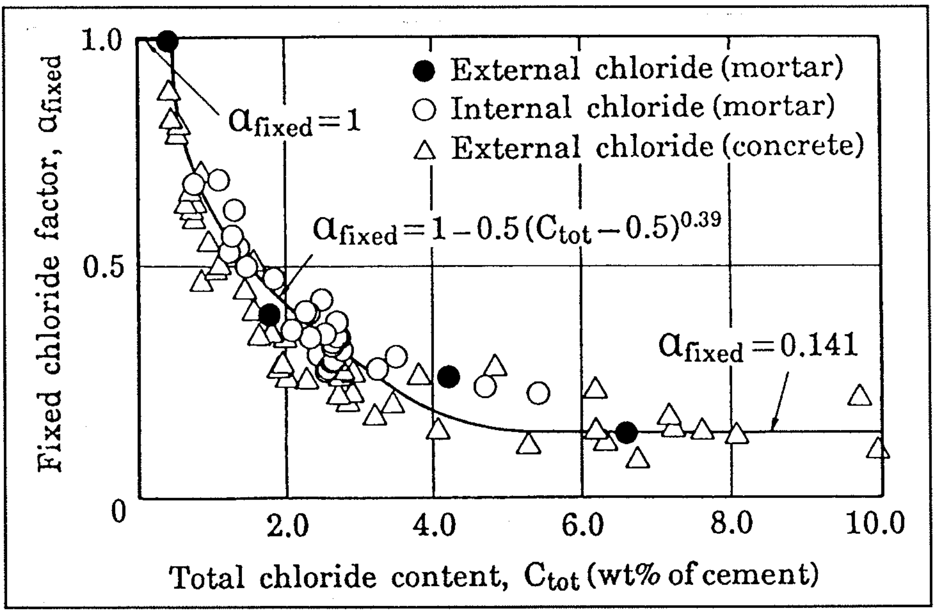


Figure 3-4. Equilibrium conditions for bound and total chlorides. Data from Maruya et al. [1992], Akita & Fujiwara [1995].

A possible binding hysteresis at low concentrations

The straight line is an oversimplification, at least when chloride concentrations increase, see Tang & Nilsson [1993a]. All chlorides are not bound at low chloride contents. For "desorption" of chlorides, as when the concentration decreases with time, the binding isotherm could be different at low chloride contents. Some of the bound chlorides could remain bound also at zero concentration in the pore solution. That would give a binding isotherm with an intercept on the axis for bound, or total, chloride content.

Linear chloride binding isotherms are not probable

A number of more or less linear binding isotherms, with no intercept at all at the y-axis, i.e. straight linearity, have been presented, eg. Tuutti [1982], Mangat & Molloy [1995]. Mangat & Molloy even found "negative" binding capacities. Those binding isotherms usually originate from field samples where the free chlorides were measured by pore water extraction. A probable explanation for these discrepancies is the temperature effect on binding, already mentioned, and minor experimental errors in the extraction technique.

The theoretical justification of the other descriptions is not yet clear and must be regarded as pure mathematics for the time being. More, and more accurate, binding data and physical and chemical models are needed to obtain better descriptions.

Binding data may be presented in many ways, some of which are preferred

Frequently the bound chlorides are shown as a function of the total amount of chlorides, cf. figure 3-2.

The two different alternatives shown in figure 3-1 are not visible in this way of presenting binding data, i.e. it is not shown how strong the non-linearity in binding is.

Sometimes the ratio between the bound and total amount of chlorides is shown instead, cf. figure 3-3. The binding properties at low concentrations are well displayed in such a presentation of data.

Akita & Fujiwara [1995] display extensive binding data from Maruya et al. [1992] in this way, see figure 3-4. According to these findings, the binding capacity is infinite at zero free concentration up to some total chloride content of 0.5 % by weight of cement.

Different binding of chlorides mixed into the concrete

Chloride binding relationships have been determined in different ways as presented further in Section 4.8. It should be noticed, however, that a lot of binding data is derived from specimens where the chlorides were mixed into the original mix. The binding in such cases is not necessarily equal to the binding when chlorides penetrate into the hardening or hardened concrete. Additionally, when chlorides are removed from concrete the content of free and bound chlorides drops with another equilibrium binding isotherm, Tang & Nilsson [1993a]. A large hysteresis seems to exist between the amount of bound chlorides when the concentration increases or decreases.

3.1.4 Binding capacity

The *binding capacity* is the capacity of a material to bind chlorides when the ion concentration changes

$$binding\,capacity = \frac{\partial c_b}{\partial c_f} \tag{3.1:13}$$

The binding capacity is the slope of the binding isotherm

This is the slope of a "binding isotherm" with linear scales as in figure 3-1. Obviously the binding capacity depends on the concentration, as seen from figure 3-1 to figure 3-4, but is sometimes assumed to be a constant.

Figure 3-5. The binding capacity at different chloride concentrations. Data from figure 3-1.

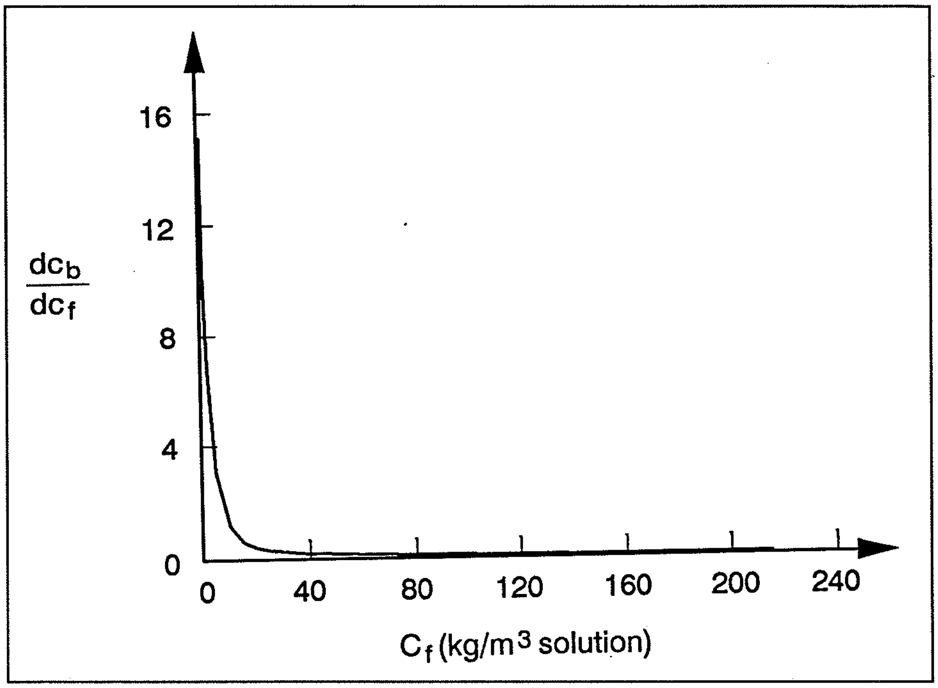
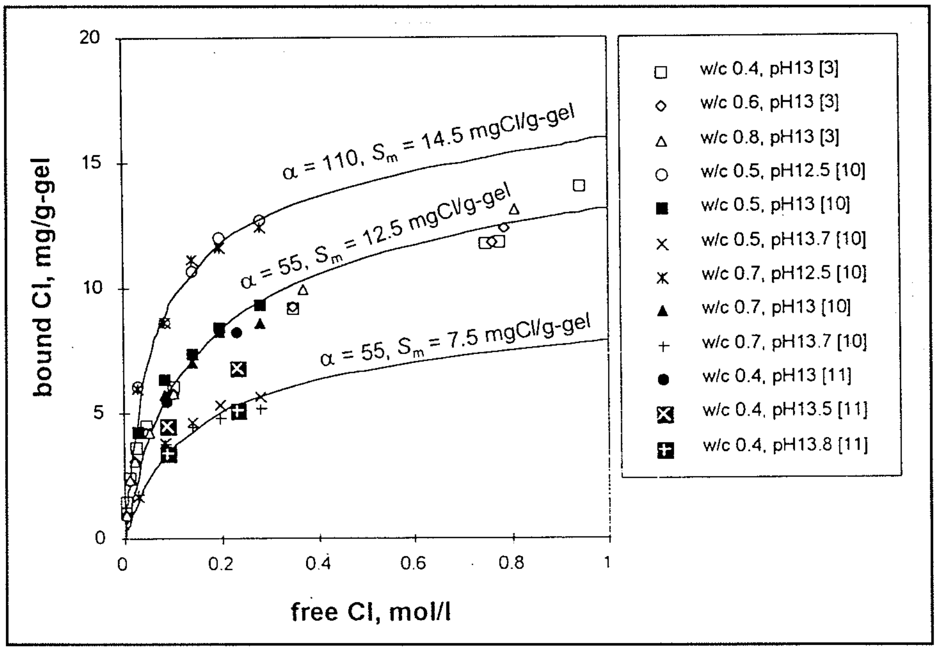


Figure 3-6. The effect of pH on chloride binding. Tang & Nilsson [1995a].



The binding capacity evaluated from the data on which figure 3-1 to figure 3-3 are based is shown in figure 3-5.

The chloride binding capacity is strongly non-linear, especially at low concentrations

The chloride binding capacity is very high at low chloride concentrations. The accuracy of the available measurements is not high enough for precise values to be obtained for the binding capacities at zero concentration. Some data, e.g. the data presented by Akita & Fujiwara [1995] and some data communicated by Massat [1993], indicates that the binding capacity is infinite or extremely high at very low concentrations. A pure chemical fixation could be a reasonable explanation. The hysterisis between increasing and decreasing concentrations must be remembered in discussing possible explanations.

The data shown also implies that the binding capacity is still larger than zero at very high concentration of chlorides. Usually the binding capacity is believed to approach zero at high concentrations.

3.1.5 Decisive parameters

From what was said in the previous section, the most decisive parameters for the amount of bound chlorides are

- concentration of chlorides
- binder content
- specific surface area or amount of gel

Effect of binder content is simple

The effect of chloride content or chloride concentration was discussed earlier. The effect of binder content is simple. The amount of bound chlorides is a linear function of the amount of binder. This is especially important to remember close to a cast surface where the binder content is elevated.

The actual effect of the binder content seems to be the amount of reaction products, i.e. the amount of gel, Tang & Nilsson [1993a]. The number of binding sites could be regarded as a "specific surface area", both of which are proportional to the amount of reaction products and not only the amount of binder. The water-binder ratio and the degree of hydration for hardening concrete should then be an important parameter for quantifying the binding of chlorides.

Other important parameters for chloride binding are

- other ions, especially hydroxides and alkalis,
- temperature,
- type of binder, binder composition,
- type of aggregate
- carbonation.

Other ions in the pore solution are decisive for chloride binding

The composition of the pore solution is decisive for chloride binding. It is important to consider the concentration of other ions present in the solution. Especially the hydroxides, i.e. the pH, have a large effect since the hydroxide ions "compete" for the binding sites with the chloride ions. Data reported by Tritthart [1989], Tang & Nilsson [1993a] and Sandberg [1995] were used to show the large effect of pH, cf. figure 3-6.

As shown in figure 3-7 the binding capacity depends on the type of chlorides that are present in the solution. With $CaCl_2$ the binding capacity is higher than with NaCl. Similar observations are reported by Gjörv & Vennesland [1987].

Figure 3-7. "Inverse sorption isotherms" for different chlorides. Tuutti [1982].

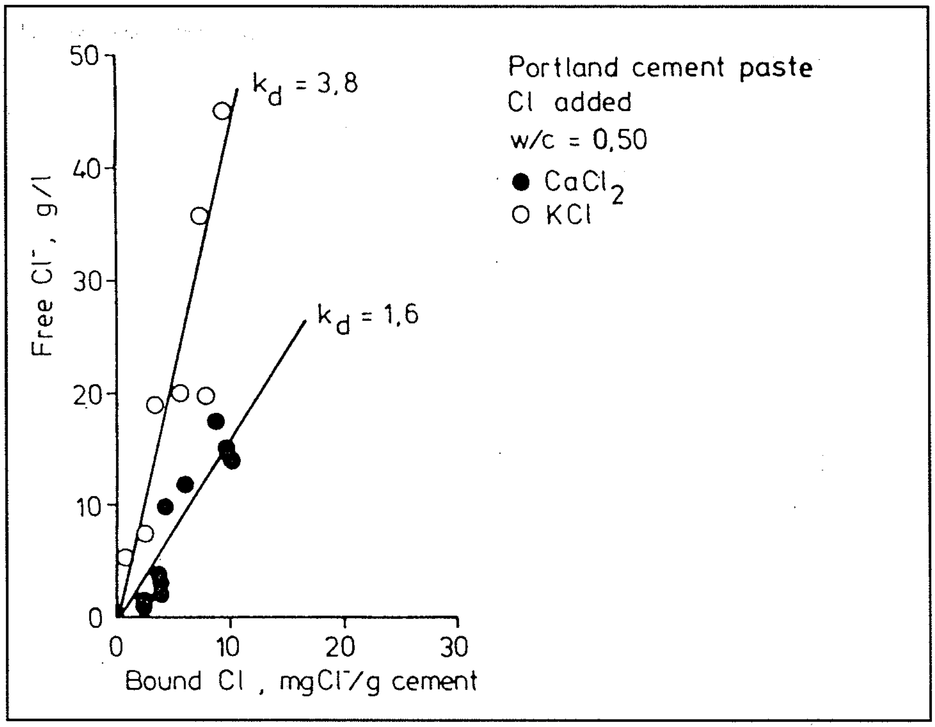
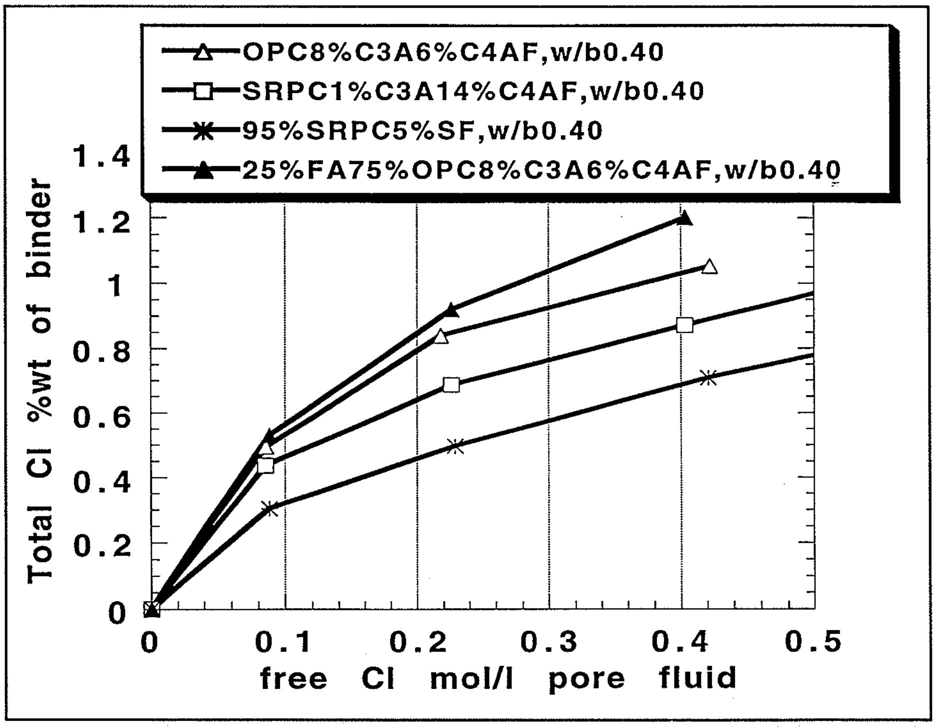


Figure 3-8. Chloride binding isotherms for different types of binders, at a water/binder ratio of 0.4 and a degree of hydration of approximately 0.6. Sandberg [1993]. The alkalinity is maintained at an equal level for all binders.



Lack of knowledge on the important effect of temperature on binding

Very little has been done regarding the effect of temperature level on chloride binding: This is a remarkable lack of knowledge since most concrete structures have temperature conditions far from the ones in laboratory conditions around +20°C, where most tests are performed. This is certainly a limiting factor for predictions of chloride penetration in structures.

A few studies on temperature effects do exist, Larsen [1995], Larsson [1995]. An increasing temperature reduces chloride binding and liberates bound chlorides into the pore solution. This effect is so large that it causes unexpectedly high free chloride concentrations in a sample from structures or field exposed specimens when taken into the laboratory, cf. Nagataki et al. [1993], Mangat & Molloy [1995].

The chloride binding properties are different for different binders, depending on what kind of Portland cement is used, especially the C_3A-content is important but also other factors, and the amount and type of pozzolans have large effects. Some of the effects of type of binder are shown in figure 3-8.

Chloride binding in different binders

The highest chloride binding in figure 3-8 was found for the fly ash binder and OPC with a high C_3A content. SRPC has a somewhat lower binding capacity and the silica fume binder the lowest in this comparison.

As mentioned above, a part of the effect of binders is the effect of the specific surface area they produce. To some extent the chloride binding properties of different binders can be estimated by measuring the specific surface area or the amount of gel. Fly ash and slag cements, however, have a significantly higher binding capacity than such an estimate gives.

Hydroxides will affect binding

The hydroxide concentrations in the pore water of unleached concretes with different binders are quite different and will be another parameter that influences chloride binding. Page et al. [1991] studied the effect of hydroxide concentration on binding and found a difference between an OPC and a SRPC binder even at constant OH-concentration.

Fly-ashes vary in binding properties

Chloride binding properties for fly ash binders vary extensively. One possible reason is the variation in aluminium content, both the total content and the reactive part. Only reactive aluminium in the glass phase participates in the fly ash reaction and chloride binding. The fly ash reaction is very slow. The crystalline part of fly ash is essentially inert. Another possible explanation is the variation in soluble alkalis and sulphates, causing large variations in pH and sulphate concentration in the pore solution.

The aluminium in a slag has a similar effect. However, for a given steel plant the composition of GGBFS is usually much more well defined.

The effect of silica fume

Silica fume influences chloride binding at least three ways. The specific surface area of the pores, or the CSH-content, increases, which should increase binding. On the other hand, the C_3A-content will be lower when silica fume replaces part of the OPC. That should decrease binding. The third effect is that the silica reaction consumes alkalis and reduces the pH. In figure 3-8 the OH-concentration is kept constant for all binders, i.e. the third effect is not included in the comparison. The combined effect of the first two factors seems to reduce the chloride binding capacity when small amounts of silica fume are used. Larger additions could reverse the combined effect. The third effect, low pH increasing the binding, is present earlier in a silica fume concrete than in OPC concrete, where pH drops eventually, due to leaching.

The type of aggregate will have an influence

Table 3-1. Factors affecting the chloride binding in concrete.

factor	increase or decrease	effect on chloride binding capacity	comments
carbonation of binder	⇑	⇓⇓⇓⇓⇓	Cl binding ≈ zero in carbonated concrete (Tuutti 1982)
temperature	⇑	⇓⇓	Larsson (1995), Larsen (1995), well known in other fields
pH (or hydroxide concentration)	⇓	⇑	Tritthart (1988), Byfors (1990), well known in other fields
relative humidity	⇓	⇓	⇓ specific surface ⇓ physical adsorption
soluble sulfates	⇑	⇓	Byfors (1990)
aluminate in cement	⇑	⇑⇑	Rasheeduzzafar et al (1992)
ferrite in cement	⇑	⇑	ferrite considered less effective as compared to aluminate
mineral adm. with reactive aluminium (fly ash, slag, etc.)	⇑	⇑⇑	3 effects: A) more reactive Al B) lower pH in pore solution C) pozzolanic reaction, more C-S-H gel
silica fume	⇑	⇑ ⇑ ⇓	SF ⇓ binding at given pH, but SF also ⇓ pH, and increase the amount of C-S-H gel. Net effect = increased binding

The type of aggregates in the concrete may influence chloride binding. Alkalis released from the aggregate may have such an effect, cf. Larsen [1995], i.e. decreased binding.

Carbonation has a dramatic effect

Carbonation dramatically changes the chloride binding capacity to almost zero, Tuutti [1982]. The specific surface area drops and the pore walls become more or less inert. Consequently, the chloride content in the surface near regions of a concrete exposed to air will be very low due to carbonation.

The factors affecting chloride binding, and their qualitative effect, are summarised in table 3-1.

From what is said above concerning chloride binding, we still have to rely upon measured data for every individual binder for quantification of the binding isotherms. Of course this is also true for the aggregates if they are not inert.

3.2 Diffusion

Diffusion in saturated, submerged concrete with no water movement

Pure diffusion models apply to saturated, submerged, mature concrete where no water movement or carbonation occur.

Pure chloride diffusion is first dealt with in Section 3.2.1. The combined effect of binding and diffusion of chlorides is then included in Section 3.2.2. The effect of simultaneous diffusion of ions other than chlorides, such as leaching of alkalis and hydroxides, is presented in Section 3.2.3. Finally the concept of “apparent diffusion coefficients” from curve-fitting chloride profiles is discussed.

The fundamentals of ion diffusion were recently reviewed by Massat et al. [1992]. Part of that work together with some later findings is included here.

3.2.1 Pure Chloride Diffusion

Fick's 1^{st} law

Pure diffusion of ions in the pore solution of a concrete occurs due to differences in the concentration of the ions. The diffusion of ions in a solution is usually believed to follow Fick's First Law, i e depend on the gradient of the concentration of *free* ions. In one dimension Fick’s 1st law will be

$$F = -D\frac{\partial c}{\partial x} \qquad (3.2:1)$$

where F is the flow of ions in [kg/(m^{2}s)] and D is the diffusion coefficient [m^2/s] according to Fick's first law.

For concrete a similar diffusivity as in (3.2:1) is determined at steady-state conditions using a diffusion cell, or in a migration test, see Chapter 4, with constant chloride concentrations in the solutions at the two sides of the specimen. The gradient of chlorides is derived from the difference in concentration in the two solutions, i.e. concentration of “free chlorides”.

The simple description of the flow as in (3.2:1) is an oversimplification. The diffusivity is not only a material property but depends on the composition of the solution. In a porous material further “complications” are added.

Chloride are not particles but charged ions that will be affected by other ions and pore walls

The movement of the chlorides is not a pure physical diffusion process. The movement of the negative Cl^--ion must be balanced by a movement of some positive ion. From experiments, by e.g. Ushiyama & Goto [1974], it is known that Na^+ and Cl^- "diffuse" at a different rate. This means that when a solution of e.g. NaCl is in contact with a concrete surface, and the salt ions diffuse inwards, diffusion of other ions, mainly OH^- and Ca^{2+}, must occur simultaneously, not only in the surface region but throughout the whole Cl-containing part, Chatterji [1995].

A salt solution in contact with the surface enables also other ions in the concrete to "leach out" into the solution by diffusion. This causes changes in the composition of the pore solution.

Changes in the composition of the pore solution with time may change the solubility and binding of substances bound to the material. Some of them may dissolve at certain conditions which then further change the composition of the pore solution and consequently the conditions for chloride "diffusion".

These "complications" are usually neglected and the chloride ion diffusion regarded as a diffusion of an inert substance in a material with a certain binding capacity for this substance. Interactions with other ions are not taken into account. Consequently, the diffusion coefficient is not only a material property but will depend on the testing conditions.

From what is said above, the diffusion of chloride ions in concrete is mathematically described by (3.2:2), "Fick's 1st law"

$$F = -D_f \frac{\partial c_f}{\partial x} = -D_{F1} \frac{\partial c_f}{\partial x} \tag{3.2:2}$$

where the concentration of free chlorides c_f is the concentration in the pore solution and the diffusion coefficient, D_f or D_{F1}, is the effective diffusion coefficient of the concrete.

Restrictivity and tortuosity are important material properties

The diffusion coefficient depends on a number of factors. The restrictivity and tortuosity of the pore system are the pure *material properties*. They depend of course on the composition and curing of the concrete. Important factors are water-binder ratio and degree of hydration. The type and amount of aggregate affect the diffusion by increasing the tortuosity with increasing aggregate content on the one hand but increasing the amount of transition zones between the aggregate and the paste, on the other hand, with the result that diffusion coefficients in concrete are higher than in the paste of the same composition.

The effect of age and maturity is significant the first six months

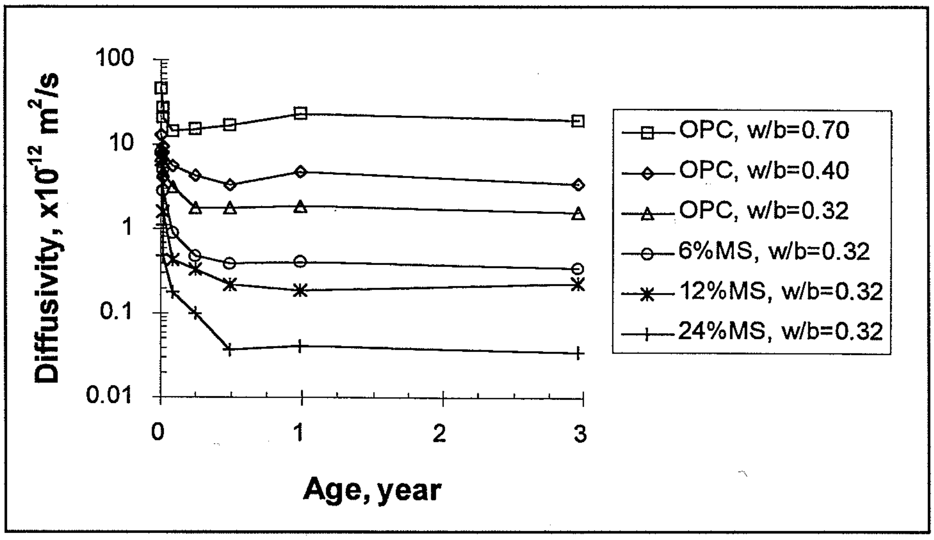
The effect of *degree of hydration*, or *age*, is shown by the measured effect of age on the diffusion coefficient, cf. figure 3-9.

The age effect is described in two steps

$$\begin{cases} \dfrac{D(t)}{D_0} = \left(\dfrac{t_0}{t+t_{ex}}\right)^{\beta} & t < t_0 - t_{ex} \\ \dfrac{D(t)}{D_0} = 1 & t \geq t_0 - t_{ex} \end{cases} \tag{3.2:3}$$

where t_{ex} is the age of the concrete when the structure is exposed to chlorides, t_0 is the age when the diffusion coefficient becomes constant, and β is a constant.

Figure 3-9. Diffusion coefficients, from migration tests, as a function of age. Tang [1995c].



A reasonable explanation for the observed age effect is simply the continuing cement hydration that stops after some time. After that time, t_0, the diffusion coefficient remains constant. That time is around half a year according to the measurements by Tang [1995c].

Studies of the effect of concrete composition parameters on the diffusion coefficient are rare. This is natural since diffusion cell experiments with thick concrete specimens take years to perform. Most studies are done on paste and a few on mortars. It is, however, important to know the theoretical effects of various parameters to understand and predict what happens in more complicated, non-steady state processes.

Important environmental conditions are the chloride concentration and the degree of saturation of the pores with water. The composition of the pore solution, i.e. the concentration of other ions, could have some effect but very little data on this is found in the literature.

The concentration dependency of the diffusion coefficient

Chatterji [1995] deduces an expression for the *concentration dependency* of ion diffusion

$$D(c) = D_0 - A\sqrt{c} \tag{3.2:4}$$

that could be written

$$\frac{D(c)}{D_0} = 1 - \frac{A}{D_0}\sqrt{c} \tag{3.2:4}$$

where D_0 is the diffusion coefficient at infinite dilution and A a parameter. He concludes that “it is obvious that the diffusivity of an ion increases with decreasing concentration”.

Achari et al. [1995] presents some experimental evidence of the concentration dependency. The distribution of chlorides in steady-state conditions through a slice of a clay, that does not bind chlorides, should be a straight line, i.e. a constant gradient in (3.2:2), if the diffusion coefficient were constant.

The distribution, however, was curved in such a way that the gradient is large at high concentrations and small at low concentrations. From a constant flow in (3.2:2) this means that the diffusion coefficient is lower at high concentrations. (3.2:4) was verified.

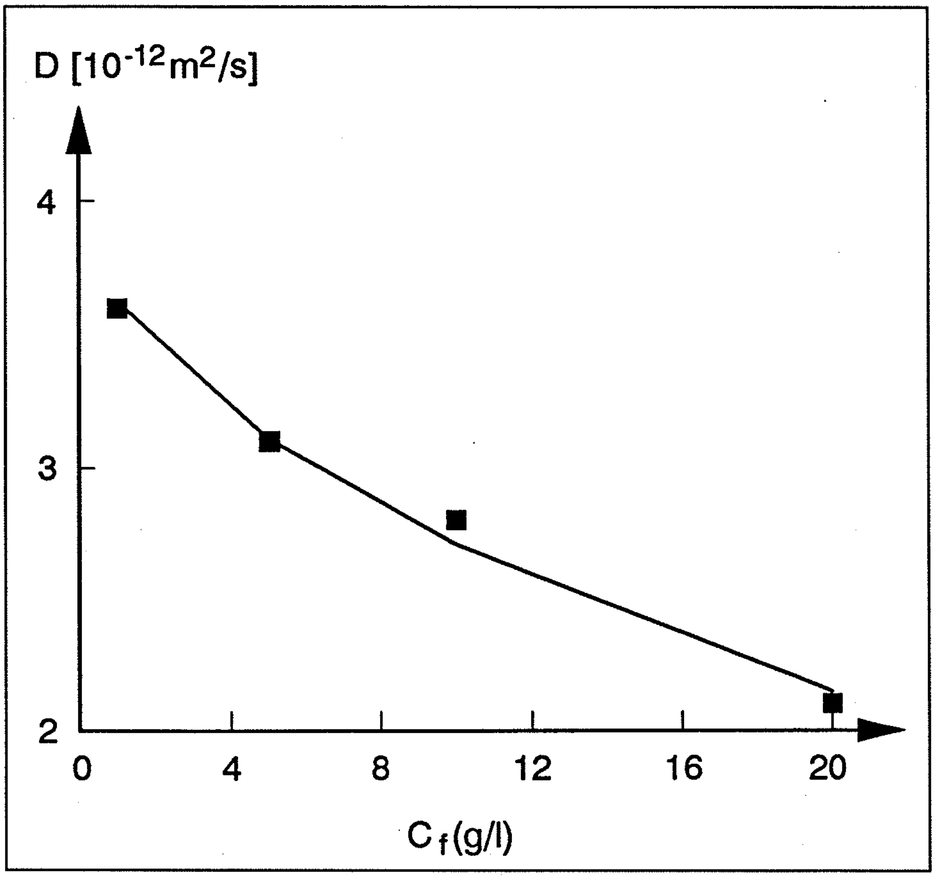
Experimental verifications of the effect of concentration gradient

A number of experimental investigations on mortar have shown the effect of the chloride concentration gradient. Bigas [1994] and Arsenault et al. [1995] found no effect of thickness but a significant decrease of the diffusion coefficient when the average concentration was increased. MacDonald & Northwood [1995] found the opposite for thin paste specimens; a certain influence of thickness but no significant effect of concentration. Gilleece et al. [1995] found a reverse effect of concentration, but they used migration tests.

Bigas′ original results are shown in figure 3-10. By integrating (3.2:4) the concentration dependency of the average diffusion coefficient in a diffusion cell experiment is derived

$$\overline{D}(c_1) = \frac{1}{c_1}\int_{c=0}^{c=c_1} D(c) = \frac{1}{c_1}\int_{c=0}^{c=c_1} (D_0 - A\sqrt{c})\,\mathrm{d}c = D_0 - \frac{2\cdot A}{3}\sqrt{c_1} \tag{3.2:5}$$

Figure 3-10. Average diffusion coefficients D_{F1} (c_1) (points) for a w/c= 0.50 mortar as a function of the concentration in the upstream cell in a series diffusion cell experiments. Bigas [1994]. The data is compared with (3.2:5) for A/D_0=0.16 (line).



The concentration dependency is experimentally verified

The concentration dependency from (3.2:5) is also shown in figure 3-10 for comparison. The measured data fits very well. As seen from the figure the concentration dependency is significant in Bigas′ measurements.

In parts of concrete structures that have been able to dry, due to surface evaporation or self-desiccation, ion diffusion still occurs in continuous water paths. Since the sizes and numbers of water paths decrease with a decreasing moisture content w or degree of water saturation S, the diffusivity of ions must decrease with the moisture content and be zero below a "critical moisture content" below which all paths contain some vapour flow. Very little has been done to quantify the effect of moisture conditions on chloride ion diffusion. Some results, however, indicate a critical moisture condition of around 80 % RH for ion diffusion. This will be further dealt with in Section 3.4.

Data lacking for temperature effect on diffusion

The temperature level probably has an influence on the diffusion coefficients. However, no data has been found to show the temperature effect.

In conclusion, the pure ("steady state") diffusion of chlorides seems to be reasonably well described by Fick's 1st law, (3.2:2). The diffusion coefficient D_{F1} for a particular concrete, however, is not at all a constant

$$D_{F1}(c_f, S, t, T, x) \tag{3.2:6}$$

but depends mainly on the concentration of chlorides c_f in the pore solution, the degree of saturation S of the pore system, the age t or degree of hydration of the concrete and the temperature T.

In a concrete member the composition may be heterogeneous because of a higher binder content close to a cast surface. That would mean that the diffusion coefficient also depends on the depth x from such a surface. The effect of other inhomogeneities and defects is treated in Chapter 5.

3.2.2 Chloride Diffusion and Binding

When the conditions change with time, the chloride flow is not constant. Consequently the chloride distribution will change with time and the binding of ions is an essential part of the process.

In a solution, however, it is very simple. The law of mass conservation in an infinitesimal volume of the solution gives the changes with time of the chloride concentration in that unit volume

$$\frac{\partial c}{\partial t} = -\frac{\partial F}{\partial x} \tag{3.2:7}$$

With the flow description as Fick′s 1st law for diffusion in a solution, (3.2:2)and with the diffusion coefficient D as a constant, one gets

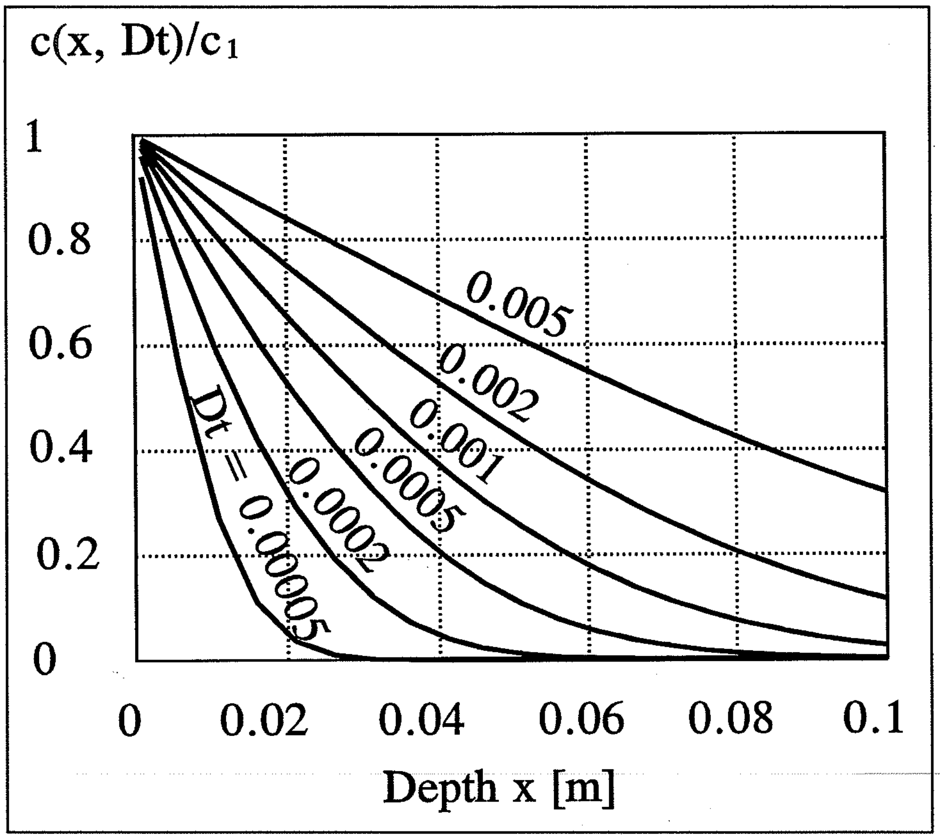
$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{3.2:8}$$

Fick′s 2^{nd} law for a solution

This equation is referred to as Fick′s 2nd law of diffusion. It should be remembered, however, that it is valid for diffusion in a solution and that the diffusion coefficient is assumed constant.

For the "penetration" of chloride ions into a solution, if the left boundary is given a constant concentration, $c(x=0, t) = c_s$, and the concentration is zero at the beginning, $c(x, t=0) = 0$, the chloride profiles are given by

Figure 3-11. The error-function solution (3.2:9) to Fick´s 2nd law for penetration of chlorides into a solution.



the common error function solution to Fick's 2nd law with these boundary and initial conditions

$$c(x,t) = c_s \left(1 - \mathrm{erf}\left(\frac{x}{2\sqrt{D \cdot t}} \right) \right) \tag{3.2:9}$$

The solution is shown in figure 3-11.

In a concrete, however, the effect of binding must be included. Additionally, the diffusion coefficient in Fick's 1st law cannot be taken as a constant.

The mass balance in concrete is different than in a solution

A correct description of the mass balance equation for an infinitesimal volume of concrete, without any assumptions or simplifications, may be written

$$\frac{\partial c_{m,tot}}{\partial t} = \frac{\partial c_{m,f}}{\partial t} + \frac{\partial c_{m,b}}{\partial t} = -\frac{\partial F}{\partial x} \tag{3.2:10}$$

where the chloride concentrations are per unit volume of concrete. The total amount of chlorides in the infinitesimal volume will change only due to differences in the flows to and from that volume. Within that volume, however, the total amount of chlorides will be distributed into free and bound chlorides.

(3.2:10) may be rearranged to

$$\frac{\partial c_{m,f}}{\partial t} = -\frac{\partial F}{\partial x} - \frac{\partial c_{m,b}}{\partial t} \tag{3.2:10'}$$

that looks similar to Fick's 2nd law of diffusion in a solution, (3.2:8), with a binding term added. However, the concentration of free chlorides $c_{m,f}$ in the pore solution, is per volume of the concrete, and the flow F is per m^2 of the material.

A separate binding term should be used

With the flow described as a diffusion process in concrete according to (3.2:2), and a non-constant diffusion coefficient, (3.2:6) the mass balance equation for a volume of concrete will be

$$\frac{\partial c_{m,f}}{\partial t} = \frac{\partial}{\partial x}\left(D_{F1} \frac{\partial c_f}{\partial x} \right) - \frac{\partial c_{m,b}}{\partial t} \tag{3.2:11}$$

with $D_{F1} = D_{F1}(c_f, S, t, T, x)$

This is the equation that is used today by some researchers to predict chloride penetration into concrete. The required input data, the material properties, is determined from independent test methods or material models for the diffusion coefficient D_{F1} and the binding isotherm. The solutions must be found numerically by computer calculations, because of the parameter's variation and interrelations.

Examples of the utilization of (3.2:11) are found e.g. in Tang & Nilsson [1994] and Tang [1995a], who developed a Windows-based finite-difference method software called *ClinConc*. It will be further used later in this section and in Chapter 7.

Fick's 2nd law is still widely used

Usually, however, Fick's 2nd law is widely used also for concrete, in its original form with the error-function solution or in modified versions. The diffusion coefficient D_{F2} in Fick's 2nd law, (3.2:8) is then taken as an "apparent" diffusion coefficient D_{app}

$$\frac{\partial c}{\partial t} = D_{F2}\frac{\partial^2 c}{\partial x^2} = D_{app}\frac{\partial^2 c}{\partial x^2} \tag{3.2:12}$$

In this equation the concentrations c must be the same on both sides. Additionally, the equation does not include a binding term. To identify the apparent diffusion coefficient, (3.2:11) may be rearranged to

$$\frac{\partial c_{m,f}}{\partial t} + \frac{\partial c_{m,b}}{\partial t} = \frac{\partial}{\partial x}\left(D_{F1}\frac{\partial c_f}{\partial x}\right) \tag{3.2:11'}$$

and, by converting the concentrations on the left hand side from chlorides per volume of the material to chlorides per volume of the pore solution, introducing the porosity p_{sol}, and by eliminating the concentration of bound chlorides, further to

$$p_{sol}\cdot\frac{\partial c_f}{\partial t}\left(1+\frac{\partial c_b}{\partial c_f}\right) = \frac{\partial}{\partial x}\left(D_{F1}\frac{\partial c_f}{\partial x}\right) \tag{3.2:11''}$$

with the parenthesis including the binding capacity $\partial c_b/\partial c_f$, cf. (3.1:13), and the porosity p_{sol} refers to the saturated pore volume that acts a solvent for chloride ions.

The "correct" Fick's 2nd law for concrete

Now, moving the porosity and the parenthesis to the other side, one gets an equation similar to Fick's 2nd law with the same concentration c_f on both sides

$$\frac{\partial c_f}{\partial t} = \frac{\partial}{\partial x}\left(\frac{D_{F1}}{p_{sol}\left(1+\frac{\partial c_b}{\partial c_f}\right)}\frac{\partial c_f}{\partial x}\right) \tag{3.2.11'''}$$

and by comparison with a Fick's 2nd law-like equation, with a non-constant diffusion coefficient D_{F2}

$$\frac{\partial c_f}{\partial t} = \frac{\partial}{\partial x}\left(D_{F2}\frac{\partial c_f}{\partial x}\right) \tag{3.2:12}$$

The apparent diffusion coefficient is complicated

the apparent diffusion coefficient can be identified as

$$D_{app} = D_{F2} = \frac{D_{F1}}{p_{sol}\left(1+\frac{\partial c_b}{\partial c_f}\right)} \tag{3.2:13}$$

Already Tuutti [1982] realised part of this relationship. Massat [1991], Nilsson [1992] and Massat et al. [1992] made it quite clear. However, a thorough experimental verification is still missing.

A lot of confusion on diffusion coefficients in Fick's two laws

Ignorance of this relationship has caused a lot of confusion about diffusion coefficients. The D:s in Fick's two laws have been compared as if they were supposed to be equal and reasons for differences have been discussed, see e.g. Tang & Nilsson [1992a].

Figure 3-12. Chloride profiles with only non-linear binding taken into account. Chloride concentration of 20 and 100 g/l respectively. Calculations with *ClinConc* by Tang & Nilsson [1994].

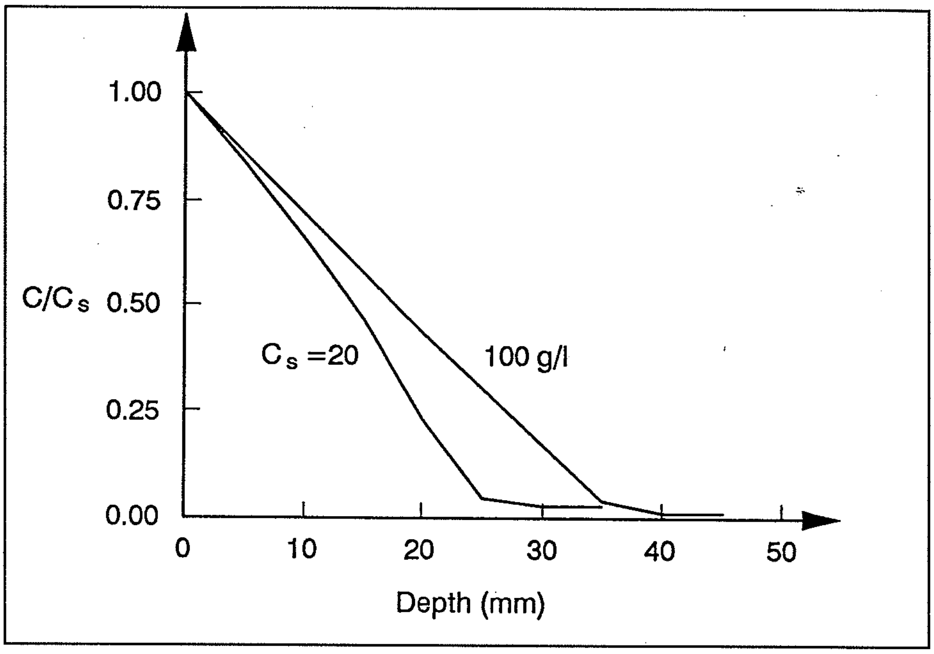
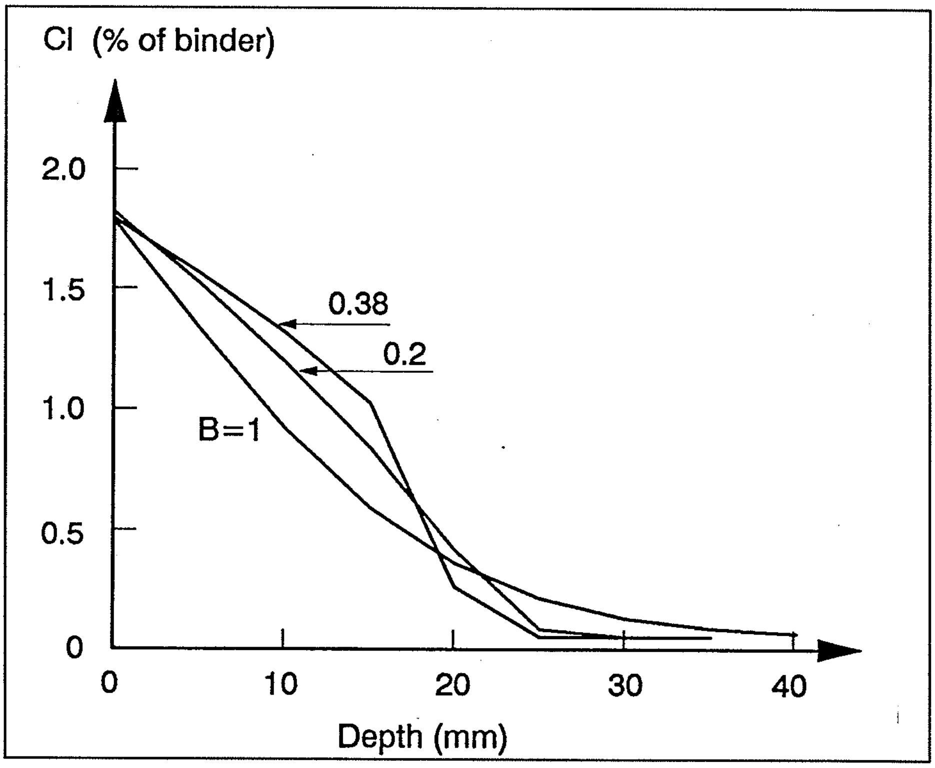


Figure 3-13. Predicted chloride profiles for different degrees of non-linearity in chloride binding. Predictions by solving (3.2:11‴) using the model by Tang & Nilsson [1994].



The two coefficients D_{F1} and D_{F2} are clearly different, but the values are not that far away from each other. The porosity for a concrete could be 10-20% and the binding capacity is between 0 and 15 for normal concentrations, cf. figure 3-5, say an average binding capacity of some 2-5, i.e. the parenthesis is between 3 and 6. With these numbers the two coefficients should normally differ by a factor of 0.8 to 3.3!

A simple approach is to assume both D_{F1} and the binding capacity R to be constants.

$$D_{app} = D_{F2} = \frac{D_{F1}}{p_{sol} \cdot (1+R)} \tag{3.2:14}$$

That would give a constant diffusion coefficient and the error-function solution would be applicable.

The utilization of Fick's 2^{nd} law was first questioned in 1992

Prediction methods using a simple error function solution to Fick's 2nd law with a constant "apparent diffusion coefficient" D_{F2} were first used already more than 25 years ago by Collepardi et al. [1970]. They are, however, still widely used. Nomograms for predictions, see e.g. Browne [1982], are published. Not until around 1992 was it realised in the Nordic countries that these prediction methods greatly overestimate chloride penetration, see below. Still in 1995 Yamamoto et al. [1995] report a number of Japanese prediction models of that type.

The "apparent" diffusion coefficient varies with concentration, age, temperature, pH etc

Today we know better. Since the binding capacity is not necessarily a constant, cf. Section 3.1, the diffusivities D_{F1} and D_{F2} cannot as a rule both be constants. On the contrary, cf. (3.2:13), they should both be concentration dependent and the diffusion coefficient in Fick's 2nd law should vary with a number of parameters, at least those that D_{F1} and the binding capacity are affected by. The diffusion coefficient D_{F1} varies with chloride concentration, moisture content, age, temperature, binder content, micro crack density etc. The binding capacity varies with concentration, moisture content, temperature, pH, presence of other ions etc., i.e. at least

$$D_{F2}(c_f, S, t, T, x, \text{pH}) \tag{3.2:15}$$

for a particular concrete. Some of these parameters are more important than others and their effects have been quantified to some extent.

If the concentration dependency is neglected, the profiles will be quite different

Part of the *concentration* dependency was quantified by Nilsson [1992] and Nilsson et al. [1994] by taking the non-linearity in chloride binding into account. With a binding capacity that varies with the concentration, cf. figure 3-5, the diffusion coefficient D_{F2} will be strongly concentration dependent, cf. (3.2:13). The solutions to (3.2:1) with a concentration dependent diffusion coefficient will strongly depend on the chloride concentration at the concrete surface; it will be totally different for the conditions similar to sea water exposure and conditions in accelerated tests, cf. figure 3-12.

Accelerated testing with concentrated solutions will give too high diffusion coefficients

Accelerated testing with extremely concentrated chloride solutions should consequently give much higher apparent diffusion coefficients than normal exposure. Predictions with a constant diffusion coefficient derived from short term accelerated tests probably overestimate the chloride penetration.

The chloride profiles also look very different, cf. figure 3-12 with figure 3-11, if only the non-linearity in binding is taken into account. A number

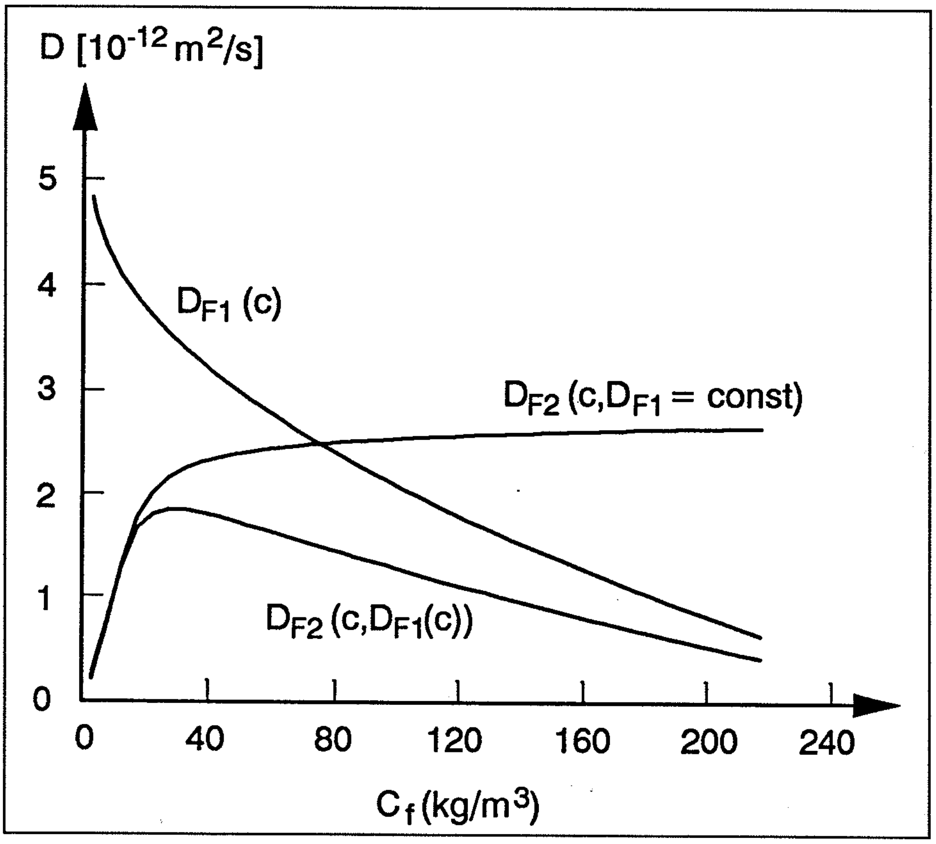


Figure 3-14. The expected concentration dependency of the diffusion coefficient D_{F2} in Fick's 2nd law (3.2:12). If both the concentration dependency of the diffusion coefficient D_{F1} in Fick's 1st law and the non-linearity in chloride binding are included.

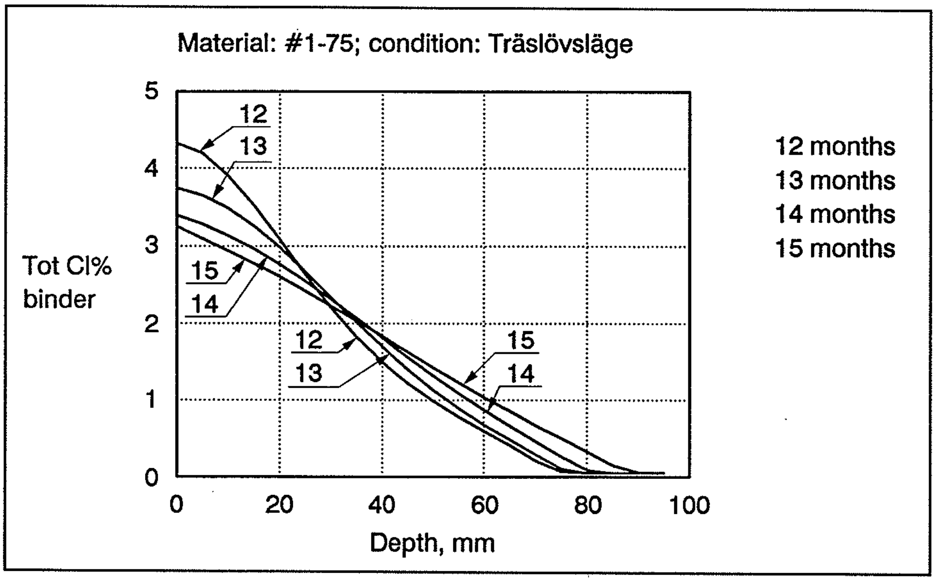


Figure 3-15. Predicted total chloride profiles during a three month period (exposure times 12-15 months) with increasing temperature. Calculation by *ClinConc.*

of measured chloride profiles actually look like the profiles in figure 3-12, but in a lot of cases the shape is quite different. The reason for this discrepancy has not been completely explained. Leaching of hydroxides is probably one decisive factor, see next section.

The effect of degree of non-linearity

The effect of the degree of non-linearity on binding properties may be estimated by solving (3.2:11′′′) with the numerical model of Tang & Nilsson [1994]. An example is shown in figure 3-13. The shape of the chloride profiles with constant boundary conditions and diffusion coefficient will strongly depend on the degree of non-linearity in the binding isotherm.

To clarify the full concentration dependency, however, the concentration dependency of D_{F1} should also be included in (3.2:11′′′) and (3.2:12), cf. (3.2:6). This has been done in figure 3-14.

The concentration dependency is much smaller than if only the non-linear chloride binding is taken into account, but it is still significant. The effect on the chloride profiles has not yet been calculated.

The effect of age and time of exposure

The effect of *age* has been quantified by Tang & Nilsson [1992] and Poulsen [1993a]. The diffusion coefficient D_{F2} can be placed outside the derivation in (3.2:11′′′) if it only depends on time

$$\frac{\partial c_f}{\partial t} = D_{F2}(t)\frac{\partial^2 c_f}{\partial x^2} \qquad (3.2:16)$$

and analytical error-function solutions can be found for this equation.

The effect of temperature

The *temperature* probably has a twofold effect on the apparent diffusion coefficient D_{F2}, cf. [3.2:13]. D_{F1} increases with increasing temperature. The binding capacity decreases with increasing temperature. Both effects increase D_{F2} with increasing temperature.

Frederiksen [1993] measured apparent diffusion coefficients in immersion tests with a high concentration of chlorides. In such an accelerated test, however, the effect of binding is small and its full effect on the diffusion coefficient may be smaller than in normal concentrations.

Tang [1994] made laboratory immersion tests for a year in solutions of different temperatures. The major effect on the chloride profiles was the very much lower chloride contents at the low temperature.

When the temperature varies, as during an annual cycle, the temperature effect on binding will dramatically change the shape of the chloride profiles. An example is shown in figure 3-15.

Temperature variations changes the concentration gradients and the surface concentrations during an annual cycle

When the temperature increases the amount of bound chlorides at the surface decreases but inside the concrete bound chlorides are liberated, increasing the concentration of free chlorides. That should increase the chloride gradients and consequently the diffusion of chlorides.

The effects of different diffusion coefficients and binding capacities in different parts of the concrete are mainly studied for a surface layer with different properties, a "*skin effect*". Hjorslev-Hansen [1993] analyses a multilayered structure in which a surface layer and the concrete mass have different properties. He concludes that the chloride concentration in the pore liquid must be used as diffusion potential, i.e. the diffusion and the binding have to be treated separately. Solutions have to be calculated numerically.

Skin effects and surface layers

Andrade et al. [1995a] used Fick's 2nd law and analytical solutions for two-layered structures to model the effect of a surface layer with proper-

Figure 3-16. Measured profiles of chlorides (total and free) and hydroxides. Sergi et al. [1992].

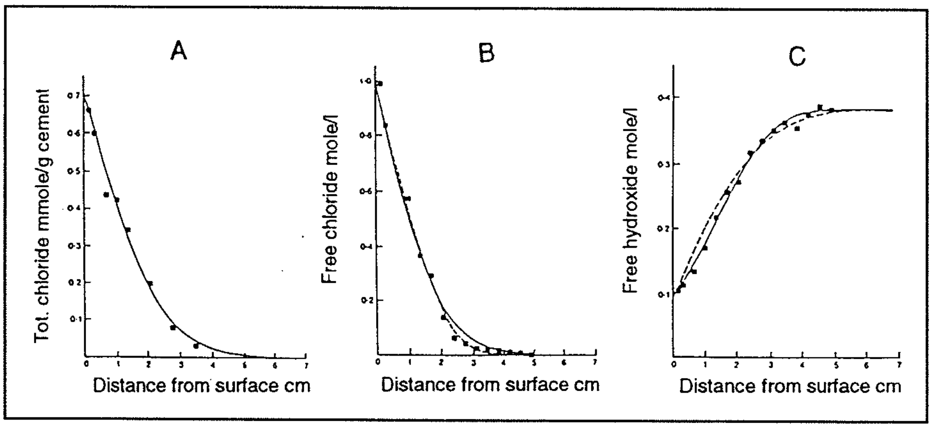
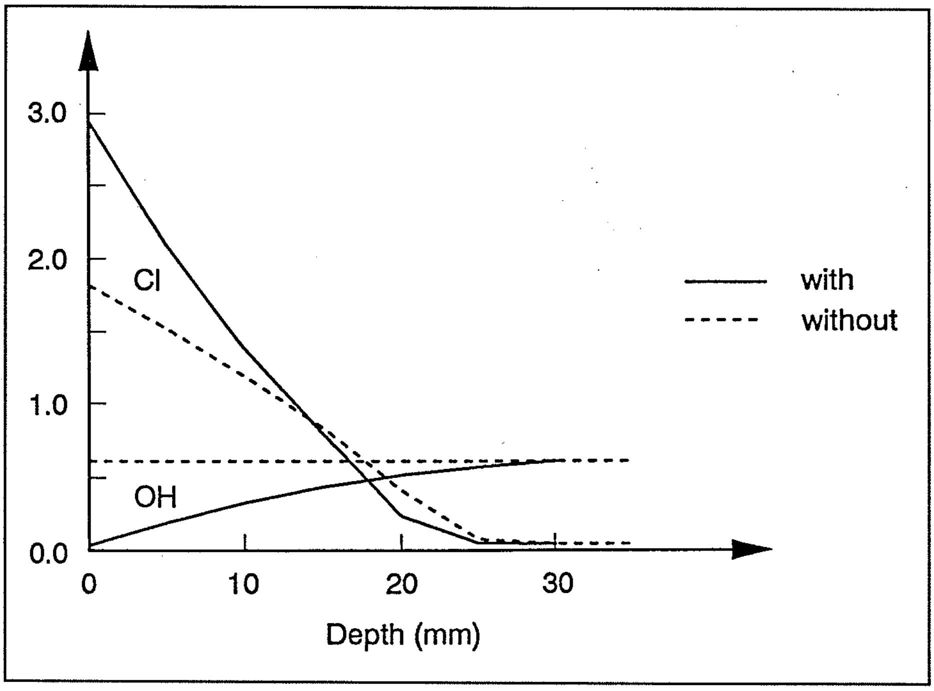


Figure 3-17. An example of a predicted chloride profile with and without considering the leaching of alkalis using the model of Tang & Nilsson [1994]. All other parameters are kept constant.



ties different from the concrete mass. The chloride profiles are of course highly dependent on the skin properties and the thickness of the skin.

To analyse skin effects in measured profiles in terms of "resistance" or diffusion coefficients, one must remember that an "apparent diffusion coefficient" includes both transport and binding properties. The boundary conditions, i.e. the chloride content at the surface, could be quite different in cases with and without a "skin", because the surface chloride content is determined by the binding properties of the outermost material.

If this effect is neglected and the total chloride profile is used for curve-fitting, the regression parameter, the apparent diffusion coefficient, will be misleading.

Variations in boundary conditions

If the *boundary conditions* are not constant but vary with time, eg. when chlorides are leached out part of the time, a numerical solution may easily be derived. Nagano & Naito [1985] published solutions for cases where the concentration at the surface has different constant values during different periods of time. Their solutions include cases where a maximum in salt concentration is found below the surface.

3.2.3 Effect of leaching of hydroxides and alkalis

Since the pH has a strong influence on chloride binding, the leaching of hydroxides and alkalis will affect measured chloride profiles. A drop in pH in surface-near regions of a concrete, due to leaching, will give a higher total content of chlorides in that region, since chloride binding increases with decreasing pH.

A few measured profiles of hydroxides and alkalis exist, cf. figure 3-16.

Leaching of hydroxides from calcium hydroxide

The leaching of hydroxides from calcium hydroxide will affect the pH only after a very long time since the buffer capacity of $Ca(OH)_2$ is large. For high quality concrete in contact with sea water it should be insignificant during the normal service life of a concrete structure. For high *w/c* concrete, or in the surface near region, further leaching of hydroxides will deteriorate the CSH gel, causing the binder content to drop. Due to this effect the amount of bound chlorides will decrease close to the surface. This might be part of the explanation for chloride profiles to drop near the surface also in the submerged zone, where carbonation is more limited.

Leaching of alkalis will change pH in a short time

The leaching of alkalis (K^+ and Na^+) will , however, affect the pH more rapidly since the available amount of alkalis is small, less than some 1 % by weight of OPC. Leaching of alkalis will cause a drop in pH from some pH=13.5-14 down to pH=12.5. That drop influences the binding capacity to a large extent, cf. Section 3.1.

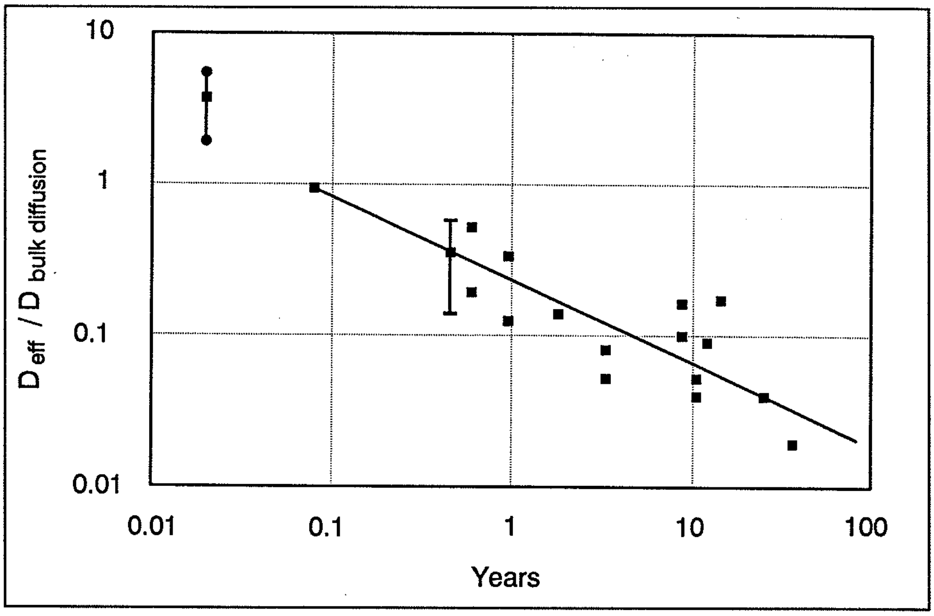
To be able to predict chloride profiles that coincide with what is measured in field concrete, the leaching of alkalis must be included in the prediction. It is included in the model of Tang & Nilsson [1994]. The effect of inclusion or non-inclusion is shown in an example in figure 3-17.

Leaching will change the shape of chloride profiles

As seen in the example the effect is large, especially close to the surface. The surface chloride concentration could be heavily misjudged if this effect was not considered in a prediction. The measured surface concentration is early affected by leaching. Using such a concentration for prediction without including the leaching effect would underestimate chloride penetration.

The drop in pH due to leaching greatly increases the binding. Not only does the chloride content increase close to the surface, but the whole shape of the chloride profile changes. The increased binding reduces the predicted chloride penetration and the "curvature" of the profile will

Figure 3-18. Constant achieved transport coefficients D_{aex} after different exposure times t_{ex} from the error-function solution to Fick´s 2nd law. The data from cores taken from old structures of different ages are compared with similar coefficients from short-term tests on the same cores. Maage et al. [1994].



change dramatically. To be able to predict chloride profiles in real structures, it is obvious that the leaching effect must be included!

3.2.4 Apparent diffusion coefficients from curve-fitting

Frequently a constant apparent diffusion coefficient D_{F2} is derived from non-steady state experiments or field measurements by curve-fitting a measured chloride profile to the error-function solution of Fick's 2nd law with a constant diffusion coefficient and a constant surface concentration. Such a curve-fitting at an exposure time t_{ex} will give two regression parameters, an "achieved transport coefficient" D_a and an "achieved concrete surface content", C_{sa}.

If the profiles in figure 3-12 were true, and nothing else than non-linear chloride binding had to be taken into consideration, very strange "apparent diffusion coefficients" would be obtained if one of them was compared with the profiles from the error-function solution to Fick's 2nd law in figure 3-9. Independent of the shape of the measured profile, a curve-fitting may always be possible, usually by excluding a number of the data points closest to the surface.

Curve-fitting a chloride profile gives regression parameters; one of which is called a diffusion coefficient

For each chloride profile one set of regression parameters will be evaluated. If two or more profiles are used, for different times of exposure, the regression parameters will not be constants. Usually the achieved transport coefficient D_a decreases with time. The surface concentration may vary irregularly.

This is what has been realised in recent years when achieved transport coefficients from chloride profiles from structures have been compared with achieved transport coefficients from short-term tests on the same concrete, Maage et al. [1994], cf. figure 3-18.

Achieved, or apparent, diffusion coefficients will decrease with time

An apparent diffusion coefficient that decreases with time is a strange phenomenon since the apparent diffusion coefficient is derived from a regression assuming the achieved transport coefficient to be constant! This is explained in detail in Chapter 7.

These findings have been utilized to set up new prediction models for chloride penetration where the apparent diffusion coefficient decreases with exposure time, Poulsen [1995b] or prediction time Sandberg [1995]. This is further treated in Chapter 7. The solutions to Fick's 2nd law with time-dependent apparent diffusion coefficients are used, cf. (3.2:9). The achieved transport coefficient, after a certain exposure time, derived from a regression analysis which assumes it is constant, is the intregrated time-dependent apparent diffusion coefficient during the exposure.

Several possible explanations for the achieved diffusion coefficient to decrease with time

No explanation has however been found as yet for the decrease in the regression parameter D_a with time. Part of the explanation is of course the true time-dependent diffusion coefficient D_{F2}, but that time-dependency does only last for half a year or so. Another part of it is probably the concentration dependency of the diffusion coefficient D_{F2}, due to the concentration dependency of the binding capacity. Variations with time of the environmental conditions are other parts of the explanation.

Curve-fitting is usually done for chloride profiles from the splash zone, where the surface concentration is far from being constant. Much more knowledge of the time dependency of the boundary conditions has to be gained before a simple prediction will come close to real chloride profiles. The numerical models have an advantage in considering relevant knowledge on a more scientific basis.

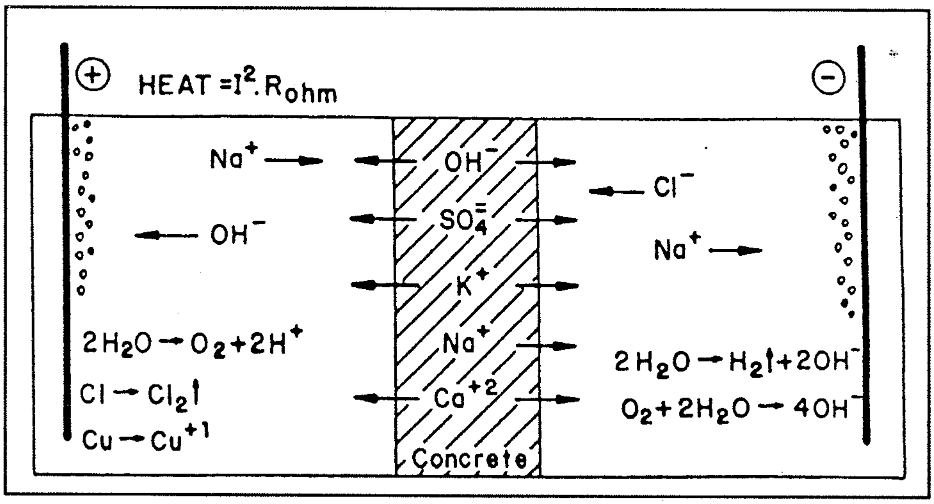


Figure 3-19. The ion migration and other phenomena in a concrete specimen when an electrical field is applied, and the solution in the right hand compartment contains sodium chloride. Andrade et al. [1995a].

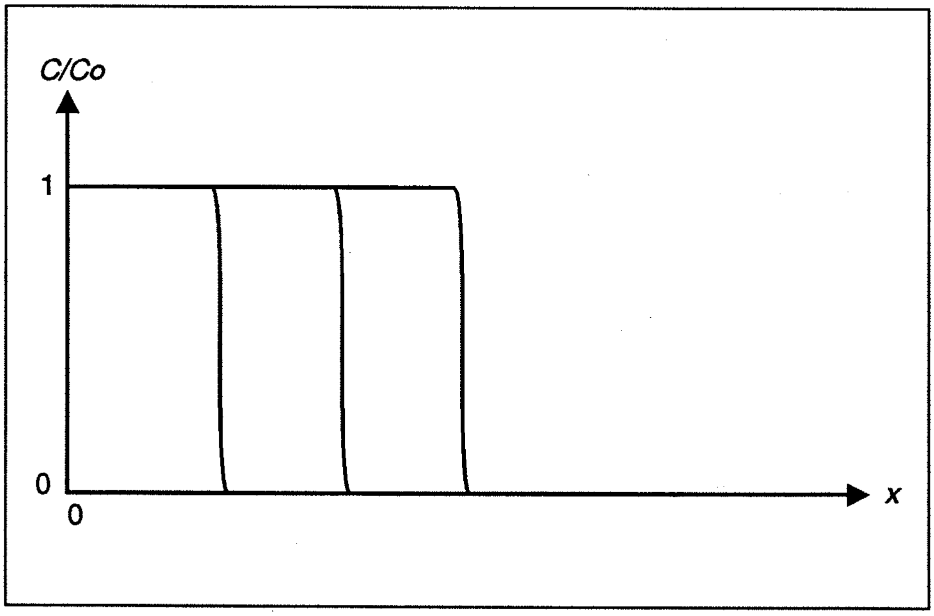


Figure 3-20. Theoretical chloride “profiles” during penetration of chlorides due to pure electrochemical migration without chloride binding or diffusion taken into account.

3.3 Migration

A number of accelerated test methods using electromigration

In recent years a number of accelerated test methods for chloride penetration have been developed in which an electrical field is applied to specimens. Additionally, in applications concerning chloride removal, repair methods use an electrical field to transport chloride ions out of a chloride contaminated concrete. Only the first matter will be treated here.

In these applications chloride ions move by migration or electrodiffusion. This section presents the present models of how to describe chloride migration in an electrical field. The first part of the presentation is to a large extent based on Andrade et al. [1995a].

The phenomena that occur in and around a concrete specimen when an electrical field is applied, are displayed in figure 3-19.

The electrical field affects the direction of movement of the ions in such a way that they move towards the electrode of opposite sign. Additionally the movement is accelerated compared with pure diffusion. This means that some of the ions will move towards a concentration gradient. For large electrical potential gradients, the current will produce a lot of heat that will raise the temperature of the concrete.

Each type of ion carries a portion of the total current i that is proportional to the concentration c_j of that ion and, its electrical charge z_j and its ionic conductivity λ_j. That portion i_j in a particular electrolyte is called the transference number t_j of the ion

$$t_j = \frac{i_j}{i} = \frac{z_j\, c_j\, \lambda_j}{\Sigma z\, c\, \lambda} \qquad (3.3:1)$$

The Nernst-Planck equation

The Nernst-Planck equation gives the total flow F of each ion

$$F_j = -D_j \frac{\partial c_j}{\partial x} + \frac{z_j F}{RT} D_j\, c_j \frac{\partial E}{\partial x} + c_j F_w \qquad (3.3:2)$$

E is the electrical potential, $\partial E/\partial x$ is the electrical potential gradient, and T is the absolute temperature. The physical constants are Faraday number F and the gas constant R.

D is the diffusion coefficient D_{F1} for ion j. F_w is the flow of the electrolyte, usually water. The last term gives the convection and is neglected in this chapter, see next section.

The ion concentrations are of course the concentration of free ions c'_f in kg/m^3 of solution.

The diffusion term may easily become insignificant

The diffusion term is insignificant if the potential gradient is higher than about 10-20 V/m. The pure electrical migration is then given by

$$F_j = \frac{z_j F}{RT} D_j\, c_j \frac{\partial E}{\partial x} \qquad (3.3:3)$$

The mass balance equation for migration without binding

If binding is not considered, the chloride profiles during penetration by electrical migration will follow from the mass balance equation with the flow description according to (3.3:3)

$$\frac{\partial c_f}{\partial t} = -\frac{\partial}{\partial x} F_j = \frac{\partial}{\partial x}\left(\frac{z_j F}{RT} D_j\, c_j \frac{\partial E}{\partial x}\right) = k \cdot D_{F1} \cdot \frac{\partial c'_f}{\partial x} \qquad (3.3:4)$$

Figure 3-21. The chloride profiles measured by Hauck [1993] after close to steady-state conditions were reached in migration tests.

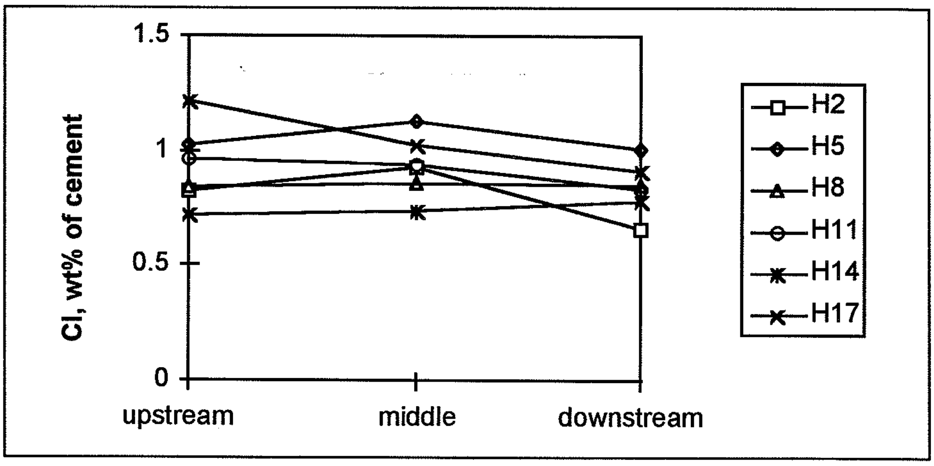


Figure 3-22. Theoretical chloride profiles during migration with the diffusion term having a significant contribution.

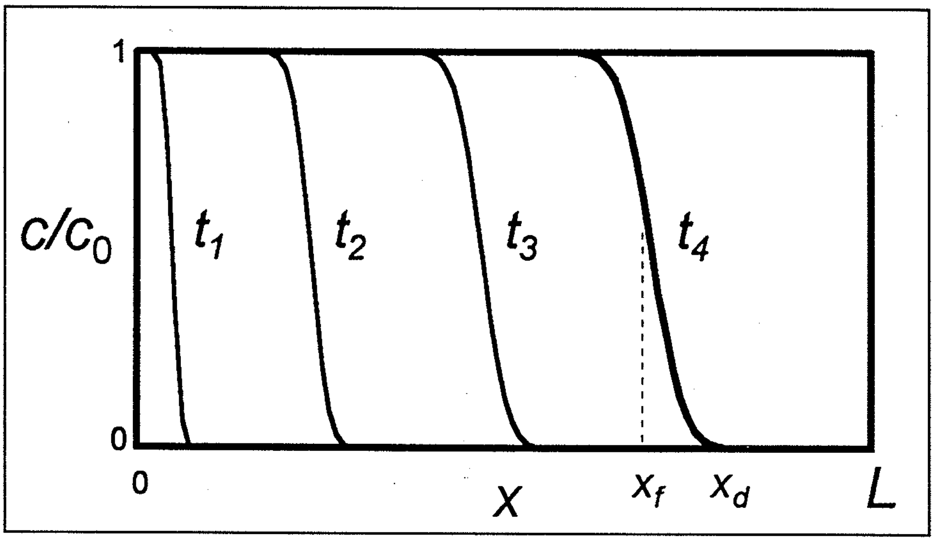
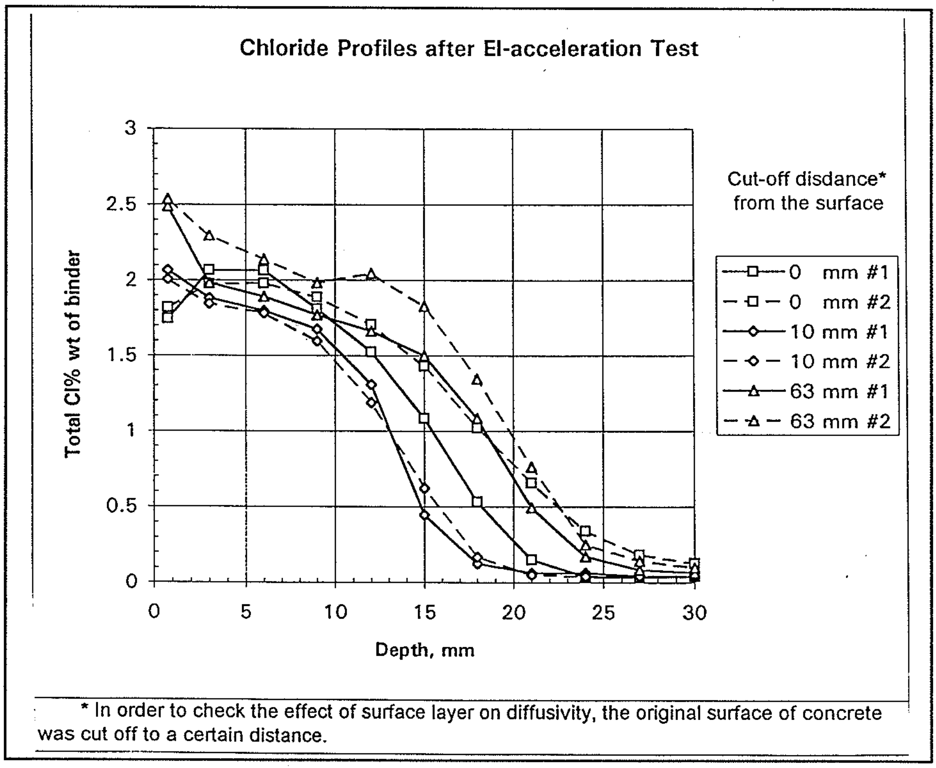


Figure 3-23. Measured total chloride profiles after non-steady state migration tests. Tang [1995d].



* In order to check the effect of surface layer on diffusivity, the original surface of concrete was cut off to a certain distance.

if the electrical potential gradient is constant E/δ throughout the concrete. The constant is $k=zFE/RT\delta$.

Theoretically a chloride front is passing through the concrete

The solution to this equation gives the chloride profiles during electrical migration, when diffusion and binding are neglected. Since the concentration on the left hand side in (3.3:4) is per volume of the material and on the right hand side per volume of solvent, a factor corresponding to that part of the porosity that acts as a solvent p_{sol}, is introduced, cf. Section 3.2.2. The solution will be

$$x(c') = k \cdot \frac{D_{F1}}{p_{sol}} \cdot t \qquad (3.3:5)$$

or simply a chloride front penetrating through the concrete, cf. figure 3-20, with a chloride concentration equal to the concentration in the solution at the concrete surface.

Hauck [1993] measured the chloride profiles through a slice of concrete after steady-state conditions had been reached. Her results are shown in figure 3-21.

Obviously (3:3:4) correctly describes the profiles during steady-state migration; with the left hand side equal to zero, the right hand side gives a slope of the chloride profile equal to zero, i.e. a constant concentration. Eventually the chloride content will approach a constant concentration throughout the material when chlorides are driven in by pure migration.

Simultaneous diffusion will make the front less steep

If the diffusion term in (3.3:2) is taken into account, the front will not be as steep as in figure 3-20, cf. figure 3-22.

The chloride front will have a reversed s-shape and a certain slope depending on the relation between the potential gradient and the diffusion coefficient.

Andrade et al published a number of papers which claim that profiles would be error-function like, Andrade, [1993,1995a]. Those ideas are obviously based on a mathematical misunderstanding of (3.3:2).

The profiles shown in figure 3-22, however, are not what we find in measurements after a non-steady state migration measurement, cf. figure 3-23.

During the penetration by migration, chloride binding will occur. That means that the concentration of free chlorides will drop with depth but that the binding will increase the total amount of chlorides. The rate of binding will be limited and the usual binding isotherms will hardly be applicable. The effect of the rate of binding is shown in figure 3-24, Tang & Nilsson [1995b]

The rate of binding will affect the chloride profiles during migration

It is seen from figure 3-24 that the rate of binding has a decisive effect on the chloride profile. The higher the binding rate, the more the profiles deviate from the front-like distribution in figure 3-20. The penetration depth of those chlorides that penetrate fastest, however, is more or less constant for the binding rates in figure 3-24.

For a very high binding rate, the penetration depth must be reduced. If an "instant" binding is assumed, but the migration is assumed to be so dominant that the concentration c_1 is maintained in the pore water, one gets, cf. figure 3-25,

Figure 3-24. The chloride profiles during migration if binding with different rates is considered.

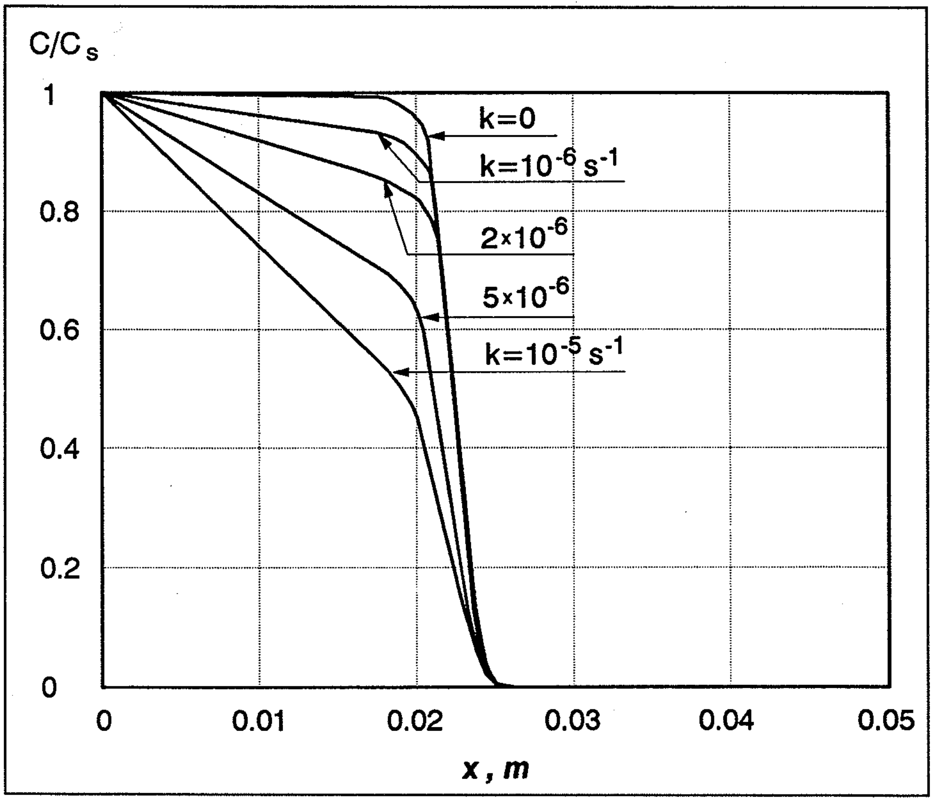
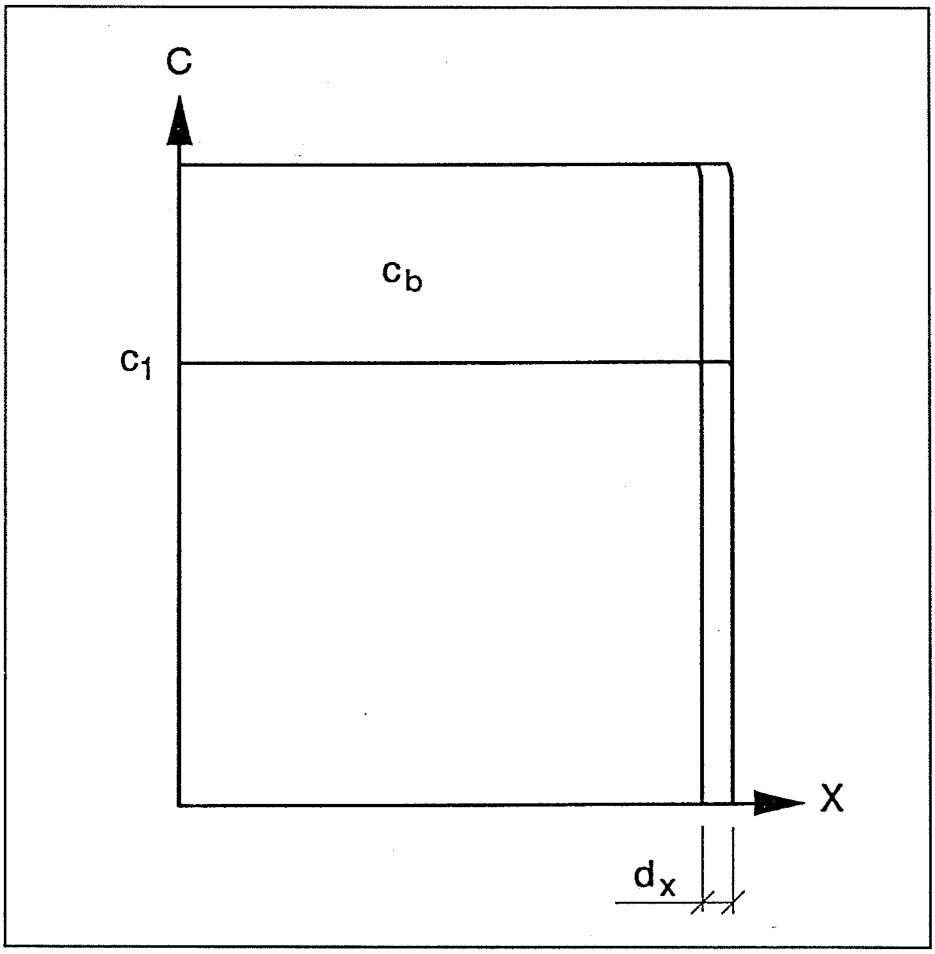


Figure 3-25. Hypothetical distributions of free and bound chlorides during migration to a certain depth if the flux dominates over an "instant" binding.



$$x(c') = k \cdot \frac{D_{F1}}{p_{sol}\left(1+\frac{c_b(c_1)}{c_1}\right)} t \qquad (3.3{:}7)$$

where the total binding capacity in the interval (0; c_1) is considered.

In reality the binding will reduce the concentration of free chlorides during migration, causing chloride profiles similar to the ones in figure 3-24. It is not yet quite clear theoretically which binding capacity to use in (3.3:7). Further work is needed to clarify these matters.

A comparison of predicted chloride profiles with measured ones needs the addition of the bound chlorides to the profiles shown in figure 3-25. Input data for those types of calculation models are still not available. Two kinds of problems are involved. The first is the lack of knowledge of the rate of binding during a migration penetration. The second problem is that the profiles that are measured after a migration experiment, are the profiles of the total amount of chlorides some time after the termination of the test. During the time between the end of the experiment, when the electrical field is removed, and the time when the analysis is done, further binding has occurred. Consequently, by the time the profiles are measured, the profiles of free and bound chlorides may have changed.

Other ions will move during migration of chlorides; uncertainties remain

Additionally, other ions will move during a migration experiment, influencing the migration itself, chloride binding and the chloride profiles. A lot of work remains to be done before we can predict the profiles accurately during migration. Until that is done, uncertainties remain on results gained from such experiments.

3.4 Combined transport

Convective flow of chlorides may be rapid

The diffusion of ions is a very slow process. Much more rapid is a convective flow of ions that moves with water or moisture in the pore system. When the pore system is not saturated with water, the diffusion of ions will have limited paths to proceed in. Once the moisture content drops below a limit where the continuous water paths cease to exist, the movement of ions, whether by diffusion or convection, is no longer possible. If the moisture flow continues as vapour flow, the chlorides will accumulate in the evaporation zone.

In most applications diffusion and convection processes are combined in different ways. In this section, the phenomena to consider are first presented together with a few examples of relevant observations. The models for mathematical description of the combined processes are then shown. Finally the current lack of knowledge is described.

3.4.1 Water flow and convection

Convection or advection

A saturated water flow due to pressure gradients moves an amount of ions that is proportional to the water flow and the concentration of ions in the pore water. This movement of ions is called convection or advection. The chloride flow is simply described by

$$F_{Cl} = \frac{c_f}{\rho_w} \cdot F_w \qquad (3.4{:}1)$$

where c_f is the concentration of free chlorides in the pore water, ρ_w is the density of water and F_w [kg/(m^{2}s)] is the flow of water.

Figure 3-26. Profiles of moisture and chlorides after a capillary suction of a salt solution. Volkwein [1991].

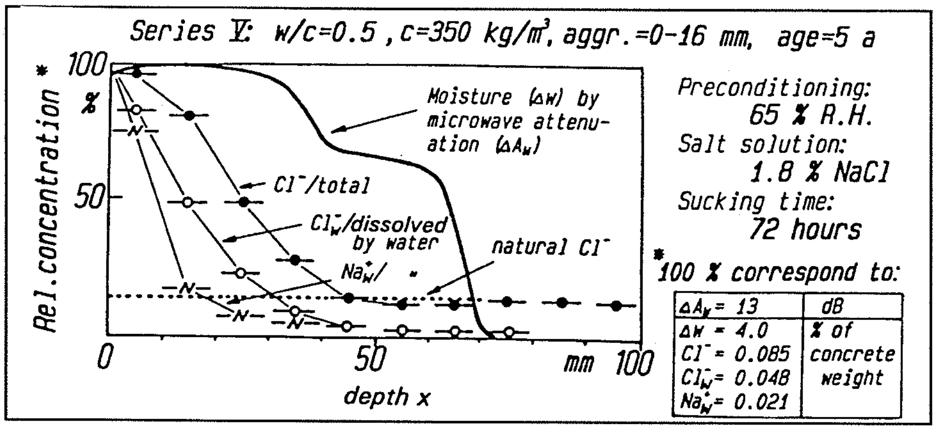


Figure 3-27. Moisture and salt distributions before and after a capillary suction from a salt solution.

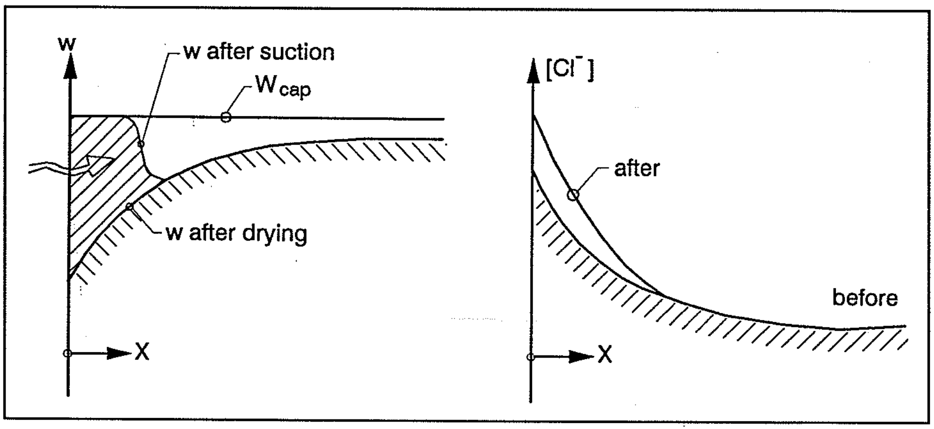
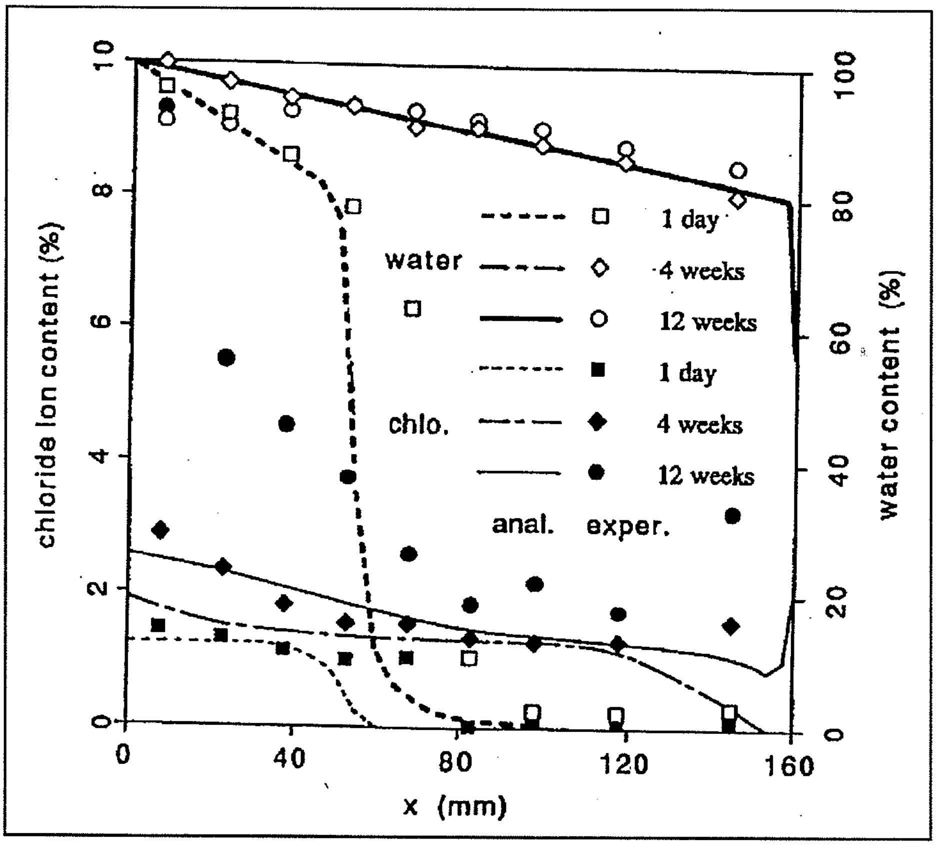


Figure 3-28. Profiles of salt content after capillary suction of a salt solution.
Akita & Fujiwara [1995].



If the flow is continuous, and no evaporation occurs, there should be no deposition of chlorides in the concrete except for those chlorides that will be bound to equilibrium with the chlorides in the pore water.

3.4.2 Capillary suction of a salt solution

A special case of moisture or water flow is a capillary suction from a salt solution in contact with the concrete surface. This will only happen if the concrete has been dried to some extent.

The amount of chlorides sucked into the concrete, Q [kg/m^2], depends on the salt concentration, c [kg/m^3], the duration of suction, t [s], and the "coefficient of capillarity", A [kg/(m$^2\sqrt{\text{s}}$)]

$$Q_{Cl}(t) = \frac{c_f}{\rho_w} \cdot A\sqrt{t} \tag{3.4:2}$$

The coefficient of capillarity depends on the moisture distribution in the concrete. The coefficient is greater for a dry concrete surface. The coefficient also depends on the salt concentration, Schimmelwitz et al. [1982], at least at high concentrations.

Binding will affect the chloride profiles during capillary suction of a salt solution

The distribution of chlorides during capillary suction of a salt solution will be highly affected by chloride binding. The binding will "filter" the salt solution from some of the passing chlorides and the concentration of chlorides in the penetrating salt solution will drop with depth. Volkwein [1991] showed this in a famous experiment, cf. figure 3-26.

The changes in the distribution of chlorides, after the capillary suction of a salt solution has stopped, depend on

- the dissolution, binding and movement of chlorides already present in the concrete
- the changes in the distribution of moisture

Moisture distribution after the suction

The moisture content after the suction should be close to an amount corresponding to capillary saturation to a depth that has been reached by the suction, cf. figure 3-27.

Redistribution of moisture and chlorides

When the suction has stopped a further inwards moisture flow will occur moving the chlorides deeper into the concrete. This will continue until the moisture content drops below the "critical moisture content" where the liquid paths begin to be discontinuous. Simultaneously an evaporation will start at the surface, causing a moisture flow to the surface and an increase in salt content near the surface.

The effect of capillary suction has been investigated by Tuutti [1982]. Before exposure to a salt solution the specimens had dried to different humidities. The effect was still clearly visible after two months of continuous suction from a salt solution.

Akita & Fujiwara [1995] treated capillary suction from a salt solution experimentally and theoretically. They measured the distribution of water and chlorides after 1 day, 4 weeks and 12 weeks of suction for specimens that were oven-dried, room-dried or wet. Figure 3-28 gives an example of their results. To fit calculations and experiments a number of assumptions are made. Moisture flow is assumed to be independent of salt conditions. A strange depth dependence of the moisture flow properties is used.

They conclude that there still is a lack of experimental data and identify some inconsistencies between data previously reported. The chloride

Figure 3-29. Chloride profiles from moisture flow and evaporation. Tuutti [1982].

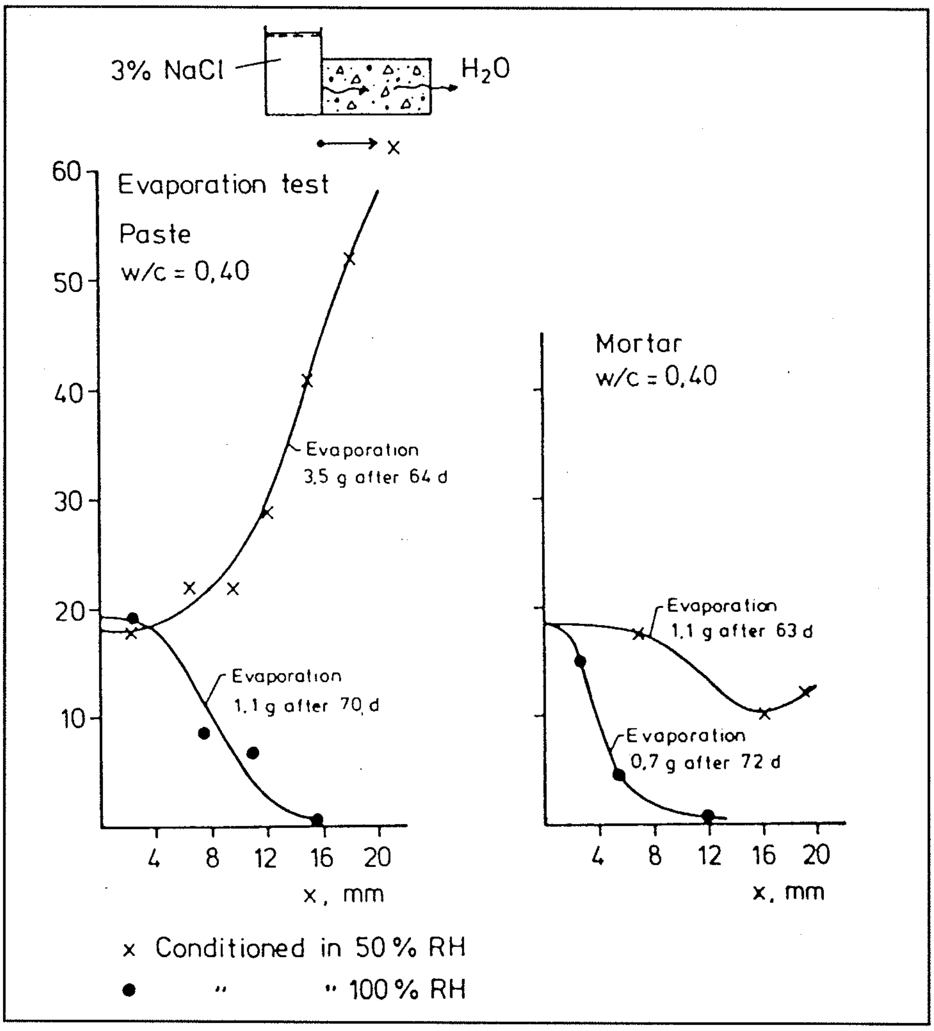
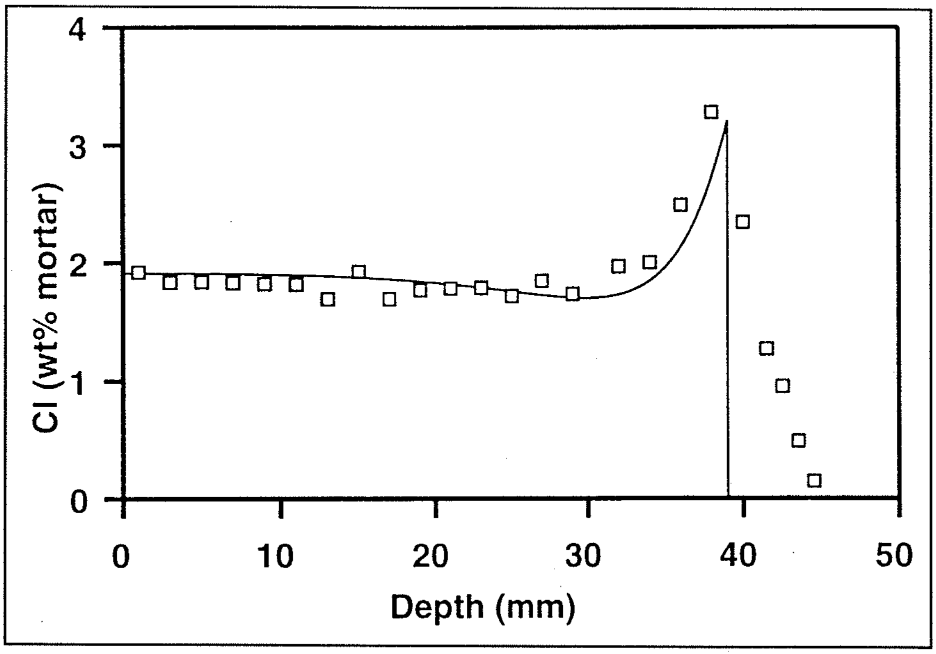


Figure 3-30. Measured and predicted chloride profiles during close to steady-state moisture flow and evaporation. Buenfeld et al. [1995].



binding properties are shown to be decisive for the predictions. They also acknowledge the importance of a more accurate analysis of moisture movement.

3.4.3 "Hydration suction"

If the curing water contains chlorides or the structure is exposed to salt water very early, the salt may penetrate deep into the young concrete since its permeability is high and the contraction sucks water into the young concrete. Kay et al. [1981] show an example. Volkwein [1991] calls this process "hydration suction".

Hydration suction should be very limited for high quality concrete

The total amount of chlorides that can be penetrated by this process must be limited to the amount of chlorides dissolved in the solution that is sucked into the concrete. It should be possible to predict the distribution of those chlorides into free and bound chlorides during and after the process has terminated or slowed down by taking the binding properties into account.

3.4.4 Moisture flow and evaporation

A non-saturated water flow, a moisture flow, usually causes internal evaporation. Some, or all, of the migrating water evaporates and continues as water vapour flow. The chlorides will deposit at the site of that kind of evaporation causing the concentration of ions to increase. The increase in chloride content is proportional to the amount of evaporation but the distribution of chloride concentration is influenced by a certain counterdiffusion. An example is shown in figure 3-29.

A moisture flow in both liquid and vapour phase is influenced by differences in salt concentrations. If the moisture flow causes changes in the salt concentration, the moisture flow will change.

Wick action is predictable

Buenfeld et al. [1995] studied the transport of chlorides due to "wick action", the movement of salt by the suction of the salt solution and evaporation at some depth. They also predicted the chloride and moisture flows and distribution, see the example in figure 3-30.

Such simple moisture and chloride flow descriptions as Buenfeld et al used seem to be accurate enough for some applications, at least for steady-state conditions. Models for the combined effect of moisture transport, evaporation and chloride transport under non-steady state conditions have not yet been developed.

Chloride convection close to a sea water table

Tang [1994] made a thorough study of the chloride distribution at different levels above an artificial sea water table in the laboratory, with and without tidal cycles. With a tidal cycle frequency of once a week, the chloride profiles in the tidal zone were very similar to the ones in the submerged zone, with one exception. Very close to the constant water table, the concentrations of chlorides were almost twice as high, see the example in figure 3-31.

Probably, close to the water table, there is a two dimensional moisture flow convecting chlorides from the submerged zone in the outer millimetres of the concrete. Due to the evaporation, they are deposited close to the surface. At a larger distance from the water table, the flow is more one-dimensional in and out of the concrete.

A number of similar, more one-dimensional, drying and wetting experiments are found in the literature. Repeated drying and wetting, by a salt solution, promotes the convection of chlorides into the concrete, if the concrete surface has time to dry, i.e. the frequency is not too short. Dry-

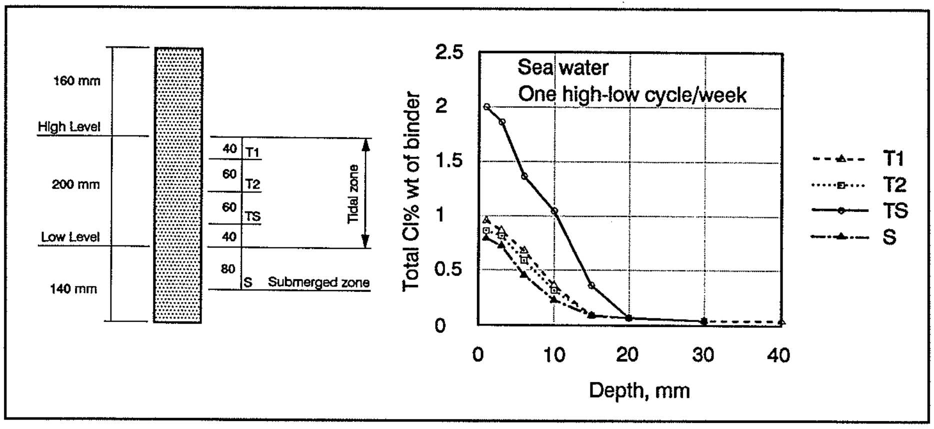


Figure 3-31. Chloride profiles at different levels in the tidal zone with a frequency of one cycle a week. Tang [1994].

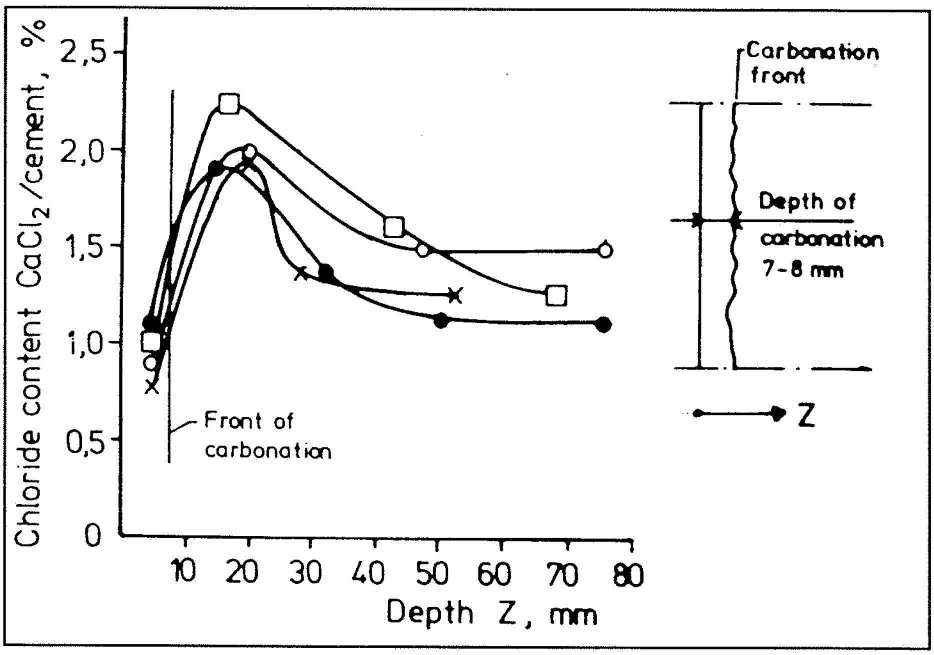


Figure 3-32. Chloride profile in a partially carbonated concrete. Tuutti [1982].

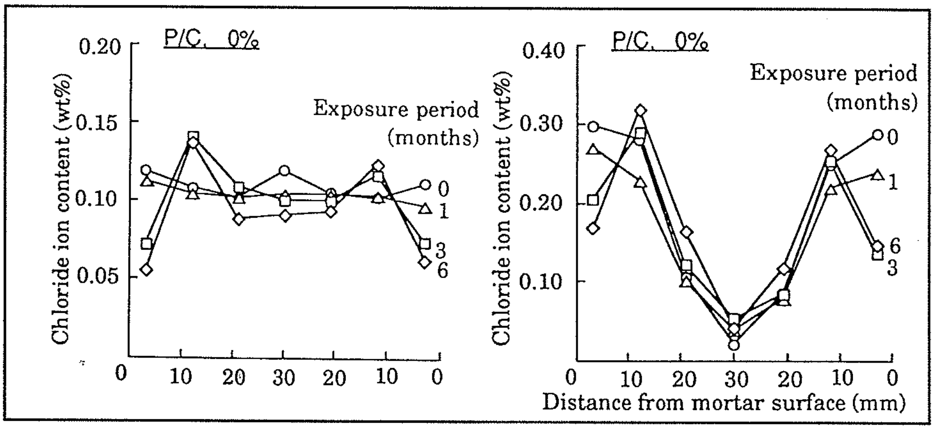


Figure 3-33. Profiles of chlorides during drying in 80 % RH; chlorides mixed in (left) or chloride immersion (right). Ohama et al. [1995].

ing conditions, on the other hand, will permit the occurrence of carbonation, that will dramatically change the chloride profiles, see the next section.

3.4.5 Carbonation and chloride penetration

Carbonation should not be a problem in high quality concrete. In short term drying and wetting tests, in the laboratory or in the field, where the chloride profiles are close to the surface and accurately measured, carbonation could interact with the chloride binding, moisture movement and chloride penetration.

In tests with high *w/c*-ratios carbonation would certainly affect the chloride profiles.

Carbonation completely alters a chloride profile

Tuutti [1982] demonstrated the extreme effect of carbonation on chloride binding, cf. figure 3-32 and section 3.1.5.

Tsutsimi et al. [1995] found a similar explanation for a chloride profile in a 25 year old bridge exposed to de-icing salts. Kamiya et al. [1995] observed a similar drop in the surface near region of chloride profiles for concretes with $w/c \geq 0.55$ but not for better concretes.

Carbonation is probably the explanation of the findings by Ohama et al. [1995] who tested mortars with w/c=0.75 by immersion or by mixing in the chlorides. Chloride profiles were measured before and during drying in two drying climates. At 50% RH the profiles did not change during drying but at 80 % RH chlorides are "moved" inwards during the drying process, cf. figure 3-33.

The effect of drying on chloride profiles may be mainly a carbonation effect

The concentration of chlorides in the tests is probably so low that more or less all the chlorides are bound. That would explain why the chlorides do not move during drying. At the surfaces, however, a probable carbonation of some millimetres changes the chloride binding and the free chlorides diffuse inwards provided the pores are water-filled. It seems as if 80% RH provides these conditions but 50% RH does not. Carbonation naturally also occurs in the dry climate but the liberated chlorides have no water paths to diffuse in.

3.4.6 Mathematical models for chloride and moisture changes

All the phenomena described above may be predicted by calculating the moisture flow and the chloride diffusion and convection. From that information, the changes in moisture and chloride distribution may be predicted.

(3.4.6.1) *Moisture transport description*

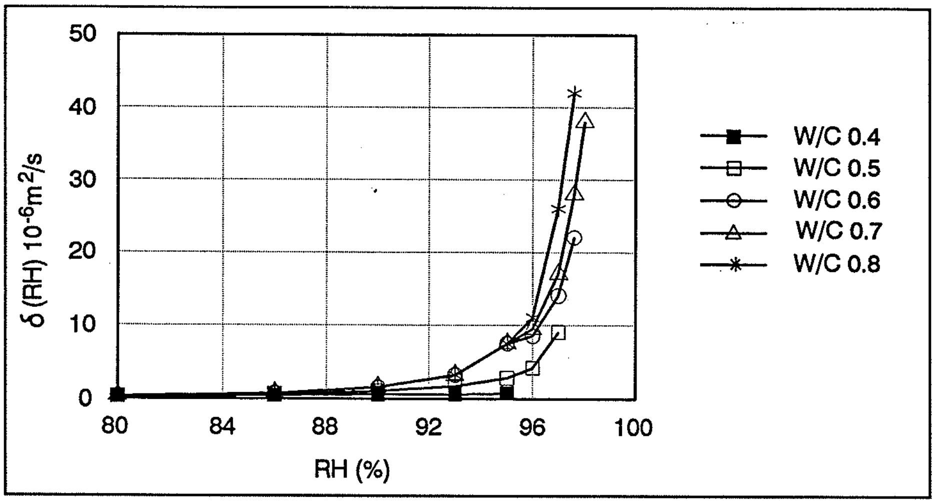
The total moisture flow F_m must be described by two terms, one describing the liquid (water) flow F_w that can carry chloride ions and one that describes the vapour flow F_v

$$F_m = F_w + F_v \qquad (3.4:3)$$

The choice of describing moisture flow depends on available data

These flow terms can be described in a number of ways. The choice of description more or less depends on the kind of measured data that is available. With a proper choice of description, lack of data may be estimated.

Figure 3-34. Moisture flow coefficients from Hedenblad [1993].



The total moisture flow, for pore water without chlorides, is commonly described by a moisture conductivity and the vapour content as moisture flow potential

$$F_m = -\delta_m \cdot \frac{\partial c_v}{\partial x} = -(\delta_w + \delta_v) \cdot \frac{\partial c_v}{\partial x} \tag{3.4:4}$$

The vapour flow coefficient is usually regarded as more or less constant. The liquid flow coefficient, however, depends very much on the moisture content or RH in the pore system. Examples of total moisture flow coefficients are shown in figure 3-34, Hedenblad [1993].

Other ways of describing the moisture flows can always be translated into the description in (3.4:4) by common moisture theory.

Chlorides seems to have little effect on liquid flow

The effect of chlorides on the moisture flow has been studied to some extent. Perrin & Bonnet [1995] found no effect of chloride concentration on liquid water transport. Buenfeld et al. [1995] could describe capillary suction of a salt solution without considering the chloride concentration.

The relative humidity, and consequently the vapour content, will be affected by the concentration of chlorides dissolved in the pore solution. RH will drop when the chloride concentration increases. A saturated solution of NaCl would reduce RH to 75 % in a saturated pore system.

Vapour flow will be greatly dependent on chloride concentration

This means that the vapour content is not a proper choice of potential for the liquid flow as in (3.4:4) when the pore water contains chlorides. The pore water pressure P_w should be used instead, with a water permeability k_P expressing the liquid flow

$$F_w = -k_P \frac{\partial P_w}{\partial x} \tag{3.4:5}$$

For the vapour flow, the last term in (3.4:4) would be suitable. However, no data is available, that really separates the two coefficients for vapour and liquid flow, at all levels of moisture contents, not even for pure pore water without chlorides. Only the total moisture flow coefficients have been measured, cf. figure 3-34. In some cases the total moisture flow is described as vapour and liquid flow using only one term at a time, assuming that vapour and liquid flow occur in different parts of the material. However, a reasonable separation into *two* terms should be possible from data like in figure 3-34, since only vapour flow occurs at low RH and the pure vapour flow should decrease to some extent at higher RH due to moisture blocking the pores. Still no verification exists to show that it works. However, a number of measurements give some information on non-saturated moisture flow processes. Baroghel-Bouny [1995] measured absorption of vapour from air with 95 % RH for saturated paste and concrete specimens. Buenfeld et al. [1995] used vapour content as driving potential for the non-saturated moisture flow and could fit measured profiles.

Experiments indicate a critical limit for convection of chlorides

The problem of describing moisture flow, however, is not only a question of separating vapour and liquid flow. Only liquid flow that occurs in continuous liquid paths will allow chlorides to be convected and to diffuse. The important thing is to find a proper way of describing that limit in RH, moisture content or degree of capillary saturation. A few observations indicate that chloride convection with moisture flow ceases around 75-80 % RH, Buenfeld et al. [1995], Baroghel-Bouny [1995] and others.

Chloride transport description

The diffusion of chloride ions in a non-saturated pore system will of course be reduced compared with diffusion in saturated concrete. The diffusion must be described by the concentration of free chlorides in the pore solution and a diffusion coefficient that includes the effect of a non-saturated pore system, i.e. a function of the content of pore water acting as a solvent w_{sol}. Adding the convection of chlorides, one gets

$$F_{Cl} = -D_{F1}(c_f', w_{sol})\frac{\partial c_f'}{\partial x} + \frac{c_f'}{\rho_w}F_w \qquad (3.4:6)$$

Mass balance equations

The change in moisture conditions with time is given by the mass balance equation for moisture

$$\frac{\partial w_e}{\partial t} = -\frac{\partial F_m}{\partial x} - \frac{\partial w_n}{\partial t} \qquad (3.4:7)$$

where the last term, the chemical fixation of water by cement hydration, is significant only in hardening concrete. If only the moisture flow can be described, this equation can be solved for relevant initial and boundary conditions. Even self-desiccation may be included in the solution, Norling-Mjörnell [1994].

Mass balance for chlorides in the pore solution

The changes in the chloride distribution with time, including convection and moisture changes, are given by the mass balance equation for the chlorides in the pore solution. For concentrations below the solubility limit, one gets

$$\frac{\partial c_f'}{\partial t} = \frac{\rho_w}{w_{sol}}\left(-\frac{\partial F_{Cl}}{\partial x} - \frac{\partial c_b}{\partial t}\right) - \frac{c_f'}{w_{sol}}\frac{\partial w_{sol}}{\partial t} \qquad (3.4:8)$$

This is another way of describing the equations of Johannesson [1995].

By solving these two equations simultaneously, the moisture and chloride profiles for combined transport processes may be derived for any of the applications mentioned above. The temperature conditions should be included in that process since some of the parts included are temperature dependent.

3.4.7 Description of boundary conditions

The solutions, however, require that the boundary conditions for moisture and chlorides are defined. For structures exposed to natural climate we have large gaps in quantitative knowledge and understanding of these conditions.

Macro climate, undisturbed by the structure

A lot of parameters in the macro climate, undisturbed by the concrete structure, are available from meteorological observations of

- air temperature
- air humidity
- solar radiation
- rain and driving rain; amount, duration, direction
- wind conditions; velocities and direction
- sea water temperatures

- sea water temperatures
- wave heights and directions.

For structures exposed to de-icing salts, the frequency of salting and amounts of salt spread may be relevant macro "climatic" parameters together with traffic data such as traffic intensity and speed.

Meso climate depends on the structure

The macro climatic parameters may be used to estimate the meso climate, influenced by the topography around the structure and the geometry of the structure. Finally the effect of detailing of parts of the structure and the properties of the concrete surface will give the boundary conditions, the micro climate at the surface.

Micro climate

The microclimate should be expressed in terms of

- equivalent air temperature
- concrete surface humidity
- wetness; time and duration
- concrete surface chloride conditions: concentration, occurrence and duration.

Very little quantitative data exists for concrete structures exposed to chlorides and micro climatic models are rare. Instead some empirical data relating to chloride surface concentrations from curve-fitted chloride profiles have been reported for some structures and environments. This is further treated in Section 5.6.

3.4.8 Lack of information

The quantification of these combined processes is not yet fully possible. A lot of data has to be collected and better understanding is needed before this will be possible. We need more information on

- water permeability of the particular concrete.
- moisture flow coefficients and their dependence on moisture and chloride concentration.
- critical moisture content for continuous liquid paths or preferably a moisture flow description that separates liquid and vapour flow.
- data on the environmental conditions (humidity, time of wetness, concentration of salt solutions, temperature, etc.)
- a model for predicting a simultaneous movement of salt water, water vapour, ions including the deposition and dissolution of ions, not only the chlorides.
- chloride binding capacity and binding rate.

3.5 Percolation models

The structure and distribution of the pore system in concrete have a decisive significance for permeability. The connectivity of the pore system is a very important factor. The concept of connectivity covers a description of the degree of continuity in the pore system. The connectivity of both the pore system and the porous hydration products is of great importance for diffusion processes like chloride diffusion into concrete. The diffusion rate will be gradually more and more controlled by the transport through gel pores as the capillary pore system loses its connectivity during the hydration process, cf. Bentz et al. [1991].

3.5.1 Limited connectivity

Nearly every model used today to describe the properties of concrete is based on the assumption that the pore structure is continuous and homogeneously distributed in the concrete. There is no reason to question this assumption when dealing with concrete without pozzolans and with *w/c* ratios above 0.45-0.50. The striving towards more and more durable concrete during the last decades has lead to addition of pozzolans and reduced *w/c* ratios. In this way the permeability of modern concrete types is substantially improved compared with more traditional concrete types.

Observations, of which some are reported later, imply that it is not possible to extrapolate the property models based on a continuous and homogeneously distributed pore structure to cover all the modern concrete types.

In cases where the pore system in concrete cannot be described as a continuous and homogeneous structure, the foundation of the property models used so far is removed. Additionally, this means that most of the test results for transport properties produced using many of the generally accepted test methods will not be valid.

3.5.2 Observations on limited connectivity

Balaguru et al. [1988] have reported that chloride penetration into two dense concrete types exposed in 8% sodium chloride solution almost ceased after exposure in the laboratory for 1 month.

It is often reported that chloride ingress in seawater exposed structures has a tendency to be overestimated by use of Fick's laws or even cease. Thomas [1991] has followed chloride penetration into concrete specimens with varying contents of pulverized fly ash. The specimens were placed in the tidal zone for several years. No increase of the chloride content in depths below 10 mm could be observed between 1 and 2 years exposure for the specimens with a PFA content of 30 % or more (by mass of binder). Similar results have been observed by Zhang et al. [1990] for concrete specimens exposed in the tidal zone for up to 5 years.

Hansson [1987] has tested an extremely impermeable microsilica modified cement paste known as Densit. Diffusion cell tests showed no penetration of chlorides through 2-3 mm thick slices during an exposure period of more than 4 months.

3.5.3 Percolation theory

The percolation theory can be considered as a tool to describe the connectivity of structures built of small units. The percolation theory is generally considered to originate from a paper by Broadbent & Hammersley [1957]. The theory is named in this paper where they discuss the general situation of a "fluid" spreading randomly through a "medium".

Later Hammersley [1983] gives his personal review of the early work with the percolation theory. Here Hammersley emphasizes that the random spreading can find expression in two quite different situations. The first situation is the well-known diffusion process, where the randomness is expressed as "random walks" of the "fluid" through the "medium". The second situation is named "percolation process" by Hammersley, because this type is comparable to the situation where water is passed through the coffee in a percolator. In this situation the randomness is kind of built into the "medium".

Often there is no distinct separation between percolation processes and diffusion processes. An example is the diffusion of particles from a source. The resulting diffusion front has a geometric structure very closely related to the fractal geometry of percolation processes, cf. Sapoval et al. [1985].

Much literature has already been written on the subject "percolation theory". Stauffer [1985] has written a good introduction, where further references can be found.

3.5.4 Percolation models for chloride penetration

So far, the percolation models describing chloride penetration into concrete have not been developed to a level where they can find practical applications in predicting chloride ingress.

Figure 4-1. Results from round robin tests on Volhard titration. Reknes [1994] and AEC [1992a].

Volhard titration - round robin tests										
Original content	0.0225	0.0474	0.0731	0.1681	0.3000	0.0225	0.0474	0.0731	0.1681	0.3000
Lab	Chloride content in % by mass of concrete					Error in % by original content				
A	0.023	0.046	0.072	0.172		2.2	-3.0	-1.5	2.3	
A	0.022	0.045	0.072	0.173		-2.2	-5.1	-1.5	2.9	
B	0.020	0.050	0.070	0.170		-11.1	5.5	-4.2	1.1	
C	0.024	0.038	0.068	0.097		8.0	-20.0	-6.4	-42.1	
C	0.027	0.056	0.062	0.170		17.8	17.3	-15.7	1.0	
D	0.028	0.043	0.069	0.171		26.2	-8.6	-5.3	1.7	
D	0.028	0.043	0.071	0.170		26.2	-8.6	-2.9	1.4	
D	0.029	0.044	0.071	0.170		26.7	-7.4	-3.0	1.4	
E					0.304					1.4
E					0.299					-0.3
E					0.296					-1.4
E					0.304					1.3
F					0.308					2.7
F					0.306					2.0
F					0.294					-2.0
F					0.308					2.7
F					0.311					3.7
F					0.294					-2.0
F					0.309					3.0
F					0.314					4.7
F					0.290					-3.3
F					0.299					-0.3

4 Test methods

Overviews of test methods for chloride penetration were recently presented by e.g. Tang et al. [1995], Andrade [1995a] and Gjørv & Sakai [1995]. In this chapter methods of measuring chloride contents and methods of measuring chloride transport properties are reviewed and commented upon.

Test results may not be applicable for predictions

It should be realised that results from laboratory test methods may not directly be used for predictions. The theories behind the methods are usually very simple and the effects of a number of parameters that influence the test results are not fully understood and quantified. Some research is needed to somewhat improve the methods and to improve the accuracy in the utilization of the test results.

Most test results are used for comparing concretes

Most of the test methods are used to make comparisons. Different concrete compositions or binders are compared but the relevance of such a comparison must of course be judged in the light of the test results. A "better" concrete in a test may not necessarily have a higher chloride resistance in practice! It depends on the test conditions and the conditions in the application in question.

4.1 *Chloride content analysis*

Chloride analysis is a part of nearly all chloride penetration tests

Almost all test methods for determining chloride penetration or diffusivity involve some kind of determination of the chloride content in the test specimen. The Nordic countries have a common standard for determination of the total content of chloride in hardened concrete, cf. Nordtest [1984b]. This reference method is based on Volhard titration.

Several alternative analytical techniques are used to measure the chloride content in hardened concrete: Potentiometric titration, spectrophotometric analysis, ionselective electrodes, Quantab strips, RCT.

4.1.1 Volhard titration

The reference method is Volhard titration

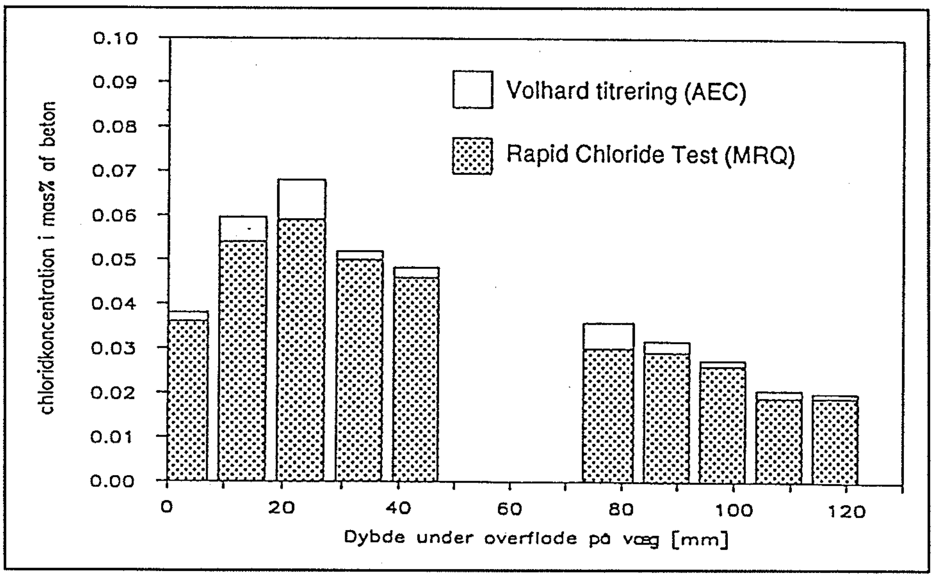
Volhard titration is a reference method for determination of the total acid-soluble chloride content in concrete. The common Nordic standard based on this technique is called NT BUILD 208, cf. Nordtest [1984b]. Each of the Nordic countries have their own corresponding national standard, e.g. DS 423.28 in Denmark, cf. Dansk Standardiseringsråd [1984].

This standard provides reliable test results if the sample size corresponds to a cement content of at least 2 g as required in the standard. Figure 4-1 shows results from two round robin tests, cf. Reknes [1994] and AEClaboratory [1992a]. The precision of the test result mainly depends on the experience and competence of the operator and also on the accuracy of the test equipment.

Diluted titrants improve precision

According to the standard the titration is carried out using solutions of 0.1 N $AgNO_3$ and 0.1 N NH_4SCN. It is possible to use more dilute solutions if a better precision is needed due to small sample sizes or low chloride concentrations.

Figure 4-2. Comparison of test results from measurement of chloride content using Volhard titration and Rapid Chloride Test.



4.1.2 Potentiometric titration

Potentiometry is an important titration method for chloride

Among the most important titration methods is potentiometric titration with silver, cf. Fritz et al. [1979]. The titration of chloride and other anions with silver(I) can be followed potentiometrically with a silver indicator electrode. The potential in volts of an immersed silver electrode is a function of the concentration of silver ions in the solution. In a potentiometric titration, the difference in potential is measured between the silver indicator electrode and a reference electrode whose constant potential is unaffected by the composition of the solution titrated.

Titration of mixtures of halide ions (chloride, bromide and iodide) with silver nitrate will give a separate potentiometric break for each halide ion. Unfortunately this titration is not very accurate, because the more soluble halide will coprecipitate. For example, chloride is coprecipitated during the titration of bromide with silver nitrate, giving high results for bromide and low results for chloride. Fortunately halide ions other than chloride are not normally present in concrete.

The titration method can be refined by replacing the silver indicator electrode by a chloride selective electrode. In this case the measured difference in potential is a function of the chloride concentration in the solution. The titration will be less sensitive to other ions present in the solution.

Potentiometric titration is very accurate

Potentiometric titration is an analytical technique of very good precision, if the operator is skilled and calibration is performed carefully.

4.1.3 Ionselective electrode

Methods using chloride selective electrodes are fast

The use of chloride selective electrodes to measure the chloride content of hardened concrete is a fast method, which is easy to use. For this reason a number of laboratories have tried to apply this technique for standard chloride analyses. However, it is difficult to obtain the same accuracy for this method as for Volhard titration. The reason is that it is very difficult to produce a good calibration curve which covers the whole range of concretes and chloride contents.

Special precausions should be taken against slag cements

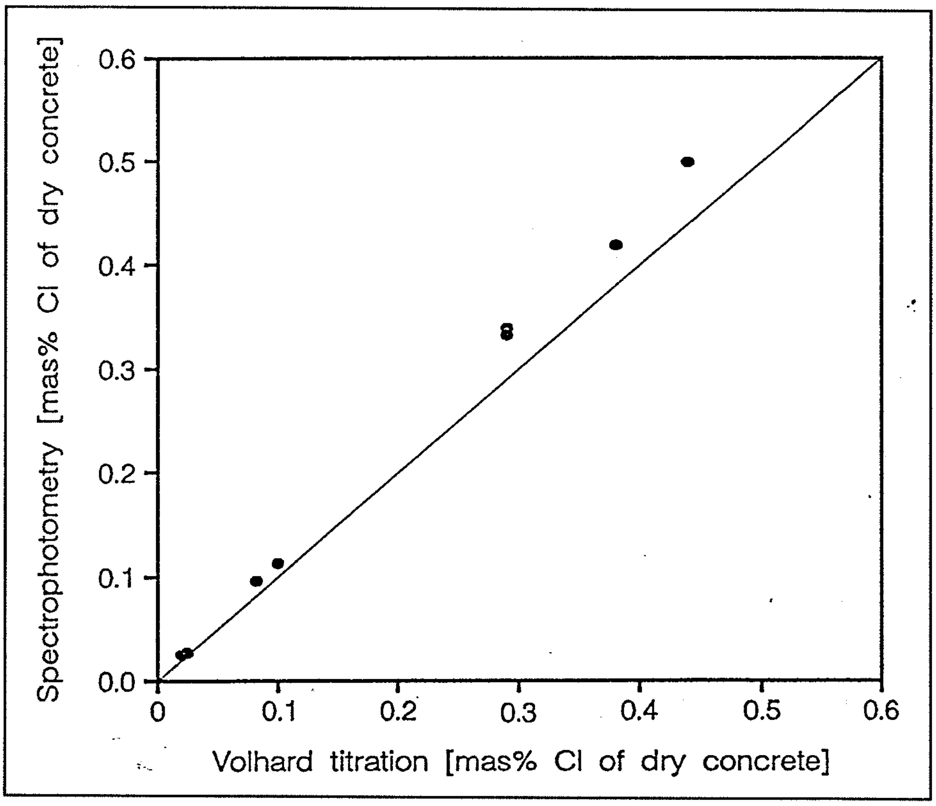
The chloride selective electrodes are interfered with by bromide, iodide, cyanide, and to a smaller degree by ammonium and hydroxide. These compounds are normally not present in sufficient concentrations to interfere in analytical samples prepared from acid digestion of concrete. But sulphide will also interfere. The concentration of sulphide must be kept lower than 10^{-4} M S^{--}. It may be necessary to remove sulphides by e.g. precipitation, especially if the concrete contains slag.

Another problem arises if the sample contains a fairly high background concentration of ions other than sought for (plus its accompanying ion). In such cases it is recommended to add so much of an indifferent salt, e.g. $NaNO_3$, to both standards and samples that the total ionic strength in all events is almost entirely governed by the $NaNO_3$ addition, cf. Radiometer [1982].

Chloride selective electrodes are used in field tests

A commercially available field test method using this technique is called RCT - Rapid Chloride Test, cf. Petersen [1987]. Figure 4-2 shows correlating values from chloride analyses using Volhard titration and RCT. The performance of the RCT method is quite good in this case.

Figure 4-3. Comparison of test results from measurement of chloride content using Volhard titration and spectrophotometry. Sørensen [1994].



4.1.4 Spectrophotometry

Spectrophotometry is an automated colorimetric method to estimate the concentration of a coloured substance in solution. In spectrophotometric analysis, a sample solution in a glass or quartz "cell" is inserted into a spectrophotometer. Radiant energy (ultraviolet, visible, or infrared) of a very narrow (monochromatic) wavelength range is selected from a source by means of a diffraction grating, and the resulting beam is directed at the cell containing the sample. Some of the radiant power incident on the cell is absorbed by the chemical substance(s) in the sample, and the remainder is transmitted. The amount of energy absorbed is proportional to the concentration of the chemical substance(s) absorbing it. This proportionality is the quantitative basis of spectrophotometry, or spectrophotometric methods.

Spectrophotometric methods for determination of macro quantities are often inaccurate

Literally thousands of spectrophotometric methods for analyzing elements and most organic compounds are described in the chemical literature. These methods are usually employed to determine small amounts, or even traces, of substances. They are not normally used to determine macro quantities of substances, because this approach would be somewhat inaccurate and inconvenient due to the dilution needed to reduce the concentration to a sufficient level for the method, cf. Fritz et al. [1979]. Titrimetric techniques are usually preferred in these cases.

The spectrophotometric analysis of chloride can be performed by several methods, cf. Vogel [1978]. One laboratory uses the mercury(II) thiocyanate method, cf. Sørensen [1994]. This method, normally used for the determination of trace amounts of chloride ions, depends upon the displacement of thiocyanate ion from mercury(II) thiocyanate by chloride ion. In the presence of iron(III) ion a highly coloured iron(III) thiocyanate complex is formed:

$$2Cl^- + Hg(SCN)_2 + Fe^{3+} \rightarrow HgCl_2 + \underset{\text{(Brown)}}{2[Fe(SCN)]^{21}}$$

The intensity of its colour is proportional to the original chloride ion concentration. The method is applicable in the range 0.5-100 ppm of chloride ion, which means that the solution from acid digestion must be given a very high degree of dilution.

It seems difficult to obtain a proper calibration for this method. The accuracy does not correspond to those of titration methods, cf. Figure 4-3.

4.1.5 Quantab chloride titrators

Quantab strips are fast but inaccurate

Determination of the chloride content using Quantab chloride titrators must be considered as a field method, which gives fast but not very accurate test results.

According to Miles Laboratories [1979] the Quantab chloride titrator consist of a thin, chemically inert plastic strip. Laminated within the strip is a capillary column impregnated with silver dichromate. When the strip is placed in an aqueous solution, fluid rises in the column by capillary action and continues to progress as long as chloride solution enters the column. The reaction of silver dichromate with chloride produces a white colour change in the capillary column. When the capillary column is completely saturated, a moisture-sensitive signal across the top of the column turns dark blue and the chloride concentration has then been measured as silver chloride. The reaction that takes place in this measurement can be explained by the chemical equation:

$$\begin{array}{lr} Ag_2Cr_2O_7 + 2Cl^- \rightarrow Cr_2O_7^- + 2AgCl & \\ \text{(Brown)} \qquad\qquad\qquad\qquad & \text{(White)} \end{array}$$

The length of the white colour change in the capillary column is proportinal to chloride concentration.

Quantab chloride titrators are specific for chlorides, but bromides, iodides, sulphides, strong acids and strong bases can react with the strips.

4.1.6 Colourimetric spray indicators

Colourimetric spray methods are used to visualise penetration depths

Colourimetric spray methods are *qualitative* methods, suited to measure the penetration depth into concrete samples. The chloride penetration depth is determined in two dimensions by spraying the colourimetric indicators on a fractured or sawn concrete surface. The penetration depth is visualized by a colour change.

Collepardi's method for free chlorides

Collepardi's method determines free chlorides

A colourimetric method based on spraying fluoresceine and silver nitrate solution on concrete surfaces has been developed by Collepardi et al. [1970]. The method is used in Italy as a national standard method to determine the chloride penetration into concrete structures, cf. Collepardi [1995].

The analysis is performed by spraying first a solution of 1g fluoresceine in an aqueous 70% ethyl alcohol solution and then a 0.1 M aqueous silver nitrate solution on a fractured surface of the concrete sample. The surface becomes dark coloured if free chlorides are present in the sample. This is due to the formation of white silver chloride, which in the presence of natural light quickly becomes dark by a photochemical process. If chloride is not present, the concrete surface becomes permanently pink coloured.

Recently it has been suggested that the test method must be modified with an initial realkalization process by spraying 10% sodium hydroxide prior to the test if the concrete sample is carbonated, cf. Collepardi [1995].

APM 321 for total chlorides

APM 321 determines total chlorides

The standard specification APM 321 describes a test method similar to Collepardi's method, but modified to analyse for total chlorides, cf. AEC-laboratory [1991b].

This method specifies that the colourimetric indicators are sprayed on sawn concrete surfaces. First a silver nitrate solution adjusted to a pH-value of approx. 2 using nitric acid is sprayed on the concrete surface, and afterwards an aqueous 5% potassium dichromate solution is applied. If chloride is not present, the concrete surface becomes red-coloured. On the other hand, if chloride is present, the concrete surface becomes more white, and will if natural light is present eventually change to dark brown.

4.1.7 Comparison of different analytical techniques

A recent Round Robin test on different chloride analysis techniques performed by six concrete testing laboratories in Sweden and Denmark has

Figure 4-4. Comparison of results from a round robin test on measurement of chloride content in concrete. Volhard titration, ionselective electrode and potentiometric titration. Sørensen [1994].

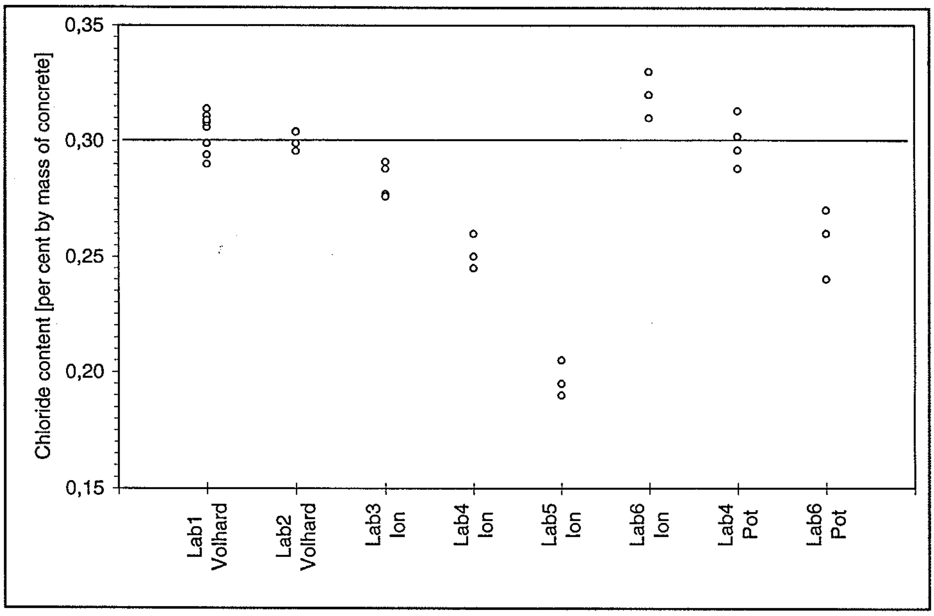


Figure 4-5. The diffusion cell test method with a sample of the material to be tested between two cells. The "upstream cell" is placed to the left and the "downstream cell" to the right.

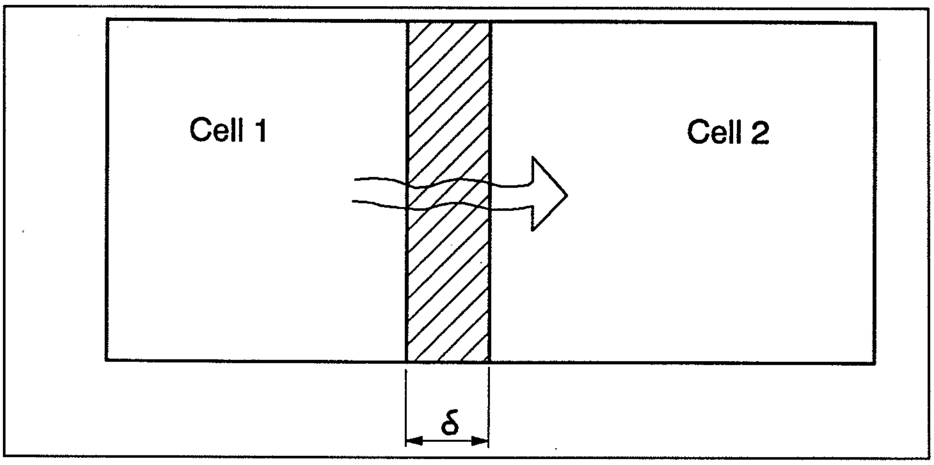
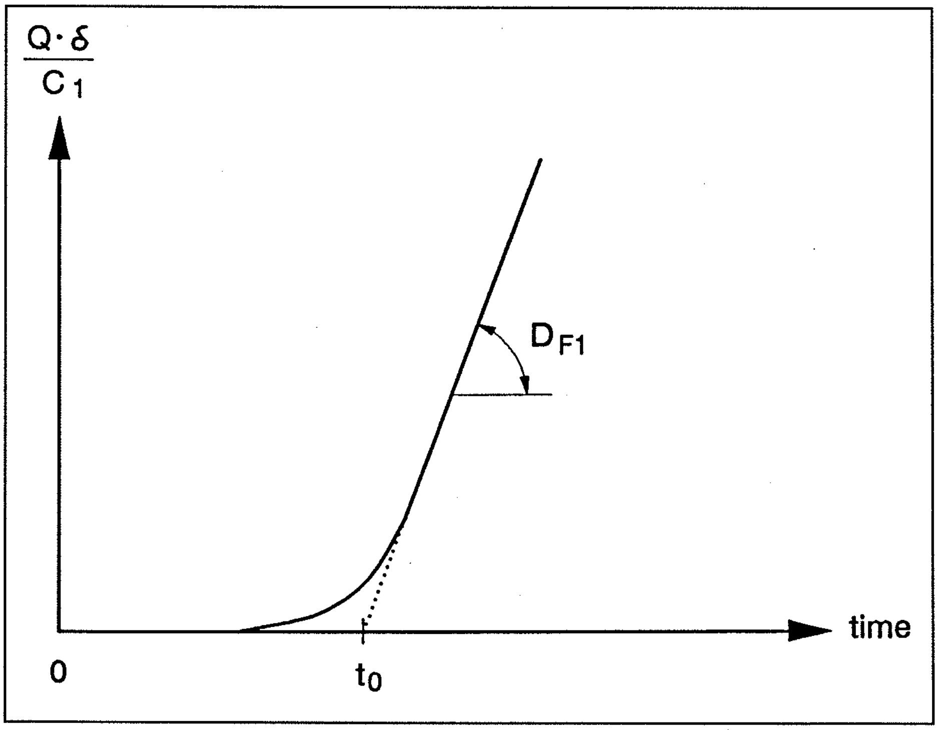


Figure 4-6. The evaluation of steady-state flow and timelag from a diffusion cell test.



demonstrated the variation in accuracy depending on the applied analytical technique, cf. Figure 4-4. The tests were carried out using pulverized concrete samples with a mixed-in chloride content of 0.300 per cent by mass of concrete.

Volhard titration gave high accuracy and small variability

In both cases where Volhard titration was applied, a high accuracy and a small variability were obtained.

Ionselective electrodes are very sensitive to workmanship

An ion selective electrode was applied in four cases. The results from this technique span from bad to fair accuracy. The variabilities are fair to good. The bad reproducibility of this method implies that it is very sensitive to workmanship and calibration.

Potentiometry is very accurate when used by experienced personnel

Potentiometric titration was applied in two cases. One case shows good accuracy and fair variability. The other case shows bad accuracy and fair variability. This method is also used by Chalmers. The experience from their laboratory is that this method is very accurate and shows small variability if careful calibration is undertaken by experienced personnel.

4.2 Diffusion cell test methods

The straightforward method applying Fick's 1^{st} law

The straightforward method to measure chloride diffusion coefficients is the diffusion cell test method. A slice of the material to be tested is placed in a sample holder between two cells containing solutions. The “upstream cell”, cell 1, contains the chloride solution with an original concentration of chlorides c_{f1}. The “downstream cell”, cell 2, collects the chlorides once they passed the specimen. By regularly analysing the content of chlorides in cell 2, the flow through the specimen is measured. Once the flow is constant in time, a steady-state flow F is obtained.

The principles of the test and the evaluation are shown in Figure 4-5 and Figure 4-6.

From the test, the diffusion coefficient in Fick's 1st law, (3.2.:2), is determined from

$$D_{F1} = \frac{F \cdot \delta}{(c_{f,1} - c_{f,2})} \qquad (4.2:1)$$

where δ is the thickness of the specimen.

The concentration c_{f2} in the downstream cell is kept close to zero by replacing the solution. If this is not done, the concentration gradient will decrease with time and the steady-state flow will not be reached, but a decline in flow will be obtained after some time. The diffusion coefficient cannot be evaluated with (4.2.1) in such a case, but an extensive correction has to be made, cf. Bigas [1994].

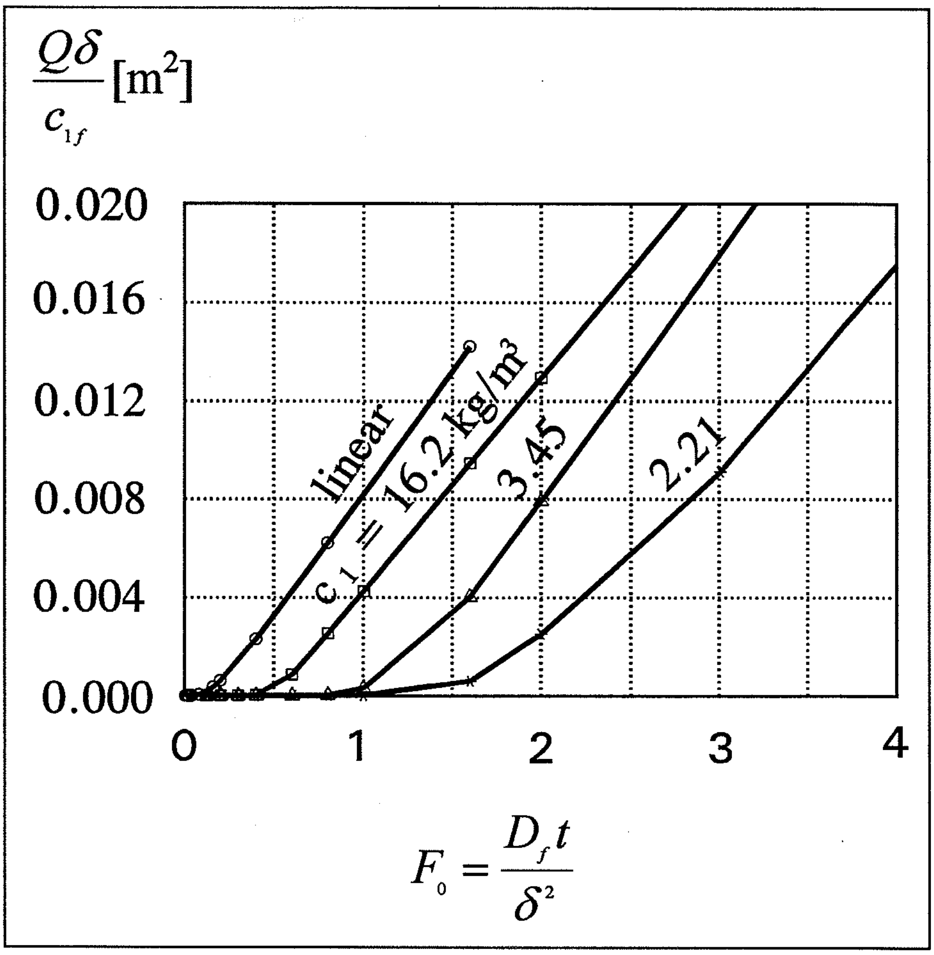
Leaching may affect the test

The very long test period used for the diffusion cell tests will of course induce leaching of hydroxides and alkalis during the test. The solutions in the cells are usually designed to prevent most of the leaching by using a saturated solution of calcium hydroxide and a concentration of potassium hydroxide that corresponds to what the binder will produce. During the test, however, ions other than chlorides will also diffuse, dissolve and precipitate, cf. the discussion in Section 3.2.1. The effects of these processes on the test results are not yet clarified.

The non steady-state part of the test may also be used

The non-steady state conditions before the steady-state flow is reached may be utilized to determine the apparent diffusion coefficient in Fick's 2nd law. From analytical solutions to Fick's 2nd law for the conditions in a diffusion cell test it is possible to evaluate the diffusion coefficient D_{F2}

Figure 4-7. The integrated flux through mortar specimens in diffusion cells with different chloride concentrations in the upstream cell.
Nilsson et al. [1993].



from the time lag, cf. Figure 4-6. If the diffusion coefficient D_{F2} is assumed constant the time lag t_0 is, according to Massat [1991]

$$t_0 = \frac{\delta^2}{6D_{F2}} \qquad (4.2:2)$$

From that evaluation the diffusion coefficient D_{F2} is determined.

Theoretical findings were experimentally verified

Nilsson [1992] and Nilsson et al. [1994] theoretically showed that the time lag depends on the non-linearity in chloride binding, cf. Figure 4-7, i.e. if the diffusion coefficient D_{F2} is concentration dependent, the time lag should depend on the concentration in cell 1. These findings were experimentally verified later by Bigas [1994], who even used the findings to develop a test method to measure chloride binding isotherms on slices of concrete, cf. Section 4.8.

Consequently, the results from the non-linear part of a diffusion cell test will depend very much on the concentration in cell 1. As discussed earlier in Section 3.2.1, the findings by Bigas [1994] and others show that the diffusion coefficient D_{F1} will also depend on the concentration in cell 1.

A very long test period is required

The diffusion cell test method is widely used, however, mostly for paste specimens and for mortar in rare cases. In a few studies, concrete specimens were used, Massat [1991]. This is of course due to the test period required to reach steady-state conditions. For mortar specimen some months or more is needed and testing of 20 mm concrete specimen may take years!

4.3 Immersion and ponding test methods

Immersion tests are based on non-steady state diffusion

Non-steady state diffusion test methods are generally based on immersion of concrete samples in liquids containing chloride salts for a certain time followed by a measurement of the chloride ingress. These methods usually involve:

- Sealing all except one surface of the specimen to prevent multidirectional penetration.
- Immersing the specimen in a solution containing specific ions for a certain time.
- Measuring penetration depth or penetration profile of chloride in the specimen.

4.3.1 APM 302 - Chloride penetration

APM 302 will be adopted as NORDTEST standard no. NT BUILD 443

The test method APM 302, cf. AEClaboratory [1991a], describes an accelerated test based on immersion of a concrete sample in a solution containing sodium chloride (NaCl). The test method will be adopted as a NORDTEST standard (NT Build 443) during 1996, cf. Sørensen [1994].

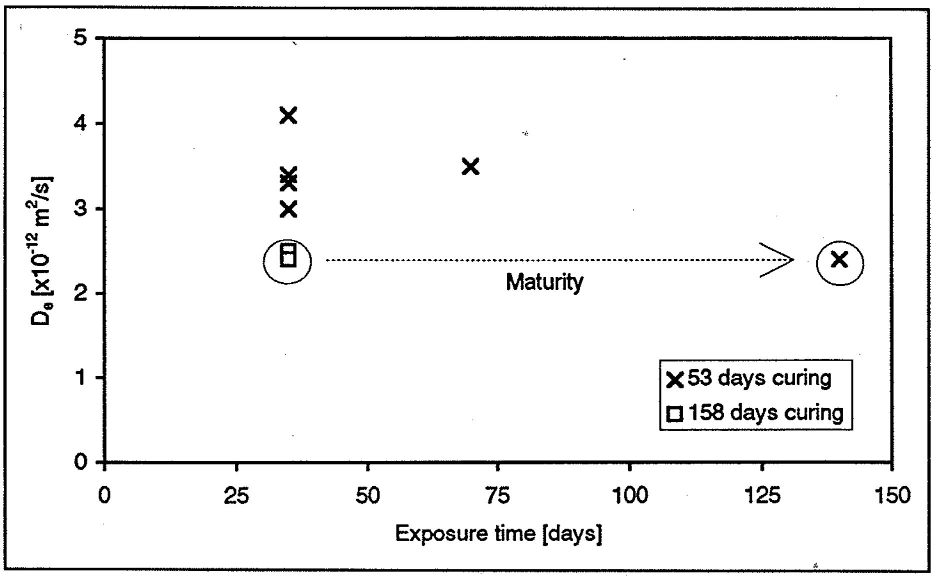
The method is used to estimate the resistance against chloride penetration into hardened concrete or other materials having cement as binder or cement as a part of the binder.

Test specimens

Cast cylinders or drilled cores are used as test specimens

The test specimens are usually cast concrete cylinders or drilled concrete cores. The exposed surface must have a certain size to minimize the influence from non-uniformly distributed aggregates. For this reason test specimens with an exposed area corresponding to at least ø100 mm are preferred.

Figure 4-8. Diffusion coefficients for different exposure periods measured by the use of APM 302 on concrete containing microsilica. The effect of curing time before exposure is illustrated. Sørensen [1994].



Due to the wall effect the content of cement paste has a large variation in the concrete near the as cast surface. To avoid influence from this effect the outmost 10 mm are cut off from the as cast surface before exposure.

To ensure a one-dimensional chloride ingress all faces other than the one to be exposed are covered with a chloride proof membrane, e.g. epoxy or polyurethane.

The test specimen must have an age corresponding to at least 28 days curing at 20°C. This is specified to ensure that the degree of hydration does not change markedly during the test. However, in some cases the specified minimum age should be higher, especially when pozzolans are used in the concrete, cf. Figure 4-8.

Exposure

Exposure time is at least 35 days

The test specimen is saturated with water before exposure to avoid capillary suction of exposure liquid containing chlorides. This is done by immersion in saturated calcium hydroxide solution until constant mass is obtained. The water saturated test specimen is then exposed to chloride by immersion in a solution containing 165 g sodium chloride (NaCl) per litre. The exposure time is at least 35 days at 23°C.

Results

The penetration of chloride into the sample is described by measuring the chloride profile. At the end of exposure the chloride profile is measured using profile grinding in steps of 0.4-1.0 mm and a chemical analysis of the chloride content in the concrete powder samples.

The measured chloride profile is described by the following penetration parameters:

The result is given C_i , C_s and D_{pex}

- The initial chloride content, C_i
- The boundary condition at the exposed surface, C_s
- The effective chloride transport coefficient, D_{pex}

The penetration parameters are calculated by means of a non-linear regression analysis of the measured chloride profile using the equation:

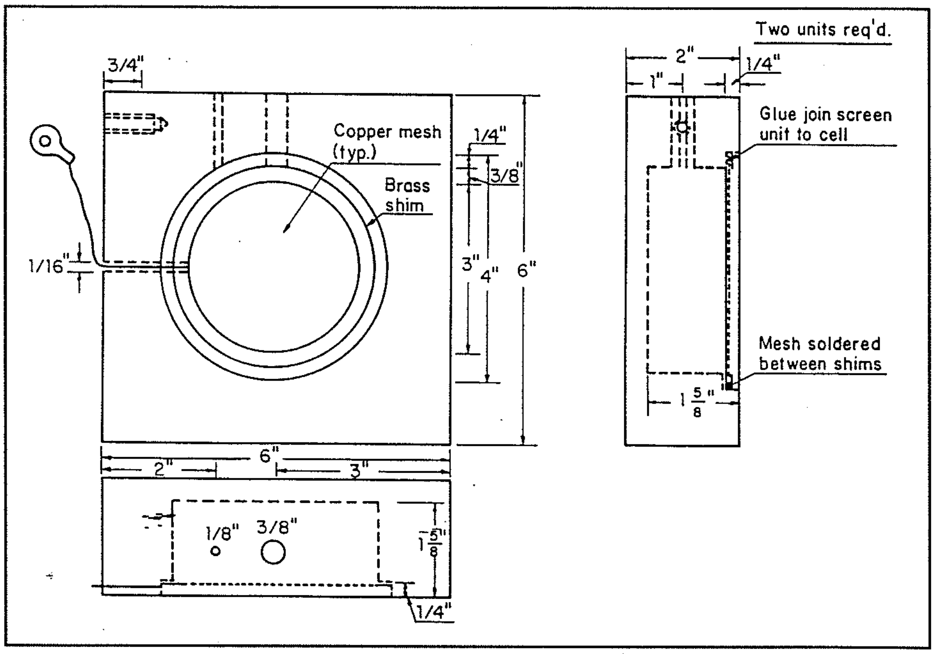
$$C_s = C_s - (C_s - C_i)\,\mathrm{erf}\left(\frac{x}{\sqrt{4D_{pex}t}}\right) \tag{4.3.1}$$

The parameter D_{pex} is often considered as the chloride diffusion coefficient of the material and has been used directly to calculate the future ingress of chloride into structures of this material. However, this is not possible without taking other factors into consideration, cf. Chapters 3, 5 and 7.

4.3.2 AASHTOO T259-80 - 90-days ponding test

The ponding test AASHTOO T259-80 is the only standardized test procedure for immersion tests so far, cf. AASHTOO [1980]. A specimen of 300◈300◈75 mm concrete slab is ponded with a 3 per cent sodium chloride solution for a period of 90 days. The chloride profile is measured subsequent to the exposure by removing the exposing solution and sampling concrete powder from various depths using a rotary hammer drill.

Figure 4-9. The migration cell in AASHTO T277-93 and ASTM C 1202-94.



4.3.3 Other immersion tests

Various other immersion test methods, for example 40°C bulk diffusion, have been used by different research groups. These methods are usually based on the same priciples and techniques as APM 302. They differ from this method only in the choice of different values for one or more of these conditions:

Varying condition in other immersion tests

- Conditioning (water saturation)
- Exposure temperature
- Exposure time
- Exposure concentration
- Chloride salt composition

4.4 Electrical field migration test methods

Migration tests may give diffusion coefficients

Because of the complexity and the very long test periods for diffusion cell tests and immersion tests, a number of electrical migration test methods have been developed. Today, these tests may even give quantitative data on chloride diffusion coefficients, applicable for predictions.

A specimen is placed between two solutions, the upstream solution containing chlorides, and is exposed to an electrical potential gradient. Two types of migration test methods are used. Non-steady state migration methods use a very short test period, while the steady-state migration tests are continued until steady-state conditions are reached.

4.4.1 Non-steady state migration cell methods

The most widely used "rapid chloride permeability test" method is AASHTO T277, dating back to the 70's, measuring the charges passing through a concrete specimen during six hours. Another non-steady state method, the CTH-method first presented in 1991, measures the penetration depth after some hours of migration by a colorimetric method and evaluates the diffusion coefficient from that depth.

AASHTO T277

Commercially available and widely used

AASHTO T277 has been developed and revised in a number of steps, described by Whiting [1981], AASHTO [1993] and ASTM Standards [1994]. Today testing equipment is commercially available and widely used for comparing concretes and for quality control.

One half of the migration cell is shown in Figure 4-9. A 50 mm thick concrete specimen is enclosed between two chambers, the upstream cell containing a salt solution. A voltage of 60 V is applied over the specimen, between the electrodes in each chamber. The test is run for six hours and during that time the amount of charge passing the specimen is measured by recording the current as a function of time.

Results in Coulombs

The test result is given in charge (coulombs). Experience and comparison with results from other methods are used to evaluate the test results.

The application for comparing different binders is questioned

The method has been heavily criticised for a number of reasons. Because the test measures only the charge which passes, and not the chlorides which penetrate, the relevance of the test results has been questioned. The composition of the pore solution probably has an important effect on the charge passing, but not necessarily on the flux of chlorides. Different binders may not be valued correctly.

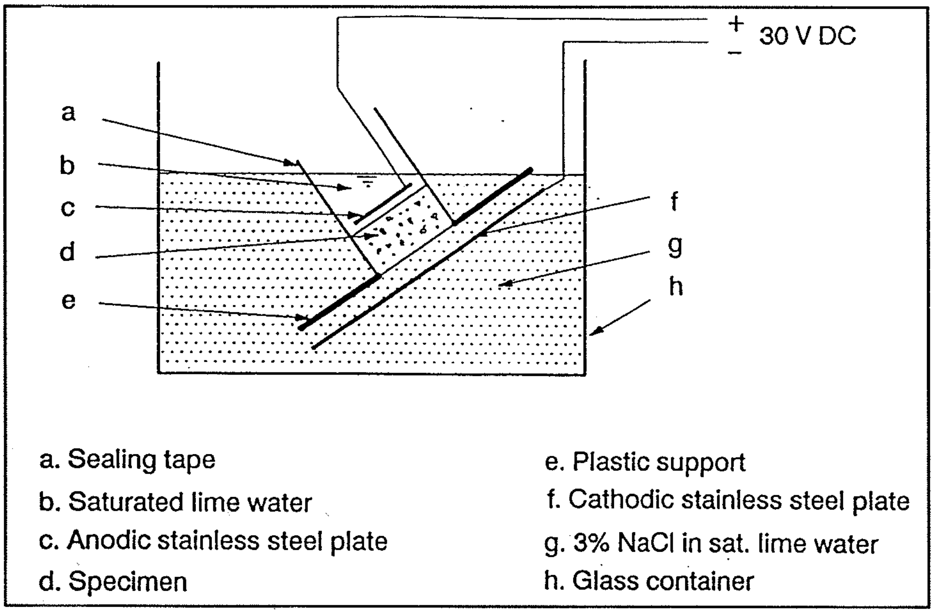


Figure 4-10. The experimental arrangement in the CTH migration method.
Tang & Nilsson [1992a].

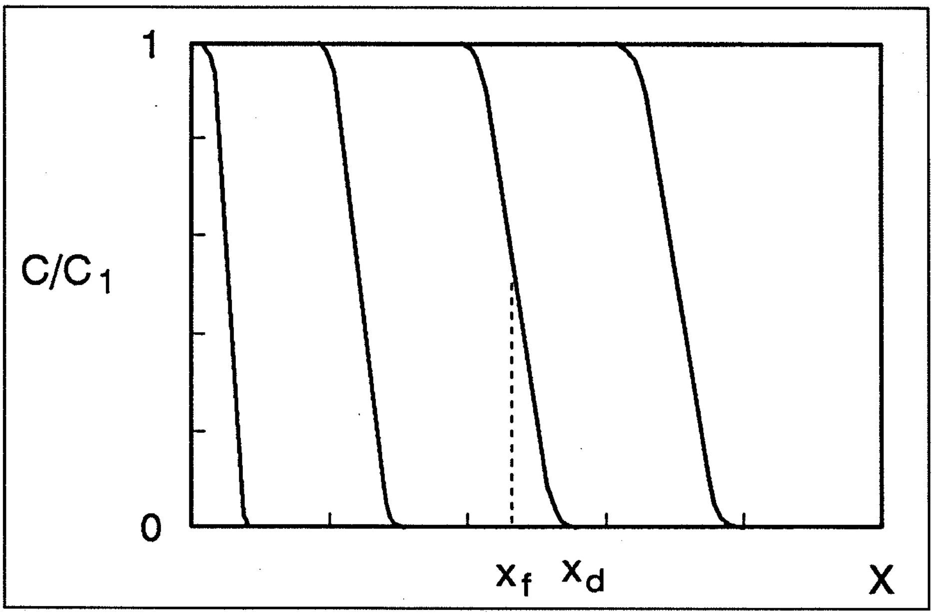


Figure 4-11. Theoretical chloride profiles during a non-steady state migration test if migration is dopunating.

Intial resistivity would give similar information

Another objection has been, eg. Arup [1993a], that measuring the initial resistivity would give the same information within a test period of a few seconds. This is nowadays suggested as an alternative test method, cf. Section 4.5.

The very high voltage of 60 V increases the temperature of the specimen. This temperature rise probably affects the transport processes in the concrete. Yamamoto et al. [1995] compared an applied voltage of 10 V with the standard 60 V and found a linear relationship between the charges passed; however, with a factor of 8 between the two cases, independent of type of binder and *w/c*. A lower voltage could be a better alternative.

The CTH method

The first migration test method to give diffusion coefficients

The CTH method was first presented in 1991 and published by Tang & Nilsson [1992a]. The most important invention was that it is the first migration test to actually give chloride transport coefficients. Extensive experience has been gained with using the method and utilizing the test results, cf. Tang [1993 and 1995].

The equipment consists of a specimen sealed with a sealing tape on all surfaces except two opposite parallel surfaces. The sealing tape is extended from the specimen to create the downstream cell, cf. Figure 4-10, with a solution of saturated lime water. The specimen with the downstream cell from the sealing tape is placed in a large container containing the upstream cell with a sodium solution of saturated lime water with a concentration c_1 of chlorides. Electrodes are placed on each side of the specimen. The specimen is tilted to make it easy for gas bubbles at the cathodic plate to escape.

A test period of hours or days only

In the standardised version, the specimen is 50 mm thick. A voltage of 30 V is applied across the specimen. The initial current is measured to give an estimate of the required test period. The test period is typically 8, 24 or 48 hours depending on the concrete quality.

Split the specimen, spray it and evaluate the penetration depth

After the test, the specimen is split and the two fractured surfaces are sprayed with a $AgNO_3$ solution to detect the depth of chloride penetration with the colorimetric method by Collepardi et al. [1970] and Collepardi [1995].

From the depth of penetration the diffusion coefficient D_{CTH} is evaluated by an equation similar to (3.3:5). The depth of penetration of the theoretical inflection point x_f in the chloride distribution, cf. Figure 4-11, is

$$x_f = k \cdot D_{CTH} \cdot t \qquad (4.4:1)$$

where t is the test period and k is a constant $k = zFU/RT\delta$. The colorimetric method, however, has a detection point at a certain chloride concentration c_d. The measured depth x_d of this concentration will give the diffusion coefficient from

$$
\begin{aligned}
D_{CTH} &= \frac{x_d - \alpha\sqrt{x_d}}{k \cdot t} \\
\alpha &= \frac{2}{\sqrt{k}} \cdot \mathrm{erf}^{-1}\left(1 - \frac{2c_d}{c_1}\right)
\end{aligned}
\qquad (4.4{:}2)
$$

as shown by Tang [1995].

Diffusion coefficients at early ages may be measured

The advantages of this method are obvious. The test period is short, only a few days. Because of this, diffusion coefficients as a function of the age of the concrete can be measured, cf. Tang & Nilsson [1992a]. The test procedure is simple and the measurements are extremely simple compared with other methods.

The test results is applicable for predictions

The test results are expressed in terms of a diffusion coefficient. This coefficient has been shown to apply for predicting chloride penetration into concrete, cf. Tang & Nilsson [1994, 1995b] and Tang [1995].

The binding capacity is involved in the test

However, the chloride profiles after a test do not coincide with the simple theoretical profiles in Figure 4-10, as discussed in Section 3.3. A certain part of the chloride binding capacity influences the distribution and consequently the penetration depth as described in (3.3:6).

Tang & Nilsson[1995b] developed the current expression for evaluating the results from the CTH method. The diffusion coefficient in Fick's 1st law, applicable for predictions, should be

$$
D_{F1} = D_{CTH} \cdot p_{sol} \cdot \left(1 + \frac{c_b(c_1)}{c_1}\right) \qquad (4.4{:}3)
$$

where c_b/c_1 is the total binding capacity that is active during the test. The experimental verification of these findings, and of the predictions using the test data, must to be extended.

4.4.2 Steady state migration cell methods

Migration cell test methods have been used for a long time to compare concretes. With migration cells similar to the ones used by the AASHTO or CTH methods, the cumulative flux has been measured by several researchers, eg. Dhir et al. [1990] and Hauck [1993]. The effect of the test parameters was thoroughly examined.

Diffusion coefficients also from steady-state migration tests

However, it was not until Tang [1993] and Andrade [1993] showed how to evaluate diffusion coefficients from the test, the relevance of the test results became clear.

The diffusion coefficient from a steady-state migration test should be equal to the D_{F1} in Fick's first law. From the steady-state flux F through a specimen with a thickness δ, Tang [1993a] showed the analytical solution

$$
D_{s-s} = \frac{F}{k} \cdot \frac{\left(e^{k\delta} - 1\right)}{\left(c_1 e^{k\delta} - c_2\right)} \qquad (4.4{:}4)
$$

where c_1 and c_2 are the concentrations in the upstream and downstream cells and the constant k is $k = zFU/RT\delta$. For large voltages, i.e. large values of k, this is simplified to

Table 4-1. "Intrinsic" migration coefficients D_0 for a series of OPC concrete.
Tang & Nilsson [1995b].

w/c	0.35	0.40	0.50	0.75
Steady-state	11.4	15.2	16.3	23.0
Non-steady state	9.4	18.1	40.8	91.8

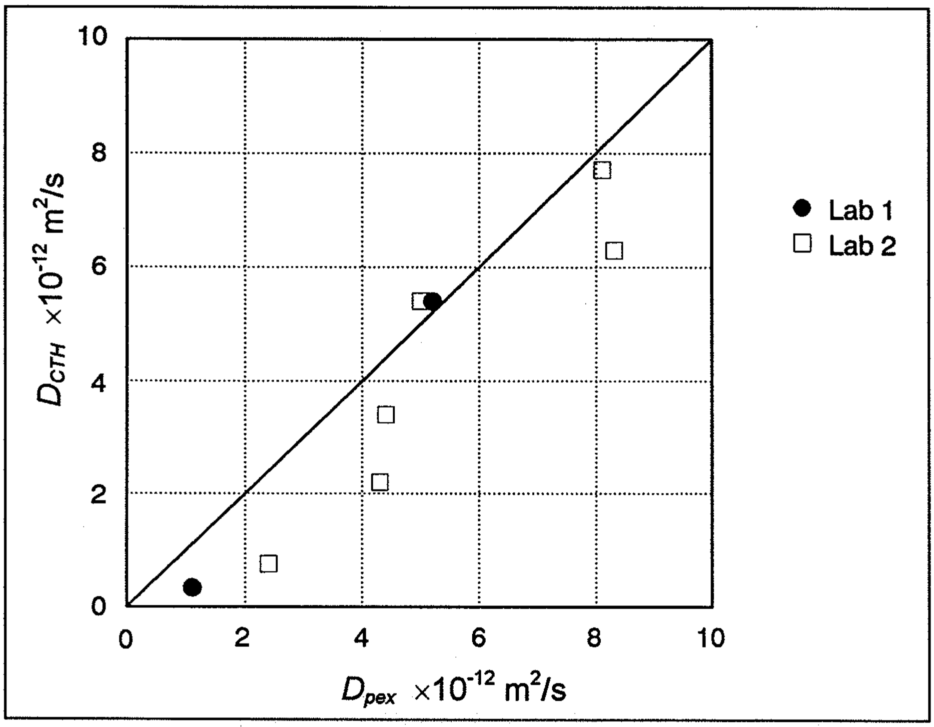


Figure 4-12. Diffusion coefficients from the APM302 immersion test and the CTH migration method.

$$D_{s-s} = \frac{F}{k \cdot c_1} \tag{4.4:5}$$

as shown by Tang [1993a] and Andrade [1993].

A fairly long test period, repeated chemical analysis and possible change of the pore solution during the test

The method has a few drawbacks. The most obvious one is the long test period required for concrete to reach steady state flow. Testing of concrete should be performed on specimens with a thickness two or three times the maximum size of stones. For high quality concrete, weeks would be required. Another drawback is the number of repeated measurements of the concentration in cell 2. A third factor is the uncertainty of the effect of direct current during a long time changing the composition of the pore solution and the sample with time during the experiment, cf. Arup [1993a]. When the steady-state flow is determined, the sample may be significantly different compared to the initial state.

A lot of test results are published. The effect of test parameters has been studied to some extent. Arsenault et al. [1995] found a small decrease in D_{s-s} when the concentration is increased. Gilleece et al. [1995] found the opposite.

4.4.3 Other migration test methods

A few other migration tests do exist, but they are not widely used. One is the embedded steel method, the "Lollipop method" (NT Build 356), that uses a reinforcement bar as a centre electrode in a concrete cylinder to drive chlorides in from the curved surface. The time for cracks to occur due to corrosion is measured. This method is heavily violating the electrochemical conditions at the steel, compared to normal conditions.

4.4.4 Relations between test results

According to (3.3:4) the steady-state migration coefficient D_{s-s} should be equal to the diffusion coefficient D_{F1} in Fick's 1st law.

D_{s-s} somewhat higher than D_{F1}

Arsenault et al. [1995] compared diffusion cell tests and steady-state migration tests for mortar. They found a factor of 1.6-2.2 between the two coefficients, D_{s-s} being higher.

The non-steady state migration coefficient D_{n-s}, evaluated from the diffusion coefficient D_{CTH}, could be compared to the coefficient from the steady-state test by the "intrinsic" diffusion coefficient

$$D_0 = \frac{D_{F1}}{p_{sol}} = \frac{D_{s-s}}{p} \tag{4.4:6}$$

Tang & Nilsson [1995b] measured both the migration coefficients for a series of concretes, cf. Table 4-1.

Migration coefficients coincide for high quality concrete

The coefficients coincide very well for the better concretes. However, for high *w/c* concrete steady-state conditions are never reached in the steady-state method. The steady-state flux decreases with time from an initial high value in a strange way, Tang [1995e].

The diffusion coefficients from immersion tests and migration tests have been compared and shown to be almost equal experimentally, cf. Figure 4-12.

The APM302 and the CTH method give quite similar diffusion coefficients. A strange coincidence?

The two methods have been found to differ by not more than a factor of two. This is a strange coincidence since the two methods are theoretically quite different. The differences, from a theoretical point of view, are explained by the differences in the binding capacity that influences the chloride transport during the tests. That may explain why especially fly ash concrete coefficients deviate in Figure 4-12.

4.5 Resistivity methods

The electrical resistivity of any material is defined as the resistance in ohms per unit length between the opposite faces of a unit cube of the material, cf. Whittington et al. [1981]. Thus, if R is the resistance of a specimen having a length δ and cross sectional area A, according to Monfore [1968] the resistivity ρ_s is expressed by the formula:

$$\rho_s = RA/\delta \quad [\Omega\text{m}] \qquad (4.5:1)$$

Resistivity, being a fundamental property of the material, is independent of the volume, whereas resistance depends upon the shape and size of the specimen, cf. Buenfeld et al. [1984]. The conductance of the material is defined as the reciprocal of resistivity, i.e.

$$\sigma_s = 1/\rho_s \quad [1/\Omega\text{m}] \qquad (4.5:2)$$

4.5.1 Electrical resistivity of concrete

Electrical conduction through concrete is almost entirely due to electrolytic conduction through the pore water, electronic conduction through the solid cement matrix and aggregate being negligible. As reported by Arup et al. [1993], the resistance of a concrete specimen is therefore dependent upon:

- Degree of saturation
- Temperature
- Resistivity of the pore solution

Concrete exhibits a negative temperature coefficient of resistivity. According to Whittington et al. [1981] the electrical resistivity of concrete at temperature, t, can be related to its resistivity at a reference temperature, Θ, by the formula:

$$\rho_t = \rho_\Theta/(1 + \alpha(t - \Theta)) \qquad (4.5.1:1)$$

where ρ_t is the resistivity at the temperature t, ρ_Θ the resistivity at the reference temperature Θ and α is the temperature coefficient for resistivity of the material. For concrete α is determined to be approximately 0.025.

Moist concrete behaves as an electrolyte with a typical resistivity of 50 Ωm, which is within the range associated with semiconductors. However, the dry concrete shows a resistivity of around 10^{-9} Ωm, which classifies such concrete as a reasonably good insulator. Just this enormous fall in conductivity due to the removal of evaporable water suggests that electric current is conducted through concrete ions in the pore water, cf. Buenfeld et al. [1984].

Figure 4-13. Schematically illustration of four different ways to measure the resistivity of a cylindrical block of concrete. Arup et al. [1993].

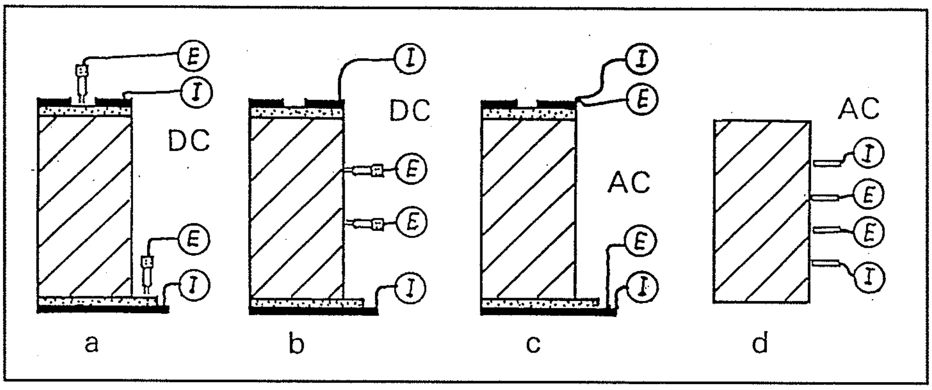
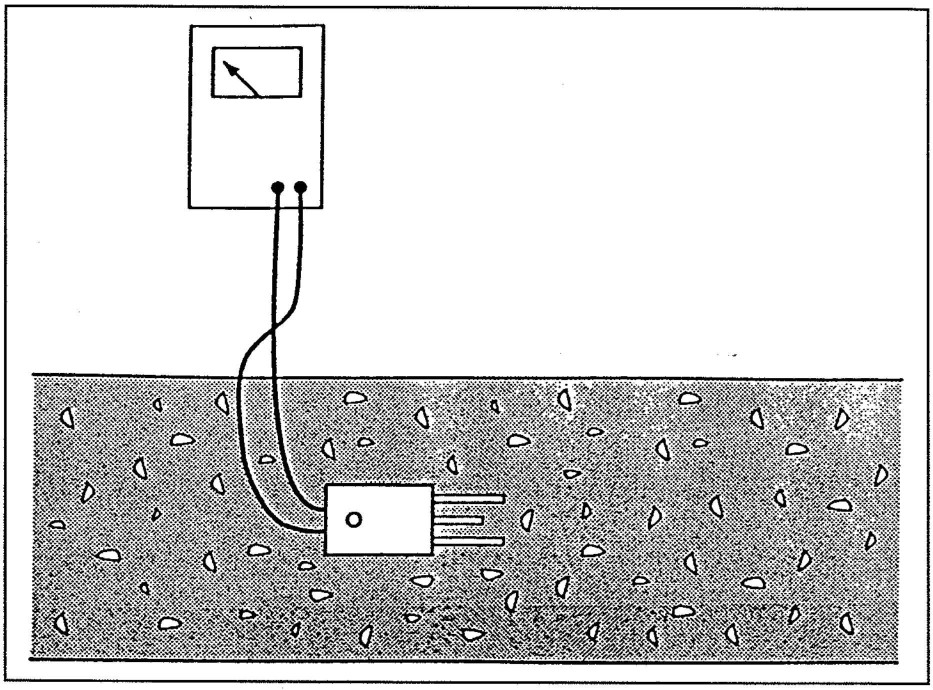


Figure 4-14. Schematically illustration of measurement of the resistivity of concrete by cast-in probes.
Klinghoffer et al. [1995].



Formation Factor

The pore water contains a solution of sodium, potassium and calcium hydroxides. The relative proportions of these hydroxides vary as hydration proceeds and hence the resistivity of the pore solution also varies. It is suggested that such changes are minimal after 28 days, cf. Diamond [1981]. On the other hand the pore water resistivity is influenced by ionic diffusion through concrete. By using a parameter called the Formation Factor (*FF*) these variations can be taken into account, cf. Buenfeld et al. [1984].

The Formation Factor describes the structure of a porous material like concrete and is defined by the equation:

$$FF = \rho_m/\rho_l \qquad (4.5.1:2)$$

where ρ_m is the resistivity of the whole material and ρ_l is the resistivity of the pore water.

If the material consists of a relatively non-conductive matrix, the resistivity of the entire solid will be influenced by the resistivity of the pore water and the continuity of the pore system (the cross sectional area of pores and length of the pores). *FF* is then a measure of the relative ability of ions to migrate through the material.

Measurement of resistivity

In practice electrical resistivity can be measured by means of either a D.C (direct current) system or A.C. (alternating current) system, cf. Hansson et al. [1983]. The use of a D.C. system results in polarization of the electrolyte (in this case the concrete) and the formation of hydrogen and oxygen at measuring electrodes. To avoid this effect an A.C. system is normally used with frequency in the range of 50 Hz to 1000Hz, cf. Millard et al. [1989]. The measuring electrodes are either surface mounted (an often used type is the Wenner probe) or embedded in concrete. Systems using two or four electrode probes are used.

Figure 4-13 shows schematically four different ways of measuring the resistivity of a cylindrical block of concrete, cf. Arup et al. [1993].

In the case of Figure 4-13a and Figure 4-13b, DC current is applied to the flat ends of the cylinder using two wetted pads. The liquid used for wetting could be any salt solution, e.g. a calcium hydroxide solution. Two metal plates, one with a central hole, are the electrodes connected to the current source. If DC current is used for resistivity measurements, voltage drop must be measured by means of closely spaced reference electrodes.

Current is measured in the circuit marked "*I*", while voltage drops are measured between leads marked "*E*". The resistance is determined as *E*/*I*, the resistivity is calculated according to formula (1).

The AC measurements shown on Figure 4-13c are also performed by applying current to the flat ends of the sample but in this case the reference electrodes are not needed.

Figure 4-13d shows an example of AC measurements by means of the Wenner 4-points method. The four pins are used to contact the concrete surface, and the distance "*a*" between them can be varied. This method is suitable for use on the flat surface of a semi-infinite body of concrete and formula (1) used for resistivity calculation can result in errors if "*a*" is not very small compared with the dimensions of the test sample.

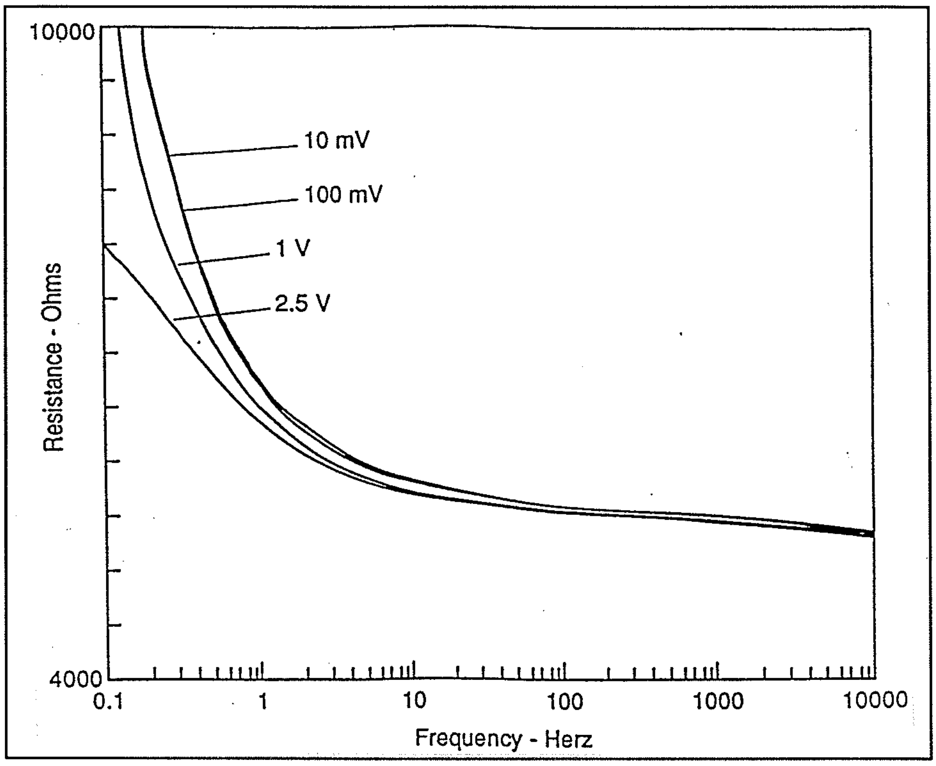


Figure 4-15. Apparent resistivity of mortar with embedded electrodes when different applied voltages and frequencies were used for the test.
Arup et al. [1993b].

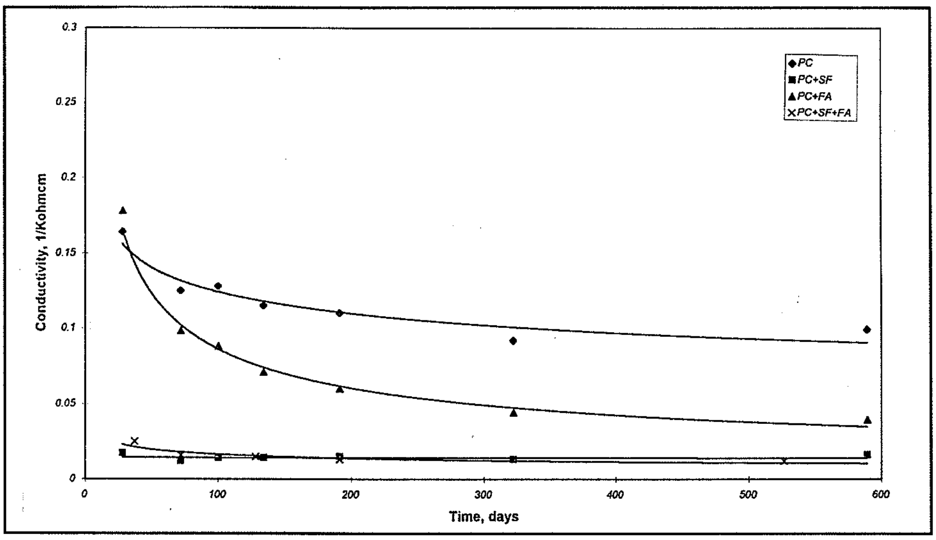


Figure 4-16. Influence of pozzolanic addition and age of samples on the electrical conductivity.
Klinghoffer et al. [1995].

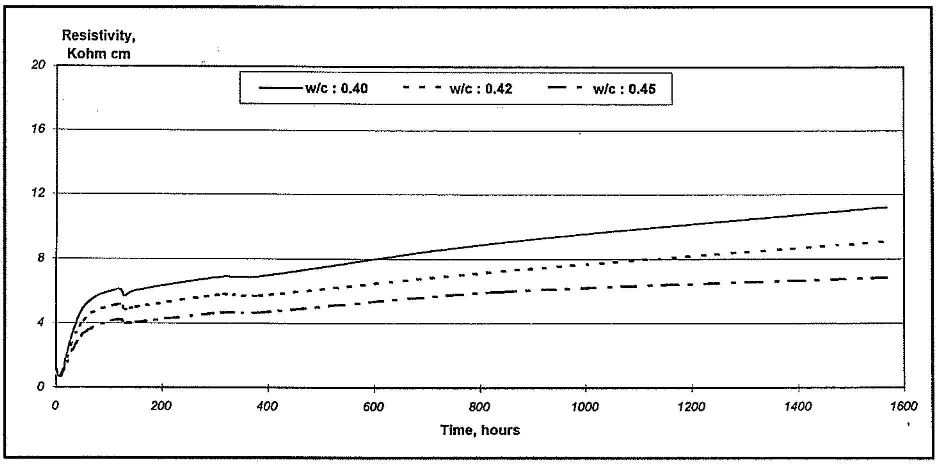


Figure 4-17. Influence of *w/c* ratio on concrete resistivity. Cement content is kept constant at 320 kg/m^3.

The resistivity of concrete can also be measured with cast-in probes, cf. Figure 4-14.

The electrodes must bond well to the concrete and the distance between them must be relatively small compared with the distance from the surface or from embedded steel, but large compared with the size of aggregate. Every configuration of electrodes can be characterized by a geometry factor, which is used to convert the measured resistance to resistivity. The geometry factor is determined by taking a measurement with the electrode set in a liquid of known resistivity prior to embedding it.

The measured resistivity may vary with the frequency and magnitude of the applied voltage. As shown in Figure 4-15 there is a little variation with frequency or voltage at a frequency of few hundred Hz, which is commonly used in commercial instruments.

The general conclusion regarding determination of resistivity is, that these measurements can be made *easily in a number of ways, quickly (it takes only few minutes from the start of the test until the results are available) and with good reproducibility.*

Due to the different possible measurement set-ups, standarization of this technique, e.g. a standard regarding recommended practice is needed, and some work is already being done on this subject.

Decisive parameters

The influence of the following parameters on the electrical resistivity of concrete is reported in the literature, cf. Hope et al. [1985]:

- Resistivity of concrete increases with the age of the concrete
- Resistivity of water saturated concrete increases with decrease in *w/c* ratio
- Resistivity of concrete increases with decrease in the moisture content
- Resistivity of concrete increases with decrease in temperature

The electrical resistivity is also dependent on the concrete composition, especially addition of pozzolans, such as microsilica and fly ash.

The influence of the pozzolanic addition and also the age of the samples on the electrical resistivity, expressed as a conductivity, is shown in Figure 4-16.

Especially samples containing micro silica show much higher resistivity (lower conductivity) values than the rest of the samples. Resistivity increases with increasing age of the samples. It should be noticed that in the sample containing fly ash the resistivity increases (conductivity decreases) at a much slower rate than in the samples which contain microsilica. It takes almost one year until the conductivity value reaches a stable level for mixes with fly ash addition.

The influence of water/cement ratio on concrete resistivity is shown in Figure 4-17.

A higher *w/c* ratio results in lower resistivity. If electrical resistivity is measured, it is possible to distinguish between samples of the same concrete type which only differ by small changes in *w/c* ratio.

These influences are of great importance when the model for comparison of electrical resistivity and chloride diffusion is considered.

4.5.2 Electrical resistivity as a measure of diffusivity

The electric current is conducted through concrete by electrolytic means and such electrolytic conduction is a special case of ion diffusion. The ions are driven by an applied electrical potential rather than by a concentration gradient, cf. Buenfeld et al. [1987].

Changes in ionic diffusivity can therefore be investigated by monitoring the electrical resistance of concrete specimens. The electrical conductivity will depend on all the ions present in the pore solution (i.e. Na^+, K^+, OH-, etc.) rather than one specific ion (e.g. Cl-).

The conductivity of concrete is dependent both on concrete microstructure and the electrical conductivity of the pore solution, cf. Kyi et al. [1994]. The electrical resistance measured in a saturated concrete sample at a constant temperature will be influenced by changes in diffusivity or by a variation in pore water composition. Changes in pore water concentration may be taken into account by measuring pore solution conductivity and, subsequently, expression of results in terms of the Formation Factor of concrete (*FF*) defined in (4.5.1:2).

The Formation Factor, *FF*,can also be expressed by the ratio of molecular diffusivity D_0 to effective diffusivity D_{Fl},, cf. Garboczi [1990].

Assuming that all ions present in the pore solution have the same diffusion coefficients D_0 in water and D_{Fl} in pore liquid saturated concrete the following relationship can be applied:

$$FF = D_0/D_{Fl} \qquad (4.5.1:3)$$

The effective diffusivity D_{Fl} represents the steady state unaffected by chemical or physical binding, cf. Taffinder et al. [1993].

By combining equations (4) and (5) the following relationship is obtained:

$$FF = \rho_m/\rho_l = D_0/D_{Fl} \qquad (4.5.1:4)$$

The ratio of diffusivities is also called the McMullin number (N_m) in chemical engineering, cf. Geankoplis [1978] and McMullin et al. [1956].

If the formation factor *FF* is determined for a concrete material by measuring its electrical resistivity, the effective diffusivity of e.g. chloride ions can be calculated using their molecular diffusivity.

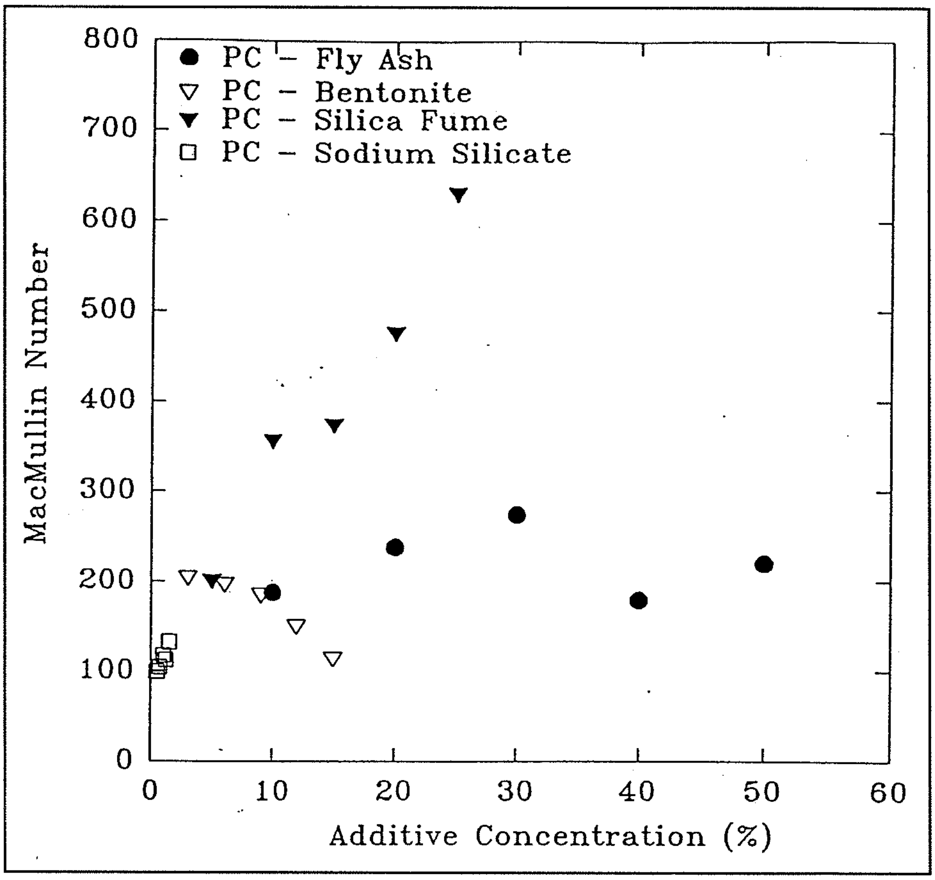
$$D_{Fl} = D_0/FF \qquad (4.5.1:5)$$

The value of molecular diffusivity is constant, e.g diffusivity of chloride ions in NaCl solution is $1.61 \cdot 10^{-9}$ m^2/s, cf. Kyi et al. [1994].

Thus measurement of electrical resistivity provides one of the possibilities to determine diffusion coefficients in concrete, cf. Kyi et al. [1994]. Other possible techniques are described in Sections 4.2 and 4.3. Compared with such methods, the electrical resistivity technique allows very rapid measurements of good reproducibility.

When the electrical resistivity measurements are used for determination of diffusivity, the following must be taken into account, cf. Arup et al. [1993]:

Figure 4-18. Effect of type and concentration of additives on McMullin Number.
Kyi & Batchelor [1994].



- The steady state diffusivity, D_{FI}, will be determined.
- The resistivity must be measured on a water saturated sample.
- The resistivity of the pore water must be known.

In the next section the practical application of the resistivity measurements for determination of diffusivity will be demonstrated based on the results available in the literature.

4.5.3 Application of electrical resistivity measurements for determination of diffusivity

Electrical resistivity measurements have been used to characterize different concrete properties. Apart from determination of diffusivity these measurements were also applied for evaluation of pozzolanic activity and indirect indication of the risk of corrosion of the embedded reinforcement.

Because the electrical resistivity measurements are sensitive to degree of hydration, moisture content and changes in water/cement ratio, this method is suitable for QA/QC procedures.

A summary of the most interesting experimental results regarding application of electrical resistivity measurements for determination of diffusivity is given below.

According to Taffinder [1993] the resistivity method has been developed to determine the effective diffusivity of contaminants through porous solids, such as hazardous waste solidified with cementitious binders. The effect of water/cement ratio, curing time and sample thickness on the Formation Factor, *FF*, was determined. The validity of this method was established through comparison with effective diffusivities measured by conventional techniques. Correlation of the Formation Factor with porosity and bulk density was developed. The electrical resistivity was found to be a rapid and reliable method for measuring the effective diffusivities. This technique offers the advantage of much more rapid analysis than conventional methods.

Buenfeld & Newman [1984,1987], have examined the electrical resistivity method for determination of diffusivity together with two other, more and less standard, techniques. They found that the resistivity method is a useful means of instantly identifying changes in the rate of ion diffusion. The same authors have also found the resistivity method to be useful for monitoring small changes in concrete permeability in a marine environment. The five investigated mixes show a drop in permeability on exposure to sea water, though the decrease was very slight for fly ash mortar. The reduction in permeability is associated with both the formation of the surface layer and a more widespread pore closing and blocking. The permeability reducing effect has a considerable effect upon absorption and could have important connotations with respect to the performance of concrete in the tidal and splash zones.

Kyi & Batchelor [1994] have used the electrical resistivity procedure to measure the effective diffusivities of compounds in cementitious systems containing the additives of fly ash, silica fume, sodium silicate, and bentonite.

The effect of type and concentration of additives on diffusivity expressed by the McMullin Number is shown in Figure 4-18.

Silica fume was found to be the most effective additive for increasing the McMullin Number (decreasing effective diffusivity).

Table 4-2. Chloride diffusion coefficient and electrical resistivity in a fog room of 5 concrete mixes. Polder [1995].

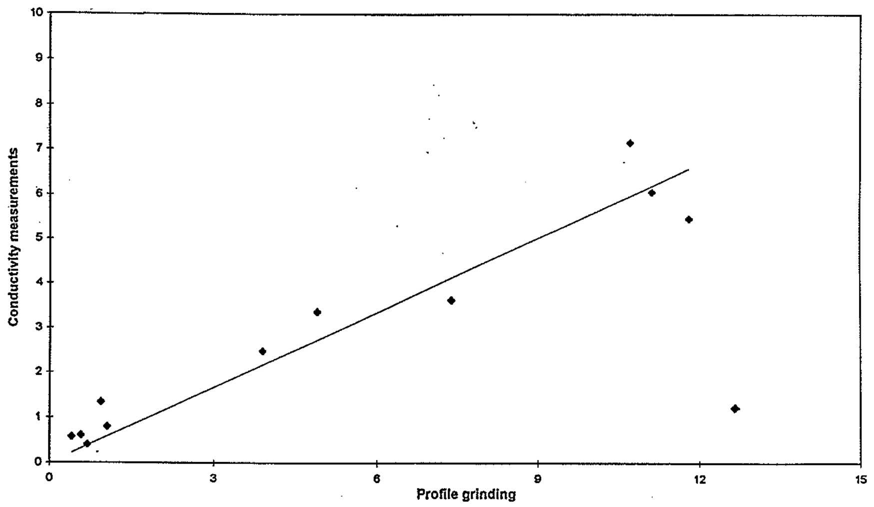
Concrete type	mix S	mix L	mix F	mix P	mix B
all w/c 0.43, 340 kg cement/m^3, superplast	5% silica fume	OPC, porous coarse aggregate	10% fly ash, 5% silica fume	OPC	BFSC (70% slag)
D_{eff} $*10^{-12}$ (m^2/s)	3	8	1	2.5	0.8
$\rho_{concrete}$ (Ω.m)	250	100	550	120	690
A $*10^{-12}$ (Ω.m^3/s)	750	800	550	300	550
Average A $*$ 10^{-12} (Ω.m^3/s)	600 (+/-200)				

Table 4-3. Comparison of diffusion coefficients obtained by conductivity measurements with values determined by immersion method (incl. profile grinding). Klinghoffer & Rislund [1995].

Mix No		Diffusion coefficients determined by means of:			
		conductivity measurements D_e [10^{-12} m^2 /s]		profile grinding method D_e [10^{-12} m^2 /s]	
Maturity		8 days	28 days	28 days	one year
1	PC	5.45	4.32	9.5	11.8
2	"	6.05	ND *	19.8	11.1
3	"	7.15	7.98	24.5	10.7
4	PC+SF	0.80	0.82	2.08	1.05
5	"	1.20	ND *	2.96	12.8
6	"	1.35	1.80	1.85	0.94
7	PC+FA	2.48	1.53	12.7	3.90
8	"	3.36	2.25	16.1	4.90
9	"	3.62	3.26	14.6	7.40
10	PC+SF+FA	0.40	0.69	3.19	0.69
11	"	0.57	0.73	3.43	0.40
12	"	0.61	0.78	4.51	0.57

* ND = Not Determined

Figure 4-19. Comparison of diffusion coefficients obtained by conductivity measurements and immersion tests (incl. profile grinding). Values from table 4-3 given in [10^{-12} m^2/s].



Diffusivities measured by techniques that rely on measurement of fluxes through the solid or concentration profiles within the solid tend to result in higher values than those measured by the electrical resistivity method. This may be due to reactions of the tracer ions in the flux-based tests. The flux based procedures may thus be measuring the combined effects of physical transport and chemical reactions, i.e. they may be measuring observed diffusivities rather than effective diffusivities. It is also concluded that porosity and bulk density are not well correlated with effective diffusivities in cementitious systems containing additives.

According to Polder [1995] a relation was found between the effective diffusion coefficients for chloride and the wet concrete resistivity. Chloride diffusion and resistivity were determined for five concrete mixes based on ordinary Portland cement with addition of fly ash and silica fume and also on blast furnace slag cement. It was shown that the additional cementing materials have a strong influence on chloride diffusion and resistivity of concrete. For the five investigated mixes, the resistivities increase in the same order as the chloride diffusion coefficients decrease. Therefore, the products of the chloride diffusion coefficient and the resistivity in wet conditions are determined, cf. Table 4-2.

By means of these products the chloride diffusion coefficient of a particular concrete can be calculated from a simple resistivity measurement with reasonable accuracy, for wide a range of concrete mixes.

4.5.4 Application of electrical resistivity measurements on hardening concrete for QA/QC procedures

Quality control procedures require rapid and reliable test methods.

As described above the electrical resistivity is influenced by a number of concrete properties. Therefore by measuring the electrical resistivity in the early stage of concrete maturity the future capability for achieving the required durability can be evaluated.

Klinghoffer & Rislund [1995] have recently described a test method based on resistivity measurements, which are useful for quality control procedures.

This work was a part of BRITE/EURAM project (BREU-CT90-0358) regarding "Quality Assurance of Concrete based on Testing of the fresh, still plastic Material". In the experimental part of this work the resistivity of twelve different concrete compositions was determined during the entire hardening period. Pore water was also squeezed at a fixed time of the sample maturity for determination of electrical resistivity.

By means of equation (4.5.1:4) and by using the resistivity values up to 28 days of sample maturity, the Formation Factor *FF* expressed as McMullin Number N_M was calculated. Then the actual and effective chloride diffusion coefficients were calculated by means of equation (4.5.1:5). The diffusivity of the fully matured concrete was calculated based on resistivity measured up to 28 days of sample maturity corrected by the empirically determined factors representing hardened concrete. Diffusion coefficients obtained by means of resistivity measurements were compared with values obtained by means of a standard test method for measuring diffusivities of Cl^- in concrete.

Some results from the work by Klinghoffer & Rislund [1995] are shown in Table 4-3 and in Figure 4-19, where diffusion coefficients obtained by means of resistivity measurements are compared with results from the standard method. The results correlate well with similar data published in the literature.

The most important conclusion of this work is therefore, that determination of diffusivity by means of resistivity measurements performed in the early stage of concrete maturity makes it possible to apply this technique in the quality control procedures, while the traditional methods require at least twice the time before the test results are available.

4.5.5 Summary

The electrical *resistivity* can directly be used as a uniformity parameter as it is well known today. This is simple and sufficient for most purposes. But the electrical resistivity is also a property which can be used as a measure of *diffusivity* when the following conditions are satisfied:

- The resistivity is measured on fully water saturated samples.
- The resistivity of pore water is known.

The second condition can cause difficulties in practice. In this case the electrical resistivity measured on the number of samples selected from the current production batch can be utilized as a measure of chloride permeability.

Depending on composition and pozzolanic addition, calibration will be needed, after which it could be possible to use resistivity measurements as a control parameter and a measure of homogeneity when the concrete is mixed.

Under these conditions the electrical resistivity measurements can be considered as a suitable technique for QA/QC procedures.

4.6 Combined transport test methods

Combined test methods are rare

Test methods involving combined transport processes are rare. A lot of experiments have been performed where combined processes were studied with various experimental methods.

Very few of the experimental methods, however, have been repeated. For each new experimental series, the set-up or conditions for the test are new.

Wetting and drying

One way to make tests is to simply let a specimen suck salt water and then dry out, with different combinations of wetting and drying periods. During, or after, the test period chloride profiles are determined. Sometimes this is done in two dimensions, by submerging a part of a specimen, with or without changing the salt water level with time.

Capillary suction of a salt solution

Exposing a specimen to a salt solution at one end and letting it dry from the other, is another method that has been used in different versions, cf. Tuutti [1982] and Buenfeld et al. [1995]. The position of the evaporation front and the distribution of moisture and chlorides during and after the test, as a function of the conditions at the two sides of the specimen, are interesting test results. These tests are time-consuming, requiring several months, or years, to come close to steady-state conditions.

Spray methods

Other methods are spray methods, where concrete specimens are exposed to an intermittent splash or fog of a salt solution.

One example is the NTH-spray method, Vennesland [1993]. In a plexiglass box concrete specimens, sealed by epoxy on all surfaces but one, are sprayed with a salt solution from nozzles. A fan is used to blow a salt fog around the specimen and to dry the specimen. The test cycle is four hours of spraying and four hours of drying, making three cycles a day for six weeks. After the test, chloride profiles are taken from the specimen and the "achieved" transport coefficient is determined by curve-fitting.

This method has been suggested as a test method and has been used to some extent. The application of the test result is not clear, however.

The relevance of accelerated combined methods is doubtful

The relevance of the results from the experiments involving combined processes is questionable. Usually the tests are heavily accelerated, in a way that is difficult to translate into real exposure.

Swamy et al. [1995], however, tried to quantify an "acceleration rate" of an intermittent ponding test from a comparison of test results for a particular concrete and reported chloride profiles in the literature for similar concretes in the splash zone.

Urgent need

We urgently need test methods that test relevant properties of concrete for quantifying the combined transport processes involving convection of chlorides, cf. Section 3.4.

4.7 *Field exposure tests*

The difference in field exposure test methods for measuring in-situ chloride penetration into concrete can generally be described by two subjects:

- Sampling technique
- Chloride analysis technique.

Furthermore the test methods fall into two groups: One group containing »quick and dirty methods« which are fast but not very precise, and one group containing more accurate methods which are more time-consuming.

It is of importance to have a knowledge of the concrete microstructure when evaluating chloride profiles in field structures. Factors like carbonation, leaching, frost damage, skin effect and crack intensity can have a decisive effect on chloride penetration. A test method to evaluate the macro- and microstructure of concrete is presented in the end of this section.

4.7.1 Sampling techniques

At the beginning of the period when measurement of the chloride content of concrete became of interest, single measurements were often used. Now there is often a wish to map the amount of chlorides penetrated into the concrete through measurements of concentration gradients or profiles. This imposes great demands not only on the chemical analysis but also on the sampling technique.

It is a principal problem that the chloride profile is not known during the sampling. Therefor one has to consider careful where to place the points of the profile. There are two risks: To make a too coarse profile having only one or two signinficant points or making a too narrow profile not showing all points down to the initial content C_i.

Generally concrete samples for chloride analysis are produced by one of the following methods:

- Chiselling by hand or machine
- Dry drilling by hand held hammer drill
- Water-cooled drilling of cores by jig-mounted drill
- In-situ grinding by profile grinding equipment

Figure 4-20. Photo showing sampling of concrete using the profile grinding technique.