Computational Modelling of Chloride Ingress in Concrete
S.J.H. Meijers
Computational modelling of chloride ingress in concrete
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of
chloride ingress in concrete

Proefschrift

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Sander Johan Helena MEIJERS

civiel ingenieur
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# GLOSSARY OF SYMBOLS AND ABBREVIATIONS

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<td>chloride ion potential: (C_{i,j}) in chloride model 0, 2 and 3</td>
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<td>$\gamma_2$</td>
<td>dry heat conductivity</td>
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<td>$\zeta_1$</td>
<td>water to cement ratio (w/c)</td>
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<tr>
<td>$\zeta_2$</td>
<td>cement content</td>
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\( \eta \) : isoparametric co-ordinate
\( \eta_i \) : moisture content parameter
\( \eta_2 \) : moisture content parameter: multiplier of T
\( \eta_3 \) : moisture content parameter: multiplier of H
\( \eta_4 \) : moisture content parameter: multiplier of TH
\( \eta_5 \) : moisture content parameter: multiplier of H²
\( \eta_6 \) : moisture content parameter: multiplier of TH²
\( \theta_1 \) : \( m^2s^{-1} \) moisture conductivity parameter: saturated moisture conductivity (at H=1)
\( \theta_2 \) : moisture conductivity parameter
\( \theta_3 \) : moisture conductivity parameter: threshold moisture potential
\( \theta_4 \) : moisture conductivity parameter: exponent
\( \kappa_1 \) : \( m^2s^{-1} \) saturated chloride ion conductivity
\( \kappa_2 \) : \( m^2s^{-1} \) dry chloride ion conductivity
\( \lambda_1 \) : Jmol⁻¹ Arrhenius function: activation energy
\( \lambda_2 \) : K Arrhenius function: reference temperature
\( \xi \) : isoparametric co-ordinate
\( \xi_1 \) : kgm⁻³ chloride binding: maximum moisture content in chloride model 1
\( \xi_2 \) : kgm⁻³ chloride binding: cement gel content in chloride model 2 and 3
\( \xi_3 \) : kgm⁻³ chloride binding: ratio of \( C_{\text{bound}} \) and \( C_{\text{free}} \) in chloride model 1
\( \xi_4 \) : kgm⁻³ chloride binding: reciprocate of \( dC_{\text{bound}}/dC_{\text{free}} \) at \( C_{\text{free}}=0 \) in chloride model 2
\( \rho_w \) : kgm⁻³ density of water
\( \tau \) : dimensionless time
\( \varphi_1 \) : carbonation parameter for moisture content
\( \varphi_2 \) : carbonation parameter for moisture conductivity
\( \varphi_3 \) : carbonation parameter: threshold moisture potential
\( \varphi_4 \) : carbonation parameter: exponent
\( \varphi_i \) : dimensionless co-ordinate in i-direction
\( \chi_1 \) : transfer coefficient
\( \chi_2 \) : ms⁻¹ moisture transfer coefficient (=\( \chi_{22} \))
\( \psi_i \) : environmental potential
\( \psi_2 \) : environmental relative humidity
\( \mathcal{C} \) : kgm⁻²s⁻¹/² scaled chloride ion potential
\( \mathcal{N} \) : kg⁻¹s⁻¹/²m⁻¹/² scaled moisture potential in moisture model 0 and 3
\( \mathcal{M} \) : m²s⁻¹ scaled moisture potential in moisture model 1, 2 and 4
\( \mathcal{G} \) : J¹/²k¹/²s⁻¹/²m⁻¹/² scaled inner energy potential

DOF : degree of freedom
FEM : finite element method
ITZ : interfacial transition zone
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<tr>
<td>REV</td>
<td>representative elementary volume</td>
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<td>w/c</td>
<td>water-cement ratio</td>
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<td></td>
<td>dimensionless</td>
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Chapter 1
INTRODUCTION

Exposure to a saline environment is a major threat to the durability of reinforced concrete structures. The chloride ions, which are present in seawater and de-icing salts, are able to penetrate the concrete up to the depth of the reinforcement. Despite the availability of oxygen, in principle the reinforcement bars in concrete do not corrode due to a passivating gamma ferric oxide film, which surrounds the steel. The highly alkaline pore liquid in concrete facilitates the formation of this protective film. However, a sufficient concentration of chloride ions at the depth of the reinforcement steel in combination with a certain electrode potential of the steel and a certain hydroxyl ion concentration, leads to breakdown of the passive oxide film. Consequently, reinforcement corrosion starts after all. The destruction of the oxide film is limited to specific sites, corrosion pits, where an acid environment is created. The severity of the corrosion process is established by the localised anodic reaction in the pits and the large cathodic area for oxygen reduction. The structural consequences of the corrosion process are twofold. Firstly, the effective cross-section of the reinforcement steel is being reduced, which causes loss of strength. Secondly, the expansion of the rust products, up to 600 %, inevitably leads to cracking of the cover, which enhances further deterioration (see figure 1.1). Clearly, the analysis of chloride ingress is an important part of the durability design of reinforced concrete structures. The costs and damage caused by the premature ending of the service life of concrete structures, enforces good durability design.

The objective of the present work was to develop a computational model for chloride ingress in reinforced concrete, which is based on the coherent processes of chloride ion transport and moisture migration. Particularly, the model was supposed to be able to deal with varying external conditions, i.e. varying environmental temperature, humidity and chloride loading. As carbonation is coupled with drying of concrete and is known to influence chloride ingress, it was to be included in the modelling as
well. The performance of the computational model was to be tested by comparing both its input and output to experimental data from literature.

The present work focuses on the so-called initiation phase, during which chloride ions move globally towards the reinforcement bars where they eventually, when the threshold chloride content has been reached, may trigger the corrosion process. The propagation phase, in which the corrosion process is going on, and the resulting cracks in concrete are disregarded. Current structural concrete design follows ‘lean and mean’ principles with typically narrow safety margins. In that respect inclusion of the corrosion propagation phase in the designed lifetime of a concrete structure is questionable, so that confining durability analysis to the corrosion initiation phase is a safe approach. For the case of marine concrete structures usually three exposure zones are distinguished: the submerged zone, the tidal and splash zone, and the atmospheric zone. In case of exposure to de-icing salts, the concrete is intermittently subjected to saturated chloride solutions during the winter season. The developed model has been set up as robust as possible and is intended for all these exposure conditions. In the model concrete is assumed to be uncracked and homogeneous in the sense that the ensemble of aggregates, cement paste and interfacial transition zones constitutes a material that can be characterised by averaged quantities.

Traditionally chloride ingress in concrete is modelled by the error-function solution corresponding to Fick’s second law. Although that model is widely applied, it is a rather coarse approach to chloride penetration in concrete and particularly omits the influence of moisture migration in concrete on chloride transport. The basis of recent models are the simultaneous and interactive processes of chloride, moisture and heat transport in concrete. Similar models and thorough thermodynamic elaborations can be found in hydrology. The resulting coupled diffusion equations are the backbone of the present model, the detailing of which grew gradually during the work. The scope of the work consisted largely of the programming and evaluation of the corresponding computer software.

Several moisture and salt transport models for porous media like concrete are discussed in chapter 2. The coupling of the processes of heat, moisture and chloride ion transport in concrete is further explained in chapter 3. In chapter 4 the implementation of the model according to the finite element method is elucidated. The model has been applied to three cases and the corresponding experimental and numerical results have been compared, which is described in chapter 5. Sensitivity analyses have been performed and they are reported in chapter 6. In that chapter also the contribution of moisture transport to chloride ingress in concrete is evaluated, partly by comparing application of the developed model and the error-
function model to a drying-wetting exposure. Conclusions are drawn and recommendations given in chapter 7.

Figure 1.1: a heavily corroded concrete pier in the North-West of Sliema on Malta (picture March 5th 2000 by L. Moors, see also cover).
Chapter 2

MOISTURE AND SALT TRANSPORT MODELS FOR POROUS MEDIA

Moisture and salt transport models have not only been developed for concrete, but also for soil. Both concrete and soil are porous media which are accessible to liquids, solutes and vapours, but the main difference is the physical and chemical instability of concrete due to the hydration process. Almost all models proposed in literature are diffusion-type models, i.e. models based on partial differential equations of the parabolic type. These models arise simply from linear or non-linear relations between flows and the gradients of the potentials that drive the flows, and the continuity requirement. The linear relations between flow and potential gradient are the well-known Darcy’s equation (moisture) and Fick’s first law (solute). Thorough thermodynamic analyses of the transport phenomena in porous media over the past decades have resulted in complex relations between flows and their driving forces. The diffusion-type models can be found in balance form, i.e. using the continuity requirement (e.g. the Richards equation and Fick’s second law), in flow (steady-state) form, i.e. without the continuity requirement, and in accumulative form, i.e. integration of the uptake or loss of liquid or solute over time (which results in a ¥t formulation). Some moisture and salt transport models are described separately in section 1 and 2 respectively. Combined approaches to moisture and salt transport in porous media are given attention to in the last section.

2.1 Moisture transport models

Moisture transport models are mainly based on partial differential equations of the parabolic type; an exception are the models based on cellular automata. The former models differ from each other in the used potentials for moisture flow and in the
definition of the coefficients (capacities, conductivities and sources). The coefficients can be related to storage and transport of moisture in the porous medium. The transport coefficient is referred to as either permeability, (hydraulic) conductivity or diffusivity. Generally two alternatives exist to describe moisture storage (capacity): a (ab- or de-) sorption curve or a capillary pressure curve. In the sorption curve the moisture content is plotted versus the environmental or pore humidity [JON94][REL99]; the capillary pressure curve gives the capillary pressure or matrix potential versus the moisture content [PEL95a][NIE00] (see figure 2.1). Usually within these diagrams distinct absorption and desorption, or wetting and draining curves appear. This effect is commonly identified as hysteresis, although some authors argue that it is due to the relatively short measurement time, an internal material change and a pore liquid composition change during the measurement [KIE83][KLO83].

Figure 2.1: two alternative (schematic) representations of moisture storage in a porous medium. The sorption diagram (left) relates the moisture content (W) to the environmental or pore humidity (h), and the capillary pressure diagram (right) the capillary pressure or matrix potential (p) to the moisture content. The difference between the absorption and desorption, and wetting and draining curves respectively is commonly attributed to hysteresis.

While in saturated porous media Darcy’s law can readily be applied, the study of the more general case of unsaturated (vadose) zones necessitated a more fundamental, thermodynamic approach. Over the past decades a tremendous amount of research has been dedicated to the modelling of moisture transport in unsaturated porous media. The models can globally be divided into single balance models and multiple balance models (with corresponding partial differential equations of the parabolic type). Mostly the multiple balance models comprise of two coupled balances: one for mass (moisture) transport and one for energy (heat) transport. The recognition of the
2.1 moisture transport models

Mutual influence of heat and moisture has lead to the additional heat balance. Obviously, the multiple balance models are more sophisticated than the single balance models. However, the latter models are easier to handle from a computational point of view and less parameters (to be determined experimentally) are involved generally. In the following the work of some authors is briefly addressed, which yields a superficial overview of this extensive field of research.

The general formulation of a single balance moisture model is:

\[
c \frac{\partial H}{\partial t} = \nabla \cdot (k \nabla H) - f
\]  \hspace{1cm} (2.1)

With \(H\) as the potential (the gradient of which is the driving force) for moisture transport, time \(t\), moisture capacity \(c\), moisture conductivity \(k\) and sink (negative source) \(f\). The coefficients \(c, k, f\) may be functions of \(H\), which makes the above partial differential equation non-linear. In [ECK85] this model, with the moisture content as \(H, c=1\) and \(f=0\), is derived from a moisture balance in which the moisture flow equals the product of permeability and gradient of the partial pressure of water vapour. The diffusivity equals then the product of permeability and the derivative of the partial pressure of water vapour with respect to moisture content. This derivative is the inverse of the slope of the sorption isotherm. A similar model is given in [SAK83][HOR85][PLE98] and in [HOR85] it is indicated that for drying of mature concrete the value of \(k\) (constant) lies between \(10^{-10}\) and \(10^{-12}\) m\(^2\)/s. Also in [REL99] the analysis of experimental results with this model yielded that \(k\) (constant in certain time spans) is in the range from \(7 \cdot 10^{-10}\) to \(4 \cdot 10^{-12}\) m\(^2\)/s for field concrete.

In [JON94] the vapour content is chosen as the potential instead of the moisture content; moreover, \(c\) equals the derivative of the evaporable moisture content with respect to the vapour content and \(f\) the time derivative of the non-evaporable moisture content. In [PEL95b][PEL96][PEL98] the last equation, with the volumetric moisture content as \(H, c=1\) and \(f=0\), is shown to hold for isothermal water absorption and desorption (drying) of bricks, gypsum and mortar. The moisture diffusivity \(k\) is in [PEL98] defined as an exponential function of the volumetric moisture content (more precisely, two different exponential functions for two separate ranges of the volumetric moisture content) and a good agreement between experimental (NMR) absorption data of mortar and model predictions is obtained for \(k\) varying (exponentially) between \(2 \cdot 10^{-10}\) and \(6 \cdot 10^{-7}\) m\(^2\)/s (depending on the way of preparing the dry samples). It is remarkable that these values of \(k\) are much higher than the ones in e.g. [REL99], despite that mortar and concrete have been analysed respectively. Note that the different definitions of \(H\) (moisture content in kg/m\(^3\) versus volumetric moisture content in m\(^3\)/m\(^3\)) do not affect the respective values of \(k\), if the respective values of \(H\) are proportional to each other (constant water density).
According to the Richards equation [NIE00] \( H \) is the water pressure head, \( c \) the specific water capacity (the derivative of the volumetric water content with respect to the water pressure head), \( k \) the unsaturated hydraulic conductivity (depending on the degree of saturation) and \( f \) the derivative of this hydraulic conductivity in vertical direction. For the case of saturated concrete, \( H \) as the hydraulic pressure in excess of atmospheric pressure, \( c = 1 \), \( f = 0 \) and \( k \) constant, Murata [HOR85] reported values of \( k \) ranging from \( 10^{-8} \) to \( 10^{-4} \, \text{m}^2/\text{s} \).

In [BAZ72] it is stated that in case of drying the linear diffusion equation overestimates the moisture loss at large time spans. In this work a non-linear diffusion equation is derived which can be considered to form a bridge between the single balance models on the one hand and the multiple balance models on the other hand. The water flux is initially modelled being proportional to the gradient of the Gibbs free energy per unit mass of evaporable water. By expressing this Gibbs free energy in terms of the pore humidity and noting that in each pore the Gibbs free energy is the same for water vapour, capillary water and unhindered adsorbed water due to thermodynamic equilibrium, the water flux becomes proportional to the gradient of the pore humidity. Next, it is stated that a change of pore humidity is proportional to a change of total water content and a change of temperature. The hygrothermic coefficient determines the relation between a change of pore humidity and a change of temperature. Application of the continuity requirement leads then to equation 2.1, in which \( H \) is the pore humidity, \( c = 1 \) and \( f \) comprises of autodesiccation and thermal effects. The thermal effect in \( f \) consists of the (negative) product of the hygrothermic coefficient and the time derivative of the temperature. The moisture diffusivity \( (k) \), since \( c = 1 \) increases with the pore humidity; this empirical functional relation is given by equation 3.102 and shown in figure 3.14. The explicit appearance of the time derivative of temperature in the moisture balance in [BAZ72] already indicates that the simultaneous consideration of heat flow is necessary, which is the case in the multiple balance models.

In most cases the multiple balance models consist of two coupled balances, given by:

\[
\begin{align*}
\frac{\partial T}{\partial t} + c_{\text{m}} \frac{\partial H}{\partial t} &= \nabla \cdot (k_{\text{m}} \nabla T + k_{\text{m}} H \nabla H) - f_T \\
\frac{\partial T}{\partial t} + c_{\text{H}} \frac{\partial H}{\partial t} &= \nabla \cdot (k_{\text{H}} \nabla T + k_{\text{H}} H \nabla H) - f_H
\end{align*}
\]

(2.2)

The upper row of this set of coupled partial differential equations constitutes the heat balance, while the lower row is the moisture balance. If \( H \) is the moisture concentration and \( T \) temperature, it holds that \( k_{\text{H}} \neq k_{\text{T}} \) according to de Groot and Mazur [HOR85], since the gradients of \( H \) and \( T \) are not the thermodynamic driving forces of the moisture and heat flux. In this respect [GRO69] states that if the fluxes are
independent and covering completely the entropy production in the system considered, the Onsager reciprocal relations are applicable, i.e. a symmetric conductance matrix (\(k_{ij} = k_{ji}\) in this case). It is further remarked in [HOR85] that the solution of this system of coupled partial differential equations "can only be obtained by sophisticated numerical procedures. The numerical solution is in itself a formidable task." Krischer [GRU97] put forward a model for simultaneous moisture and heat transport analogous to the last equation with the potentials temperature and partial pressure of water vapour. In Krischer's moisture balance also the volumetric moisture content is differentiated with respect to time and space; in the heat balance the specific phase change enthalpy liquid-vapour of water is explicitly taken into account. The work of Luikov [GRU97] is similar to that of Krischer, however as opposed to Krischer, the temperature gradient in the moisture balance is included in Luikov's model. Moreover, the ratio of vapour and moisture transport is constant in Luikov's model.

In the model of Philip and de Vries [PHI57][VRI58][GRU97] for porous media, in particular soils, gravity and the matrix potential (negative capillary pressure) gradient drive capillary liquid transport. The partial pressure of water vapour depends on the matrix potential and temperature. The matrix potential, in turn, depends on water content and temperature. Hence (volumetric) moisture content and temperature are the basic variables (H and T respectively in the last equation) in the model of Philip and de Vries. In this model \(f_0=0\) and \(f_1\) equals the (negative) partial derivative of the unsaturated hydraulic conductivity with respect to the vertical co-ordinate. The tentative formulation of the heat flux in [VRI58] is composed of a common part consisting of the product of the thermal conductivity (in the absence of moisture movement) and the temperature gradient, a part describing transfer of latent heat by vapour movement and a part describing transfer of sensible heat in vapour and liquid form. Furthermore, in [PHI57] moisture transfer through liquid (water) islands in the pore space due to diffusing vapour is described.

In the work of Kießl [KIE83] for building materials H and T are also represented by the volumetric moisture content and temperature respectively. Besides, Kießl defines a moisture potential in order to be able to describe moisture transport across material boundaries. This moisture potential equals the relative humidity for relative humidities lower than or equal to 0.9 and it is a logarithmic function of the capillary radius (related to the Kelvin equation) for relative humidities greater than 0.9 [KIE83][GRU97]. In [GRU97] it is stated that several parameters of Kießl's model cannot be determined experimentally. Based on Kießl's definition of the moisture flux and the moisture potential, an extension for hardening concrete by incorporating cement hydration has been proposed in [ROE94]. For that purpose the degree of hydration is introduced in the moisture balance and \(f_1\) is defined as a non-linear function. In [ROE89] an
additional differential equation is formulated which defines the rate of the degree of hydration as a function of the degree of hydration itself, the water to cement ratio, temperature and the ratio of pore vapour pressure and pore vapour pressure at saturation.

The model of Neiß [GRU97] has been set up for soils and allows for temperatures lower than the freezing point of water. Neiß derives equation 2.2 with H as the matrix potential (capillary pressure) and T temperature from separate balances for water (liquid), vapour, heat and enthalpy flow. These flows are driven by gradients of the matrix potential, vapour pressure and temperature. The influence of gravity on the liquid phase is included in \( t_T \) and \( t_H \); gravity effects are also incorporated in \( k_{HH} \) and \( k_{TH} \). The coefficients \( k_{HH} \) and \( k_{TH} \) comprise of liquid and vapour components. According to [GRU97] the determination of some parameters in Neiß' model is not clear. The work of Häupl and Stopp [GRU97] in the field of building physics is based on Krischer's model. All material parameters are a function of water content and temperature. In later work, together with Grunewald, they added a balance for air, considering air flow through the pores to be laminar.

A completely different approach to the modelling of moisture transport in unsaturated porous media is described in [KÜN01]. The non-linear diffusion equation is simulated by means of a lattice gas automaton, which is a type of cellular automaton. Discrete fluid particles move in a triangular mesh and obey collision rules. The particle collisions lead to redistribution of velocities, while the total mass and total momentum is conserved.

### 2.2 Salt transport models

In this section salt transport models, in particular chloride ion transport models for concrete, are reviewed which do not consider moisture movements. The means of transportation of the chloride ions is therefore by diffusion only. In general, chloride models require input of material parameters, exposure (boundary) conditions and initial (internal) conditions. This input must be provided by measurements or assumptions. The output of chloride models is essentially the chloride content at the depth of the reinforcement bars at a certain point in time, which is to be compared to the threshold value of the chloride content for reinforcement corrosion. This concept has been depicted in figure 2.2.

The measurement of material parameters has mainly been focused on chloride diffusion coefficients, determined by either diffusion tests or electro-migration tests [TAN96][AND00], and chloride binding [TRI89][TAN93]. When interpreting these
Figure 2.2: the input (1, 2 and 3) and output (4) of chloride transport models. The chloride transport model is supposed to predict the chloride content at the depth of the reinforcement bars at a certain point in time. When this chloride content exceeds a certain threshold value (5), reinforcement (pitting) corrosion is likely to occur.

measured diffusion coefficients, it has to be noted firstly that they reflect diffusion of ions not in a pure substance but in a porous medium, secondly that the porous medium was not necessarily water-saturated during the entire measurement period, and thirdly that adsorption (binding) of ions to the porous material is inherent in the measurement. For these reasons the measured chloride ion diffusion coefficient in concrete is referred to as the apparent diffusion coefficient. Chloride ion diffusion coefficients have also been determined from measured chloride profiles in concrete structures by curve-fitting of the diffusion equation (Fick's second law). These diffusion coefficients can hardly be called material properties, since they have been affected by the actual exposure conditions; they are referred to as effective diffusion coefficients [BAM97]. The definition and variability of the exposure conditions (environmental temperature and humidity, chloride loading) to which concrete structures are subjected, is a problem for the predictions of any chloride model; these exposure conditions have been investigated by e.g. [LIN00]. The reliability of model predictions is further complicated by the variability of the threshold value of the chloride content for reinforcement corrosion. According to measurements the value of this threshold chloride content is between 0.2 and 2 % on cement mass [VAS84].
Traditionally, chloride ion transport in concrete has been modelled by a linear diffusion equation, also known as Fick's second law:

$$\frac{\partial C}{\partial t} = D \nabla^2 C$$  \hspace{1cm} (2.3)

with C as the total chloride content or as the free chloride ion concentration, time t and diffusion coefficient D. On the following conditions:
1. A single spatial dimension x, ranging from 0 to ∞ (semi-infinite)
2. C=C₀ at x=0 and t>0 (boundary condition)
3. C=0 at x>0 and t=0 (initial condition)

An analytical solution of the last equation can be obtained, viz.:

$$C = C₀ \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right]$$  \hspace{1cm} (2.4)

or alternatively:

$$C = C₀ \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right)$$  \hspace{1cm} (2.5)

in which C₀ is a constant and with the error-function erf() and the error-function complement erfc() as:

$$\text{erf}(p) = \frac{2}{\sqrt{\pi}} \int_0^p e^{-q^2}dq , \quad \text{erfc}(p) = \frac{2}{\sqrt{\pi}} \int_p^\infty e^{-q^2}dq , \quad \text{erfc}^{-1}(p) = 1 - \text{erf}(p)$$ \hspace{1cm} (2.6)

The error-function ranges from 0 (p=0) to 1 (p=∞), see also appendix A. Equation 2.4 can also be written as [BAM98]:

$$x = 2\text{erf}^{-1} \left( \frac{C₀ - C}{C₀} \right) \sqrt{Dt}$$ \hspace{1cm} (2.7)

in which erf⁻¹() is the inverse of the error-function.

**Bamforth**

In conjunction with the above analytical solution a time dependence of the diffusion coefficient has been proposed in [BAM97]:

$$D(t) = D_{ce} \left( \frac{t}{t_m} \right)^n$$ \hspace{1cm} (2.8)

in which D_{ce} is the effective chloride diffusion coefficient determined from a chloride profile at time tₘ. The age factor n is negative and thus the diffusion coefficient D decreases over time. This is motivated by the progress of hydration over time and the consequential densification of the pore system. The value of C₀ is defined as the notional surface chloride level Cₘₚ, which is not a true surface chloride level [AND], but the value which, together with D_{ce}, provides the best fit of the measured chloride profile at tₘ. It is emphasized in [BAM] that D_{ce} is an average diffusion coefficient over the period from t=0 until tₘ. This chloride transport model serves further a
2.2 salt transport models

probabilistic analysis, in which a distribution of values for $C_{cn}$ and $D_{ce}$ is introduced [BAM98].

Andrade

In [AND95][AND97] an analysis is performed with a solution of the linear diffusion equation for two regions:

1. the skin layer with thickness $e$ (from the surface to depth $e$), diffusion coefficient $D_1$ and total chloride content $C_1(x,t)$
2. the bulk beyond depth $e$ with diffusion coefficient $D_2$ and total chloride content $C_2(x,t)$

With the initial conditions $C_1(x,0)=0$ for $0<x<e$ and $C_2(x,0)=0$ for $x>e$, and the boundary conditions $C_1(0,t)=C_s$ and $RC_1(e,t) = C_2(e,t)$ for $t \geq 0$ it can be derived that:

$$C_1(x,t) = C_s \sum_{n=0}^{\infty} \alpha^n \left[ \text{erfc} \left( \frac{2ne+x}{2\sqrt{D_1 t}} \right) - \alpha \text{erfc} \left( \frac{(2n+1)e-x}{2\sqrt{D_1 t}} \right) \right]$$

$$C_2(x,t) = \frac{2kC_s R}{k+1} \sum_{n=0}^{\infty} \alpha^n \text{erfc} \left( \frac{(2n+1)e+k(x-e)}{2\sqrt{D_2 t}} \right)$$

in which $C_s$ is the surface chloride content, $R$ the resistance at the interface and:

$$k = \frac{D_1}{D_2}, \quad \alpha = \frac{1-k}{1+k}$$

In case of $D_1 = D_2$ and $R=1$ the expressions for $C_1(x,t)$ and $C_2(x,t)$ (equation 2.9) reduce to equation 2.5. The resistance $R$ can represent the reduced binding capacity of the skin layer, when this layer is carbonated; the total chloride content is then lower just in front of depth $e$ than just behind depth $e$ ($R>1$). In [AND95][AND97] the influence of the ratio of $D_1$ and $D_2$, the skin layer thickness $e$, the absolute value of $D_2$ and the resistance $R$ has been investigated. It was found that, when comparing diffusion coefficient $D_2$ to the diffusion coefficient $D$ used in the ordinary error-function solution (equation 2.5), the two diffusion coefficients may differ by more than one order of magnitude.

Sergi

In [SER92] the total chloride content $M_i$ (in mmole Cl- per g concrete) consists of a quantity of chloride ions in the pore solution $C_i$ (in mole Cl- per litre) and a quantity of bound ions $S_i$ (in mmole Cl- per g concrete). The change of $M_i$ over time $t$ is defined as:

$$\frac{1}{w} \frac{\partial M_i}{\partial t} = \frac{\partial C_i}{\partial t} + \frac{1}{w} \frac{\partial S_i}{\partial t}$$

1 Note that $\alpha^2 = 1$. 
which reveals that the water content \( w \) in which diffusion occurs (per unit weight of concrete) is considered to be constant. Chloride binding is assumed to be according to Langmuir:
\[
S_i = \frac{\alpha C_i}{1 + \beta C_i}
\]
(2.12)
The ionic flux in the pores \( J_i \) is defined as:
\[
J_i = -\varepsilon D_i \frac{\partial C_i}{\partial x}
\]
(2.13)
in which \( x \) is the spatial co-ordinate, \( \varepsilon \) the (constant) volume fraction of water in which diffusion occurs and \( D_i \) the (constant) diffusivity in the pore solution. With the chloride balance:
\[
\frac{1}{w} \frac{\partial M_i}{\partial t} = \frac{1}{\varepsilon} \frac{\partial J_i}{\partial x}
\]
equation 2.11, 2.12 and 2.13 the following partial differential equation is derived for the pore solution:
\[
\left[ 1 + \frac{\alpha}{w(1+\beta C_i)^2} \right] \frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2}
\]
(2.15)
It is shown that the resulting diffusion coefficients in a balance in \( C_i \) (in the pores) versus a balance in \( M_i \) (in concrete) are identical in case of no binding (\( \alpha=0 \)) and linear binding (\( \beta=0 \)) respectively.

**Tang**

In [TAN96] moisture movements are disregarded and the chloride transport model is intended for the submerged zone. Essentially the following chloride balance is solved:
\[
\frac{\partial Q_{\text{tot}}}{\partial t} = \frac{\partial}{\partial x} \left( AD \frac{\partial c}{\partial x} \right)
\]
(2.16)
with \( t \) time, \( x \) the spatial co-ordinate, \( Q_{\text{tot}} \) the total quantity of chlorides (in kg Cl\(^-\) per m\(^3\) concrete), \( c \) the free chloride ion concentration (in kg Cl\(^-\) per m\(^3\) solution), \( D \) the intrinsic diffusion coefficient and \( A \) the effective diffusion path (in m\(^3\) solution per m\(^3\) concrete). At water-saturation \( A \) equals the capillary porosity. The solution of the above equation is obtained in two successive procedures. In the first procedure the net inflow (or outflow) of free chlorides \( q_c \) in a concrete slice of unit area and thickness \( \Delta x \):
\[
q_c = -AD \frac{\partial c}{\partial x}
\]
(2.17)
with:
\[
D = D_0 f_0(T) g(t) f(x)
\]
(2.18)
is calculated by means of an explicit finite difference formulation. The intrinsic diffusion coefficient \( D_0 \) at temperature \( T_0 \) is determined by a non-steady-state migration test (CTH rapid method). The temperature dependent coefficient \( f_D(T) \) equals the Arrhenius law:

\[
f_D(T) = e^{\frac{E_D}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right)}
\]

the age effect is included by factor \( g(t) \):

\[
g(t) = \begin{cases} 
    \left( \frac{t_D}{t} \right)^{\beta}, & t < t_D \\
    1, & t \geq t_D 
\end{cases}
\]

and the depth effect by factor \( f(x) \):

\[
f(x) = \begin{cases} 
    \varphi + (1-\varphi) \left( \frac{x}{x_s} \right)^{\beta}, & x < x_s \\
    1, & x \geq x_s 
\end{cases}
\]

In the last equations \( E_D \) is the activation energy for chloride diffusivity, \( R \) the gas constant, \( t_0 \) the age when the diffusivity becomes constant, \( \beta \), a constant, \( \varphi \) the relative diffusivity in the surface zone, \( x_s \) the thickness of the surface zone and \( \beta_s \) a constant. The temperature inside the concrete as well as the (external) chloride concentration in sea water can be varied sinusoidally. In the second procedure the total quantity of chlorides in the concrete slice of thickness \( \Delta x \) is augmented with the calculated net inflow of free chlorides (see equation 2.16). The free chloride concentration is then determined from:

\[
Q_{\text{tot}} = cW + Q_{\text{bound}}
\]

with Freundlich binding:

\[
Q_{\text{bound}} = f_{\text{OH}} f_s(T) W_{\text{gel}} \frac{f_{u} - c^{\beta}}{1000}
\]

In the last two equations \( W \) is the water content (in m\(^3\) solution per m\(^3\) concrete), \( Q_{\text{bound}} \) the quantity of bound chlorides (in kg Cl\(^-\) per m\(^3\) concrete), \( W_{\text{gel}} \) the quantity of hydrate gel (in kg gel per m\(^3\) concrete), and \( f_u \) and \( \beta \) adsorption constants. The factor 1000 in the last equation is due to a unit conversion. The hydroxide dependent coefficient is defined as:

\[
f_{\text{OH}} = e^{\frac{\alpha_{\text{OH}}}{1 - \left( \frac{[\text{OH}^-]}{[\text{OH}^-]_{\text{m}}} \right) \Delta x}}
\]

with hydroxide concentration in the pore solution \([\text{OH}^-]_{\text{in}}\), initial hydroxide concentration in the pore solution \( [\text{OH}^-]_{\text{in}} \) and constant \( \alpha_{\text{OH}} \). Again Arrhenius law is used to include the temperature effect on chloride binding via \( f_s(T) \):
\[ f_D(T) = e^{\frac{E_b}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)} \] (2.25)

with \( E_b \) the activation energy for chloride binding. Note the subtle difference between equations 2.19 and 2.25: the exponent is positive in the former and negative in the latter equation for \( T > T_0 \). The hydroxide concentrations are calculated on the basis of a diffusive flux analogous to equation 2.17; the hydroxide ion diffusivity is considered to be proportional to the chloride ion diffusivity in concrete. The distribution of water contents inside submerged concrete is assumed to consist of three regions. The water content in the skin region, up to the depth of water suction \( s_d \), equals the saturated water content. The water content in the bulk region, deeper than depth \( x_c \), is a factor times the saturated water content. The water content in the remaining region, between \( s_d \) and \( x_c \), varies with \( x \). Apparently, this non-uniform water distribution inside concrete is considered to be stable for submerged concrete. Furthermore, it is pointed out in [TAN96] that the non-steady-state diffusion coefficient in a diffusion equation for free chlorides includes the chloride binding capacity, such that it decreases if the binding capacity increases.

### 2.3 Combined models

The modelling of ionic transport in porous media has been further advanced by not only considering ion diffusion in the pores, but also the simultaneous transport of moisture in the porous medium. Since ions are dissolved in the pore water, movement of water in the pores generally implies also movement of the ions. This phenomenon is referred to as convection or advection of ions. Some combined models are not confined to moisture and salt transport, but also take other processes into account, e.g. heat flow and cement hydration.

The complexity of the combined models necessitates numerical solution strategies. Therefore, in addition to the input as shown in figure 2.2, numerical parameters (timestep, mesh, solution tolerance, etc.) must be provided in order to obtain a solution resulting from the model. While analytical solutions are unambiguously defined, numerical solutions, being sequences of numbers, are not at all transparent. Moreover, depending of the complexity of the model, several physical and non-physical (numerical artefacts) solutions may exist, on the understanding that the numerical solution process has converged properly and the results are insensitive to changes of the temporal and spatial discretisation parameters. Numerical solutions must therefore be produced and presented with great care, and any apparently curious behaviour of these solutions must in the first instance be attributed to the numerical solution process. Then, after the numerical solution process has been thoroughly evaluated, the obtained solution can be analysed in a physical sense.
2.3 combined models

Nilsson

In [HET97][NIL00] a model for chloride ion transport in concrete is presented which is basically a convection-diffusion equation. The forward finite difference method is deployed and first the moisture flow is calculated, which yields the convective chloride ion flow, next the diffusive chloride ion flow and finally the new free chloride concentrations and bound chloride contents. The liquid moisture flux \( q_l \) (in \( \text{kgm}^{-2}\text{s}^{-1} \)) is defined as:

\[
q_l = -k_{RLH} \left( \varphi_{eq} \right) \frac{\partial \varphi}{\partial x}
\]

where \( x \) is the spatial co-ordinate, \( k_{RLH} \) the liquid flow coefficient (in \( \text{kgm}^{-1}\text{s}^{-1} \)), depending on the equivalent relative humidity \( \varphi_{eq} \) and \( \varphi \) the relative humidity. It is stated that \( \varphi_{eq} \) is the liquid flow potential, which implies that \( \varphi \) in the last equation should be replaced by \( \varphi_{eq} \). The chloride ion flux \( q_{CI} \) is defined as:

\[
q_{CI} = -D_{CI} \left( w, T, c_i^f \right) \frac{\partial c_i^f}{\partial x} + q_c c_i^f
\]

with \( D_{CI} \) as the chloride diffusion coefficient, depending on moisture content \( w \), temperature \( T \) and free chloride concentration \( c_i^f \) (in \( \text{kg Cl}^{-1} \text{ per m}^3 \text{ pore solution} \)). However, the dependency of \( D_{CI} \) on \( T \) and \( c_i^f \) has not been defined. The first term on the righthand-side of the last equation is the diffusive chloride ion flux and the second the convective chloride ion flux. The unit of the diffusive chloride ion flux is \( \text{kgm}^{-2}\text{s}^{-1} \). However, the unit of the convective chloride ion flux according to the last equation is \( \text{kgm}^{-2}\text{m}^{-1}\text{s}^{-1} \). This error can be repaired by dividing the convective chloride ion flux by the density of water (in \( \text{kg/m}^3 \)). The relative humidity \( \varphi \) depends on the moisture content \( w \) and the free chloride concentration \( c_i^f \):

\[
\varphi\left( w, c_i^f \right) = \varphi_{sat} - \frac{w_{cap} - w}{\frac{dw}{d\varphi}}
\]

with \( w_{cap} \) the capillary (probably maximum) moisture content and \( \varphi_{sat} \) the relative humidity at water-saturation (75 % if the pore solution is saturated with NaCl). Clearly, the dependency of \( \varphi \) on \( c_i^f \) is not explicitly defined by the last equation. If the moisture capacity \( \frac{dw}{d\varphi} \) were constant, \( \varphi \) would be a linear function of \( w \), which can be seen be rearranging the last equation:

\[
\frac{w_{cap} - w}{\varphi_{sat} - \varphi\left( w, c_i^f \right)} = \frac{dw}{d\varphi}
\]

The figures in [HET97][NIL00] suggest a piece-wise linear or even non-linear relation between \( \varphi \) and \( w \); the last equation does not exactly represent this relation. The equivalent relative humidity is obtained from the last equation with \( \varphi_{eq}=1 \) and probably with \( c_i^f=0 \text{ kg/m}^3 \). The amount of solute \( w_{sol} \) is smaller than the total moisture content \( w \):
\[ w_{\text{sol}} = w - w_{\text{atol}} \] (2.30)

with \( w_{\text{atol}} \) the part of the moisture content that does not act as solvent (corresponding to 11 % relative humidity). The total chloride content \( c_{\text{tot}} \) (in kg per m\(^3\) concrete) generally comprises of a free and bound part:

\[ c_{\text{tot}} = p_{\text{sol}} c_f + c_b \] (2.31)

with \( p_{\text{sol}} \) the part of the pore water that acts as solvent (in m\(^3\) water per m\(^3\) concrete), being equal to the ratio of \( w_{\text{sol}} \) and the density of water \( p_w \) and \( c_b \) the bound chloride content (in kg Cl\(^-\) per m\(^3\) concrete). The last equation is further specified by assuming linear chloride binding (constant binding capacity \( dc_b/dc_f \)). Then the free chloride concentration \( c_f \) is calculated from the total chloride content (resulting from the net diffusive and convective influx) as follows:

\[
c_f = \begin{cases} 
0, & c_{\text{tot}} < c_{b0} \\
\frac{c_{\text{tot}} - c_{b0}}{w_{\text{sol}}} + \frac{dc_b}{dc_f}, & c_{\text{tot}} \geq c_{b0}, \quad c_f < c_{f0} \\
\rho_w c_{f0}, & c_f \geq c_{f0}
\end{cases} \] (2.32)

with \( c_{b0} \) the bound chloride content up to which no free chlorides can be present and \( c_{f0} \) probably the saturated free chloride concentration. The temperature effect on chloride binding has been disregarded. For convergence of the numerical solution maximum timesteps are calculated throughout the time marching. It is questionable, however, whether these maximum timesteps alone indeed guarantee converged solutions, since generally, for a non-linear system as defined in this paragraph, several iterations have to be performed within every timestep.

Grace

In [GRA87] also a convection-diffusion equation is used to model chloride ingress in concrete:

\[
\frac{\partial c}{\partial t} = \left( D_c + kv \right) \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \tag{2.33}
\]

in which \( t \) is time, \( x \) the spatial co-ordinate, \( c \) the free chloride concentration, \( D_c \) the chloride diffusion coefficient and \( k \) the dispersion distance (constant). Two causes of bulk flow of water, with velocity \( v \), are considered, viz. due to capillarity:

\[
v = \frac{S}{2\varepsilon \sqrt{t}} \tag{2.34}
\]

and due to moisture diffusion:

\[
v = D_m \frac{\partial m(x,t)}{\partial x} \frac{1}{m(x,t)} \tag{2.35}
\]
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in which \( \varepsilon \) denotes the porosity, \( D_w \) the moisture diffusion coefficient and \( m \) the moisture concentration (a function of \( x \) and \( t \)). In the last equation a minus sign is probably missing. Moisture diffusion occurs beyond the saturation depth \( x_s \). The sorptivity coefficient \( S \) is defined as:

\[
S = s_0 \sqrt{1 - 1.08 \frac{m(x)}{\varepsilon}}
\]  
(2.36)

with constant \( s_0 \) (\( S=s_0 \) when \( m=0 \)). For some reason the moisture concentration \( m \) ceases to be a function of time in the last equation. It is stated that the depth of saturation \( x_s \) equals:

\[
x_s(t) = \frac{S \sqrt{t}}{\varepsilon}
\]  
(2.37)

and its time derivative equals flow velocity \( v \) according to equation 2.34 (on the condition that \( S \), via \( m \), does not depend on time). The ionic flux \( q_c \) is defined as:

\[
q_c = -(D_w + kv) \frac{\partial c}{\partial x} + vc
\]  
(2.38)

which is inconsistent with the chloride balance (equation 2.33), since \( v \) is generally a function of \( x \). At the exposed surface the (boundary) ionic flux \( q_{cb} \) is considered to be equal to:

\[
q_{cb} = vep - \frac{D_w}{a} (c - ep)
\]  
(2.39)

in case of wetting, with \( p \) the chloride concentration in seawater, \( e \) some factor and \( a \) a small distance from the concrete surface where \( c = ep \). In case of drying the boundary ionic flux is put equal to zero. Linear chloride binding is assumed, i.e. a constant ratio of total and free chlorides for a certain concrete type. A finite difference technique is deployed to obtain solutions. It is suggested in [GRA87] that the observed time-dependency of the chloride diffusion coefficient is caused by the reduction of flow velocities over time.

**Buendfeld**

In [BUE95] a convection-diffusion for the water content \( \theta \) (in kg/m\(^3\)) has been suggested for the description of ‘wick action’:

\[
\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left( D(\theta) \frac{\partial \theta}{\partial x} \right) - \frac{S^2}{2 \varepsilon} \frac{\partial \theta}{\partial x}
\]  
(2.40)

with time \( t \), spatial co-ordinate \( x \), hydraulic diffusivity \( D \) (in m\(^2\)/s), sorptivity \( S \) (in m/\( \sqrt{s} \)) and \( \varepsilon \) as the distance of the wet/dry interface from the wet face. Wick action is defined as "the transport of water (and any species it may contain) through a concrete element from a face in contact with water to a drying face". For the steady-state it has been derived that \( x \) equals:
\[ x_i = \frac{L}{1 - \frac{2D_x}{S^2} \ln \left( \frac{\rho - \theta_s}{\rho - \theta_L} \right)} \]  

(2.41)

and that the amount of water leaving the dry face \( Q \) (in kgm\(^{-2}\)s\(^{-1}\)) equals:

\[ Q = \frac{\rho P}{L} \left[ \frac{1}{2} S^2 - D_x \ln \left( \frac{\rho - \theta_s}{\rho - \theta_L} \right) \right] \]

(2.42)

In the last two equations the thickness of the element is denoted by \( L \), the density of water (liquid) by \( \rho \) (in kg/m\(^3\)), the concentration of saturated vapour by \( \theta_s \) (in kg/m\(^3\)), the concentration of vapour at the dry face by \( \theta_L \) (in kg/m\(^3\)) and the porosity involved in sorption by \( P \). An explicit formulation of chloride transport is missing in [BUE95]. It is however suggested that chloride ions are convected by the moisture movement as described by equation 2.40. Moreover, it is claimed that the model includes chloride diffusion according to Fick’s law, chloride binding and chloride precipitation (after excess of its solubility). The finite difference method is deployed to obtain solutions.

**Pel**

The model in [PEL00] involves a moisture and ion balance. The volumetric moisture content \( \theta \) is governed by:

\[ \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left( D(\theta) \frac{\partial \theta}{\partial x} \right) \]

(2.43)

with \( t \) time, \( x \) the spatial co-ordinate and \( D \) the isothermal moisture diffusivity. Ion transport is described by the following convection-diffusion equation:

\[ \frac{\partial}{\partial t} \left( \theta C_{\text{free}} \right) = -\frac{\partial}{\partial x} \left[ \theta \left( C_{\text{free}} v_i - D_h \frac{\partial C_{\text{free}}}{\partial x} \right) \right] - \frac{\partial C_{\text{bound}}}{\partial t} \]

(2.44)

in which \( C_{\text{free}} \) is the free ion concentration in water, \( v_i \) the (liquid) fluid velocity, \( D_h \) the hydrodynamic dispersion coefficient and \( C_{\text{bound}} \) the bound ion content. The first term in the brackets on the righthand-side of the last equation is the convective (or advective) ion flux, the second term the diffusive ion flux. Note that with the total ion content \( C_{\text{tot}} \) as:

\[ C_{\text{tot}} = \theta C_{\text{free}} + C_{\text{bound}} \]

(2.45)

equation 2.44 can be written as:

\[ \frac{\partial C_{\text{tot}}}{\partial t} = -\frac{\partial}{\partial x} \left[ \theta \left( C_{\text{free}} v_i - D_h \frac{\partial C_{\text{free}}}{\partial x} \right) \right] \]

(2.46)

In the model Freundlich adsorption is assumed:

\[ C_{\text{bound}} = K C_{\text{free}}^m (1 - e^{-t/\tau}) \]

(2.47)

with \( t \), the relaxation time, and \( K \) and \( m \) experimental parameters.
2.3 combined models

Boddy

The model described in [BOD99] is basically a convection-diffusion equation for chloride ions:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} + \rho \frac{\partial S}{\partial t}
\]  

(2.48)

with time \( t \), spatial co-ordinate \( x \), \( C \) the free chloride in solution, \( D \) the diffusion coefficient, \( \rho \) the concrete density, \( n \) the porosity and \( S \) the bound chloride content. The average linear (saturated) flow velocity is defined as:

\[
v = \frac{k}{n} \frac{\partial h}{\partial x}
\]  

(2.49)

with hydraulic conductivity (or permeability coefficient) \( k \) and hydraulic head \( h \). The plus sign in equation 2.48 ought to be replaced by a minus sign, which can be seen by rearranging this equation:

\[
n \frac{\partial C}{\partial t} - \rho \frac{\partial S}{\partial t} = nD \frac{\partial^2 C}{\partial x^2} - nV \frac{\partial C}{\partial x}
\]  

(2.50)

The righthand-side of the last equation equals the global (i.e. not referring to the pores only, but to the entire porous medium) net influx of free chlorides. The lefthand-side must therefore be identical to the change of total chlorides \( C_{tot} \) over time:

\[
\frac{\partial C_{tot}}{\partial t} = n \frac{\partial C}{\partial t} - \rho \frac{\partial S}{\partial t}
\]  

(2.51)

The last equation implies that the total chloride content equals the difference between free and bound chlorides, which is obviously not correct. The diffusion coefficient is dependent on time and temperature as follows:

\[
D(t,T) = D_{ref} \left( \frac{t_{ref}}{t} \right)^m \left( \frac{T_{ref}}{T} \right)^n \left( \frac{U}{t_{ref}} \right)^{-1/2}
\]  

(2.52)

with \( D_{ref} \) the diffusion coefficient at reference time \( t_{ref} \) and reference temperature \( T_{ref} \), \( m \) a constant, \( U \) the activation energy of the diffusion process and \( R \) the gas constant. The hydraulic conductivity is defined as:

\[
k(t,T) = \frac{k_{ref}}{Z} \left( \frac{t_{ref}}{t} \right)^n
\]  

(2.53)

with \( k_{ref} \) the hydraulic conductivity at \( t_{ref} \) and \( Z \) a viscosity-temperature correction factor. Chloride binding is modelled by the Langmuir isotherm:

\[
S = \frac{\alpha C}{1 + \beta C}
\]  

(2.54)

with \( \alpha \) and \( \beta \) constants. The model assumes water-saturation, except in the case of wick action. The wick action model of [BUE95], described earlier, has been incorporated in this model. The finite difference method is used to solve the system in
one spatial dimension. There are two boundaries: one at the exposed surface and one at the bottom of the concrete element. At the latter boundary the chloride flux is put equal to zero.

Martín-Pérez
In [MAR01] four coupled balances are set up in two spatial dimensions x and y: for chloride transport, moisture diffusion, heat transfer and oxygen transport. Their potentials are free chloride concentration \( C_{f} \), pore relative humidity \( h \), temperature \( T \) and amount of oxygen dissolved in the pore solution of concrete \( C_{o} \) respectively. The choice of the potential for the oxygen balance is remarkable, since the amount of oxygen in the air space of the pore system is likely to be much more decisive for its transport through concrete. The system of balances is defined as:

\[
\begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & \frac{\partial w_{p}}{\partial t} & 0 & 0 \\
0 & 0 & \rho_{c}c_{q} & 0 \\
0 & 0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
\frac{\partial C_{f}}{\partial t} \\
\frac{\partial h}{\partial t} \\
\frac{\partial T}{\partial t} \\
\frac{\partial C_{o}}{\partial t}
\end{bmatrix}
= \nabla \begin{bmatrix}
D_{c}^{*}C_{f}D_{h} & 0 & 0 & 0 & \nabla C_{f} \\
0 & C_{h}D_{h} & 0 & 0 & \nabla h \\
0 & 0 & 0 & 0 & \nabla T \\
C_{o}D_{o} & 0 & 0 & 0 & \nabla C_{o}
\end{bmatrix}
\tag{2.55}
\]

with time \( t \), moisture capacity \( \partial w_{p}/\partial t \), concrete density \( \rho_{c} \) (constant), specific heat capacity of concrete \( c_{q} \) (constant), apparent chloride diffusion coefficient \( D_{c}^{*} \), humidity diffusion coefficient \( D_{h} \), thermal conductivity of concrete \( \lambda \) (constant) and oxygen diffusion coefficient \( D_{o} \). The off-diagonal entries \( C_{h}D_{h} \) and \( C_{o}D_{o} \) in the matrix on the righthand-side of the last equation establish sorptive (convective) terms in the chloride and oxygen balance respectively. The oxygen diffusion coefficient \( D_{o} \) is claimed to be a function of the degree of water-saturation; this function has however not been defined. The apparent chloride diffusion coefficient \( D_{c}^{*} \) is specified as:

\[
D_{c}^{*} = \frac{D_{c}}{1 + \frac{1}{w_{d}} \frac{\partial C_{f}}{\partial C_{f}}}
\tag{2.56}
\]

in which \( w_{d} \) is the evaporable water content (in m³ pore solution per m³ concrete) and \( \partial C_{f}/\partial C_{f} \) the chloride binding capacity (not specified). Chloride diffusivity \( D_{c} \) is further specified as:

\[
D_{c} = D_{c,ref}F_{1}(T)F_{2}(t)F_{3}(h)
\tag{2.57}
\]

with chloride diffusivity reference value \( D_{c,ref} \) at time \( t_{ref} \) and temperature \( T_{ref} \), and:

\[\text{The divergence operator } \nabla \text{ affects each row individually.}\]
2.3 combined models

\[ F_1(T) = e^{\frac{U_c}{R}\left(\frac{1}{t_{ref}} - \frac{1}{t}\right)} \]

\[ F_2(t) = \left(\frac{t_{ref}}{t}\right)^m \]

\[ F_3(h) = \frac{1}{1 + \left(\frac{1 - h}{1 - h_c}\right)^4} \]  \hspace{1cm} (2.58)

in which \( U_c \) is the activation energy of the chloride diffusion process, \( R \) the gas constant, \( m \) an age reduction factor and \( h_c \) a constant (0.75). However, equation 2.56 seems to be inconsistent with the chloride balance. This balance has probably been derived from:

\[ \frac{\partial C_{bc}}{\partial t} = \nabla \cdot \left( w_c D_c \nabla C_e + C_e D_h \nabla h \right) \]  \hspace{1cm} (2.59)

with \( C_{bc} \) the total chloride content and:

\[ C_e = w_c C_{bc} + C_h \]  \hspace{1cm} (2.60)

in which \( C_{bc} \) denotes the bound chloride content. Then it follows that:

\[ C_{bc} \frac{\partial w_c}{\partial t} + \left( w_c + \frac{\partial C_{bc}}{\partial C_e} \right) \frac{\partial C_e}{\partial t} = \nabla \cdot \left( w_c D_c \nabla C_e + C_e D_h \nabla h \right) \]  \hspace{1cm} (2.61)

Equation 2.56 can be derived directly from the last equation only if:
1. the evaporable water content \( w_e \) is constant in time and space, and
2. the chloride binding capacity \( \frac{\partial C_{bc}}{\partial C_e} \) is constant in space.
The first condition is probably not satisfied. Moreover, in principle the multiplier of \( \nabla h \) (being \( C_{bc} D_h \)) should have been modified along with the multiplier of \( \nabla C_e \) (being \( w_c D_c \)). The humidity diffusion coefficient \( D_h \) is further specified as:

\[ D_h = D_{h,rel} G_1(h) G_2(T) G_3(t_e) \]  \hspace{1cm} (2.62)

with reference humidity diffusivity \( D_{h,rel} \) and:

\[ G_1(h) = 0.05 + \frac{0.95}{1 + \left(\frac{1 - h}{1 - h_c}\right)^n} \]

\[ G_2(T) = e^{\frac{U_c}{R}\left(\frac{1}{t_{ref}} - \frac{1}{t}\right)} \]

\[ G_3(t_e) = 0.3 + \sqrt{\frac{13}{t_e}} \]  \hspace{1cm} (2.63)

in which \( n \) is a constant (ranging from 6 to 16), \( U_c \) the activation energy of the moisture diffusion process and \( t_e \) the equivalent hydration period of concrete (in s). The model is dealt with numerically by means of the finite element method. Boundary
conditions are of the Robbins type (convective), also for chlorides. The solution process is staggered, i.e. in every timestep first the heat balance (linear diffusion) is solved, next the moisture balance and finally the chloride balance. The oxygen balance is only solved after the chloride threshold concentration has been exceeded.

Roelfstra

In the model of [ROE96] first the moisture state in concrete, characterised by moisture potential \( h \), is obtained by means of the finite element method from the following set of coupled partial differential equations:

\[
\begin{bmatrix}
C_{\theta\theta} & C_{\theta h} & -Q \\
C_{h\theta} & C_{hh} & C_{ho} + P \\
0 & 0 & 1 
\end{bmatrix}
\begin{bmatrix}
\frac{\partial \theta}{\partial t} \\
\frac{\partial h}{\partial t} \\
\frac{\partial \alpha}{\partial t}
\end{bmatrix}
= \begin{bmatrix}
\nabla \cdot \left( \lambda_{\theta\theta} \nabla \theta + \lambda_{\theta h} \nabla h \right) \\
\nabla \cdot \left( \lambda_{h\theta} \nabla \theta + \lambda_{hh} \nabla h \right) \\
F_1(\alpha) F_2(\theta) F_3(h)
\end{bmatrix}
\tag{2.64}
\]

with time \( t \), temperature \( \theta \), degree of hydration \( \alpha \), total heat of hydration \( Q \), total amount of water consumed in the hydration process \( P \), water to cement ratio \( w/c \), capacitances \( C_{ij} \), permeabilities \( \lambda_{ij} \) and functions \( F_i \) (with their arguments in parentheses). Next, the free chloride ion concentrations \( e \) (in kg Cl\(^-\) per m\(^3\) water) are obtained from the following convection-diffusion equation:

\[
\frac{\partial b}{\partial t} we + (b - 1) \frac{\partial w}{\partial t} e + bw \frac{\partial e}{\partial t} - D_c \nabla^2 e + v \nabla e = 0
\tag{2.65}
\]

with:

\[
b = \frac{C_i}{C_f} = 1 + (1 - p) \gamma
\tag{2.66}
\]

in which \( C_i \) is the total chloride content (in kg Cl\(^-\) per m\(^3\) concrete), \( C_f \) the free chloride content (in kg Cl\(^-\) per m\(^3\) concrete), \( p \) the porosity (in m\(^3\) pores per m\(^3\) concrete), \( w \) the evaporable moisture content (in m\(^3\) water per m\(^3\) concrete), \( D_c \) the (constant) chloride diffusion coefficient, \( v \) the moisture flux (in m/s), \( \gamma \) the ratio between \( C_i \) and \( C_f \), and \( C_p \) the physically bound chloride content (in kg Cl\(^-\) per m\(^3\) solid). A moving mesh technique is deployed to compute \( \nabla e \), next the diffusive part is dealt with. The chloride balance (equation 2.65) has been derived as follows. The total chloride content comprises of a free and a bound part:

\[
C_i = C_f + (1 - p) C_c
\tag{2.67}
\]

Note the different units of \( C_i \) and \( e \): kg Cl\(^-\) per m\(^3\) concrete corresponding to the former and kg Cl\(^-\) per m\(^3\) water corresponding to the latter. Note also that the unit of factor \( 1 - p \) equals m\(^3\) solid per m\(^3\) concrete. Equation 2.66 follows then with:

\[
\gamma = \frac{C_c}{C_f}
\tag{2.68}
\]
The free chloride content \( C_f \) and free chloride concentration \( e \) are related via the (volumetric) moisture content \( w \):
\[
C_f = w e
\]  
(2.69)

and hence:
\[
C_i = b w e
\]  
(2.70)

The flux of free chloride ions \( J_c \) (in kg Cl\(^-\) per m\(^2\) concrete per s) is defined as:
\[
J_c = -D_c w \nabla e - D_e e \nabla w
\]  
(2.71)

with \( D_w \) the (constant) moisture transport coefficient (in m\(^2\)/s). The first term on the right-hand-side of the last equation is the diffusive chloride flux and the second the convective chloride flux. Requiring that the net influx of free chloride ions balances the increase of the total chloride content in time:
\[
\frac{\partial C_i}{\partial t} = -\nabla \cdot J_c
\]  
(2.72)

yields:
\[
\frac{\partial C_i}{\partial t} = D_c w \nabla^2 e + (D_c + D_w) \nabla e \nabla w + D_e e \nabla^2 w
\]  
(2.73)

with:
\[
\frac{\partial C_i}{\partial t} = \frac{\partial b}{\partial t} w e + b \frac{\partial w}{\partial t} e + b w \frac{\partial e}{\partial t}
\]  
(2.74)

Equation 2.65 follows then from equation 2.73 and 2.74 upon substitution of moisture balance:
\[
\frac{\partial w}{\partial t} = D_w \nabla^2 w
\]  
(2.75)

and the moisture flux \( v \) as:
\[
v = -(D_c + D_w) \nabla w
\]  
(2.76)

In fact two moisture balances are used in the model: equation 2.75 and the middle row of equation 2.64. These balances are probably not identical, which then seems to limit the temperature and degree of hydration variations. Moreover, the definition of the moisture flux \( v \) should be consistent with the moisture balance in equation 2.75; apparently it has been assumed that \( D_c \ll D_w \).

Saetta
In [SAE93] chloride transport in concrete is modelled related to moisture migration and heat flow. The balance for the total chloride content \( C_i \) (in kg Cl\(^-\) per m\(^3\) concrete) is a kind of convection-diffusion equation:
\[
\frac{\partial C_i}{\partial t} = \nabla \cdot (D_a \nabla C_i) + \frac{C_i}{\alpha} \frac{\partial w}{\partial t}
\]  
(2.77)

with \( t \) time, \( D_a \) the apparent chloride diffusion coefficient, \( \alpha \) the ratio between \( C_i \) and \( C_i \), \( C_i \) the free chloride concentration (in kg Cl\(^-\) per m\(^3\) water) and \( w \) the effective
water content (in m$^3$ water per m$^3$ concrete). The last equation is elucidated later in this paragraph. Moisture and heat transport in concrete are described by:

$$
\begin{bmatrix}
\rho c & 0 \\
-K & 1
\end{bmatrix}
\begin{bmatrix}
\frac{\partial T}{\partial t} \\
\frac{\partial h}{\partial t}
\end{bmatrix}
= \nabla \cdot \left( \begin{bmatrix}
\lambda & 0 \\
0 & D_h(h,T,t_e)
\end{bmatrix}
\begin{bmatrix}
\nabla T \\
\nabla h
\end{bmatrix} \right) + \begin{bmatrix}
0 \\
\frac{dh_e}{dt}
\end{bmatrix}
$$

(2.78)

with temperature $T$, relative humidity in concrete $h$, concrete specific mass $\rho$ (constant), specific heat capacity $c$ (constant), coupling factor moisture-heat $K$, thermal conductivity $\lambda$ (constant), humidity diffusion coefficient $D_h$ (an undefined function of $h$, $T$ and $t_e$), equivalent maturation time $t_e$ (in days) and $dh_e/dt$ as the relative humidity variation due to self-desiccation. The effective water content $w$ is determined by the relative humidity in concrete $h$:

$$
w = \begin{cases}
w_{sat}h & , h \downarrow \\
w_{sat}h(1.16h^3 - 1.05h^2 - 0.11h + 1) & , h \uparrow
\end{cases}
$$

(2.79)

As the desorption branch ($h \downarrow$) differs from the sorption branch ($h \uparrow$), hysteresis is included in the model. The total chloride content is composed of a part related to the free chloride concentration and a part related to the bound chloride content $C_i$ (in kg Cl$^-$ per m$^3$ solid):

$$
C_i = wC_f + (1-w_{sat})C_s
$$

(2.80)

with $w_{sat}$ the saturated water content. Note that the unit of factor $1-w_{sat}$ is m$^3$ solid per m$^3$ concrete. Linear chloride binding has been assumed:

$$
C_s = \gamma C_f
$$

(2.81)

with $\gamma$ the constant of proportionality. Combination of the last two equations gives:

$$
C_i = \alpha C_f
$$

(2.82)

with:

$$
\alpha = w + (1-w_{sat})\gamma
$$

(2.83)

The initial chloride balance is:

$$
\frac{\partial C_i}{\partial t} = \nabla \cdot (D_i \nabla C_i)
$$

(2.84)

where $D_i$ is called intrinsic diffusion coefficient. The unit of $C_i$ being kg Cl$^-$ per m$^3$ concrete, the unit of the chloride flow in the last equation ($-D_i \nabla C_i$) must be kg Cl$^-$ per m$^2$ concrete per s. The adjective ‘intrinsic’ is therefore misleading, since $D_i$ is not to be associated with the pore water only, but with the entire porous medium. Next, equation 2.82 is substituted in the last equation, giving the diffusive part of equation 2.77:

$$
\frac{\partial C_i}{\partial t} = \nabla \cdot (D_a \nabla C_i)
$$

(2.85)

with:
2.3 combined models

\[ D_a = \frac{D_i}{\alpha} \]  

(2.86)

Such substitution of \( C_i \) can only be performed if \( w \) is constant in space (e.g. equal to \( w_{sat} \)). However, the effective water content \( w \) does generally vary in time and space (see equations 2.78 and 2.79, and function \( f_3 \) in equation 2.88). Nevertheless, note that \( D_i \) is associated with the free chloride concentration and does not include chloride binding, whereas \( D_a \) is associated with the total chloride content and includes chloride binding. Chloride diffusion coefficient \( D_i \) is further specified as:

\[ D_i = D_{i,ref} f_i(T) f_2(t_e) f_3(h) \]  

(2.87)

with:

\[ f_i(T) = e^{\frac{U(1+1)}{R(T-1)}} \]

\[ f_2(t_e) = \zeta + (1-\zeta) \frac{28}{t_e} \]  

(2.88)

\[ f_3(h) = \frac{1}{1 + \left(\frac{1-h}{1-h_c}\right)^4} \]

in which \( U \) is the activation energy of the diffusion process, \( R \) the gas constant, \( T_0 \) the reference temperature (296 K), \( \zeta \) (ranging from 0 to 1) the ratio between the diffusion coefficient at \( t_e \rightarrow \infty \) and the one at \( t_e = 28 \) days, and \( h_c \) a constant (75 %).

The convective part of equation 2.77 is obtained by first balancing the convective chloride ion flux \( J_c \) with the total chloride content \( C_i \):

\[ \frac{\partial C_i}{\partial t} = -\nabla \cdot J_c \]  

(2.89)

with:

\[ J_c = C_f J_w \]  

(2.90)

in which \( J_w \) is the moisture flux (in m\(^3\) water per m\(^2\) concrete per s). Substitution of the last equation in equation 2.89 yields in principle:

\[ \frac{\partial C_i}{\partial t} = -C_f \nabla \cdot J_w - J_w \nabla C_f \]  

(2.91)

However, the last term of the last equation has been neglected in [SAE93]. Then a second moisture balance appears (the first was the second row of equation 2.78):

\[ \frac{\partial w}{\partial t} = -\nabla \cdot J_w \]  

(2.92)

which is substituted, together with equation 2.82, in equation 2.91 with the following result:

\[ \frac{\partial C_i}{\partial t} = \frac{C_i}{\alpha} \frac{\partial w}{\partial t} \]  

(2.93)
The change of the total chloride content in time is then the sum of the righthand-sides of the last equation and equation 2.85 (see equation 2.77). It is questionable whether the two moisture balances (equation 2.92 and the second row of equation 2.78) are identical; if not, the model is inconsistent. A non-zero value for dh/dt and w being independent of T (according to equation 2.79) seem to cause contradictions. Robbins (convective) boundary conditions are defined for heat, humidity and chloride transport:

\[ J_{hn} = B_T (T - T_{en}) \]

\[ J_{hn} = B_h (h - h_{en}) \]

\[ J_{Cn} = B_C (C_f - C_{en}) + C_{en} \frac{d}{d} \]

with \( J_{hn} \) the heat flux normal to the surface, \( J_{hn} \) the humidity flux normal to the surface, \( J_{Cn} \) the moisture flux normal to the surface, \( J_{Cn} \) the chloride flux normal to the surface, \( B_T \), \( B_h \) and \( B_C \) transfer coefficients, \( T_{en} \) the environmental temperature, \( h_{en} \) the environmental humidity and \( C_{en} \) the chloride concentration of the external solution. The additional term \( C_{en} J_{Cn} \) in the definition of \( J_{Cn} \) is due to entering water. The chloride boundary condition according to the last equation corresponds to continuous or discontinuous immersion. In case of marine atmospheres the chloride boundary condition is defined as:

\[ \frac{dQ_C}{dt} = k_{dep} C_{atm} - k_{dl} C_f \]

with \( \frac{dQ_C}{dt} \) probably as the change of total chloride content per m² concrete surface per s, \( k_{dep} \) the deposition coefficient (in m/s), \( C_{atm} \) the ion concentration in the atmosphere (in kg/m³) and \( k_{dl} \) the washing-away coefficient (in m/s). The finite element method is deployed to obtain solutions. A staggered scheme is applied: first solution of the heat balance (linear diffusion), next the humidity balance and finally the chloride balance.
Chapter 3

A UNIFIED APPROACH TO HEAT, MOISTURE AND CHLORIDE ION TRANSPORT IN CONCRETE

Among the various processes that occur in concrete, two of them are considered to have a major influence on chloride ingress: moisture migration and heat flow. In fact, chloride transport is affected by moisture migration and moisture migration, in turn, is affected by heat flow. These three interactive processes are modelled explicitly in the present work. Properties of concrete change in time, notably by cement hydration and carbonation. It is acknowledged that these processes also influence chloride ingress. In the present work they are modelled implicitly. A value for the degree of hydration can be chosen in the implemented models, but it is a constant during the computations. Carbonation effects are linked to the moisture and chloride balances.

The three coupled balances for heat flow, moisture migration and chloride ingress are the backbone of the global model. These processes have been captured in one global model in order to arrive at a comprehensive approach to chloride ingress. This unification extends to the incorporation of the three coupled balances in a single finite element (see chapter 4). In the first section of this chapter the level of observation of concrete in the present work is set. Next, the global framework of the three coupled balances is discussed. Then, in the third section, the physical and thermodynamic backgrounds are addressed. This chapter concludes with a description of the implemented models, which together form the global model.
3.1 Level of observation

Generally the distance from the concrete surface to the reinforcement bars amounts to a few centimeters. This layer of concrete, the cover, protects the steel reinforcement from the detrimental effects of chloride ions. In design for service life the target is to avoid that chloride ions travel from the exterior to the reinforcement and exceed a threshold concentration with respect to corrosion of that reinforcement. The space domain of the chloride ingress problem is thus in the order of a few centimeters. At this level of observation two components of concrete can be distinguished: mortar and aggregates. On a lower level of observation it appears that interfacial transition zones (ITZ) form the interfaces between aggregates and mortar; the width of these zones is about 30 μm [BRE91]. Mortar is a mixture of water, cement and sand particles and therefore mortar also contains aggregates. Still, on the centimetre-level mortar can be considered to be homogeneous. The aggregates are then gravel particles, with dimensions of 4 mm and bigger\(^1\). The distinction between levels of observation of concrete is illustrated in figure 3.1. An example of a computational representation of heterogeneity of concrete is shown in figure 3.2.

In computations this explicit heterogeneity allows for attributing different characteristics to the individual components. Concrete properties show a large scatter and this follows – at least partly – from different mixture compositions and different component properties. Moreover, the role of the ITZ in transport phenomena can be investigated. Suggestions about the transport properties of the ITZ have been made by several researchers (e.g. [LAR91]), but their determination is troublesome. With explicit heterogeneity some properties of this zone could be estimated by inverse analysis: deducing these properties from comparisons between results of calculations on heterogeneous meshes and experimental results for the corresponding concrete.

Concrete is heterogeneous on many levels of observation. Scale transitions in a porous medium, i.e. shifts to other levels of observation of that porous medium, can be made upon definition of a representative elementary volume (REV) [BEA84]. The REV is the minimum volume which can be represented by a single point on a higher level of observation, while the properties of that volume of material are independent of the position of its center in the material. The material properties and state variables (e.g. temperature) in this point are the averages of the REV. The computational advantage of upward scale transitions is obvious: instead of performing computations for a whole volume, only its representative point is involved in computations.

\(^1\) The transition from sand to gravel particles is chosen at 4 mm.
3.1 level of observation

As the maximum aggregate size in concrete is around 32 mm and the distance from the concrete surface to its reinforcement bars is in the order of a few centimetres, the role of heterogeneity should be addressed in adequate chloride ingress modelling. However, all of the computations in the present work have been performed with homogeneous meshes. These computations must therefore be regarded as an exploration of the transport phenomena in concrete without consideration of the effects of the large aggregates. As the finite element method is deployed in the present work (see chapter 4), an extension to analyses of the effects of heterogeneity on chloride ingress is straightforward though.

Although the choice of the centimetre-level seems logical for the modelling of chloride ingress into reinforced concrete, a lower-level approach could have been

Figure 3.1: schematic representation of the centimetre- and micrometre-level of observation of concrete. On a lower level of observation a new heterogeneity emerges.
followed. Then the material behaviour has to be described with other mathematical expressions and the field of other scientific disciplines is entered. Moreover, the transition to the centimetre-level, where the eventual prediction has to be made, becomes more and more cumbersome with lower-level approaches. Moreover, there is the matter of the parameters, which have to be determined. For levels of observation such as the micrometre-level, this would require rather specialised equipment.

Figure 3.2: Finite-element-method mesh for concrete as a three-component-material [STR99]. The total mesh consists of elements representing mortar, aggregates and interfacial transition zones (from left to right). The width of the ITZ is over-dimensioned.

### 3.2 Three coupled balances

The computational model for heat, moisture and chloride ion transport in concrete is based on three coupled balances. First an uncoupled balance is considered and next the extension is made to the coupled system. Figure 3.3 schematically shows heat accumulation (or loss) in a certain area $\Omega$ in a 2-dimensional space. In this figure $\mathbf{q}_E$ is the heat flux vector (in $\text{Jm}^{-2}\text{s}^{-1}$), $\partial E/\partial t$ the change of specific internal energy with respect to time (in $\text{Jm}^{-3}\text{s}^{-1}$), $f_i$ the heat generation within $\Omega$ (in $\text{Jm}^{-3}\text{s}^{-1}$) and $\mathbf{n}$ the unit vector normal to boundary $\Gamma$ pointing outwards. Application of the first law of thermodynamics to this system yields the following heat balance:

$$\iiint_{\Omega} \frac{\partial E}{\partial t} \, d\Omega = \int_{\Gamma} -\mathbf{q}_E \cdot \mathbf{n} \, d\Gamma + \iint_{\Omega} f_i \, d\Omega \tag{3.1}$$

which states that the change of internal energy in $\Omega$ per unit of time equals the net heat influx through the boundaries $\Gamma$ plus the heat generated within $\Omega$. Evaluation of the first term on the right-hand-side of the equation sign results in:

- the components of $\mathbf{q}_E$ tangential to $\Gamma$ being removed and its components perpendicular to $\Gamma$ remaining

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Footnote: Although a 2-dimensional case is discussed here, the units of the quantities apply to 3 spatial dimensions.
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- A heat flux into \( \Omega \) (briefly: a heat influx) being positive and a heat flux out of \( \Omega \) (briefly: a heat outflux) being negative.

The specific internal energy and the heat flux can be related to the temperature by the following constitutive relations:

\[
\frac{\partial E}{\partial T} = \rho c
\]

\[q_\epsilon = -k_{1i} \nabla T\]

in which \( \rho \) is the density (in kg/m\(^3\)), \( c \) the specific heat (in J/kg K\(^{-1}\)) and \( k_{1i} \) the heat conductivity (in J/(K m s\(^{-1}\)));

the product of \( \rho \) and \( c \) is the heat capacity \( c_{1i} \) (in J/(kg K\(^{-1}\)).

Substitution of these constitutive relations in the heat balance yields:

\[
\iint_{\Omega} \rho c \frac{\partial T}{\partial t} \, d\Omega = \int_{\Gamma} k_{1i} \nabla T \cdot \mathbf{n} d\Gamma + \iint_{\Omega} f_i d\Omega
\]

(3.3)

With the help of Gauss' divergence theorem the line integral can be replaced by an area integral:

\[
\iint_{\Omega} \frac{\partial T}{\partial t} \, d\Omega = \iiint_{\Omega} \nabla \cdot (k_{1i} \nabla T) \, d\Omega + \iint_{\Omega} f_i \, d\Omega
\]

(3.4)

As this equation is valid for any area \( \Omega \), all integrals can be removed:

\[
c_{1i} \frac{\partial T}{\partial t} = \nabla \cdot (k_{1i} \nabla T) + f_i
\]

(3.5)

Figure 3.3: uncoupled heat balance in 2 dimensions (x and y). The change of inner energy \( dE/dt \) inside \( \Omega \) is the result of heat flows through boundary \( \Gamma \) and heat generation \( f_i \) inside \( \Omega \).
Equation 3.5 is a second order partial differential equation; it is also referred to as a diffusion equation and as a partial differential equation of the parabolic type.

The heat balance, as given in equation 3.1, can be extended as follows. The heat flux through boundary \( \Gamma \) \( \mathbf{q}_E \) is thought to consist of three contributions: one due to a temperature gradient \( \mathbf{q}_{ET} \) (as has already been discussed), one due to a moisture gradient \( \mathbf{q}_{EH} \) and one due to a chloride-ion concentration gradient \( \mathbf{q}_{EC} \):

\[
\mathbf{q}_E = \mathbf{q}_{ET} + \mathbf{q}_{EH} + \mathbf{q}_{EC}
\]  

(3.6)

After elaboration of the three components it is obvious that, in fact, the constitutive relation for heat flux has been extended:

\[
\mathbf{q}_E = -k_{11} \nabla T - k_{12} \nabla H - k_{13} \nabla C
\]  

(3.7)

Now this constitutive relation is inserted in the heat balance equation:

\[
\int_\Omega \frac{\partial \mathbf{E}}{\partial t} \, d\Omega = \int_\Gamma (k_{11} \nabla T + k_{12} \nabla H + k_{13} \nabla C) \cdot \mathbf{n} \, d\Gamma + \int_\Omega \int f_i \, d\Omega
\]  

(3.8)

The extent to which the heat flux \( \mathbf{q}_{ET} \) (proportional to \( k_{11} \) and \( \nabla T \)) through boundary \( \Gamma \) can influence the specific internal energy \( E \) inside \( \Omega \) is obvious and this has already been dealt with. However, the extent to which the heat flux \( \mathbf{q}_{EH} \) (proportional to \( k_{12} \) and \( \nabla H \)) through boundary \( \Gamma \) can influence the specific internal energy \( E \) inside \( \Omega \) is not immediately obvious. At this point it is important to notice that \( \Omega \) represents a porous medium. In [GRO69] the contribution of \( \mathbf{q}_{EH} \) is called thermofiltration; the heat flux \( \mathbf{q}_{EC} \), induced by a gradient of the chloride content, is known as the Dufour-effect [GRO69][GRU97]. Both fluxes \( \mathbf{q}_{EH} \) and \( \mathbf{q}_{EC} \) have been neglected in the present work (see also [VR85]).

The other constitutive relation in equation 3.2 can be formally extended as follows. Suppose that the specific internal energy \( E \) is not only dependent on the temperature, but also on the moisture potential and the chloride ion content: \( E(T,H,C) \). Then the heat balance equation can be written as follows:

\[
\int_\Omega \left( \frac{\partial \mathbf{E}}{\partial T} + \frac{\partial \mathbf{H}}{\partial H} + \frac{\partial \mathbf{C}}{\partial C} \right) \, d\Omega = \int_\Gamma (k_{11} \nabla T + k_{12} \nabla H + k_{13} \nabla C) \cdot \mathbf{n} \, d\Gamma + \int_\Omega \int f_i \, d\Omega
\]  

(3.9)

or

\[
\int_\Omega \left( c_{11} \frac{\partial E}{\partial T} + c_{12} \frac{\partial E}{\partial H} + c_{13} \frac{\partial E}{\partial C} \right) \, d\Omega = \int_\Gamma (k_{11} \nabla T + k_{12} \nabla H + k_{13} \nabla C) \cdot \mathbf{n} \, d\Gamma + \int_\Omega \int f_i \, d\Omega
\]  

(3.10)

with

\[
c_{11} = \frac{\partial E}{\partial T} , \quad c_{12} = \frac{\partial E}{\partial H} , \quad c_{13} = \frac{\partial E}{\partial C}
\]  

(3.11)

A possible interpretation of \( c_{12} \) and \( c_{13} \) can be found in [GRU97]. Particularly, the heat of evaporation and condensation related to the moisture in concrete can be included
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in $c_{12}$. In the present work, however, both capacities $c_{12}$ and $c_{13}$ have been neglected.

The processes of heat flow, moisture migration and chloride ion transport are based on the same principles in the model [MEI01]. The change of a quantity over time in a reference volume (or surface area, in case of two dimensions) equals the net influx from outside the reference volume plus the production within that reference volume. The quantity in such a balance can be either inner energy $E$, moisture $W$ or chlorides $C$. Furthermore, there are three potentials: temperature $T$, moisture potential $H$ and chloride content $C$. Usually the temperature is associated with the heat balance, the moisture potential with the moisture balance and the chloride content with the chloride balance. But also cross-links are possible [GRO69][ROEB99][GRU97]. In this way the net influx of a quantity is composed of three contributions: the first is proportional to the gradient of the temperature, the second is proportional to the gradient of the moisture potential and the third is proportional to the gradient of the chloride ion content. Also the change of a quantity over time can be decomposed into three terms:

- the derivative of a quantity with respect to temperature multiplied by the time-derivative of temperature
- the derivative of that quantity with respect to the moisture potential multiplied by the time-derivative of the moisture potential
- and the derivative of that quantity with respect to the chloride ion content multiplied by the time-derivative of the chloride ion content.

This concept is illustrated in figure 3.4.

After integration and application of Gauß' divergence theorem, the three coupled balances for heat, moisture and chloride ion transport are represented mathematically by:

$$
\begin{bmatrix}
    c_{11} & c_{12} & c_{13} \\
    c_{21} & c_{22} & c_{23} \\
    c_{31} & c_{32} & c_{33}
\end{bmatrix}
\begin{bmatrix}
    \frac{\partial T}{\partial t} \\
    \frac{\partial H}{\partial t} \\
    \frac{\partial C}{\partial t}
\end{bmatrix}
= \nabla \cdot \left( \begin{bmatrix} k_{11} & k_{12} & k_{13} \\
                        k_{21} & k_{22} & k_{23} \\
                        k_{31} & k_{32} & k_{33} \end{bmatrix}
\begin{bmatrix} \nabla T \\ \nabla H \\ \nabla C \end{bmatrix} \right) + \begin{bmatrix} f_1 \\ f_2 \\ f_3 \end{bmatrix}
$$

(3.12)

in which the divergence operator affects each individual row and the derivatives of the quantities ($E$, $W$ and $C$) with respect to the potentials ($T$, $H$ and $C$) have been replaced by $c_{ij}$. The capacities ($c_{ij}$) form the capacitance matrix, the conductivities ($k_{ij}$) the conductance matrix and the sources ($f_i$) the source vector; they are in principle functions of the potentials, and in case of explicit heterogeneity functions of the spatial co-ordinates as well. This yields a set of coupled non-linear second order
partial differential equations (see also section 3.4). The ensemble of capacities, conductivities and source terms is referred to as material functions. Since chloride ions are particles bearing an electrical charge, the set of equations could have been completed with a fourth balance for electrical charge. In the present work electrical neutrality is assumed.

\[ \begin{align*}
-k_1 \nabla T & \\
-k_2 \nabla H & \\
-k_3 \nabla C & \\
\frac{\partial T}{\partial t} & = \frac{\partial E}{\partial T} + \frac{\partial E}{\partial H} + \frac{\partial E}{\partial C}
\end{align*} \]

\[ \begin{align*}
-k_1 \nabla T & \\
-k_2 \nabla H & \\
-k_3 \nabla C & \\
\frac{\partial C}{\partial t} & = \frac{\partial E}{\partial T} + \frac{\partial E}{\partial H} + \frac{\partial E}{\partial C}
\end{align*} \]

\[ \begin{align*}
-k_1 \nabla T & \\
-k_2 \nabla H & \\
-k_3 \nabla C & \\
\frac{\partial E}{\partial t} & = \frac{\partial T}{\partial T} + \frac{\partial T}{\partial H} + \frac{\partial T}{\partial C}
\end{align*} \]

\[ \begin{align*}
-k_1 \nabla T & \\
-k_2 \nabla H & \\
-k_3 \nabla C & \\
\frac{\partial H}{\partial t} & = \frac{\partial E}{\partial T} + \frac{\partial E}{\partial H} + \frac{\partial E}{\partial C}
\end{align*} \]

\[ \begin{align*}
-k_1 \nabla T & \\
-k_2 \nabla H & \\
-k_3 \nabla C & \\
\frac{\partial C}{\partial t} & = \frac{\partial E}{\partial T} + \frac{\partial E}{\partial H} + \frac{\partial E}{\partial C}
\end{align*} \]

Figure 3.4: three coupled balances for heat \((E)\), moisture \((W)\) and chloride-ion \((C)\) transport. In each balance it holds that the change of a quantity over time equals the net-influx from outside plus the inner generation of that quantity \((f_i, f_2 \text{ or } f_3)\). The fluxes are driven by the temperature \((T)\), the moisture potential \((H)\) and the chloride content \((C)\) respectively.

The terms on the diagonal of the conductance matrix \((k_{ij})\) are the traditional transport properties for heat (Fourier), moisture\(^3\) and chloride ions (Fick). The cross-terms in this matrix provide couplings between the three balances: osmosis \((k_{23})\), reversed osmosis \((k_{32})\), thermo-osmosis \((k_{21})\), thermodiffusion \((k_{12})\), Soret- \((k_{31})\) and Dufour-effect \((k_{13})\) [GRO69]. The significance of some of the latter processes in concrete is questionable. Preliminary experiments have been carried out to determine the relevance of \(k_{22}\) [MANN1]. These experiments indicated that certain osmotic effects are present in concrete, as was also pointed out in [BAK82]. However, osmosis has been

\(^3\) if \(H\) would have been interpreted as a hydraulic pressure head, then \(k_{22}\) would have represented Darcy's law.
3.2 three coupled balances

further disregarded in the modelling by putting $k_{23}=0$. Although thermofiltration and reversed osmosis, primarily in $k_{12}$ and $k_{32}$ respectively, have been neglected, these coefficients can also be considered to establish couplings for heat and chloride convection respectively, which is elaborated later in this section. Note that couplings between the balances are not only established by the off-diagonal terms in the capacitance and conductance matrices, but also arise as a result of the dependencies of the diagonal terms and entries in the source vector on the potentials.

Experiments have also been carried out to determine the relevance of $c_{23}$ (see appendix B) [MAN01][WAR01]. As will be explained in the next section, the saturation vapour pressure and surface tension of salt solutions differs from demineralised water. Hence, it is to be expected that the presence of chloride ions in the pore water influences the moisture content. Since $c_{23}$ is defined as the moisture content change per chloride content change, this coefficient represents hygroscopic effects in concrete. From the experiments it followed that the value of $c_{23}$ depends on the cement type and the moisture potential (see table 3.1). These hygroscopic effects, however, have not been incorporated in the model, i.e. it has been assumed that $c_{23}=0$.

| Table 3.1: measured values of $c_{23}$ at 293 K in mortar specimens (see also appendix B). The values correspond to moisture content $W$ in kg/m$^3$ and total chloride content $C_{tot}$ in kg/m$^3$. |
|---------------------------------|------------------|------------------|
|                                | Portland cement  | blastfurnaceslag cement |
| $H=0.50$                       | 1.7              | 2.0              |
| $H=0.85$                       | 3.3              | 1.6              |

Although in [GRO69] it is inferred that $k_{21}$ represents thermo-osmosis, which is based on the increased mobility of water molecules at higher temperatures, this coefficient could also be associated with moisture flow induced by a water density change and a surface tension change due to a temperature change. None of these effects have been taken into account in the model and thus $k_{21}=0$. The moisture capacity $c_{22}$ represents the moisture content change per moisture potential change; this is in fact the conventional moisture sorption and desorption isotherms. These moisture sorption and desorption isotherms relate the moisture content at a certain temperature to either the macroscopic pore humidity [ROE89] or to the capillary pressure [PEL95a]. The moisture capacity $c_{21}$ accounts for the influence of temperature on the moisture content.

The capacities of the chloride balance $c_{31}$, $c_{32}$ and $c_{33}$ are determined by the choice of the chloride potential. If the chloride potential is the total chloride content $C_{tot}$ (kg
Cl⁻ per m³ concrete) then \(c_{31} = 0\ kgm^{-2}K^{-1}\), \(c_{32} = 0\ kgm^{-3}\) (if the moisture potential \(\Pi\) is dimensionless) and \(c_{33} = 1\). For the free chloride concentration \(C_{\text{free}}\) as the chloride potential all chloride capacities can have non-zero values. This is further explained in section 3.4.3; in that section expressions for the chloride conductivities \(k_{31}\), \(k_{32}\) and \(k_{33}\) are derived as well. Theoretically also the osmotic pressure could be chosen as the potential in the chloride balance [GRO69]. For concrete, however, this is not a suitable choice, since the pore water also contains other ions.

The source terms (or sink terms, in case of negative values) \(f_1\), \(f_2\) and \(f_3\) can be used to model the generation or disappearance of heat, moisture and chloride ions respectively. Heat generation in concrete can refer to heat of hydration. Heat of hydration only plays a significant role for young concrete, so that it is not directly relevant for chloride ingress analyses, which cover large time spans. The same reasoning holds for autodesiccation, which can be associated with \(f_2\). Chloride adsorption and precipitation can be attributed to \(f_3\). In that case, in fact, the adsorption and precipitation speed is modelled; moreover, the potential in the chloride balance must be the free chloride content \(C_{\text{free}}\). Chloride precipitation, i.e. excess of the solubility of \(\text{Cl}^-\) in combination with some cation, is not modelled in the present work. Since chloride adsorption is covered in an other way (see section 3.4.3), the complete source vector equals zero in the model.

**Convection**

It can be shown that heat and chloride ion convection can be included in \(k_{12}\) and \(k_{32}\) respectively. These convective parts are additional to thermo-filtration and reversed osmosis. However, since thermo-filtration and reversed osmosis have been neglected, \(k_{12}\) and \(k_{32}\) contain only the convective parts. In literature the transport of quantities by a flow of other quantities is referred to as convection or advection; in the present work the term ‘convection’ is used. The heat convection-diffusion equation is derived on the basis of the heat balance in figure 3.5, in which \(\rho\) (in kg/m³) denotes the density of the medium in which heat diffuses and is convected, \(c\) (in Jkg⁻¹K⁻¹) the specific heat, \(\lambda\) (in JK⁻¹m⁻¹s⁻¹) the heat conductivity and \(f\) (in Jm⁻³s⁻¹) a heat source. The convection speed in x- and y-direction is represented by \(v_x\) and \(v_y\) (in m/s). The net diffusive heat influx in x-direction is then given by:

\[
-\left(\frac{-\lambda \frac{\partial T}{\partial x}}{x_{\text{in}}} - \left(\frac{-\lambda \frac{\partial T}{\partial x}}{x_{\text{out}}}\right)\right)dy = \lambda \frac{\partial^2 T}{\partial x^2}dxdy
\]  
(3.13)

in which it is assumed that \(\lambda\) is independent of \(x\) (and \(y\)). The net convective heat influx in x-direction is:
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\begin{align*}
\begin{aligned}
\left(-\lambda \frac{\partial T}{\partial y}\right)_{y+dx} & \quad dx \\
\left(\rho c v, T\right)_{y+dx} & \quad dx \\
(-\lambda \frac{\partial T}{\partial x})_y & \quad dy \\
\left(\rho c v, T\right)_y & \quad dy \\
(\rho c v, T)_x & \quad dy \\
\frac{\partial \rho c T}{\partial t} \quad dxdy \\
\left(-\lambda \frac{\partial T}{\partial x}\right)_{x+dx} & \quad dy \\
\left(\rho c v, T\right)_{x+dx} & \quad dy \\
\left(-\lambda \frac{\partial T}{\partial y}\right)_x & \quad dx \\
\left(\rho c v, T\right)_x & \quad dx
\end{aligned}
\end{align*}

Figure 3.5: 2-dimensional heat balance with diffusive and convective heat fluxes.

\[ -\left[\left(\rho c v, T\right)_{x+dx} - \left(\rho c v, T\right)_{x}\right] \frac{dy}{c} = -c \frac{\partial \rho v, T}{\partial x} dxdy \quad (3.14) \]

in which it is assumed that \( c \) is independent of \( x \) (and \( y \)). Analogous expressions are obtained for the \( y \)-direction. Next, the heat balance requires that \( [SM173] \):

\[ \iint_{\Omega} \left( c \frac{\partial \rho T}{\partial t} - \lambda \frac{\partial^2 T}{\partial x^2} - \lambda \frac{\partial^2 T}{\partial y^2} + c \frac{\partial \rho v, T}{\partial x} + c \frac{\partial \rho v, T}{\partial y} - f \right) dxdy = 0 \quad (3.15) \]

in which it is assumed that \( c \) is independent of \( t \) as well. The reference area is denoted by \( \Omega \). As this equation holds for any area \( \Omega \), the integrand (enclosed in parentheses) must be zero. The same equation would have been obtained by applying Gauß' divergence theorem to the following balance:

\[ \iint_{\Omega} \frac{\partial \rho c T}{\partial t} \quad dxdy + \oint_{\Gamma} (-\lambda V T + \rho c T \mathbf{v}) \cdot \mathbf{n} ds - \iiint_{\Omega} f dxdy = 0 \quad (3.16) \]

in which \( \mathbf{v} \) is the velocity vector with components \( v_x \) and \( v_y \), and \( \Gamma \) the edge of the reference area with co-ordinate \( s \). Further elaboration of the last two equations yields:
\[ cT \frac{\partial \rho}{\partial t} + c\rho \frac{\partial T}{\partial t} - \lambda \frac{\partial^2 T}{\partial x^2} - \lambda \frac{\partial^2 T}{\partial y^2} + cT \frac{\partial \rho v_x}{\partial x} + c\rho v_x \frac{\partial T}{\partial x} + cT \frac{\partial \rho v_y}{\partial y} + c\rho v_y \frac{\partial T}{\partial y} = f \]  

(3.17)

For the medium in which and by which heat is transported, a new balance can be set up; this is illustrated in figure 3.6. The net mass influx in x-direction is:

\[ -[(\rho v_x)_{x+}\text{dx}] \text{dy} = -\frac{\partial \rho v_x}{\partial x} \text{dx}\text{dy} \]  

(3.18)

With the analogous expression for the net mass influx in y-direction, the mass balance becomes:

\[ \iint_{\Omega} \left( \frac{\partial \rho}{\partial t} + \frac{\partial \rho v_x}{\partial x} + \frac{\partial \rho v_y}{\partial y} \right) \text{dxdy} = 0 \]  

(3.19)

Again, the above equation holds for any area \( \Omega \), so the integrand must be zero:

\[ \frac{\partial \rho}{\partial t} + \frac{\partial \rho v_x}{\partial x} + \frac{\partial \rho v_y}{\partial y} = 0 \]  

(3.20)

This equation is called the equation of continuity [SMI73]. Summarising, convection-
diffusion is governed by equation 3.17 and the equation of continuity. Substitution of the equation of continuity into equation 3.17 yields:

\[ c \rho \frac{\partial T}{\partial t} - \lambda \left( \frac{\partial^2 T}{\partial x^2} - \frac{\partial^2 T}{\partial y^2} \right) + c \rho \nu_z \frac{\partial T}{\partial x} + c \rho \nu_y \frac{\partial T}{\partial y} - f = 0 \]  

(3.21)

or

\[ c \rho \frac{\partial T}{\partial t} - \lambda \nabla^2 T + c \rho \nu \cdot \nabla T - f = 0 \]  

(3.22)

This is the traditional convection-diffusion equation (with \( c \) independent of time and space and \( \lambda \) independent of space) [HOO91]. With the substantial (barycentric) derivative [HOO91]:

\[ \frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \]  

(3.23)

the convection-diffusion equation appears as:

\[ c \rho \frac{D T}{D t} - \lambda \nabla^2 T - f = 0 \]  

(3.24)

In concrete pore water can serve as a means of transportation of heat and chlorides with velocity \( \mathbf{v} \). While \( k_{11} \) represents diffusive heat transport, the convective heat transport must then be represented by \( k_{12} \), since this coefficient links the moisture balance to the heat balance. The equation of continuity (equation 3.20) is equivalent to the moisture balance in the model (equation 3.12). So, the heat balance (omitting the terms with \( c_{13} \) and \( k_{13} \)) must be equivalent to equation 3.17. Obviously, it holds that:

\[ k_{11} = \lambda \quad , \quad f_i = f \]  

(3.25)

Note that in concrete the density \( \rho \) and specific heat \( c \) of the convective flux (water) differ from the ones in the reference area \( \Omega \) (concrete). The latter quantities appear in the first two terms of equation 3.17. Elaboration of these terms yields:

\[ c^* \rho^* \frac{\partial T}{\partial t} + c^* \rho^* \frac{\partial T}{\partial t} = c_{11} \frac{\partial T}{\partial t} + c_{12} \frac{\partial H}{\partial t} \]  

(3.26)

with:

\[ c_{11} = c^* \rho^* + c^* T \frac{\partial W}{\partial T} \quad , \quad c_{12} = c^* T \frac{\partial W}{\partial H} \]  

(3.27)

in which the * refers to the reference area and the moisture content \( W \) is a function of temperature \( T \) and moisture potential \( H \). Then, if the two heat balances are to be equivalent, the following should hold:

\[ - \frac{\partial}{\partial x} \left( k_{12} \frac{\partial H}{\partial x} \right) - \frac{\partial}{\partial y} \left( k_{12} \frac{\partial H}{\partial y} \right) = c^* T \frac{\partial \rho v_x}{\partial x} + c \rho v_z \frac{\partial T}{\partial x} + c^* T \frac{\partial \rho v_y}{\partial y} + c \rho v_y \frac{\partial T}{\partial y} \]  

(3.28)

The terms on the righthand-side of the equation sign describe convection. In concrete the speed of moving moisture is generally not known a priori, but obviously it is proportional to the gradient of the moisture potential \( H \). And the moisture fluxes
\( \rho v \) and \( \rho v \) are proportional to this gradient as well. The moisture flux has already been defined in the second row of equation 3.12, so it follows that:

\[
\rho v = -k_{22} \nabla H
\]  

(3.29)

Substitution of the last equation into equation 3.28 yields:

\[
-\frac{\partial}{\partial x} \left( k_{12} \frac{\partial H}{\partial x} \right) - \frac{\partial}{\partial y} \left( k_{12} \frac{\partial H}{\partial y} \right) =
- cT \frac{\partial}{\partial x} \left( k_{22} \frac{\partial H}{\partial x} \right) - ck_{22} \frac{\partial H}{\partial x} \frac{\partial T}{\partial x} - cT \frac{\partial}{\partial y} \left( k_{22} \frac{\partial H}{\partial y} \right) - ck_{22} \frac{\partial H}{\partial y} \frac{\partial T}{\partial y}
\]  

(3.30)

which is an equality for:

\[
k_{12} = ck_{22}T
\]  

(3.31)

Note that this material function is determined by a factor related to moisture movement (\( k_{22} \)) and a factor related to heat flow (\( cT \)). Analogously it can be derived that convection in the chloride balance results for:

\[
k_{32} = \frac{k_{32}C}{\rho}
\]  

(3.32)

This is further elaborated in section 3.4.3.

The heat diffusion coefficient \((k_{11}/c_{11})\) through concrete is in the order of \(10^6\) m\(^2\)/s, the moisture diffusion coefficient \((k_{22}/c_{22})\) is in the order of \(10^{-10}\) m\(^2\)/s and the chloride ion diffusion coefficient \((k_{33}/c_{33})\) in the order of \(10^{-12}\) m\(^2\)/s. This means that the heat transport process is several orders of magnitude faster than the moisture transport process; the moisture transport process in turn is two orders of magnitude faster than the chloride ion transport process. Consequently, heat convection by moving moisture inside concrete is insignificant [VRI58], in contrast with chloride convection in concrete. As a result of the mentioned omissions the set of coupled equations is in fact:

\[
\begin{bmatrix}
c_{11} & 0 & 0 \\
c_{21} & c_{22} & 0 \\
c_{31} & c_{32} & c_{33}
\end{bmatrix}
\begin{bmatrix}
\frac{\partial T}{\partial t} \\
\frac{\partial H}{\partial t} \\
\frac{\partial C}{\partial t}
\end{bmatrix}
= \nabla \cdot \left( \begin{bmatrix}
k_{11} & 0 & 0 \\
0 & k_{22} & 0 \\
k_{31} & k_{32} & k_{33}
\end{bmatrix}
\begin{bmatrix}
\nabla T \\
\nabla H \\
\nabla C
\end{bmatrix}\right)
\]  

(3.33)

which is an unsymmetrical system.

### 3.3 Physical and thermodynamic backgrounds

Its heterogeneity, different compositions and identity as a porous medium makes concrete a complex material to model. Moreover, its properties change in time due
to ongoing hydration. To provide a basis for further modelling in the following section, some features of concrete as a porous medium are discussed here. A more general section about surface tension and capillarity follows and finally the relation of transport phenomena in porous media with entropy production is indicated.

3.3.1 CONCRETE AS A POROUS MEDIUM

Concrete is basically a mixture of cement, water and aggregates. Traditionally aggregates are (small) sand and (big) gravel particles. A mixture of cement, water and sand is referred to as mortar, so in fact mortar can be regarded as concrete without gravel. Cement reacts with water to form cement gel (CSH-gel); the entire product of (hydrated and unhydrated) cement plus water is called (hardened) cement paste.

The porosity of cement paste is a function of the degree of hydration. Initially the mixture of cement and water is a suspension; the water surrounding the cement particles can be regarded as the initial pore space. As hydration progresses the solid matrix is formed. During this process the external volume hardly changes. The mass of water needed for the complete hydration of cement is 40 % of its mass (25 % chemically bound and 15 % physically bound) [REI85]. The degree of hydration \( \alpha \) can be defined as the ratio of the mass of cement that has already reacted with water (to form hydration products) to the initial mass of cement, or alternatively as the ratio of the mass of chemically bound water (again for the formation of hydration products) to the mass of water that can possibly be bound (25 % of the initial cement mass).

The hydration process is fast in the beginning, but then slows down to approach \( \alpha = 1 \) asymptotically; hydration may still be going on years after casting [SOU98]. For a water to cement ratio \( \zeta_1 < 0.4 \) complete hydration cannot be achieved and thus \( \alpha = 1 \) will never be reached. Thus the mass of cement gel per volume of concrete equals [REI85][TAN93]:

\[
\zeta = 1.25 \alpha \zeta_2
\]

(3.34)

with \( \zeta_2 \) as the cement content. The volume of the total pore space in cement paste \( V_{\text{pore}} \) as referred to the volume of the initial mixture of cement and water \( V_{\text{ini}} \) \( p_{\text{tot}} \) is given by [REI85]:

\[
p_{\text{tot}} = \frac{V_{\text{pore}}}{V_{\text{ini}}} = \frac{\zeta_1 - 0.19 \alpha}{\zeta_1 + \frac{\rho_w}{\rho_c}}
\]

(3.35)

in which \( \rho_w \) the specific mass of water (998 kg/m\(^3\)) and \( \rho_c \) the specific mass of cement (3150 kg/m\(^3\) for Portland cement; 2950 kg/m\(^3\) for blastfurnaceslag cement). This pore space can be subdivided into two categories, namely the gel pores (again
their total volume as referred to the volume of the initial mixture of cement and water:

$$p_{gel} = \frac{V_{gel}}{V_{ini}} = \frac{0.21\alpha}{\zeta_1 + \frac{\rho_w}{\rho_c}}$$

(3.36)

with \(V_{gel}\) the volume of the gel pores, and the capillary pores:

$$p_{cap} = \frac{V_{cap}}{V_{ini}} = \frac{\zeta_1 - 0.40\alpha}{\zeta_1 + \frac{\rho_w}{\rho_c}}$$

(3.37)

with \(V_{cap}\) the volume of the capillary pores. It should be noted that in the derivation of equation 3.36 (and 3.37) 71% of the volume of gel pores is supposed to be filled by physically bound water; this amount of water is already included in the 40% mentioned earlier. Since the cement paste is distributed all over the concrete and assuming that the pore space in the aggregates is negligible, the total pore volume of concrete can be calculated on the basis of equation 3.35 (see e.g. table 3.3).

The diameter of gel pores ranges from 10 nm to less than 0.5 nm, the diameter of capillary pores from 10 μm to 10 nm (see figure 3.7). The small gel pores are located inside the hydration products; they do not participate in moisture transport under normal circumstances. The bigger capillary pores lie around the hydration products and are channels for moisture transport. The ionic radius of Cl⁻ is 181 pm [BiN86] [ATK86] and the radius of the H₂O-molecule is 170 pm [ATK86], so both of them are smaller than the smallest gel pore.

![Figure 3.7: pore-sizes in concrete (middle column). The diameter of the gel pores is in the order of nanometres, while the one of the capillary pores is in the order of micrometres. Picture taken from [SET77] with permission of the publisher.](image-url)
3.3.2 Surface Tension and Capillarity

The molecules near the surface of a liquid experience a resulting force directed towards the interior of the liquid, see figure 3.8. Consequently, a liquid tends to minimize its surface-volume ratio. The quantity associated with this tendency is the surface tension \( \gamma \) of a liquid (in N/m), i.e. the force tangent to the surface of the liquid that tries to minimize this surface [KRO66]. Hence, in the absence of gravity, the shape of a liquid is spherical. The surface tension is equal to the surface energy per unit of area (in J/m\(^2\)), provided that there is no heat exchange. The fact that liquids strive after a minimum surface area can be explained thermodynamically with the Helmholtz function: systems try to lower their Helmholtz function and this can be achieved by a decrease of the surface area. Thermodynamics are the subject of the next section.

The internal pressure of bubbles and cavities is higher than their external pressure; this is due to the surface tension, which balances, together with the external pressure, the internal pressure. Bubbles are thin films of liquid containing air and vapour, and cavities are vapour filled holes in a liquid [ATK86]. If the bubble or cavity is spherical, force equilibrium requires that:

\[
4\pi r^2 p_{\text{inside}} = 4\pi r^2 p_{\text{outside}} + 8\pi r \gamma \tag{3.38}
\]

in which \( r \) denotes the radius of the bubble or cavity (in m), \( p_{\text{inside}} \) and \( p_{\text{outside}} \) the internal and external pressure respectively (in N/m\(^2\)), and \( \gamma \) the surface tension of the liquid (in N/m). Elaboration yields the Laplace equation:

\[
p_{\text{inside}} = p_{\text{outside}} + \frac{2\gamma}{r} \tag{3.39}
\]

In case of a flat liquid surface, \( r \) approaches infinity and the pressure difference across the surface disappears. Also the pressure inside drops of liquid is higher than in a bulk of liquid; this higher internal pressure is due to the curvature of the drops. As a result, the saturation vapour pressure of a liquid which is dispersed as drops, is increased. This phenomenon can be explained by considering the chemical potentials of the vapour and liquid phase. At vapour saturation the chemical potential of the vapour and the one of the liquid are equal. A higher pressure on the liquid causes a shift of the equilibrium state. Then the change in the chemical potential of the vapour must be equal to the one of the liquid [ATK86]:

\[
V_{m,v} dp_v = V_{m,l} dp_l \tag{3.40}
\]

\(^4\) The surface tension is sometimes called ‘constant of capillarity’ [KRO66].
in which $V_{nv}$ is the molar volume of the vapour, $\Delta p$, its pressure change, $V_{nl}$, the molar volume of the liquid and $\Delta p$, its pressure change. In the last equation the temperature is assumed to be constant. If it is further assumed that the vapour behaves like a perfect gas and that the molar volume of the liquid is constant, the previous equation transforms, after integration, into:

$$\int_{p_v}^{p_f} \frac{dp_v}{p_v} = \frac{V_{nl}}{RT} \int_{p}^{p_f+\Delta p} dp_l$$  \hspace{1cm} (3.41)

in which $p_v$ denotes the saturation pressure, $p_{sd}$ the new saturation pressure of the dispersion and $\Delta p$ the increased pressure on the drops of liquid. In this equation $V_{nv}$ has been substituted by the law of Boyle-Bay-Lussac. The lower integration boundary is the saturation pressure of the vapour, which is the initial equilibrium pressure for both vapour and liquid. Then, at the new equilibrium state, the pressure on the liquid is augmented with $\Delta p$ and the new saturation pressure of the vapour is $p_{sd}$ (the upper integration boundary). Elaboration of the last equation yields:

$$\ln \left( \frac{p_{sd}}{p_v} \right) = \frac{V_{nl} \Delta p}{RT}$$  \hspace{1cm} (3.42)

which is equal to:

$$p_{sd} = p_v e^{\frac{V_{nl} \Delta p}{RT}}$$  \hspace{1cm} (3.43)

Insertion of the Laplace equation into this equation yields the Kelvin equation\(^5\):

$$p_{sd} = p_v e^{\frac{2\gamma_{lv}}{RT}}$$  \hspace{1cm} (3.44)

in which the following equality has been used:

$$\Delta p = p_{inside} - p_{outside}$$  \hspace{1cm} (3.45)

Note that in the last but one equation spherical drops have been assumed. According to this equation the saturation vapour pressure of a liquid which is dispersed as (spherical) drops, is higher than the one of a bulk of liquid (see figure 3.9). Analogously, the saturation vapour pressure in a (spherical) cavity is lower than the saturation vapour pressure in contact with a bulk of liquid:

$$p_{sv} = p_v e^{\frac{2\gamma_{lv}}{RT}}$$  \hspace{1cm} (3.46)

(see figure 3.10) in which $p_{sv}$ is the reduced saturation vapour pressure inside the cavity with radius $r$. The Kelvin equation for drops (equation 3.44) explains the instability of small drops of water, when water vapour has reached its saturation pressure; consequently, the vapour becomes supersaturated. The Kelvin equation for cavities (equation 3.46) explains the collapse of small cavities in unstirred water that has just attained the boiling point; as a result, the liquid can be superheated (above its boiling point).

---

\(^5\) The Kelvin equation is sometimes referred to as the Helmholtz-Thomson equation (possibly with a minus sign in the exponent for the case of cavities) [MAG55][SBR66]. The former name of Baron Kelvin of Largs was William Thomson [KRO66].
When a solid, a liquid and a vapour are in contact with each other, there are generally three boundary surfaces. Each boundary surface is subjected to its individual surface tension: the surface tension of the solid-liquid boundary is $\gamma_{sl}$, the surface tension of the liquid-vapour boundary $\gamma_{lv}$, and the surface tension of the vapour-solid boundary $\gamma_{vs}$. Then the total surface energy of this system $E$ – on the condition of no heat exchange – is given by:

$$E = \gamma_{sl} A_{sl} + \gamma_{lv} A_{lv} + \gamma_{vs} A_{vs}$$

(3.47)

in which $A_{sl}$ is the surface area of the solid-liquid boundary, $A_{lv}$ the surface area of the liquid-vapour boundary and $A_{vs}$ the one of the vapour-solid boundary. The system minimizes this total surface energy. In general, the molecules of the solid and liquid exert attractive forces on each other: adhesion. The attractive forces that molecules inside the liquid exert on each other are called cohesion. Adhesion reduces the surface tension of the solid-liquid boundary $\gamma_{sl}$ with an amount $\Delta \gamma$. Now, suppose that $\gamma_{sl}$ is smaller than $\gamma_{vs}$, which can be due to adhesion. In order to minimize its total surface energy, the system decides to attribute more surface area to the solid-liquid boundary than to the vapour-solid boundary. This means that the surface area of the solid covered by the liquid is increased at the expense of the one covered by the vapour. This happens e.g. when an amount of water is poured in a glass beaker, see figure 3.11. In that case the boundary surfaces are: glass-water, water-air and air-glass. The growth of area $A_{sl}$ and the decline of area $A_{vs}$ are accompanied by a growth of area $A_{lv}$. The growth of this area $A_{lv}$ ultimately restrains the growth of area $A_{sl}$; then it holds that$^6$:

$$(\gamma_{vs} - \gamma_{sl}) dA_{sl} = \gamma_{lv} dA_{lv}$$

(3.48)

At this point the energy that is gained by attributing surface area of the solid to the liquid instead of to the vapour, is lost by an increase of the contribution of the last

$^6$ Note that in this case $dA_{lv} = dA_{vs}$. 
but one term in equation 3.47. With the definition of the contact angle $\alpha$ in figure 3.11 the relation between $dA_w$ and $dA_d$ is the following:

$$\cos \alpha = \frac{dA_w}{dA_d}$$  \hspace{1cm} (3.49)

Substitution of this equation into the previous one results in:

$$\cos \alpha = \frac{\gamma_v - \gamma_{sl}}{\gamma_{lv}}$$  \hspace{1cm} (3.50)

If the liquid doesn’t adhere to the solid at all, it follows that:

$$\alpha = \pi \rightarrow \cos \alpha = -1 \rightarrow \gamma_{sl} = \gamma_v + \gamma_{lv}$$  \hspace{1cm} (3.51)

This is approximately the case when mercury is in a glass beaker, see figure 3.11. For the general case of adhesion the surface energy of the solid-liquid boundary must be reduced with $\Delta \gamma$:

$$\gamma_{sl} = \gamma_v + \gamma_{lv} - \Delta \gamma$$  \hspace{1cm} (3.52)

Substitution of this equation in equation 3.50 yields:

$$\cos \alpha = -1 + \frac{\Delta \gamma}{\gamma_{lv}}$$  \hspace{1cm} (3.53)

This equation states that the contact angle between liquid and solid only depends on the adhesion of the liquid to the solid and the surface tension of the liquid in contact with vapour. For water in a glass beaker the value of $\cos \alpha$ is close to 1: a convex meniscus is visible. For mercury in a glass beaker the value of $\cos \alpha$ is close to minus 1: a concave meniscus can be seen.

\footnote{on the condition of no heat exchange}
When a glass cylinder with a very small radius – a capillary – is placed vertically in water, the water lifts itself in the cylinder, see figure 3.12. This was not possible in the beaker, where only a meniscus was formed; however, the physical causes of both phenomena are the same. Again, in the case of the glass cylinder, the system glass-water-air aims at minimization of its surface energy. For that purpose it is now possible to cover the glass surface with water by pulling the water upwards in the cylinder. The energy gain effected by substitution of the air-glass boundary by an air-water boundary, cannot be balanced by an increase of the water-air surface area, since this increase is insignificant. However, the potential energy of the water in the cylinder is augmented. Finally, the energy gain by covering the glass surface with water and thus lifting the water column is entirely consumed by the potential energy increase of this water column:

\[2\pi rdz(\gamma_w - \gamma_a) = \pi^2dz\rho g\Delta h\]  \hspace{1cm} (3.54)

in which \(z\) is the vertical co-ordinate (in m), \(\rho\) the density of water (in kg/m\(^3\)) and \(g\) the gravitational acceleration (in m/s\(^2\)). At this point the minimum of the total energy of the system is reached and the water stops moving upwards. The (final) elevation of the water column is denoted by \(\Delta h\) (in m), see figure 3.12; this elevation can be both positive, e.g. in the case of water in a glass cylinder, and negative, e.g. in the case of mercury in a glass cylinder. After substitution of equation 3.50 in the last equation it follows that the elevation of the water column is [KRO66]:

\[\Delta h = 2\frac{\gamma_w \cos \alpha}{\rho g}\]  \hspace{1cm} (3.55)

Now it is obvious that if the radius is large, e.g. in the case of the glass beaker, the elevation of the water column is approximately nil. An other way to explain capillary rise is by considering the curved water surface inside the cylinder. If this curvature is spherical, which implies that \(\alpha\) is equal to zero, there must be a pressure difference
across this curvature, which is given by the Laplace equation:

\[ p_{\text{water}} = p_{\text{air}} - 2 \frac{Y_{lv}}{r} \]  \hspace{1cm} (3.56)

The hydrostatic water pressure has to be the same at a horizontal level. At the water surface outside the cylinder the water pressure equals the air pressure; in the cylinder, however, the water pressure at the (curved) water surface is initially lower than the air pressure. This disturbance can be cancelled by moving the water upwards in the cylinder and thus augmenting the water pressure at the base of the created water column. The hydrostatic pressure at the base of the water column in the cylinder is restored, when the pressure of the water column with elevation \( \Delta h \) is equal to the pressure loss due to the curvature of the water surface in the cylinder:

\[ \rho g \Delta h = 2 \frac{Y_{lv}}{r} \]  \hspace{1cm} (3.57)

From this equation the (final) elevation of the water column in the cylinder can be obtained \([ATK86]\):

\[ \Delta h = 2 \frac{Y_{lv}}{\rho g} \]  \hspace{1cm} (3.58)

This is the same result as equation 3.55 with \( \alpha \) equal to zero.

Concrete

Capillary suction of water into concrete follows the principles as described above. Capillary condensation of water vapour in concrete is characterised by equation 3.46 \([HOU92],[WIT97]\). With a surface tension of \( 7.275 \cdot 10^{-2} \) N/m and a molar volume of \( 1.80 \cdot 10^{-5} \) m\(^3\) the ratio of the reduced saturation vapour pressure in the pore and the saturation vapour pressure over a flat surface is 0.999 for a pore-radius of 1 \( \mu \)m \([KIE83]\) and 0.341 for a pore-radius of 1 nm at 293 K. The relation of the Kelvin-equation to moisture storage in concrete can be elucidated as follows. Consider 4 capillaries in concrete with radii \( r_1 \) (big) to \( r_4 \) (small) and lengths \( l_1 \) to \( l_4 \) (see figure 3.13). All saturation vapour pressures in the capillaries \( p_{\text{sc}} \) are reduced compared to the environmental saturation vapour pressure (over a flat surface) \( p_e \). The saturation vapour pressure is lower in capillaries with smaller radii, so it holds that (assuming isothermal conditions):

\[ p_4 > p_{\text{sc}1} > p_{\text{sc}2} > p_{\text{sc}3} > p_{\text{sc}4} \]  \hspace{1cm} (3.59)

In case of equilibrium the partial pressure of water vapour inside the concrete equals the environmental partial pressure \( p \). Suppose that this partial pressure equals the saturation vapour pressure corresponding to capillary 1: \( p = p_{\text{sc}1} \). If this equation is devided by \( p_4 \) it follows that:
3.3 physical and thermodynamic backgrounds

Figure 3.13: model of concrete consisting of capillaries with different radii \( r_i \) and lengths \( l_i \). When the partial pressure \( p \) drops, the water in the capillaries evaporates in the order of decreasing radii.

\[
\frac{P_{\text{sat1}}}{P_s} = \frac{P}{P_s} = h_i
\]  

since the environmental relative humidity \( h_i \) is defined as the ratio of the partial pressure and the saturation pressure of water vapour. So, in case of a pressure equilibrium the environmental relative humidity \( h_i \) equals the ratio of the reduced saturation vapour pressure in a certain capillary and the saturation vapour pressure over a flat surface. A drop of the partial pressure of water vapour from \( P_{\text{sat1}} \) to \( P_{\text{sat2}} \) causes only capillary 1 to be emptied, as the partial pressure is lower than the saturation vapour pressure of capillary 1. Capillaries 2, 3 and 4 remain filled with water. Then the length of capillary 1 \( l_1 \) determines the volume of water that vapourises. At this point it holds that:

\[
\frac{P_{\text{sat2}}}{P_s} = \frac{P}{P_s} = h_i
\]  

meaning that the environmental relative humidity \( h_i \) has gone down and now equals the ratio of the saturation vapour pressure corresponding to capillary 2 and the saturation vapour pressure over a flat surface. In this sense a certain value of the environmental relative humidity can be associated with a certain pore-size \( r_i \), which is just about to be emptied as its saturation vapour pressure \( P_{\text{sat}} \) is reached.

A subsequent drop of the partial pressure of water vapour from \( P_{\text{sat2}} \) to \( P_{\text{sat3}} \) causes capillary 2 to be emptied, while capillaries 3 and 4 stay filled. Again the length of this capillary \( l_2 \) determines the amount of moisture loss. Capillaries 3 and 4 are emptied upon subsequent drops of \( p \) to \( P_{\text{sat4}} \) and lower. In this way a graph can be
obtained relating environmental relative humidity to water content in concrete. The shape of such a graph depends on the radii \( r \) and lengths \( l \) of the involved capillaries. Generally the moisture content of a concrete with many big pores is low compared to a concrete with many small pores. It should be noted that the representation of the pore system of concrete as depicted in figure 3.13, is very schematic and simplified; it does not include e.g. the ink-bottle effect.

Apart from the reduction of the saturation pressure of water vapour in pores due to the Kelvin equation, salts in aqueous solutions also reduce the saturation vapour pressure. Moreover, the surface tension of salt solutions differs from the one of demineralised water [HAN71] (see also the discussion of \( c_{23} \) in the previous section). Consequently, the chloride ions in the pore solution exert an additional influence on the hygral behaviour of concrete.

3.3.3 Entropy Production

The first law of thermo-dynamics states that the energy of an isolated system is constant. Spontaneous changes in nature are characterized by an increase of disorder. The amount of disorder or chaos is called entropy, for which the symbol \( S \) is used. The second law of thermo-dynamics states that the entropy of an isolated system increases in the course of a spontaneous change [ATK86]. In other words, entropy is produced by spontaneous natural processes [GRO69]. Moreover, for any change in an isolated system which obeys the first law, it holds that:

\[
\Delta S_{\text{isolated system}} \geq 0
\]  

(3.62)

according to the second law. This means that in an isolated system the first law dictates the permissible changes and the second law selects from this set of permissible changes those changes which do not decrease the entropy of the (isolated) system.

The entropy change of a certain system is defined as:

\[
\Delta S = \frac{q}{T}
\]  

(3.63)

in which \( q \) denotes the amount of heat (in J) transported to or from the system and \( T \) the temperature (in K) of the system. If an isolated system is split into two separate systems \( a \) and \( b \), then the sum of their entropy changes has to be positive:

\[
dS_a + dS_b \geq 0
\]  

(3.64)

According to the first law the amount of heat entering system \( a \) has to originate from system \( b \):

\[
dq_a = -dq_b
\]  

(3.65)

If these systems are in thermal equilibrium it holds that:
Substitution of the last two equations into equation (3.64) yields the Clausius inequality:

\[ dS_a \geq \frac{dq_a}{T_a} \tag{3.67} \]

Note that by putting \( dq_a \) equal to zero and thus isolating system \( a \), the initial equation (equation (3.62)) is obtained. If the heat \( dq_a \) is transported at constant volume \( V_a \) and no non-pressure-volume-work is done, then the transported amount of heat \( dq_a \) is converted entirely to a change of the internal energy \( dU_a \):

\[ dq_a = dU_a \tag{3.68} \]

Substitution of the last equation into the Clausius inequality yields:

\[ dU_a - T_a dS_a \leq 0 \tag{3.69} \]

The Helmholtz function or the (maximum) work function of system \( a \) \( A_a \) is defined as:

\[ A_a = U_a - T_a S_a \tag{3.70} \]

If the state of system \( a \) changes at constant temperature, it holds that the change of the Helmholtz function has to be non-positive:

\[ dA_a \leq 0 \tag{3.71} \]

If the heat \( dq_a \) is transported at constant pressure \( p_a \) and no non-pressure-volume-work is done, then the transported amount of heat \( dq_a \) is converted entirely to an enthalpy change \( dH_a \):

\[ dq_a = dH_a \tag{3.72} \]

with:

\[ H = U + pV \tag{3.73} \]

Substitution of the last but one equation in the Clausius equation yields:

\[ dH_a - T_a dS_a \leq 0 \tag{3.74} \]

The Gibbs function or the free energy of system \( a \) \( G_a \) is defined as:

\[ G_a = H_a - T_a S_a \tag{3.75} \]

If the state of system \( a \) changes at constant temperature, it holds that the change of the Gibbs function has to be non-positive:

\[ dG_a \leq 0 \tag{3.76} \]

The first and the second law of thermo-dynamics can be combined in the following way. A change of internal energy \( dU \) can be caused by heat transport \( dq \) and work \( dw \):

\[ dU = dq + dw \tag{3.77} \]

For the case of reversible change in an isolated system and no non-pressure-volume-work the following substitutions can be performed:

\[ dw = -pdV \]

\[ dq = TdS \tag{3.78} \]
The result is the so-called fundamental equation:
\[ dU = TdS - pdV \]  
(3.79)
This result is also valid for irreversible change, since \( dU \) is an exact differential. The fundamental equation can be used in the Helmholtz and Gibbs functions. For the Helmholtz function this yields:
\[ dA = -pdV - SdT \]  
(3.80)
Analogously, the Gibbs function can be elaborated, with the following result:
\[ dG = Vdp - SdT \]  
(3.81)
By omitting the last term (on the righthand-side) of the last equation, the pressure dependence of the Gibbs function for solids, liquids and vapours and gases can be shown. Then integration yields:
\[ G(p_2) = G(p_1) + \int_{p_1}^{p_2} Vdp \]  
(3.82)
For solids and liquids the volume change upon a pressure change can often be neglected. Then it follows that:
\[ G(p_2) = G(p_1) + V(p_2 - p_1) \]  
(3.83)
For ideal vapours and ideal gases the law of Boyle-Gay-Lussac can be substituted:
\[ G(p_2) = G(p_1) + nRT \ln \left( \frac{p_2}{p_1} \right) \]  
(3.84)
If the last equation is divided by the number of moles \( n \) and if \( p_1 \) is replaced by a standard pressure \( p_0 \) of \( 1 \times 10^5 \) Pa (which is equal to 1 bar) and \( p_2 \) by \( p \), the chemical potential \( \mu \), of an ideal vapour or ideal gas is obtained:
\[ \mu = \mu_0 + RT \ln \left( \frac{p}{p_0} \right) \]  
(3.85)
Since any system tries to lower its Gibbs function, its chemical potential decreases accordingly. Consequently, the interpretation of the chemical potential is analogous to other classical potentials, such as the electrical potential, the diffusion potential, etc.

The Helmholtz function explains the tendency of a liquid to minimize its surface-volume ratio, as already mentioned in the previous section. The amount of work \( dw \) needed for a change of the surface area \( dO \) is equal to:
\[ dw = \gamma dO \]  
(3.86)
This amount of work must be added to the incremental Helmholtz function (equation 3.80):
\[ dA = -pdV - SdT + \gamma dO \]  
(3.87)
Now it is obvious that in order to lower the Helmholtz function, the surface area can be decreased.
3.3 Physical and thermodynamic backgrounds

It can be derived from the Gibbs equation and conservation equations that entropy production in porous media can be expressed as the sum of products of fluxes and their conjugated driving forces [GRO69]. For the soil-water system (hydrology) it has been shown that the entropy production $\sigma$ at temperature $T$ can be written as

$$
T\sigma = -j^s \nabla P - j^D \nabla \pi - j_q \frac{\nabla T}{T} - I \nabla E
$$

(3.88)

with $P$ as the pressure-equivalent of the hydraulic head, $\pi$ the osmotic pressure and $E$ the electric potential. Each flux $j^s$ (total volume flux), $j^D$ (diffusion flux), $j_q$ (caloric heat flux) and I (electric current) is related to the thermodynamic forces $-\nabla P$, $-\nabla \pi$, $-(\nabla T)/T$ and $-\nabla E$ in the following way:

$$
\begin{bmatrix}
  j^s_q \\
  j^s_r \\
  j^D \\
  I
end{bmatrix} =
\begin{bmatrix}
  L_T & L_{Tv} & L_{Td} & L_{Te} \\
  L_{VT} & L_v & L_{Vd} & L_{Ve} \\
  L_{Df} & L_{Dv} & L_D & J_D \\
  L_{EF} & L_{Ev} & L_{ED} & L_E
end{bmatrix}
\begin{bmatrix}
  \nabla T \\
  T \\
  \nabla P \\
  \nabla \pi
end{bmatrix}
$$

(3.89)

with coefficients $L_i$. Clearly, the definition of the fluxes in section 3.2 is analogous to the last equation.

Ion diffusion

The chemical potential leads to Fick’s first law of diffusion in the following way. Consider a solution of particles in a liquid. Let the chemical potential of the solution at position $x$ be $\mu_1$, and at position $x+dx$ be $\mu_2$. When 1 mole of particles moves from position $x$ to $x+dx$, this requires an amount of work equal to:

$$
dw = \mu_2 - \mu_1 = \left(\mu_1 + \frac{\partial \mu_1}{\partial x} \, dx\right) - \mu_1 = \frac{\partial \mu_1}{\partial x} \, dx
$$

(3.90)

When particles move in positive $x$-direction and if the direction of an imaginary force $F$, which acts on the particles, is opposite to the positive $x$-direction, this amount of work can also be expressed as:

$$
dw = -F \, dx
$$

(3.91)

Hence it follows that:

$$
F = -\frac{\partial \mu_1}{\partial x}
$$

(3.92)

The chemical potential of an ideal solution is analogous to the chemical potential of an ideal vapour:

$$
\mu_s = \mu_{s0} + RT \ln c
$$

(3.93)
with \( c \) the concentration of particles in the liquid. Substitution of \( \mu_\tau \) in the last but one equation yields:

\[
F = -\frac{RT}{c} \frac{\partial c}{\partial x}
\]  

(3.94)

Note that temperature and pressure still have to be constant. Now it is clear that \( F \) forces the particles to move in the direction of decreasing concentration. The result is a flow of particles \( Q \), which is equal to the product of the average particle velocity \( v \), the particle concentration and the constant of Avogadro:

\[
Q = v c N_A
\]  

(3.95)

Since the average particle velocity is proportional to the driving force:

\[
v = k F
\]  

(3.96)

with \( k \) the constant of proportionality, it follows that:

\[
Q = -kRTN_A \frac{\partial c}{\partial x}
\]  

(3.97)

which is Fick's first law of diffusion. According to this law a particle concentration gradient starts the diffusion process and causes a particle flow which is proportional to that concentration gradient.

### 3.4 Implemented models

Several models for heat, moisture and chloride ion transport in concrete have been used in the present work. The starting point for the modelling were existing models, like the Bazant-Roelfstra moisture model [BAZ72][ROE89] and Saetta's chloride model [SAE93]. Adjustments have been made to some of those models and new models have been developed within the present work. Next, the models have been implemented in the finite element program FEAP [ZIE97][TAY99]; implementation issues are addressed in chapter 4. All models are of the diffusion-type, as they are part of the three coupled balances (see section 3.2). However, convective and other effects are introduced by the couplings.

The models can be linear or non-linear. Non-linearity arises as a consequence of the dependence of the material functions \( c_\nu \), \( k_\nu \) and \( f \) on the potentials \( u_\nu \). Furthermore, the models correspond to either the heat, moisture or chloride balance. The models have been numbered for convenience. The linear heat, moisture and chloride model have number 0. There is one non-linear heat model (number 1), four non-linear moisture models (number 1 to 4) and three non-linear chloride models (1 to 3). Moisture model 4 and chloride model 3 are models in which carbonation effects have been included. Table 3.2 summarises the numbering of the implemented models.
<table>
<thead>
<tr>
<th></th>
<th>linear</th>
<th>non-linear</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat</td>
<td>0</td>
<td>1, 2, 3, 4</td>
</tr>
<tr>
<td>moisture</td>
<td>0</td>
<td>1, 2, 3</td>
</tr>
<tr>
<td>chloride</td>
<td>0</td>
<td>1, 2, 3</td>
</tr>
</tbody>
</table>

The linear models do not need further explanation, since application just involves choosing a (constant) value for the capacities \( c_{ij} \), conductivities \( k_{ij} \), and sources \( f_i \). The potential in the heat balance is temperature \( T \). In the moisture balance the potential is either macroscopic pore humidity \( H \) or moisture content \( W \). The potential of the chloride balance can be total chloride content \( C_{tot} \) or free chloride concentration \( C_{free} \). The non-linear models are explained in the following sections.

### 3.4.1 Heat

In heat model 1 the heat capacity \( c_{11} \) and heat conductivity \( k_{11} \) are scaled linearly with the moisture content [KIE83]:

\[
\begin{align*}
    c_{11}(T,H) &= (\beta_1 - \beta_2) \frac{W(T,H) - W_r(T)}{W_s(T) - W_r(T)} + \beta_2 \\
    k_{11}(T,H) &= (\gamma_1 - \gamma_2) \frac{W(T,H) - W_r(T)}{W_s(T) - W_r(T)} + \gamma_2
\end{align*}
\]  \hspace{1cm} (3.98)

in which \( W_s \) is the saturated moisture content and \( W_r \) the residual moisture content. The calculation of the moisture content \( W \) will be explained in section 3.4.2. The parameters \( \beta_1 \) and \( \beta_2 \) denote the heat capacities at \( W_s \) and \( W_r \) respectively; \( \gamma_1 \) and \( \gamma_2 \) denote the heat conductivities at \( W_s \) and \( W_r \) respectively. This is a general formulation, which allows for a residual moisture content, but usually \( W \) is put equal to 0 kg/m\(^3\) for all temperatures. The coefficients \( c_{12}, c_{13}, k_{12} \) and \( k_{13} \) are zero; a constant heat source can be specified by a non-zero value of \( f_1 \).

The value of \( \beta_1 \) is 2.40-10\(^6\) Jm\(^{-3}\)K\(^{-1}\) approximately. Then the value of \( \beta_2 \) can be calculated as follows. Let the total pore space (both capillary and gel pores) in 1 m\(^3\) of concrete be 130 l. In case of \( H=1 \) the entire pore space is water-filled; this corresponds to 130 kg water. The specific heat of water\(^8\) is 4.18-10\(^3\) Jkg\(^{-1}\)K\(^{-1}\). Then to heat up this amount of water 1 degree K, 130-4.18-10\(^3\)=0.543-10\(^6\) J is needed. To heat up 1 m\(^3\) of saturated concrete 1 degree K 2.40-10\(^6\) J is needed. So, it takes 2.40-0.543=1.86 MJ to heat up 1 m\(^3\) of dry concrete (\( H=0 \)) 1 degree K, if the energy needed to heat up the air in the empty pores is neglected. The mass of air in

---

8 The specific heat of seawater (3 % salt) is 3.93-10\(^3\) Jkg\(^{-1}\)K\(^{-1}\).
the pores is low and the specific heat of air\(^9\) is \(1.00 \times 10^3 \ J/kg \cdot K\), so this contribution is negligible. The value of \(\beta_2\) is thus \(1.86 \times 10^6 \ J/m^2 \cdot K\) approximately; this value is 23 % lower than the value of \(\beta_1\).

The value of \(\gamma_1\) is 2.40 \(Js^{-1}m^{-1}K^{-1}\) approximately. This is the amount of heat flowing through 1 \(m^2\) of saturated concrete per s due to a temperature gradient of 1 \(K/m\). An indication of the value of \(\gamma_2\) can be given in the following way. Assume that the above mentioned porosity of 13 % (130 l pores per \(m^3\) of concrete) is the same in the cross-section of the flow. This corresponds e.g. to a cylinder with a cross-section of 0.13 \(m^2\) and an axial length of 1 \(m\) in the direction of the heat flow. In the case of \(H=1\) this tube is completely water-filled. The heat conductivity of water is 0.60 \(Js^{-1}m^{-1}K^{-1}\), the one of air 0.024 \(Js^{-1}m^{-1}K^{-1}\). The water-filled tube transports then 0.13 \(0.60=0.078\) J/s under a temperature gradient of 1 \(K/m\). If the tube is air-filled (at \(H=0\)), the amount of heat flowing through 1 \(m^2\) of (dry) concrete due to a temperature gradient of 1 \(K/m\) is 2.40 \(0.078=0.232\) J/s. Here the contribution of air to heat transport has been neglected. The value of \(\gamma_2\) is thus 2.32 \(Js^{-1}m^{-1}K^{-1}\) approximately; this value is 3 % lower than the value of \(\gamma_1\). In this simple parallel steady state approach a secondary heat flow in the plane normal to the axis of the cylinder is not present. However, the water in the tortuous pores and the solid matrix should be connected in both a parallel and serial fashion. In a serial steady state analysis the low heat conductivity of air determines the value of \(\gamma_2\) to a large extend; values much lower than 2.32 \(Js^{-1}m^{-1}K^{-1}\) can be found, e.g. 0.178 \(Js^{-1}m^{-1}K^{-1}\) (see appendix C). Thus the parallel analysis provides an upper bound for the value of \(\gamma_2\).

### 3.4.2 Moisture

Moisture models 1, 2, 3 and 4 are all based on the following moisture balance:

\[
\frac{\partial W}{\partial t} = \frac{\partial W}{\partial T} \frac{\partial T}{\partial t} + \frac{\partial W}{\partial H} \frac{\partial H}{\partial t} = \nabla (k_w \nabla H)
\]

(3.99)

in which \(k_w\) is the moisture conductivity (in \(kg/m^2/s\)). The moisture flow, as defined by the negative product of \(k_w\) and \(\nabla H\), consists of water in both liquid and vapour phase. The partial derivatives \(\partial W/\partial T\) and \(\partial W/\partial H\) appear in the last equation, since the moisture content \(W\) (in \(kg/m^3\)) is a function of temperature \(T\) and moisture potential \(H\). The moisture potential \(H\) is interpreted as the macroscopic pore humidity, i.e. the moisture state in the pore system of concrete that is in equilibrium with a certain environmental relative humidity [PAR88]. The gradient of the macroscopic pore humidity drives — according to the definition of a potential — a moisture flow.

\(^9\) at constant pressure \(c_v\) and \(T=273 \, K\)
3.4 implemented models

This macroscopic pore humidity is related to the experimental determination of moisture content in concrete. In such experiments concrete specimens are stored in a climate chamber with a constant temperature and humidity. After some time (several months, depending on a.o. specimen size) the moisture content in the specimens is stable: equilibrium is reached with the constant environmental conditions. In this steady state the distribution of the macroscopic pore humidity is uniform over the specimen and equal to the environmental relative humidity. Then this macroscopic pore humidity corresponds to a certain moisture content in the specimen and this pair yields one point on a so-called desorption isotherm. Several experiments with different constant environmental temperatures and relative humidities yield other points on these desorption isotherms.

The experimentally determined pairs of macroscopic pore humidity and moisture content are deployed in generally transient analyses, in which the concrete is not (yet) in equilibrium with its environment. Then the distribution of the macroscopic pore humidity is not uniform over the concrete specimen anymore and the different values of the macroscopic pore humidity yield generally different values of the moisture content over the specimen. Only at the exposed surface of the specimen the macroscopic pore humidity equals the environmental relative humidity, if a possible surface resistance (with a certain moisture transfer coefficient) is neglected. During such a transient analysis the macroscopic pore humidity in a certain point inside the specimen changes in time and so does the corresponding moisture content.

The complex moisture state on the pore level of concrete is represented by the macroscopic pore humidity on a higher level of observation, on which analyses are performed. As explained in section 3.3.2, the saturation vapour pressure of water is different for the various pore sizes. Consequently, in a steady state the uniformly distributed partial vapour pressure is equal to the saturation vapour pressure of only the pores with the corresponding radius. Only for these pores the ratio of their typical saturation water vapour pressure and the saturation water vapour pressure over a flat surface (with an infinite radius) equals the environmental relative humidity, defined as the ratio of the partial water vapour pressure and the saturation water vapour pressure over a flat surface. In a steady state these pores are (partially) filled with condensed water. Other pores are either empty due to evaporation or completely filled with condensed water because of the pressure equilibrium. For these pores the ratios of their typical saturation water vapour pressures and the saturation water vapour pressure over a flat surface do not equal the environmental relative humidity.

So, in an equilibrium state some pores are (partially) filled, others are empty. If pore humidity were defined as the ratio of partial water vapour pressure and saturation water vapour pressure for that pore radius, it would be different in every pore (with a different radius). Such a definition would be analogous to the definition of relative
humidity. Now, by characterising a certain moisture state in the pore system of concrete with an equilibrium environmental relative humidity, a single value is obtained. This is in fact an upscaling procedure. As this equilibrium environmental relative humidity can be associated with the macro-level and it represents the moisture state in the pore system, it is called macroscopic pore humidity.

In the moisture balance and in the global model the moisture potential $H$ and temperature $T$ are considered to be independent variables. This applies to concrete, for which the model is used. The environmental relative humidity $h$, (or $\psi_2$), however, is strongly influenced by temperature (see table 5.15). Of course, the environmental relative humidity is a quantity outside the concrete. This is an important difference between moisture potential, i.e. macroscopic pore humidity, and environmental relative humidity.

In moisture model 1, 2 and 4 the moisture balance (equation 3.99) is divided by $\partial W/\partial H$ in accordance with [BAZ72]:

$$\frac{\partial W}{\partial W} \frac{\partial H}{\partial H} + \frac{\partial H}{\partial H} = \frac{1}{\partial W} \nabla \left( k_w \nabla H \right)$$

(3.100)

Next, the righthand-side of the last equation can be replaced by [BAZ72]:

$$\frac{1}{\partial W} \nabla \left( k_w \nabla H \right) = \nabla \left( k_h \nabla H \right)$$

(3.101)

with:

$$k_h(H) = \theta_1 \left( \theta_2 + \frac{1 - \theta_2}{1 + \frac{1 - H}{1 - \theta_2}} \right)$$

(3.102)

(in $m^2/s$). Thus moisture model 1 and 2 are based on the following equation [MEI02a]:

$$\frac{\partial W}{\partial W} \frac{\partial H}{\partial H} + \frac{\partial H}{\partial H} = \nabla \left( k_h \nabla H \right)$$

(3.103)

Clearly $k_h = \theta_1$ for $H=1$ and therefore $\theta_1$ is the saturated moisture conductivity (in $m^2/s$). The value of parameter $\theta_2$ determines the moisture conductivity at low moisture potentials. For large values of $\theta_2$ the moisture conductivity at $H=0$ approaches the product of $\theta_1$ and $\theta_2$. Parameters $\theta_3$ locates approximately the
transition from high to low moisture conductivities; parameter $\theta_4$ determines the slope at this point. Usually the parameter-set \((\theta_2, \theta_3, \theta_4) = (0.05, 0.7, 4)\) is used; figure 3.14 depicts $k_w/\theta_i$ for this set.

In moisture model 3 the moisture balance is not divided by $\partial W/\partial H$, since this factor may get a value of 0. This issue will be addressed later after introducing the moisture data. With $k_h$ as given in equation 3.102, an expression for $k_w$ can be found by elaborating equation 3.101:

$$V \left[ \frac{\partial W}{\partial H} k_h \nabla H \right] - k_h \frac{\partial^2 W}{\partial T \partial H} (\nabla T)^T \nabla H - k_h \frac{\partial^2 W}{\partial H^2} (\nabla H)^T \nabla H = \nabla (k_w \nabla H)$$

(3.104)

in which the $T$ in superscript denotes transposition. Assuming that the second order derivatives in the second and third term on the left-hand-side of the last equation can be neglected, the following substitution is valid:

$$k_w \approx \frac{\partial W}{\partial H} k_h$$

(3.105)

The negative product of moisture conductivity $k_w$ and the moisture potential gradient $\nabla H$ yields a moisture flux $q_w$ in $\text{kgm}^{-2}\text{s}^{-1}$, whereas the negative product of moisture conductivity $k_c$ and the moisture potential gradient yields a moisture flux in $\text{ms}^{-1}$. The former will be referred to as a real moisture flux and the latter as a pseudo-moisture flux. Obviously, this pseudo-moisture flux is the consequence of the division of the moisture balance by $\partial W/\partial H$, i.e. by $\text{kgm}^3$. This issue becomes important when defining the convective chloride ion flux (see section 3.4.3), since only a real moisture flux can carry chloride ions.

Mathematical expressions for the moisture content $W$ as a function of the moisture potential $H$ and temperature $T$ can be found in [ROE89]. These mathematical expressions are based on experimental desorption isotherms for cement paste obtained by Hundt and Kantelberg. The moisture content is expressed as the ratio of the retained moisture content (in kg moisture per m$^3$ of concrete) and the cement content $\xi_2$ (in kg cement per m$^3$ of concrete). Equations are given for two regimes: $0.35 < H < H_1$ (regime II) and $H_1 < H < 1$ (regime I). The moisture content is proportional
to the degree of hydration $\alpha$ in the former regime. The value of moisture potential $H_c$ is defined as:

$$H_c = 1 - 0.161\alpha$$  \hspace{1cm} (3.106)

The equations for the two regimes are successively:

$$\frac{W}{\zeta_2} = \left(c_1 + c_4H_t + c_3H_t^2\right)\alpha$$ \hspace{1cm} (3.107)

$$\frac{W}{\zeta_2} = a + bH_t + cH_t^2$$

The coefficients $a$, $b$ and $c$ are defined as:

$$\begin{bmatrix}
a \\
b \\
c
\end{bmatrix} = \frac{1}{\left(1 - H_c\right)^2} \begin{bmatrix}
H_c^2 & 1 - 2H_c & H_c^2 - H_c \\
-2H_c & 2H_c & 1 - H_c^2 \\
1 & -1 & H_c - 1
\end{bmatrix} \begin{bmatrix}
\zeta_2 - c_4\alpha \\
(c_1 + c_2H_c + c_3H_c^2)\alpha \\
(c_2 + 2c_3H_c)\alpha
\end{bmatrix}$$  \hspace{1cm} (3.108)

with $\zeta_2$, the water to cement ratio. In the last set of equations a new coefficient has been introduced: $c_4$. Finally the coefficients $c_1$ to $c_4$ are defined as:

$$c_1 = 0.125$$

$$c_2 = 0.173 - 0.431\left(\frac{T - 293}{25}\right)$$

$$c_3 = 0.060 + 0.392\left(\frac{T - 293}{25}\right)$$  \hspace{1cm} (3.109)

$$c_4 = 0.170 + \left[0.035 + 0.029\left(\frac{\zeta_2 - 0.4}{0.15}\right)\right]\left(\frac{T - 293}{25}\right)$$

with temperature $T$ in K. The validity of this data fit is in principle restricted to:

$$293 \leq T \leq 343 \hspace{1cm} K$$

$$0.35 < H < 1.00$$

$$0.7 \leq \alpha \leq 0.9$$  \hspace{1cm} (3.110)

$$0.40 \leq \zeta_2 \leq 0.55$$

Since all coefficients $a$, $b$, $c$, $c_1$, $c_2$ and $c_3$ are linear functions of the temperature, the above equations can be replaced by a single equation:

$$W(T,H) = \zeta_2\left(\eta_1 + \eta_3T + \eta_4H + \eta_5TH + \eta_6H^2 + \eta_7TH^2\right)$$  \hspace{1cm} (3.111)

in which the coefficients $\eta_1$ to $\eta_6$ are different for the two regimes. It can be calculated that in the lower regime ($0.35 < H < H_l$) the values of these coefficients are:
3.4 implemented models

\[
\begin{align*}
\begin{pmatrix}
\eta_1^n \\
\eta_2^n \\
\eta_3^n \\
\eta_4^n \\
\eta_5^n \\
\eta_6^n \\
\end{pmatrix}
&= \begin{pmatrix}
0.125 \\
0 \\
5.22 \\
-0.0172 \\
-4.53 \\
0.0157 \\
\end{pmatrix} \\
&= \alpha\begin{pmatrix}
1 \\
\alpha \\
\alpha \zeta_1 \\
\frac{1}{\alpha} \\
\frac{\alpha}{\zeta_1} \\
\frac{\alpha^2}{\zeta_1^2} \\
\end{pmatrix}
\tag{3.112}
\end{align*}
\]

and that in the upper regime (H ≤ H < 1) the values of these coefficients are:

\[
\begin{align*}
\begin{pmatrix}
\eta_1^l \\
\eta_2^l \\
\eta_3^l \\
\eta_4^l \\
\eta_5^l \\
\eta_6^l \\
\end{pmatrix}
&= \begin{pmatrix}
18.4 & -1.36 & -27.1 & 2.27 & -57.1 & 75.0 & 38.6 \\
-4.04 \cdot 10^{-2} & 3.25 \cdot 10^3 & 9.61 \cdot 10^{-2} & -7.73 \cdot 10^{-3} & 0.126 & -0.298 & 0 \\
-18.4 & 5.22 & 28.1 & 0 & 114 & -162 & -77.2 \\
4.04 \cdot 10^{-2} & -1.72 \cdot 10^{-2} & -9.61 \cdot 10^{-2} & 0 & -0.251 & 0.597 & 0 \\
0 & -4.53 & 0 & 0 & -57.1 & 87.4 & 38.6 \\
0 & 1.57 \cdot 10^{-2} & 0 & 0 & 0.126 & -0.298 & 0 \\
\end{pmatrix}
\end{align*}
\tag{3.113}
\]

Clearly, the coefficients \( \eta_1 \) to \( \eta_6 \) depend only on the degree of hydration \( \alpha \) in the lower regime (II), whereas they depend on both the degree of hydration and the water to cement ratio \( \zeta_1 \) in the upper regime (I). At the connection of the two regimes (H = H_1) \( W \) and its partial derivatives \( \partial W / \partial T, \partial W / \partial H, \partial^2 W / \partial T \partial H \) are continuous, however \( \partial^3 W / \partial H^2 \) is discontinuous.

At this point a comparison can be made between the total porosity as given by [REI85] (see equation 3.35) and the moisture content at H = 1 according to [ROE89]. The maximum moisture content is reached when all pores are water-filled. The moisture content at H = 1 should approximate this maximum moisture content. The calculations are performed on concrete mixtures from chapter 5 and shown in table 3.3. At H = 1 the moisture content according to [ROE89] still depends on temperature for a certain degree of hydration \( \alpha \), water to cement ratio \( \zeta_1 \) and cement content \( \zeta_2 \). In table 3.3 the moisture contents at T = 293 and T = 303 K have been calculated. It appears that the correspondence of the resulting moisture contents based on [REI85] and [ROE89] respectively is acceptable; the maximum deviation is 7 %. It is noticeable, however, that the moisture contents at H = 1 according to [ROE89] are mostly higher than the moisture contents according to [REI85].

An extension of the description of the moisture content in [ROE89] has been made for the regime 0 ≤ H ≤ 0.35 (regime III). Again a parabola in H has been proposed:
\[ W = \zeta_2 \left( d + eH + fH^2 \right) \]  

(3.114)

with coefficients \(d\), \(e\), and \(f\). The values of these three coefficients have been determined by imposing the following three constraints:

- \( W = 0 \) kg/m\(^3\) at \( H = 0 \)
- \( W \) is continuous at \( H = 0.35 \)
- \( dW/dH \) is continuous at \( H = 0.35 \)

**Table 3.3:** Comparison of total porosity according to [REI85] and moisture content at \( H = 1 \) according to [ROE89]. The assumption that all pores are water-filled leads to \( W_{\text{w}} \). The moisture contents at \( H = 1 \) are calculated at \( T = 293 \) K \( (W_{\text{w}, 293}) \) and at \( T = 303 \) K \( (W_{\text{w}, 303}) \).

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>mixture 1</th>
<th>mixture 2</th>
<th>mixture 3</th>
<th>mixture 4</th>
<th>mixture 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_w )</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>( \rho_c )</td>
<td>999</td>
<td>999</td>
<td>999</td>
<td>999</td>
<td>999</td>
</tr>
<tr>
<td>( w )</td>
<td>3150</td>
<td>3150</td>
<td>3150</td>
<td>3150</td>
<td>3150</td>
</tr>
<tr>
<td>( \zeta_2 )</td>
<td>1.200</td>
<td>1.200</td>
<td>1.200</td>
<td>1.200</td>
<td>1.200</td>
</tr>
<tr>
<td>( \zeta_1 )</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
<td>0.100</td>
</tr>
<tr>
<td>( V_{\text{w}} )</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>( V_{\text{w}} )</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>( W_{\text{w}} )</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>( W_{\text{w}, 293} )</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>( W_{\text{w}, 303} )</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

As a consequence of the first constraint \( d = 0 \). From the other two constraints it follows then that:

\[ e = \frac{1}{0.35} \frac{W''_{H=0.35}}{W''_{H=0.35}} \left( \frac{\partial W}{\partial H} \right)_{H=0.35} \]

(3.115)

\[ f = -\frac{1}{(0.35)^2} W''_{H=0.35} + \frac{1}{0.35} \left( \frac{\partial W}{\partial H} \right)_{H=0.35} \]

Elaboration yields the coefficients \( \eta_1 \) to \( \eta_6 \) for regime III:

\[
\left[ \begin{array}{c}
\eta_1'' \\
\eta_2'' \\
\eta_3'' \\
\eta_4'' \\
\eta_5'' \\
\eta_6''
\end{array} \right] = \left[ \begin{array}{c}
0 \\
0 \\
\frac{1}{0.35} \eta_1'' + \eta_2'' \\
\frac{1}{0.35} \eta_2'' + \eta_4'' \\
- \frac{1}{(0.35)^2} \eta_1'' + \eta_5'' \\
- \frac{1}{(0.35)^2} \eta_2'' + \eta_6''
\end{array} \right] \alpha
\]

(3.116)

Also at the connection of regimes II and III (\( H = 0.35 \)) \( W \) and its partial derivates \( \partial W/\partial T, \partial W/\partial H \) and \( \partial^2 W/\partial T^2 \partial H \) are continuous, whereas \( \partial^2 W/\partial H^2 \) is discontinuous.
In a porous medium the moisture contents for descending moisture potentials are generally higher than for ascending moisture potentials, i.e. at a certain moisture potential the corresponding moisture content depends on the moisture history. This effect is called hysteresis (e.g. in [REL99]). As a consequence of this hysteresis a range of moisture contents is possible at a certain value of the moisture potential. In the present work hysteresis has not been taken into account and the desorption isotherms are considered to be valid for both ascending and descending moisture potentials.

With the definition of the moisture content as explained above, moisture capacity \( c_{21} \) in moisture model 1 becomes:

\[
\frac{\partial W}{\partial T} = \frac{\partial T}{\partial W} = \frac{\eta_2 + \eta_4 H + \eta_5 H^2}{\eta_1 + \eta_4 T + 2\eta_5 H + 2\eta_6 TH}
\] (3.117)

Obviously, material functions \( c_{21} \) and \( c_{22} \) in moisture model 3 are equal to the numerator and denominator of the last equation respectively, multiplied by the cement content \( \zeta_2 \). As the partial derivative \( \partial W/\partial H \) becomes 0 for some combinations of \( \alpha, \zeta_1, T \) and \( H \), asymptotes may arise in moisture capacity \( c_{21} \) with the above definition. This problem occurs at low moisture potentials and high temperatures (see section 5.3). The moisture content \( W \) and moisture capacity \( c_{21} \) according to equation 3.117 are shown in figure 3.15 and 3.16 respectively.

![Figure 3.15: moisture contents at three different temperatures for \( \alpha=0.8, \zeta_1=0.54 \) and \( \zeta_2=300 \text{ kg/m}^3 \).](image1)

![Figure 3.16: moisture capacity \( c_{21} \) in moisture model 1 and 2 at three different temperatures for \( \alpha=0.8, \zeta_1=0.54 \) and \( \zeta_2=300 \text{ kg/m}^3 \).](image2)

From \( \alpha=0.8 \) it follows that \( H_1=0.87 \). The transition from regime I to II at this value of the moisture potential is observable in figures 3.15 and 3.16. While the transition
from regime II to III at $H=0.35$ is smooth for the moisture content, it is marked by negative peaks for $c_{21}$. Figure 3.16 also clearly shows the discontinuity of $\partial^2 W/\partial H^2$ at $H=0.35$ and $H=0.87$, as this factor is included in the derivative of $c_{21}$ with respect to $H$. It can be observed in Figure 3.15 that for a constant moisture potential an increase of temperature leads to a decrease of moisture content, and that a certain moisture content can correspond to different combinations of moisture potential and temperature.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3.17.png}
\caption{piecewise-linear approximation of moisture content in concrete for $\alpha=0.8$, $\zeta_1=0.54$ and $\zeta_2=300$ kg/m$^3$. Linear interpolation is performed between the two extreme temperatures.}
\end{figure}

In moisture model 2 the moisture content has been formulated in a piecewise-linear fashion: a linear branch for each regime. For a certain $\alpha$, $\zeta_1$, and $\zeta_2$ the moisture contents are calculated for the following six pairs $(T,H)$ according to equation 3.111: $(293,0.35)$, $(293,H_1)$, $(293,1)$, $(338,0.35)$, $(338,H_1)$ and $(338,1)$. Next, for a certain $H$ is determined to what regime it belongs and the moisture contents at $T=293$ and $T=338$ K are calculated by interpolation using the predefined pairs. Then the moisture content at temperature $T$ is interpolated between these moisture contents. Clearly, the partial derivative $\partial W/\partial H$ is discontinuous at $H=0.35$ and $H=H_r$. Consequently, if this formulation of the moisture content is used in $c_{21}$ according to equation 3.117, $c_{21}$ is discontinuous as well at these values of $H$, which is undesirable from a computational point of view (see chapter 4).

Carbonation

Moisture model 4 has been developed to take into account carbonation effects. Carbonation affects the pore structure of concrete [NGA97] and thus induces changes to the desorption isotherms [HOU92][REL99] and to the moisture conductivity. Generally, the total porosity decreases while the capillary porosity increases. In blastfurnace slag cement concrete a greater increase of the capillary porosity occurs than in Portland cement concrete. Consequently, a lowering of the desorption isotherms and a reduction of the moisture conductivity occurs in case of Portland cement concrete. In case of blastfurnace slag cement concrete the desorption isotherms are also lowered, however the moisture conductivity increases. These
carbonation effects are irreversible. Consequently, carbonation produces two zones with permanently different moisture properties: the uncarbonated zone, with the unaffected moisture properties, and the carbonated zone, with the changed moisture properties. The boundary between the two zones is generally not fixed.

As carbonation is related to drying of concrete, the computational criterion for the triggering of carbonation has in the present work been attached to the moisture potential. If the moisture potential at a certain point in the concrete surpasses the carbonation threshold in terms of the moisture potential, then this point becomes part of the carbonated zone. If a carbonation criterion of $H=0.6$ is adopted, this implies that below $H=0.6$ the concrete is carbonated. The transition to the new moisture properties in case of carbonation must be prepared by a function which is continuous itself and continuously differentiable. S-shaped functions analogous to the definition of $k_s$ (equation 3.102) are suitable for this purpose:

$$f_w(H) = \varphi_1 + \frac{1-\varphi_1}{1+\left(\frac{1-H}{1-\varphi_1}\right)^{\psi_1}} \quad f_k(H) = \varphi_2 + \frac{1-\varphi_2}{1+\left(\frac{1-H}{1-\varphi_2}\right)^{\psi_2}}$$

(3.118)

Function $f_w$ is a multiplier for the moisture content $W$ (equation 3.111) and $f_k$ a multiplier for the moisture conductivity $k_s$ (equation 3.102) in the uncarbonated zone. Each of the multiplicative functions utilises three parameters: $\varphi_1$ or $\varphi_2$ to denote the factor for the changed moisture content or moisture conductivity respectively, $\varphi_3$ for the value of $H$ at which the moisture properties change and $\varphi_4$ for the radicalness of the transition. For a carbonation threshold of $H=0.6$, 0.7 and 20 are suitable choices for $\varphi_3$ and $\varphi_4$ respectively. Then $f=1$ in the $H$-range $[0.8 \ldots 1.0]$, $f=\varphi_1$ and $f=\varphi_2$ respectively in the $H$-range $[0.0 \ldots 0.6]$ and in the remaining $H$-range $[0.6 \ldots 0.8]$ a smooth transition takes place; this is shown in figure 3.18.

![Figure 3.18](image)

Figure 3.18: multiplicative function $f_w$ for $\varphi_1=2$ (left) and $\varphi_2=0.8$ (right); $\varphi_3=0.7$ and $\varphi_4=20$ in both figures. This function models the transition from uncarbonated to carbonated concrete. In case of concrete with ordinary Portland cement or blastfurnace slag cement $\varphi_4<1$. 
Thus, in moisture model 4 the moisture content in the uncarbonated zone (with subscript 'uncarb') and carbonated zone (with subscript 'carb') respectively is defined as:

$$W_{\text{uncarb}}(T, H) = \xi_2 \left( \eta_1 + \eta_2 T + \eta_3 H + \eta_4 TH + \eta_5 H^2 + \eta_6 TH^2 \right) f_w$$

$$W_{\text{carb}}(T, H) = \phi_1 \xi_2 \left( \eta_1 + \eta_2 T + \eta_3 H + \eta_4 TH + \eta_5 H^2 + \eta_6 TH^2 \right)$$

and the moisture conductivity in these respective zones as:

$$k_{22,\text{uncarb}}(H) = \theta_1 \left( \theta_2 + \frac{1-\theta_2}{1+\left(1-H\frac{\alpha}{1-\theta_2}\right)^{\phi_2}} \right)$$

$$k_{22,\text{carb}}(H) = \phi_2 \theta_1 \left( \theta_2 + \frac{1-\theta_2}{1+\left(1-H\frac{\alpha}{1-\theta_2}\right)^{\phi_2}} \right)$$

(3.120) The last equations show that after the carbonation threshold has been surpassed, the moisture properties of this carbonated zone differ from the moisture properties of the uncarbonated zone by a constant factor ($\phi_1$ or $\phi_2$). The definitions $W_{\text{uncarb}}$ and $k_{22,\text{uncarb}}$ are applied in the uncarbonated zone, where $H$ has never been lower than the carbonation threshold ($H=0.6$). The definitions $W_{\text{carb}}$ and $k_{22,\text{carb}}$ are applied for the carbonated zone, in which $H$ can have any value between 0 and 1, but in which the carbonation threshold has been surpassed at least once. In this way the irreversibility of carbonation is modelled. In general for ordinary Portland cement concrete it holds that $\phi_1<1$ and $\phi_2<1$, while for concrete with blastfurnace slag cement it holds that $\phi_1<1$ and $\phi_2>1$. In figure 3.19 and 3.20 the effect is illustrated of carbonation on the moisture content and the moisture conductivity respectively according to moisture model 4.

![Figure 3.19: Desorption isotherm for $\alpha=0.7$, $\zeta=0.415$, $\zeta'=420$ kg/m$^3$ and $T=293$ K in the uncarbonated zone ('uncarb') and carbonated zone ('carb'). The transition between the curves is provided by multiplicative function $f_w$ with $\phi_1=2$, $\phi_2=0.7$ and $\phi_3=20$.](image1)

![Figure 3.20: Moisture conductivity for $\theta_1=5\cdot10^{-11}$ m$^2$/s, $\theta_2=0.05$, $\theta_3=0.7$ and $\theta_4=4$ in the uncarbonated zone ('uncarb') and carbonated zone ('carb'). The transition between the curves is provided by multiplicative function $f_k$ with $\phi_2=0.8$, $\phi_3=0.7$ and $\phi_4=20$.](image2)
The basic equation of moisture model 4 is equation 3.103, like moisture model 1 and 2. Due to the altered definition of the moisture content $W$, moisture capacity $c_{21}$ becomes:

$$
c_{21,\text{unw}}(T,H) = \frac{\partial W}{\partial T} = \frac{1}{\left(\eta_3 + \eta_4 T + 2\eta_5 H + 2\eta_6 TH \right) f_w + \frac{df_w}{dH}}
$$

(3.121)

$c_{21,\text{w}}(T,H) = c_{21}(T,H)$

for the uncarbonated and carbonated zone respectively, with $W$ according to equation 3.111 and $c_{21}$ according to equation 3.117. The derivative $df_w/dH$ is given by:

$$
\frac{df_w}{dH} = \frac{(1-\varphi_1)\varphi_4}{(1-\varphi_3)^{\varphi_1}} \frac{(1-H)^{\varphi_1-1}}{1 + 2\left(\frac{1-H}{1-\varphi_3}\right)^{\varphi_1} + \left(\frac{1-H}{1-\varphi_3}\right)^{2\varphi_1}}
$$

(3.122)

Summary

It is assumed that the discussed models are applicable to both a situation in which concrete dries out and a situation in which concrete acquires moisture. In the former situation evaporation of pore water takes place at the exposed concrete surface. In the latter situation, gaseous and liquid environments can be distinguished. In the models it is assumed that an environment with 100% relative humidity is the same as a liquid environment, e.g. in case of submerged concrete; both environments correspond to $H=1$ on the concrete surface (in case of a Dirichlet boundary condition, see section 5.1). The complex process of capillary water uptake in concrete from the various environments is implicitly included in the meso-level material functions of the implemented models, possibly in combination with the interface element for moisture transfer at the concrete surface (a Robbins boundary condition, see chapter 4 and section 5.1). Table 3.4 summarises the characteristics of the four moisture models.
Table 3.4: overview of implemented moisture models. Carbonation effects are included in moisture model 4 only. A constant negative source term $f_2$ may be specified to model an overall moisture sink.

<table>
<thead>
<tr>
<th>model 1</th>
<th>model 2</th>
<th>model 3</th>
<th>model 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>equation 3.111</td>
<td>piecewise-linear</td>
<td>equation 3.111</td>
<td>equation 3.119</td>
</tr>
<tr>
<td>$\frac{\partial W}{\partial T}$</td>
<td>$\frac{\partial W}{\partial T}$</td>
<td>$\frac{\partial W}{\partial T}$</td>
<td>$\frac{\partial W}{\partial T}$</td>
</tr>
<tr>
<td>$\frac{\partial W}{\partial H}$</td>
<td>$\frac{\partial W}{\partial H}$</td>
<td>$\frac{\partial W}{\partial H}$</td>
<td>$\frac{\partial W}{\partial H}$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>$\frac{\partial W}{\partial H}$</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$k_h$</td>
<td>$k_h$</td>
<td>$k_w$</td>
<td>equation 3.120</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

3.4.3 Chloride

Chloride transport in concrete is the main focus of the present work. However, heat flow and moisture migration in concrete needed to be discussed first, since chloride transport depends on these processes. The dependencies of the chloride balance on the other two balances are elaborated in this section.

Two categories of chloride ions are commonly distinguished: free and bound chloride ions. Free chloride ions are dissolved in the pore water in concrete and can be transported, whereas bound chloride ions are stuck to (specific sites on) the solid matrix. This adsorption of chloride ions in cement-based materials has been investigated e.g. by [TRIB91][TAN93]. The free chloride ion concentration in the pore water of concrete $C_{\text{free}}$ is expressed in kg Cl$^{-}$ per m$^3$ pore water. The unit of the bound chloride ion content in concrete $C_{\text{bound}}$ depends on how the chloride adsorption is defined. According to a general formulation chloride ions can be bound to the entire solid matrix (chloride model 1): the unit of $C_{\text{bound}}$ is then kg Cl$^{-}$ per m$^3$ of solid matrix. If bound chloride ions can only be adsorbed by the cement paste component in concrete (chloride models 2 and 3) [TAN93], then a suitable unit for $C_{\text{bound}}$ is kg Cl$^{-}$ per kg cement paste component. The sum of free and bound chloride ions is total chloride ions $C_{\text{tot}}$ (in kg Cl$^{-}$ per m$^3$ concrete).

Free chloride ions can become bound chloride ions and vice versa. Equilibrium states exist between free and bound chlorides, i.e. for a certain total chloride content a typical amount of chlorides is present in the pore water and the rest is adsorbed.
3.4 implemented models

So, if this total chloride content increases due to a net influx of free chloride ions, the equilibrium between free and bound chlorides must shift to a new state. It is assumed in the present work that this equilibrium shift is instantaneous, i.e. no time is needed for the conversion of free chlorides to bound chlorides, neither for the conversion of bound chlorides to free chlorides. Due to the coupling with the moisture balance, an equilibrium shift can not only be evoked by a net influx or outflux of chloride ions, but also by a net influx or outflux of moisture, since this changes the free chloride concentration.

In moisture model 1 the main variable is the total chloride content \( C_{\text{tot}} \) (in kg Cl\(^-\) per m\(^3\) concrete), while the free chloride concentration \( C_{\text{free}} \) (in kg Cl\(^-\) per m\(^3\) pore water) is the driving force of the chloride diffusion process. Diffusion of chloride ions in concrete takes place via continuous water paths in the pores. The diffusion process of ions in the pore water is influenced by the simultaneous convection of these ions, which on a higher level of observation – the meso-level – is referred to as dispersion. Following [SAE93] the relation between \( C_{\text{tot}} \), \( C_{\text{free}} \) and \( C_{\text{bound}} \) (in kg Cl\(^-\) per m\(^3\) of solid matrix) is:

\[
C_{\text{tot}} = W^* C_{\text{free}} + (1 - W_{\text{max}}^*) C_{\text{bound}}
\]  \( (3.123) \)

with \( W^* \) the volumetric moisture content (in m\(^3\) water per m\(^3\) concrete) and \( W_{\text{max}}^* \) the maximum volumetric moisture content (constant). The maximum volume of moisture plus the volume of the solid matrix in concrete equals its total volume. Consequently, the factor \( 1 - W_{\text{max}}^* \) equals the volumetric solid matrix content (in m\(^3\) solid matrix per m\(^3\) concrete), onto which chlorides can be adsorbed. The volumetric moisture content \( W^* \) is related to moisture content \( W \) (in kg water per m\(^3\) concrete) as follows:

\[
W = \rho_w W^*
\]  \( (3.124) \)

with \( \rho_w \) the density of water (998 kg/m\(^3\)). Then equation 3.123 can be written as:

\[
C_{\text{tot}} = \frac{W}{\rho_w} C_{\text{free}} + \left(1 - \frac{\xi_1}{\rho_w} \right) C_{\text{bound}}
\]  \( (3.125) \)

in which chloride binding parameter \( \xi_1 \) represents the maximum moisture content (in kg/m\(^3\)). In moisture model 1 a linear relation is assumed between the chloride ions adsorbed on the solid matrix and the free chloride ions in the pore water [SAE93]:

\[
C_{\text{bound}} = \xi_2 C_{\text{free}}
\]  \( (3.126) \)

with chloride binding parameter \( \xi_2 \) (dimensionless) as the constant of proportionality. The effect of temperature on chloride binding [HET96] has been disregarded. Note that although the ratio between \( C_{\text{bound}} \) and \( C_{\text{free}} \) is fixed (and equal to \( \xi_2 \)), the ratio between the mass of bound and free chloride ions per volume concrete is generally variable due to the variable moisture content \( W \). The latter ratio corresponds to the ratio of the second and the first term on the righthand-side of equation 3.125.
At this point an example can elucidate an earlier statement, namely that upon a net moisture influx or outflux the equilibrium between $C_{\text{bound}}$ and $C_{\text{free}}$ is shifted. Suppose that the net chloride influx equals zero; consequently $C_{\text{tot}}$ is constant (see equation 3.129). Table 3.5 shows two different equilibrium states corresponding to the different moisture contents. Note that $C_{\text{free}}$ and $C_{\text{bound}}$ cannot simply be added to yield $C_{\text{tot}}$, in spite of their identical units, since $C_{\text{free}}$ and $C_{\text{bound}}$ are related to different phases in concrete (water and solid matrix respectively).

Table 3.5: example of two different equilibrium states between $C_{\text{bound}}$ and $C_{\text{free}}$ for constant $C_{\text{tot}}$. Verify that in both cases equations 3.125 and 3.126 are satisfied with $\xi_1 = 163 \text{ kg/m}^3$ and $\xi_2 = 0.35$.

<table>
<thead>
<tr>
<th>$W$ [kg/m$^3$]</th>
<th>$C_{\text{tot}}$ [kg/m$^3$]</th>
<th>$C_{\text{free}}$ [kg/m$^3$]</th>
<th>$C_{\text{bound}}$ [kg/m$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>7</td>
<td>18.8</td>
<td>6.57</td>
</tr>
<tr>
<td>60</td>
<td>7</td>
<td>19.8</td>
<td>6.94</td>
</tr>
</tbody>
</table>

Next, substitution of equation 3.126 in equation 3.125 gives a relation between $C_{\text{tot}}$ and $C_{\text{free}}$:

$$C_{\text{tot}} = f_a(T,H)C_{\text{free}}$$  \hspace{1cm} (3.127)

with adsorption function $f_a$ as:

$$f_a(T,H) = \frac{W}{\rho_w} + \left(1 - \frac{\xi_1}{\rho_w}\right)\xi_2$$  \hspace{1cm} (3.128)

which is a function of temperature and moisture potential, since it depends on the moisture content $W$. The total chloride content $C_{\text{tot}}$ at a certain point in concrete can increase in time $t$ due to a net diffusive or convective chloride influx. This leads to the following chloride balance:

$$\int_{\Omega} \frac{\partial C_{\text{tot}}}{\partial t} d\Omega = \int_{\Gamma} \left(\mathbf{q}_{\text{c, diff}} + \mathbf{q}_{\text{c, conv}}\right) \cdot \mathbf{n} d\Gamma$$  \hspace{1cm} (3.129)

in which $\Omega$ is the reference volume (in m$^3$), $\Gamma$ its surface area (in m$^2$), vector $\mathbf{q}_{\text{c, diff}}$ is the diffusive chloride flux (in kgm$^{-2}\text{s}^{-1}$), vector $\mathbf{q}_{\text{c, conv}}$ the convective chloride flux (in kgm$^{-2}\text{s}^{-1}$) and vector $\mathbf{n}$ the normal vector of surface $\Gamma$. As the normal vector $\mathbf{n}$ points outward of $\Omega$, the negative inner product of $\mathbf{n}$ and a flux in a certain direction makes an influx into $\Omega$ positive and an outflux out of $\Omega$ negative (see section 3.2). Moreover, this inner product removes the components of the flux tangential to $\Gamma$, so that only the component of the flux perpendicular to $\Gamma$ remains. Thus, indeed equation 3.129 states that a positive change of the total amount of chlorides in volume $\Omega$ in time equals a positive net chloride influx, diffusive and convective, into $\Omega$ through its surface area $\Gamma$.

Diffusion of chloride ions in the pore water is driven by a gradient of the free chloride concentration $\nabla C_{\text{free}}$. The dispersive chloride ion flux on the meso-level depends on
the amount of water paths in the pore system which is available for this diffusion process. It is assumed that the efficiency of the chloride ion diffusion process in the porous material is proportional to its moisture content, see figure 3.21. Furthermore, the diffusion process is sensitive to temperature via the Arrhenius function [SAE93]. This leads to the following definition of the diffusive chloride ion flux in concrete:

$$q_{c, \text{diff}} = -k_c(T, H) \nabla C_{\text{pve}}$$  \hspace{1cm} (3.130)

with the macroscopic chloride conductivity \( k_c \) as:

$$k_c(T, H) = \left( \kappa_1 - \kappa_2 \right) \frac{W(T, H) - W_s(T)}{W_s(T) - W_r(T)} + \kappa_2 e^{\frac{E_\alpha}{R \left( \frac{T}{T_0} - 1 \right)}}$$  \hspace{1cm} (3.131)

in which parameter \( \kappa_1 \) is the saturated chloride conductivity (at \( W_s \), in m²/s), \( \kappa_2 \) the chloride conductivity at \( W_r \) (in m²/s), \( W_s \) the saturation moisture content and \( W_r \) the residual moisture content. The Arrhenius function includes the following constants: \( \lambda_1 \) as the activation energy of the diffusion process (in J/mol), \( R \) the gas constant (8.3143 J/mol·K⁻¹) and \( \lambda_2 \) the reference temperature. The bracketed factor in equation 3.131 is a general formulation (analogous to equation 3.98), which allows for a residual moisture content; usually \( W_r = 0 \) kg/m³ (for all temperatures) and \( \kappa_2 = 0 \) m²/s. The diffusive chloride flux could also have been called dispersive chloride flux, but the former name is thought to better indicate the underlying mechanism.

![Figure 3.21: dependence of the chloride conductivity \( k_c \) in concrete on the moisture content \( W \). While the free chloride concentration \( C_{\text{free}} \) (the mass of chloride ions per volume of pore water) on the lefthand-side of A is equal to \( C_{\text{free}} \) on the lefthand-side of B, and while \( C_{\text{free}} \) on the righthand-side of A is equal to \( C_{\text{free}} \) on the righthand-side of B, the diffusive chloride ion flow \( q_{c, \text{diff}} \) (the mass of chloride ions passing per unit of time through a unit of concrete cross-section) is greater in B than in A.](image)

Convection of chloride ions in concrete is migration of pore water containing chloride ions. This phenomenon is also referred to as ‘advection’ of chloride ions. The mechanism of convection (or advection) of chloride ions is in essence different
from diffusion of chloride ions. In case of convection the chloride ions are not actively involved in their transport; they are just carried by the moisture flow. So, in order to obtain an expression for the convective chloride ion flux, the volume of moisture passing through a surface area of 1 m$^2$ per s can be multiplied by the mass of chloride ions in that volume. Since the negative product of $k_w$ and $\nabla H$ yields a moisture flux in kgm$^{-2}$s$^{-1}$, this moisture flux can be divided by the density of water $\rho_w$ to arrive at a volume of moisture passing through 1 m$^2$ per s. Then the convective chloride ion flux $\mathbf{q}_{c,\text{conv}}$ (in kgm$^{-2}$s$^{-1}$) becomes:

$$\mathbf{q}_{c,\text{conv}} = -\frac{C_{\text{free}}}{\rho_w} k_w \nabla H$$  \hspace{1cm} (3.132)

Clearly, convection of chloride ions is driven by a gradient of the moisture potential. Now, only the liquid component of the moisture flow carries chloride ions. This means that the vapour component of the moisture flow in the last equation must be removed. As the associated moisture flux in the last equation is in kgm$^{-2}$s$^{-1}$ and assuming that the mass of water vapour in this flux can be neglected, the last equation can be considered to take into account only the liquid component of moisture flow. An approximation of $k_w$ has already been given in equation 3.105 and hence:

$$\mathbf{q}_{c,\text{conv}} \approx -\frac{C_{\text{free}}}{\rho_w} \frac{\partial W}{\partial H} k_h \nabla H$$  \hspace{1cm} (3.133)

Now the chloride balance can be elaborated. Insertion of the expressions for the chloride fluxes into equation 3.129 yields:

$$\int_{\Omega} \frac{\partial C_{\text{tot}}}{\partial t} \, d\Omega = \int_{\Omega} \left( k_c \nabla C_{\text{free}} + \frac{C_{\text{free}}}{\rho_w} \frac{\partial W}{\partial H} k_h \nabla H \right) \cdot \mathbf{n} \, d\Gamma$$  \hspace{1cm} (3.134)

Application of Gauß' divergence theorem yields:

$$\int_{\Omega} \frac{\partial C_{\text{tot}}}{\partial t} \, d\Omega = \int_{\Omega} \nabla \cdot \left( k_c \nabla C_{\text{free}} + \frac{C_{\text{free}}}{\rho_w} \frac{\partial W}{\partial H} k_h \nabla H \right) \, d\Omega$$  \hspace{1cm} (3.135)

The integration over volume $\Omega$ can be omitted, since the balance must hold for an arbitrary volume. Now a choice must be made for the main chloride variable: either $C_{\text{tot}}$ or $C_{\text{free}}$. Following [SAE93] $C_{\text{tot}}$ is the main chloride variable in chloride model 1 and substitution of equation 3.127 leads to:

$$\frac{\partial C_{\text{tot}}}{\partial t} = \nabla \cdot \left[ k_c(T,H) \nabla \left( \frac{C_{\text{tot}}}{f_a(T,H)} \right) + \frac{C_{\text{tot}}}{\rho_w f_a(T,H)} \frac{\partial W(T,H)}{\partial H} k_h(H) \nabla H \right]$$  \hspace{1cm} (3.136)

in which the dependencies on T and H have been explicitly mentioned. Substitution of equation 3.126 in the chloride balance (equation 3.129) implies that the chloride binding equilibrium is forced at all times. This means that chloride binding is
3.4 implemented models

assumed to be instantaneous [PER84]. Elaboration of the first term between the brackets on the righthand-side of the last equation results in:

\[
k_C \nabla \left( \frac{C_{\text{tot}}}{f_a} \right) = k_C \nabla C_{\text{tot}} - \frac{k_C}{\rho_w f_a^2} C_{\text{tot}} \frac{\partial W}{\partial T} - \frac{k_C}{\rho_w f_a} C_{\text{tot}} \frac{\partial W}{\partial H} \nabla H \tag{3.137}
\]

Then the conductivities \(k_{31}\), \(k_{32}\) and \(k_{33}\) in chloride model 1 are successively:

\[
k_{31}(T,H,C_{\text{tot}}) = -\frac{k_C C_{\text{tot}}}{\rho_w f_a^2} \frac{\partial W}{\partial T}
\]

\[
k_{32}(T,H,C_{\text{tot}}) = \left( k_h - \frac{k_C}{f_a} \right) \frac{C_{\text{tot}}}{\rho_w f_a} \frac{\partial W}{\partial H} \tag{3.138}
\]

\[
k_{33}(T,H) = \frac{k_v}{f_a}
\]

The couplings in the chloride balance to the heat and moisture balance are established by these conductivities. The capacities \(c_{31}\), \(c_{32}\) and \(c_{33}\) in chloride model 1 are 0, 0 and 1 respectively; the source term \(f_3\) equals 0.

Alternative formulation

In chloride model 2 the description of chloride adsorption differs from the one in chloride model 1. Here the total chloride content \(C_{\text{tot}}\) (in kg Cl\(^{-}\) per m\(^3\) concrete) is defined as:

\[
C_{\text{tot}} = \frac{W}{\rho_w} C_{\text{free}} + \xi_1 C_{\text{bound}} \tag{3.139}
\]

with \(C_{\text{free}}\) again in kg Cl\(^{-}\) per m\(^3\) of pore water, but with \(C_{\text{bound}}\) in kg Cl\(^{-}\) per kg cement gel. Consequently, chloride binding parameter \(\xi_1\) now represents the cement gel (CSH) content in concrete (in kg cement gel per m\(^3\) concrete), see equation 3.34. A Langmuir-type\(^{10}\) function is deployed for the relation between bound and free chloride ions [ATK86]:

\[
C_{\text{bound}} = \frac{C_{\text{free}}}{\xi_2 + \xi_3 C_{\text{free}}} \tag{3.140}
\]

in which \(\xi_2\) (in kg/m\(^3\)) and \(\xi_3\) (dimensionless) are binding parameters, see figure 3.22. These parameters can be chosen to fit measurements performed by e.g. [TRI89][TAN93]. Obviously the choice of \(\xi_3 = 0\) leads to linear chloride adsorption. Again, the effect of temperature on chloride binding [HET96] has been disregarded. Freundlich adsorption is not suitable from a computational point of view (see appendix C).

\(^{10}\) In the original Langmuir function it holds that \(\xi_3 = 1\).
In [TAN93] chloride adsorption measurements have been described for cement pastes and mortars with water to cement ratios $z$, of 0.4, 0.6 and 0.8. The samples were first dried and vacuumed and next put in a chloride solution, so that the chloride ions were sucked into the samples. Chloride desorption data were obtained after the adsorption measurements by removing the chloride solution and putting the samples in a solution without chlorides. It appeared that the measurements follow the same trend, if the mass of bound chlorides is taken relative to the cement gel (CSH) content. This is shown in figure 3.23, in which one symbol is used for the cement pastes with $z=0.4$, 0.6 and 0.8, and another symbol for the mortars with $z=0.4$, 0.6 and 0.8.

![Figure 3.22: Langmuir-type chloride adsorption. The slope at $C_{\text{free}}=0$ equals $1/\xi_2$, and a horizontal asymptote is located at $C_{\text{bound}}=1/\xi_3$.](image)

![Figure 3.23: measurements [TRI89][TAN93] and modelling of chloride adsorption. The measurements of [TRI89][TAN93] (see also appendix D) show that cement pastes and mortars with different water to cement ratios follow the same trend regarding chloride adsorption. In chloride model 2 the adsorption of chloride ions in concrete is described by a generalisation of Langmuir’s equation, in which linear adsorption is a particular case. The two curves are deployed in section 5.3 and 6.1.4.](image)

- Tang & Nilsson, sucked, cement paste
- Tang & Nilsson, sucked, mortar
- Tritthart, mixed-in, Ca, $w/c=0.6$
- Tritthart, mixed-in, Ca, Cal=1 %
- Tritthart, diffused, 0.1 n NaOH, $w/c=0.5$
- Tritthart, diffused, 0.1 n NaOH, $w/c=0.7$
- Langmuir, ksi2=247 kg/m3, ksi3=71
- linear, ksi2=956 kg/m3, ksi3=0
Also in [TRI89] chloride adsorption measurements have been described for cement pastes with water to cement ratios $\zeta_1$ in the range [0.4 ... 1.0] at increments of 0.1. Two experimental procedures were followed: adding chlorides to the mixing water of the pastes and putting wet chloride-free cement pastes in chloride solutions. In the latter case the chloride ions diffused into the samples where they were partially bound. Moreover, in [TRI89] the influence of the cation was investigated: chloride ions were added to the mixing water as NaCl and as CaCl$_2$ in the one experimental procedure, and in the other experimental procedure the chloride solutions contained also either Ca(OH)$_2$ (saturated), 0.1n NaOH or 0.5n NaOH. In [TRI89] graphs are presented relating the free chloride concentration in ppm to the total chloride content as a percentage of the cement mass. These graphs have been transformed into plots of $C_{\text{free}}$ in kg Cl$^{-}$ per m$^3$ water versus $C_{\text{bound}}$ in kg Cl$^{-}$ per kg cement gel (see appendix D). Four data series from [TRI89] agreed well with the measurements of [TAN93]; they are shown also in figure 3.23. The other six data series, which diverge somewhat from the measurements in [TAN93], are shown in figure 3.24.

![Graph](image)

Figure 3.24: measurements of chloride adsorption in cement pastes with different water to cement ratios [TRI89] (see also appendix D) and two approximating curves of the Langmuir-type. These measurements diverge somewhat from the measurements in [TAN93] (see figure 3.23).

From figures 3.23 and 3.24 it follows that the water to cement ratio hardly influences the relation between bound chlorides, expressed in kg Cl$^{-}$ per kg cement gel, and free chlorides, expressed in kg Cl$^{-}$ per m$^3$ water. However, still with these units, the total chemical composition of the pore solution affects the adsorption of chloride ions in cement paste, as shown in figure 3.24. In the present work no further
attention has been paid to this phenomenon and for chloride model 2 the choice of the binding parameters $\xi_2$ and $\xi_3$ has been based on the data in figure 3.23. Comparison of the chloride adsorption and desorption measurements in [TAN93] indicates that also with respect to chloride binding some hysteresis may occur. It is assumed, however, that equation 3.140 is valid both in the case of ascending and descending free chloride ion concentrations. Two chloride adsorption curves, which are used in section 5.3 and 6.1.4, are already shown in figure 3.23.

In chloride model 2 the diffusive and convective chloride ion fluxes are the same as in chloride model 1 (see equations 3.130 and 3.133). Also the same chloride balance is applied (see equation 3.129). In the elaboration of this balance, however, the free chloride concentration $C_{\text{free}}$ has been chosen as the main chloride variable. Consequently, upon substitution of equations 3.139 and 3.140 the lefthand-side of the chloride balance becomes:

$$\frac{\partial C_{\text{tot}}}{\partial t} = \frac{C_{\text{free}}}{\rho_w} \frac{\partial W}{\partial T} + \frac{C_{\text{free}}}{\rho_w} \frac{\partial W}{\partial H} \frac{\partial H}{\partial t} + \left[ \frac{W}{p_w} + \frac{\xi_2 \xi_3}{\left( \xi_2 + \xi_3 C_{\text{free}} \right)^2} \right] \frac{\partial C_{\text{free}}}{\partial t}$$  \hspace{1cm} (3.141)

so that the chloride balance now is:

$$c_{31} \frac{\partial T}{\partial t} + c_{32} \frac{\partial H}{\partial t} + c_{33} \frac{\partial C_{\text{free}}}{\partial t} = \nabla \cdot \left( k \nabla C_{\text{free}} + \frac{C_{\text{free}}}{\rho_w} \frac{\partial W}{\partial H} k_h \nabla H \right)$$  \hspace{1cm} (3.142)

with capacities $c_{31}$, $c_{32}$ and $c_{33}$:

$$c_{31} \left( H, C_{\text{free}} \right) = \frac{C_{\text{free}}}{\rho_w} \frac{\partial W}{\partial T}$$

$$c_{32} \left( T, H, C_{\text{free}} \right) = \frac{C_{\text{free}}}{\rho_w} \frac{\partial W}{\partial H}$$  \hspace{1cm} (3.143)

$$c_{33} \left( T, H, C_{\text{free}} \right) = \frac{W}{\rho_w} + \frac{\xi_2 \xi_3}{\left( \xi_2 + \xi_3 C_{\text{free}} \right)^2}$$

Again, substitution of the chloride binding relation (equation 3.140) into the balance implies that chloride binding is assumed to be instantaneous. Clearly, the conductivities $k_{32}$ and $k_{33}$ in chloride model 2 are:

$$k_{32} \left( T, H, C_{\text{free}} \right) = \frac{C_{\text{free}}}{\rho_w} \frac{\partial W}{\partial H} k_h$$

$$k_{33} \left( T, H \right) = k_i$$  \hspace{1cm} (3.144)

and both $k_{31}$ and $f_3$ equal zero.
Carbonation

Chloride model 2 has been extended with the effect of carbonation on chloride binding; the result is chloride model 3. Carbonation leads to a decrease of alkalinity, which reduces the chloride binding capacity of concrete, regardless of the cement type [TUU82][AND95][HET96]. In chloride model 3 this effect is taken into account by multiplying the relation between bound and free chloride ions (equation 3.140) with an s-shaped function \( f_c \). This function models the transition from uncarbonated to carbonated concrete:

\[
 f_c(H) = \frac{1}{1 + \left(\frac{1-H}{1-\varphi_1}\right)^{\varphi_2}}
\]  

(3.145)

Clearly, this function \( f_c \) is identical to \( f_s \) and \( f_i \) in moisture model 4 with \( \varphi_1=0 \) and \( \varphi_2=0 \) respectively. It is assumed that carbonation irreversibly reduces the amount of bound chlorides to zero. For a carbonation threshold of \( H=0.6 \), a suitable choice for the parameters is \( \varphi_3=0.7 \) and \( \varphi_4=20 \), as already mentioned in section 3.4.2. Function \( f_c \) is depicted in figure 3.25 for these parameter values. The bound chloride content \( C_{\text{bound}} \) (in kg Cl\(^-\) per kg cement gel) in chloride model 3 is thus defined as:

\[
 C_{\text{bound}}(H,C_{\text{free}}) = \frac{C_{\text{free}}f_c}{\xi_2 + \xi_3C_{\text{free}}}
\]  

(3.146)

meaning that, for \( \varphi_3=0.7 \) and \( \varphi_4=20 \), in the \( H \)-range [0.8 ... 1.0] chloride binding is as in equation 3.140, in the \( H \)-range [0.0 ... 0.6] only free chloride ions are present and in the remaining \( H \)-range [0.6 ... 0.8] the chloride binding capacity gradually changes. Once the moisture potential \( H \) has been below the carbonation threshold (\( H=0.6 \)), the zone has become carbonated and can no longer accommodate bound chlorides. So, the modelling is such that, if the moisture potential at a certain point in the concrete was below the carbonation threshold and later rises again above this threshold, the concrete remains carbonated and contains only free chloride ions at that point. Thus, the total chloride content \( C_{\text{tot}} \) (in kg Cl\(^-\) per m\(^3\) concrete) in the uncarbonated ('uncarb') and carbonated ('carb') zone are respectively:

![Figure 3.25: multiplicative function \( f_c \) for \( \varphi_3=0.7 \) and \( \varphi_4=20 \). This function models the transition from uncarbonated to carbonated concrete. In chloride model 3 carbonation cancels chloride binding.](image-url)
\[ C_{\text{tot, uncarb}} = \frac{W}{\rho_w} C_{\text{free}} + \frac{\xi_1 C_{\text{free}} f_c}{\xi_2 + \xi_3 C_{\text{free}}} \]

\[ C_{\text{tot, carb}} = \frac{W}{\rho_w} C_{\text{free}} \]

Substitution of the last equations in the chloride balance leads to different capacities \( c_{32} \) and \( c_{33} \) for the uncarbonated and carbonated zone. For the uncarbonated zone it holds that:

\[ c_{31, uncarb}(H, C_{\text{free}}) = \frac{C_{\text{free}}}{\rho_w} \frac{\partial W}{\partial T} \]

\[ c_{32, uncarb}(T, H, C_{\text{free}}) = \frac{C_{\text{free}}}{\rho_w} \frac{\partial W}{\partial H} + \frac{\xi_1 C_{\text{free}}}{\xi_2 + \xi_3 C_{\text{free}}} \frac{df_c}{dH} \]

\[ c_{33, uncarb}(T, H, C_{\text{free}}) = \frac{W}{\rho_w} + \frac{\xi_1 \xi_2 f_c}{\left( \xi_2 + \xi_3 C_{\text{free}} \right)^2} \]

with:

\[ \frac{df_c}{dH} = \frac{\varphi_4}{(1-\varphi_3)^{\varphi_4} + \left( 1 + \varphi_4 \right) \left( \frac{1-H}{1-\varphi_3} \right)^{2\varphi_4}} \]

\[ = \frac{\varphi_4}{(1-\varphi_3)^{\varphi_4} + \left( 1 + \varphi_4 \right) \left( \frac{1-H}{1-\varphi_3} \right)^{2\varphi_4}} \]

and for the carbonated zone that:

\[ c_{31, carb}(H, C_{\text{free}}) = \frac{C_{\text{free}}}{\rho_w} \frac{\partial W}{\partial T} \]

\[ c_{32, carb}(T, H, C_{\text{free}}) = \frac{C_{\text{free}}}{\rho_w} \frac{\partial W}{\partial H} \]

\[ \frac{c_{33, carb}(T, H)}{\rho_w} = \frac{W}{\rho_w} \]

In chloride model 3 the conductivities \( k_{32} \) and \( k_{33} \) are unchanged as compared to chloride model 2 (see equation 3.144) and a distinction between \( k_{32} \) or \( k_{33} \) in the uncarbonated and carbonated zone respectively does not have to be made, since the chloride binding relation is relevant neither for the diffusive nor for the convective chloride ion flux. Also in chloride model 3 conductivity \( k_{31} \) and source term \( f_3 \) both equal zero.

**Summary**

If linear chloride binding is considered, chloride models 1 and 2 are basically identical, despite the different main chloride variables (\( C_{\text{tot}} \) in chloride model 1 and
3.4 implemented models

$C_{\text{free}}$, in chloride model 2) and the different units of $C_{\text{bound}}$ (kg Cl$^{-}$ per m$^3$ solid matrix in chloride model 1 and kg Cl$^{-}$ per kg cement gel in chloride model 2). As the units of $C_{\text{tot}}$ and $C_{\text{free}}$ are the same in both models (kg Cl$^{-}$ per m$^3$ concrete and kg Cl$^{-}$ per m$^3$ water respectively), equivalent chloride binding parameters $\xi_1$ and $\xi_2$ can be calculated for the two models. Let a second index for $\xi$ denote the associated model, then the chloride binding parameters are related as follows:

\[
\begin{pmatrix}
1 - \frac{\xi_{11}}{\rho_n} \\
\frac{\xi_{12}}{\rho_n}
\end{pmatrix}
\begin{pmatrix}
\xi_{21} \\
\xi_{22}
\end{pmatrix} = \begin{pmatrix}
\xi_{11} \\
\xi_{12}
\end{pmatrix}
\]

in case of linear binding. In principle $\xi_{11}$ and $\xi_{12}$ are calculated with equations 3.111 and 3.34 respectively. Then $\xi_{21}$ can be related to $\xi_{22}$ via figure 3.23 and equation 3.140. An example of equivalent binding parameters is given in table 3.6. An overview of the three non-linear chloride models is given in table 3.7.

| Table 3.6: example of equivalent chloride binding parameters for $\alpha=0.7$, $\xi_1=0.59$, $C_p=320$ kg/m$^3$ and T=293 K. |
|---|---|---|
| $\xi_1$ | 151 | 280 kg/m$^3$ |
| $\xi_2$ | 0.343 | 956 kg/m$^3$ |
| $\xi_3$ | 0 | --- |
Table 3.7: overview of implemented chloride models. Carbonation effects are included in chloride model 3 only; in the corresponding column the expression for the uncarbonated zone has been written on the first line and the one for the carbonated zone on the second line, if the expressions are different for these two zones.

<table>
<thead>
<tr>
<th>model 1</th>
<th>model 2</th>
<th>model 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \frac{W}{\rho_w} C_{free} + \left( 1 - \frac{\xi_1}{\rho_w} \right) C_{bound} ]</td>
<td>[ \frac{W}{\rho_w} C_{free} + \xi_1 C_{bound} ]</td>
<td>[ \frac{W}{\rho_w} C_{free} + \xi_1 C_{bound} ]</td>
</tr>
<tr>
<td>[ \xi_2 C_{free} ]</td>
<td>[ C_{free} ]</td>
<td>[ \frac{C_{free,f_c}}{\xi_2 + \xi_3 C_{free}} ]</td>
</tr>
<tr>
<td>0</td>
<td>[ \frac{\partial W}{\rho_w} \frac{\partial T}{\partial T} ]</td>
<td>[ \frac{\partial W}{\rho_w} \frac{\partial T}{\partial T} ]</td>
</tr>
<tr>
<td>0</td>
<td>[ \frac{C_{free} \partial W}{\rho_w \partial H} ]</td>
<td>[ \frac{C_{free} \partial W}{\rho_w \partial H} + \frac{\xi_1 C_{free}}{\xi_2 + \xi_3 C_{free}} \frac{df_c}{dH} ]</td>
</tr>
<tr>
<td>1</td>
<td>[ \frac{W}{\rho_w} + \frac{\xi_1 \xi_2}{\left( \xi_2 + \xi_3 C_{free} \right)^2} ]</td>
<td>[ \frac{W}{\rho_w} + \frac{\xi_1 \xi_2 f_c}{\left( \xi_2 + \xi_3 C_{free} \right)^2} ]</td>
</tr>
<tr>
<td>[ \frac{-k_c C_{tot} \partial W}{\rho_w f_a^2 \partial T} ]</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>[ \left( k_h - \frac{k_c}{f_a} \right) \frac{C_{tot} \partial W}{\rho_w \partial H} ]</td>
<td>[ \frac{C_{free} \partial W}{\rho_w \partial H} k_h ]</td>
<td>[ \frac{C_{free} \partial W}{\rho_w \partial H} k_h ]</td>
</tr>
<tr>
<td>[ \frac{k_c}{f_a} ]</td>
<td>[ k_c ]</td>
<td>[ k_c ]</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Chapter 4
NUMERICAL ELABORATION

For the analysis of the set of coupled differential equations, as described in chapter 3, several subroutines have been developed based on the finite element method (FEM). A 1- and 2-dimensional element for the three coupled balances and a 1-dimensional element for surface resistance have been implemented in the program FEAP [ZIE97; TAY99]. At the level of complexity resulting from the individual heat, moisture and chloride models (see section 3.4), a numerical procedure is virtually the only option to obtain solutions of the global model. Following the procedure of the FEM a weak form of the coupled balances and the natural boundary conditions is derived in the first section, from which a set of discretised equations is obtained in the second section. The weak formulation has been set up according to a monolithical scheme and consequently each finite element deals with heat flow, moisture migration and chloride transport simultaneously. Non-linearity and time marching are addressed in the third section. Due to the different time scales of the individual diffusion processes, the element matrices are in principle ill-conditioned. The conditioning of the element matrices can be improved by scaling of the balances. This subject and the related dimensional analysis are discussed in the last section.

4.1 Weak monolithic formulation

The three coupled balances for heat, moisture and chloride ion transport in concrete (see equation 3.12) in space $\Omega$ can be written as:

$$c_y \frac{\partial u_j}{\partial t} - \frac{\partial}{\partial x_i} \left( k_y \frac{\partial u_j}{\partial x_i} \right) - f_i = 0$$

(4.1)
using index notation and the Einstein convention (for summation over repeated
indices). The potentials temperature $T$, macroscopic pore humidity $H$ and chloride
ion content $C$ have been replaced by the degrees of freedom $u_1$, $u_2$ and $u_3$
respectively:

$$u_1 \equiv T, \quad u_2 \equiv H, \quad u_3 \equiv C$$

(4.2)

The capacities $c_{ij}$, conductivities $k_i$, and sources $f_i$ are generally functions of
the degrees of freedom, time $t$ and spatial dimensions $x_i$:

$$c_{ij}(u_1, u_2, u_3, t, x_1, x_2, x_3), \quad k_i(u_1, u_2, u_3, t, x_1, x_2, x_3), \quad f_i(u_1, u_2, u_3, t, x_1, x_2, x_3)$$

The specific definitions of the above quantities have been given in section 3.4. Note
that isotropy is implied for the fluxes in equation 4.1 (enclosed in parentheses), since
the same conductivity $k_i$ applies to all spatial dimensions $x_i$. The boundary of space
$\Omega$ consists of two parts for each degree of freedom $u_i$: the forced boundary condition
on boundary $\Gamma_{\text{f}}$ and the natural boundary condition on boundary $\Gamma_{\text{n}}$. The forced
boundary condition is known as a Dirichlet boundary condition:

$$u_i - \bar{u}_i = 0$$

(4.3)

The natural boundary condition can either be a Neumann boundary condition:

$$-k_i \frac{\partial u_i}{\partial x_i} n_i - \bar{q}_i = 0$$

(4.4)

or a Robbins boundary condition:

$$-k_i \frac{\partial u_i}{\partial x_i} n_i - g_i(u_1, u_2, u_3, t, x_1, x_2, x_3) = 0$$

(4.5)

in which the overbar has been used to indicate known values of potentials $u_i$ (on
boundary $\Gamma_{\text{f}}$) and known values of fluxes $q_i$ (on boundary $\Gamma_{\text{n}}$), $n_i$ is the component in
1-direction of the normal vector, and $g_i$ certain function of the degrees of freedom,
time and space. The Robbins boundary condition can be deployed to model surface
resistance, i.e. a convective (linear) or radiation (non-linear) boundary condition. The
convective boundary condition is defined as:

$$-k_i \frac{\partial u_i}{\partial x_i} n_i - \chi_{ij} (u_j - \Psi_j) = 0$$

(4.6)

and the radiation boundary condition as:

$$-k_i \frac{\partial u_i}{\partial x_i} n_i - \chi_{ij} (u_j^* - \Psi_j^*) = 0$$

(4.7)

with transfer matrix $\chi_{ij}$ and environmental potentials $\Psi_j$. As the coefficients of
the transfer matrix and the environmental potentials are known, their negative products
can be replaced by known fluxes $\bar{q}_i$ and hence the convective boundary condition
can be written as:

$$-k_i \frac{\partial u_i}{\partial x_i} n_i - \chi_{ij} u_j - \bar{q}_i = 0$$

(4.8)
and the radiation boundary condition as:
\[-k_y \frac{\partial u_j}{\partial x_i} n_i - \chi_y u_j^* - \tilde{q}_i = 0\]  \hspace{1cm} (4.9)

So, in case of convective and radiation boundary conditions an extra term appears compared to the Neumann boundary condition, which is a first or fourth order function of the degrees of freedom \( u \).

Following the method of weighted residuals the differential equation is multiplied with an arbitrary weight function \( v_i \) and integrated over area \( \Omega \), and the boundary condition on boundary \( \Gamma \) is multiplied with an arbitrary weight function \( w_i \), and integrated over \( \Gamma \). The sum of these two integrals is required to be zero:
\[
\int_{\Omega} v_i \left[ c_y \frac{\partial u_j}{\partial t} - \frac{\partial}{\partial x_i} \left( k_y \frac{\partial u_j}{\partial x_i} \right) - f_j \right] d\Omega + \int_{\Gamma} w_i \left[ k_y \frac{\partial u_j}{\partial x_i} n_i + \chi_y u_j + \tilde{q}_i \right] d\Gamma = 0 \hspace{1cm} (4.10)
\]
in which the convective boundary condition has been inserted. This equation replaces the differential equation and the natural boundary condition (on \( \Gamma \)); the first boundary condition (on \( \Gamma \)) still has to be fulfilled. The integrands in the last equation comprise of all balances (the first factor in brackets) and corresponding natural boundary conditions (the last factor in brackets) and that equation is therefore a monolithic formulation. Next Green’s lemma is applied to the second term on the left-hand-side of the last equation:
\[
\int_{\Omega} v_i \frac{\partial}{\partial x_i} \left( k_y \frac{\partial u_j}{\partial x_i} \right) d\Omega = -\int_{\Gamma} \frac{\partial v_i}{\partial x_i} k_y \frac{\partial u_j}{\partial x_i} d\Omega + \int_{\Gamma} v_i k_y \frac{\partial u_j}{\partial x_i} n_i d\Gamma \hspace{1cm} (4.11)
\]
Substitution of the last equation into the last but one equation yields:
\[
\int_{\Omega} \left( v_i c_y \frac{\partial u_j}{\partial t} + \frac{\partial v_i}{\partial x_i} k_y \frac{\partial u_j}{\partial x_i} - v_i f_j \right) d\Omega - \int_{\Gamma} v_i k_y \frac{\partial u_j}{\partial x_i} n_i d\Gamma + \int_{\Gamma} w_i \left( k_y \frac{\partial u_j}{\partial x_i} n_i + \chi_y u_j + \tilde{q}_i \right) d\Gamma = 0 \hspace{1cm} (4.12)
\]
By putting \( v_i = w_i \) the weak form is obtained:
\[
\int_{\Omega} \left( v_i c_y \frac{\partial u_j}{\partial t} + \frac{\partial v_i}{\partial x_i} k_y \frac{\partial u_j}{\partial x_i} - v_i f_j \right) d\Omega - \int_{\Gamma} v_i k_y \frac{\partial u_j}{\partial x_i} n_i d\Gamma + \int_{\Gamma} v_i \left( \chi_y u_j + \tilde{q}_i \right) d\Gamma = 0 \hspace{1cm} (4.13)
\]
Note that \( \Gamma = \Gamma_{11} + \Gamma_{12} \). If the choice of weight functions \( v_i \) is restricted to functions which give \( v_i = 0 \) on boundary \( \Gamma_{11} \), then the integral over \( \Gamma_{11} \) in the last equation disappears:
\[
\int_{\Omega} \left( v_i c_y \frac{\partial u_j}{\partial t} + \frac{\partial v_i}{\partial x_i} k_y \frac{\partial u_j}{\partial x_i} - v_i f_j \right) d\Omega + \int_{\Gamma} v_i \left( \chi_y u_j + \tilde{q}_i \right) d\Gamma = 0 \hspace{1cm} (4.14)
\]
This equation is clarified in appendix C for three degrees of freedom \( u_i \) (T, H and C) and two spatial co-ordinates \( x \) (x and y).

### 4.2 Discretised equations

According to the finite element method the total space domain is divided into finite subdomains (see figure 4.1). These subdomains are called finite elements. It is also possible to divide both time and space into finite elements: a space-time formulation. However, this procedure is not followed in the present work; time marching is addressed in the following section.

![Figure 4.1: subdivision of the total space \( \Omega \) into finite elements (with \( e \) in superscript). The boundary conditions of the entire mesh are generally different for each degree of freedom. The first index of boundary \( \Gamma_e \) refers to the associated degree of freedom \( u_i \) and the second to the boundary condition type (1 for 'forced' and 2 for 'natural').](image)

Separate integration over every subdomain \( \Omega^e \) yields equation 4.14. So, for a single finite element it holds that (in vector-matrix notation):

\[
\int_{\Omega^e} v^T \mathbf{C} \hat{u}' d\Omega + \int_{\Gamma^e} \left\{ \left( \nabla v_1 \right)^T \left( \nabla v_2 \right)^T \left( \nabla v_3 \right)^T \right\} \mathbf{K}^e \begin{bmatrix} \nabla u_1^e \\ \nabla u_2^e \\ \nabla u_3^e \end{bmatrix} d\Omega - \int_{\Gamma^e} v^T \mathbf{f}^e d\Omega + \int_{\Gamma_{12}, \Gamma_{23}, \Gamma_{31}} v^T \left( \mathbf{G} u^e + \mathbf{q} \right) d\Gamma = 0
\]  

(4.15)

in which \( T \) in superscript symbolises transposition and the dot over vector \( \mathbf{u}^e \) the time derivative of its components. The last integration of the last equation must be interpreted as follows:
4.2 discretised equations

\[ \int_{\Gamma_i} \mathbf{v}^T (\mathbf{G} \mathbf{u} + \mathbf{q}) d\Gamma = \int_{\Gamma_i} v_1 (\chi_{11} u_1 + \chi_{12} u_2 + \chi_{13} u_3 + \vec{q}_1) d\Gamma + \]
\[ + \int_{\Gamma_i} v_2 (\chi_{21} u_1 + \chi_{22} u_2 + \chi_{23} u_3 + \vec{q}_2) d\Gamma + \]
\[ + \int_{\Gamma_i} v_3 (\chi_{31} u_1 + \chi_{32} u_2 + \chi_{33} u_3 + \vec{q}_3) d\Gamma \] (4.16)

since in general the natural boundary conditions differ for each degree of freedom (DOF) \( u_i \) (see figure 4.1). Clearly, the integrals of the last equation are not applicable to every element in the mesh; a distinction is made later in this section. The three DOFs have been assembled in vector \( \mathbf{u}^* \), the three source terms in vector \( \mathbf{f} \), the three prescribed fluxes in vector \( \mathbf{q} \) and the three weight functions in vector \( \mathbf{v} \).

The transfer matrix \( \mathbf{G} \) is in general:

\[ \mathbf{G} = \begin{bmatrix}
\chi_{11} & \chi_{12} & \chi_{13} \\
\chi_{21} & \chi_{22} & \chi_{23} \\
\chi_{31} & \chi_{32} & \chi_{33}
\end{bmatrix} \] (4.17)

However, the off-diagonal terms of \( \mathbf{G} \) are unused in the present work (i.e. set to zero). In case of a convective boundary conditions the entries in \( \mathbf{G} \) are constants; in case of a radiation boundary conditions the entries in \( \mathbf{G} \) are third order functions of the potentials (\( T, H \) and \( C \)). The capacitance and conductance matrices are denoted by \( \mathbf{C} \) and \( \mathbf{K} \) respectively:

\[ \mathbf{C}^* = \begin{bmatrix}
c_{11} & c_{12} & c_{13} \\
c_{21} & c_{22} & c_{23} \\
c_{31} & c_{32} & c_{33}
\end{bmatrix}, \quad \mathbf{K}^* = \begin{bmatrix}
K_{11} & K_{12} & K_{13} \\
K_{21} & K_{22} & K_{23} \\
K_{31} & K_{32} & K_{33}
\end{bmatrix} \] (4.18)

in which matrix \( \mathbf{K}^* \) has been decomposed into submatrices \( \mathbf{K}_{ij} \) which relate DOF (potential) \( i \) to DOF (potential) \( j \). Assuming isotropy within an element, it follows that submatrix \( \mathbf{K}_{ij} \) (for two spatial dimensions) is defined by:

\[ \mathbf{K}_{ij} = \begin{bmatrix}
k_{ij} & 0 \\
0 & k_{ij}
\end{bmatrix} \] (4.19)

In case of orthotropy the terms on the diagonal of the last matrix differ from each other, if the principal directions of orthotropy coincide with the co-ordinate directions. The off-diagonal terms of the last matrix are non-zero in case of orthotropy, if the angle between the principal directions of orthotropy and the co-ordinate directions is not equal to \( 0^\circ \) and not equal to \( 90^\circ \). In case of anisotropy the entries of submatrix \( \mathbf{K}_{ij} \) can have any value.

Each potential in the vector \( \mathbf{u}^* \) is approximated by a finite number of nodal values and continuity is obtained by interpolating between these nodal values with the help of shape functions \( \mathbf{N}^* \). If there are \( r \) nodes per element, it holds that:
\[
\begin{pmatrix}
  u^e_1 \\
  u^e_2 \\
  u^e_3 \\
  \end{pmatrix}
\approx
\begin{pmatrix}
  N^e_1 & 0 & 0 & N^e_2 & 0 & 0 & N^e_3 & 0 & 0 \\
  0 & N^e_2 & 0 & 0 & N^e_2 & 0 & \cdots & 0 & N^e_3 \\
  0 & 0 & N^e_3 & 0 & 0 & N^e_3 & 0 & \cdots & 0
\end{pmatrix}
\begin{pmatrix}
  u_1^{e1} \\
  u_2^{e1} \\
  u_3^{e1} \\
  u_2^{e2} \\
  u_2^{e3} \\
  u_3^{e3} \\
  \vdots \\
  u_1^{e\alpha} \\
  u_2^{e\alpha} \\
  u_3^{e\alpha}
\end{pmatrix}
\]

or shortly\(^1\):

\[\mathbf{u}^e = N^e \mathbf{u}^{\alpha}\]

in which the subindex refers to the DOF (the potential), the superindex to the element (indicated by 'e') node number, and in which \(\mathbf{u}^{\alpha}\) is the vector containing the nodal DOFs. In principle different shape functions can be deployed for the respective DOFs, however in the present work no distinction has been made, so that:

\[N^e_1 = N^e_2 = N^e_3 = N^e_\alpha\]

(4.22)

For example, a (2-dimensional) 4-noded isoparametric (quadrilateral) element can be used (see figure 4.2), the shape functions of which are:

\[N^{e1} = (\frac{1}{2} - \xi)(\frac{1}{2} - \eta)\]
\[N^{e2} = (\frac{1}{2} + \xi)(\frac{1}{2} - \eta)\]
\[N^{e3} = (\frac{1}{2} + \xi)(\frac{1}{2} + \eta)\]
\[N^{e4} = (\frac{1}{2} - \xi)(\frac{1}{2} + \eta)\]

(4.23)

![Figure 4.2: 4-noded isoparametric (quadrilateral) element.](image)

\(^1\)The approximating character of the righthand-side of the equation is not expressed explicitly anymore.
The sum of the shape functions equals unity in every point \((\xi, \eta)\). At each node there are three degrees of freedom: \(u_1\) (T), \(u_2\) (H) and \(u_3\) (C). As \(N^u\) is a function of the spatial co-ordinates only (\(\xi\) and \(\eta\)) and \(u^{\text{no}}\) a function of time only, the time derivative of \(u^e\) is given by:

\[
\dot{u}^e = N^u u^{\text{no}}
\]

and the gradient vector of \(u^e\) (for two spatial dimensions) by:

\[
\{\nabla u^e_1\} = \begin{bmatrix}
\frac{\partial N_1^{\text{el}}}{\partial x} & 0 & 0 & \frac{\partial N_1^{\text{el}}}{\partial y} & 0 & 0 & \frac{\partial N_1^{\text{el}}}{\partial \xi} & 0 & 0 \\
\frac{\partial N_2^{\text{el}}}{\partial x} & 0 & 0 & \frac{\partial N_2^{\text{el}}}{\partial y} & 0 & 0 & \frac{\partial N_2^{\text{el}}}{\partial \xi} & 0 & 0 \\
\frac{\partial N_3^{\text{el}}}{\partial x} & 0 & 0 & \frac{\partial N_3^{\text{el}}}{\partial y} & 0 & 0 & \frac{\partial N_3^{\text{el}}}{\partial \xi} & 0 & 0 \\
0 & \frac{\partial N_1^{\text{el}}}{\partial x} & 0 & 0 & \frac{\partial N_1^{\text{el}}}{\partial y} & 0 & 0 & \frac{\partial N_1^{\text{el}}}{\partial \xi} & 0 \\
0 & \frac{\partial N_2^{\text{el}}}{\partial x} & 0 & 0 & \frac{\partial N_2^{\text{el}}}{\partial y} & 0 & 0 & \frac{\partial N_2^{\text{el}}}{\partial \xi} & 0 \\
0 & \frac{\partial N_3^{\text{el}}}{\partial x} & 0 & 0 & \frac{\partial N_3^{\text{el}}}{\partial y} & 0 & 0 & \frac{\partial N_3^{\text{el}}}{\partial \xi} & 0 \\
0 & 0 & \frac{\partial N_1^{\text{el}}}{\partial x} & 0 & 0 & \frac{\partial N_1^{\text{el}}}{\partial \xi} & 0 & 0 & \frac{\partial N_1^{\text{el}}}{\partial \xi} \\
0 & 0 & \frac{\partial N_2^{\text{el}}}{\partial x} & 0 & 0 & \frac{\partial N_2^{\text{el}}}{\partial \xi} & 0 & 0 & \frac{\partial N_2^{\text{el}}}{\partial \xi} \\
0 & 0 & \frac{\partial N_3^{\text{el}}}{\partial x} & 0 & 0 & \frac{\partial N_3^{\text{el}}}{\partial \xi} & 0 & 0 & \frac{\partial N_3^{\text{el}}}{\partial \xi}
\end{bmatrix}
\]

(4.25) or shortly:

\[
\begin{bmatrix}
\nabla u^e_1 \\
\nabla u^e_2 \\
\nabla u^e_3
\end{bmatrix} = B^e u^{\text{no}}
\]

(4.26)

The derivates of the shape functions with respect to \(x\) and \(y\) are related to their derivates with respect to \(\xi\) and \(\eta\) in the following way:

\[
\begin{bmatrix}
\frac{\partial N^*(\xi, \eta)}{\partial \xi} \\
\frac{\partial N^*(\xi, \eta)}{\partial \eta}
\end{bmatrix} = \begin{bmatrix}
\frac{\partial N^*(\xi, \eta)}{\partial \xi} \\
\frac{\partial N^*(\xi, \eta)}{\partial \eta}
\end{bmatrix}\begin{bmatrix}
\frac{\partial N^*(\xi, \eta)}{\partial \xi} \\
\frac{\partial N^*(\xi, \eta)}{\partial \eta}
\end{bmatrix}^{-1}
\]

(4.27)

The matrix on the righthand-side is the Jacobi-matrix \(J\). So, in order to obtain the derivates of the shape functions with respect to \(x\) and \(y\), the Jacobi-matrix has to be inverted:

\[
\begin{bmatrix}
\frac{\partial N^*(\xi, \eta)}{\partial x} \\
\frac{\partial N^*(\xi, \eta)}{\partial y}
\end{bmatrix} = \frac{1}{|J|}\begin{bmatrix}
\frac{\partial N^*(\xi, \eta)}{\partial \xi} & \frac{\partial N^*(\xi, \eta)}{\partial \eta} \\
\frac{\partial N^*(\xi, \eta)}{\partial \xi} & \frac{\partial N^*(\xi, \eta)}{\partial \eta}
\end{bmatrix}\begin{bmatrix}
\frac{\partial N^*(\xi, \eta)}{\partial \xi} \\
\frac{\partial N^*(\xi, \eta)}{\partial \eta}
\end{bmatrix}^{-1}
\]

(4.28)
in which \(|J|\) symbolises the Jacobian, i.e. the determinant of the Jacobi-matrix. The cartesian co-ordinates \(x\) and \(y\) are interpolated in the same way as the potentials. With \(x^e\) and \(y^e\) as the cartesian co-ordinates of node \(i\) of element \(e\), it follows for the quadrilateral that the entries of the Jacobi-matrix are:

\[
\frac{\partial x(\xi, \eta)}{\partial \xi} = -\left(\frac{1}{2} - \eta\right)x^e + \left(\frac{1}{2} - \eta\right)x^{e2} + \left(\frac{1}{2} + \eta\right)x^{e3} - \left(\frac{1}{2} + \eta\right)x^{e4}
\]

\[
\frac{\partial x(\xi, \eta)}{\partial \eta} = -\left(\frac{1}{2} - \xi\right)x^e - \left(\frac{1}{2} + \xi\right)x^{e2} + \left(\frac{1}{2} + \xi\right)x^{e3} + \left(\frac{1}{2} - \xi\right)x^{e4}
\]

\[
\frac{\partial y(\xi, \eta)}{\partial \xi} = -\left(\frac{1}{2} - \eta\right)y^e + \left(\frac{1}{2} - \eta\right)y^{e2} + \left(\frac{1}{2} + \eta\right)y^{e3} + \left(\frac{1}{2} - \eta\right)y^{e4}
\]

\[
\frac{\partial y(\xi, \eta)}{\partial \eta} = -\left(\frac{1}{2} - \xi\right)y^e - \left(\frac{1}{2} + \xi\right)y^{e2} + \left(\frac{1}{2} + \xi\right)y^{e3} - \left(\frac{1}{2} - \xi\right)y^{e4}
\]

(4.29)

According to the Galerkin method the shape functions \(N^e\) are also substituted for the weight functions \(v\):

\[
v^T \to (N^e)^T
\]

(4.30)

The gradient row vector of the weight functions then becomes:

\[
\left\{ (\nabla v_1)^T, (\nabla v_2)^T, (\nabla v_3)^T \right\} \to (B^e)^T
\]

(4.31)

Consequently, equation 4.15 can be written as:

\[
\left[ \int_{\Omega} (N^e)^T C' N^e d\Omega \right] \hat{u}^e + \left[ \int_{\Gamma_1} (B^e)^T K' B' d\Gamma + \int_{\Gamma_2} (N^e)^T G N^e d\Gamma \right] u^e + \int_{\Gamma_2} (N^e)^T f^e d\Gamma + \int_{\Gamma_1} (N^e)^T \bar{q}^e d\Gamma = 0
\]

(4.32)

The left-hand-side of the last equation is the so-called residual vector \(r^e\), which is equal to – within the preset numerical tolerance – the zero vector for a properly converged solution. Note that as a consequence of the Galerkin method the number of equations per element has increased from 1 (equation 4.15) to the product of the number of DOFs \(3\) and the number of nodes on the element \(a\), equation 4.32.

The unknown discrete (nodal) DOFs, assembled in vector \(u^e\), can be obtained from the above set of (discretised) equations. As only specific elements in the mesh are located along boundaries \(\Gamma_{12}^e, \Gamma_{22}^e\) and \(\Gamma_{32}^e\), the last equation is split up into a part for all elements:

\[
\left[ \int_{\Omega} (N^e)^T C' N^e d\Omega \right] \hat{u}^e + \left[ \int_{\Omega} (B^e)^T K' B' d\Omega \right] u^e - \int_{\Omega} (N^e)^T f^e d\Omega = 0
\]

(4.33)

and an additional part for elements at boundaries \(\Gamma_{12}^e, \Gamma_{22}^e\) and \(\Gamma_{32}^e\):
\[
\left[ \int_{r_{12}r_{12}}^{r_{12}r_{12}} (N^e)^T G N^e d\Gamma \right] u^{\omega} + \int_{r_{12}r_{12}}^{r_{12}r_{12}} (N^e)^T \bar{q} d\Gamma = 0
\]

(4.34)

The last equation must be read as:

\[
\left[ \int_{r_{12}}^{r_{12}} \bar{g}^e d\Gamma + \int_{r_{12}}^{r_{12}} \bar{h}^e k^e d\Gamma + \int_{r_{12}}^{r_{12}} \bar{l}^e l^e d\Gamma \right] u^{\omega} + \int_{r_{12}}^{r_{12}} \bar{g}^e \bar{q}_i d\Gamma + \int_{r_{12}}^{r_{12}} \bar{h}^e \bar{q}_j d\Gamma + \int_{r_{12}}^{r_{12}} \bar{l}^e \bar{q}_l d\Gamma = 0
\]

(4.35)

in which the vectors \( \bar{g}^e, \bar{h}^e \) and \( \bar{l}^e \) are contained in matrix \( N^e \) and the vectors \( \bar{j}, \bar{k}, \bar{l} \) in transfer matrix \( G \):

\[
N^e = \begin{pmatrix}
(g^e)^T \\
(h^e)^T \\
(l^e)^T
\end{pmatrix}, \quad G = \begin{pmatrix}
\bar{j}^T \\
\bar{k}^T \\
\bar{l}^T
\end{pmatrix}
\]

(4.36)

Since the order of integration of equation 4.34 is one lower than the order of integration of equation 4.33, the element associated with the former equation possesses one dimension less than the one associated with the latter. In case of two spatial dimensions a quadrilateral element can be used in conjunction with equation 4.33, while a line element (see figure 4.3) is used in conjunction with equation 4.34. Then at boundaries \( \Gamma_{12}, \Gamma_{22} \) and \( \Gamma_{32} \) both the quadrilateral and line element are placed, while the rest of the mesh consists of only quadrilateral elements.

Equation 4.33 can be written as:

\[
r^{\omega e} = C^{\omega e} u^{\omega e} + K^{\omega e} u^{\omega e} - f^{\omega e} = 0
\]

(4.37)

with element capacitance matrix \( C^e \) (or element damping matrix in a mechanical analogue):

\[
C^e = \int_{\Gamma^e} (N^e)^T C^e N^e d\Omega
\]

(4.38)

element conductance matrix \( K^e \) (or element stiffness matrix in a mechanical analogue):

\[
K^e = \int_{\Omega^e} (B^e)^T K^e B^e d\Omega
\]

(4.39)
and element source vector $\mathbf{f}^e$ (or external force vector in a mechanical analogue):

$$
\mathbf{f}_e^e = \int_{\Omega^e} \mathbf{f}^e d\Omega = \begin{bmatrix} f_1^{\alpha} \\ f_2^{\alpha} \\ \vdots \\ f_{n_{\alpha}}^{\alpha} \end{bmatrix}
$$

(4.40)

The $3 \times 3$ (square of the number of DOFs) submatrices $\mathbf{C}_{pq}$ and $\mathbf{K}_{pq}$ relate element node $p$ to element node $q$, while subvector $\mathbf{f}_p^e$ is related to element node $p$:

$$
\mathbf{C}_{pq} = \begin{bmatrix} c_{11}^{pq} & c_{12}^{pq} & c_{13}^{pq} \\ c_{21}^{pq} & c_{22}^{pq} & c_{23}^{pq} \\ c_{31}^{pq} & c_{32}^{pq} & c_{33}^{pq} \end{bmatrix}, \quad \mathbf{K}_{pq} = \begin{bmatrix} k_{11}^{pq} & k_{12}^{pq} & k_{13}^{pq} \\ k_{21}^{pq} & k_{22}^{pq} & k_{23}^{pq} \\ k_{31}^{pq} & k_{32}^{pq} & k_{33}^{pq} \end{bmatrix}, \quad \mathbf{f}_p^e = \begin{bmatrix} f_1^p \\ f_2^p \\ f_3^p \end{bmatrix}
$$

(4.41)

Entries $c_{rs}^{pq}$ and $k_{rs}^{pq}$ relate degree of freedom $r$ to degree of freedom $s$, while entry $f_r^p$ is related to degree of freedom $r$. They are defined by:

$$
c_{rs}^{pq} = \int_{\Omega^p} N_r^{pq} c_{rs} N_s^{pq} d\Omega
$$

$$
k_{rs}^{pq} = \int_{\Omega^p} \left( \frac{\partial N_r^{pq}}{\partial x} k_{rr} N_s^{pq} + \frac{\partial N_r^{pq}}{\partial y} k_{rs} \right) d\Omega
$$

$$
f_r^p = \int_{\Omega^p} N_r^{pq} f d\Omega
$$

(4.42)

For 2-dimensional isoparametric elements all entries in matrices $\mathbf{N}^*$ and $\mathbf{B}^*$ are functions of $\xi$ and $\eta$. For the integration over $\Omega^*$ (in two spatial dimensions: $x$ and $y$) of a function $f$ of the isoparametric co-ordinates $\xi$ and $\eta$ it holds in general that [ZIE97]:

$$
\int f(\xi, \eta) d\xi d\eta = \int \int f(\xi, \eta) J |d\xi d\eta|
$$

(4.43)

which implies for the entries in matrix $\mathbf{C}^*$, matrix $\mathbf{K}^*$ and vector $\mathbf{f}^e$ that:

$$
c_{rs}^{pq} = \int_{-\frac{1}{2}}^{\frac{1}{2}} \int_{-\frac{1}{2}}^{\frac{1}{2}} N_r^{pq} c_{rs} N_s^{pq} J |d\xi d\eta|
$$

$$
k_{rs}^{pq} = \int_{-\frac{1}{2}}^{\frac{1}{2}} \int_{-\frac{1}{2}}^{\frac{1}{2}} \left( \frac{\partial N_r^{pq}}{\partial x} k_{rr} N_s^{pq} + \frac{\partial N_r^{pq}}{\partial y} k_{rs} \right) J |d\xi d\eta|
$$

$$
f_r^p = \int_{-\frac{1}{2}}^{\frac{1}{2}} \int_{-\frac{1}{2}}^{\frac{1}{2}} N_r^{pq} f J |d\xi d\eta|
$$

(4.44)

\(^2\) without summation over repeated indices
All the integrals are evaluated numerically by determining the value of the integrand in so-called Gauss points \((\xi_i, \eta_j)\) and then multiplying each value with its weight factor \(w_i\) (integration over \(\xi\)) or \(w_j\) (integration over \(\eta\)) [KOK95]:

\[
\int_{-\frac{1}{2}}^{\frac{1}{2}} \int_{-\frac{1}{2}}^{\frac{1}{2}} g(\xi, \eta) \, d\xi \, d\eta = \sum_{i=1}^{p} \sum_{j=1}^{p} g(\xi_i, \eta_j) w_i w_j \tag{4.45}
\]

in which \(g\) is some function depending on \(\xi\) and \(\eta\), and \(p\) the number of Gauss points per integration. If two Gauss points are used per integration and if integration is carried out over \(-\frac{1}{2} \leq \xi \leq \frac{1}{2}\) and over \(-\frac{1}{2} \leq \eta \leq \frac{1}{2}\), then there are four Gauss points \((\xi_i, \eta_j)\) and four corresponding weights \(w_i w_j\) as shown in table 4.1. With \(f(\xi, \eta) = 1\) it follows from equations 4.43 and 4.45 that the surface area of an element (in an orthogonal reference system) equals the sum of the products of the Jacobian \(|J|\) in Gauss point \((\xi_i, \eta_j)\) and weight \(w_i w_j\).

**Table 4.1:** 2×2 numerical integration of \(g(\xi, \eta)\) over \(-\frac{1}{2} \leq \xi \leq \frac{1}{2}\) and \(-\frac{1}{2} \leq \eta \leq \frac{1}{2}\). The integration is performed by summation of the products of \(g(\xi_i, \eta_j)\) and weights \(w_i w_j\).

<table>
<thead>
<tr>
<th>(i)</th>
<th>(j)</th>
<th>(\xi)</th>
<th>(\eta)</th>
<th>(w_i)</th>
<th>(w_j)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>(-\frac{1}{6}\sqrt{3})</td>
<td>(-\frac{1}{6}\sqrt{3})</td>
<td>(\frac{1}{2})</td>
<td>(\frac{1}{2})</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>(-\frac{1}{6}\sqrt{3})</td>
<td>(\frac{1}{6}\sqrt{3})</td>
<td>(\frac{1}{2})</td>
<td>(\frac{1}{2})</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>(\frac{1}{6}\sqrt{3})</td>
<td>(-\frac{1}{6}\sqrt{3})</td>
<td>(\frac{1}{2})</td>
<td>(\frac{1}{2})</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>(\frac{1}{6}\sqrt{3})</td>
<td>(\frac{1}{6}\sqrt{3})</td>
<td>(\frac{1}{2})</td>
<td>(\frac{1}{2})</td>
</tr>
</tbody>
</table>

This 2×2 numerical integration procedure is exact for any polynomial up to the third order; a pxp numerical integration procedure is exact for any polynomial up to order \(2p-1\). As the entries in matrix \(\mathbf{C}\) are third order polynomials, the ones in matrix \(\mathbf{f}^a\) second order polynomials and the ones in matrix \(\mathbf{N}\) first order polynomials, the 2×2 numerical integration procedure is adequate for the shape functions as defined in equation 4.23.

Equation 4.34 can be written as:

\[
\mathbf{r}^a = \mathbf{K}^a \mathbf{u}^a - \mathbf{f}^a = 0 \tag{4.46}
\]

with \(\mathbf{K}^a\) now as the element transfer matrix and \(\mathbf{f}^a\) the element external flux vector. If boundary \(\Gamma^e\) is 1-dimensional, the shape function matrix \(\mathbf{N}^e\) and element nodal DOF-vector \(\mathbf{u}^e\) can be reduced to size \(a=2\), corresponding to a line element (see figure 4.3). The shape functions of the line element are:

\[
N^e_1 = \frac{1}{2} - \xi, \quad N^e_2 = \frac{1}{2} + \xi \tag{4.47}
\]
The entries of matrix $K^e$ and vector $f^o$ can then be determined using 2-point integration with Gauss-points and weights according to table 4.1 (in which only columns $i$, $\xi$, and $w$ are applicable). The Jacobian reduces to the length of the line element in a cartesian $(x,y)$ reference system. This line element can be placed on the edge $\Gamma^e$ of a quadrilateral element at which a natural boundary condition for one of the three balances (heat, moisture and chloride) is to be modelled. However, the line element incorporates the natural boundary conditions for all three balances. Since not all balances necessarily have a natural boundary condition at that edge $\Gamma^e$, i.e. $\Gamma^e_{12}$, $\Gamma^e_{22}$ and $\Gamma^e_{32}$ do not necessarily coincide, it must be possible to disable the inactive natural boundary conditions. This can be achieved by putting the subvectors $j$, $k$ and $l$ of the transfer matrix $G$ which are associated with the inactive (Robbins) boundary conditions, equal to the zero vector, and by putting the prescribed fluxes $\bar{q}$, associated with the inactive (Neumann and Robbins) boundary conditions, equal to zero (see equation 4.35).

The element matrices $C^e$ and $K^e$ and the element vectors $u^{eo}$ and $f^o$ are assembled into global matrices $C$ and $K$ and global vectors $u$ and $f$ respectively for the entire finite element mesh [ZIE97]. After imposing the prescribed nodal DOFs (the Dirichlet boundary condition) and discretising the time derivative of vector $u$, a set of linear algebraic equations results from which the solution $u$ can be obtained by Gaussian elimination, if the entries in $C^e$, $K^e$ and $f^o$ are not a function of the entries in $u^{eo}$. However, as explained in section 3.4, the capacities $c_q$ and conductivities $k_q$, generally depend on $T$ (temperature), $H$ (moisture potential) and $C$ (chloride content). As these DOFs (potentials) are discretised in vector $u^{eo}$ (and $u$), a set of non-linear equations needs to be solved. The issues non-linearity and time marching are discussed in the next section.

### 4.3 Time marching and non-linearity

In the previous section a set of equations for an element (equation 4.32) has been derived from the weak monolithic formulation (equation 4.14). While the space $\Omega$
has been discretised by means of finite elements with nodal degrees of freedom (DOFs), the time dimension still needs to be discretised in order to solve for nodal DOF-vector $u$, since both this vector and its time derivative $\dot{u}$ appear in equation 4.32. The relation between these two vectors can be elaborated as follows. Obviously it holds that:

$$\dot{u} = \frac{du}{dt}$$  \hspace{1cm} (4.48)

Integration of the last equation over the time increment $\Delta t$ yields:

$$\int_0^{\Delta t} \dot{u} dt = \int_0^{\Delta t} \frac{du}{dt} dt$$  \hspace{1cm} (4.49)

The lefthand-side of the last equation can be approximated by (see also figure 4.4):

$$\int_0^{\Delta t} \dot{u} dt = \left[ \alpha \dot{u}^{t+\Delta t} + (1-\alpha) \dot{u}^t \right] \Delta t$$  \hspace{1cm} (4.50)

in which $\alpha$ is a parameter with values between 0 and 1. The trapezoidal rule of numerical integration results for $\alpha = \frac{1}{2}$.

![Figure 4.4: numerical integration of entries of velocity vector $\dot{u}$ with respect to time $t$. According to the trapezoidal rule the grey surface area equals $\Delta t(\dot{u} + \dot{u}^{t+\Delta t})/2$.](image)

The righthand-side of equation 4.49 equals simply the difference between $u^{t+\Delta t}$ and $u^t$. So, it follows that [HUG87]:

$$\left[ \alpha \dot{u}^{t+\Delta t} + (1-\alpha) \dot{u}^t \right] \Delta t = u^{t+\Delta t} - u^t$$  \hspace{1cm} (4.51)

Substitution of the last equation into equation 4.37 yields the residual at time $t+\Delta t$

$$r^{t+\Delta t} = \left( \frac{1}{\alpha \Delta t} C^{t+\Delta t} + K^{t+\Delta t} \right) u^{t+\Delta t} \frac{1}{\alpha \Delta t} C^{t+\Delta t} u^t - \frac{1-\alpha}{\alpha} C^{t+\Delta t} \dot{u}^t - f^{t+\Delta t} = 0$$  \hspace{1cm} (4.52)
from which \( \mathbf{u}^{i+\Delta t} \) can be calculated, since \( \mathbf{u}' \) and \( \dot{\mathbf{u}}' \) are known at time \( t+\Delta t \). Time marching with \( \alpha = 1 \) is referred to as Euler backward; use of \( \alpha = \frac{1}{2} \) is known as a Crank-Nicolson scheme. The Crank-Nicolson scheme possesses a higher order of accuracy than the Euler backward scheme, but the former scheme can produce oscillations [KAN91][ZIE97]. In the present work only Euler backward time marching has been deployed.

If the entries in \( \mathbf{C}, \mathbf{K} \) and \( \mathbf{f} \) are not functions of entries in \( \mathbf{u} \), the last equation can be written as the following set of linear algebraic equations:

\[
\mathbf{Ku} = \mathbf{f}
\]

with:

\[
\mathbf{K} = \frac{1}{\alpha\Delta t} \mathbf{C}^{i+\Delta t} + \mathbf{K}^{i+\Delta t}
\]

\[
\mathbf{u} = \mathbf{u}^{i+\Delta t}
\]

\[
\mathbf{f} = \frac{1}{\alpha\Delta t} \mathbf{C}^{i+\Delta t} \mathbf{u}' + \frac{1-\alpha}{\alpha} \mathbf{C}^{i+\Delta t} \dot{\mathbf{u}}' + \mathbf{f}^{i+\Delta t}
\]

from which the solution \( \mathbf{u} \) follows, since \( \mathbf{K} \) and \( \mathbf{f} \) are known. In case of an Euler backward scheme, the solution process is unconditionally stable [HUG87][KAN91][ZIE97], however a smaller timestep \( \Delta t \) leads to a more accurate solution [ROE89]. Since the entries in \( \mathbf{C} \) and \( \mathbf{K} \) are functions of the potentials \( \mathbf{T}, \mathbf{H} \) and \( \mathbf{C} \) and therefore functions of the entries in \( \mathbf{u} \) (see section 4.2), equation 4.52 is in fact a set of non-linear equations and the solution \( \mathbf{u}^{i+\Delta t} \) can be found by iterating within a timestep according to a Newton-Raphson scheme. In order to iterate towards a solution, the residual vector \( \mathbf{r}^{i+\Delta t} \), which is a non-linear function of \( \mathbf{u}^{i+\Delta t} \), is linearised [ZIE97][TAY99]:

\[
\mathbf{r}^{i+\Delta t}_i = \mathbf{r}^{i+\Delta t}_i + \left. \frac{d\mathbf{r}}{d\mathbf{u}} \right|_{\mathbf{u}^{i+\Delta t}} \cdot d\mathbf{u}^{i+\Delta t}_i
\]

(4.55)

where \( i \) denotes the iteration number. As the residual vector must become equal to the zero vector, it is required in every iteration that:

\[
\mathbf{r}^{i+\Delta t}_i + \left. \frac{d\mathbf{r}}{d\mathbf{u}} \right|_{\mathbf{u}^{i+\Delta t}} \cdot d\mathbf{u}^{i+\Delta t}_i = \mathbf{0}
\]

(4.56)

The derivative of the residual vector \( \mathbf{r} \) with respect to the nodal DOF-vector \( \mathbf{u} \) is called the tangent matrix \( \mathbf{S} \):

\[
\mathbf{S} = \left. \frac{d\mathbf{r}}{d\mathbf{u}} \right|_{\mathbf{u}^{i+\Delta t}}
\]

(4.57)

While \( \mathbf{r}^{i+\Delta t} \) and \( \mathbf{S}^{i+\Delta t} \) are known, the incremental nodal DOF-vector \( d\mathbf{u}^{i+\Delta t}_i \) can be obtained from the last but one equation by Gaussian elimination:

\[\text{The mechanical analogue of this equation is } \mathbf{S}d\mathbf{u} = \mathbf{f}_e - \mathbf{f}_i. \text{ In this case the residual } \mathbf{r} \text{ equals the difference between internal } \mathbf{f}_i \text{ and external forces } \mathbf{f}_e, \text{ while the internal forces are equal to the product of stiffness matrix } \mathbf{K} \text{ and displacement vector } \mathbf{u} \text{ (if damping } \mathbf{C} \text{ is not taken into account).} \]
\[
S_i^{i+\Delta t} \Delta u_i^{i+\Delta t} = -r_i^{i+\Delta t}
\]

(4.58)

After every iteration the former nodal DOF-vector is augmented with this incremental vector:

\[
u_i^{i+\Delta t} = u_i^{i+\Delta t} + \Delta u_i^{i+\Delta t}
\]

(4.59)

In general, substitution of this new nodal DOF-vector \( \mathbf{u}_{i,1}^{i+\Delta t} \) into the residual vector does not yield the required zero vector yet, since the linearisation of \( \mathbf{r} \) was just an approximation of its non-linear shape. Also substitution of \( \mathbf{u}_{i,1}^{i+\Delta t} \) into the tangent matrix causes generally a different version from the former one. Therefore, a new incremental nodal DOF-vector must be determined on the basis of the new residual vector and tangent matrix, and again this incremental vector is added to the last nodal DOF-vector. This iteration proceeds until the residual vector has effectively – within some tolerance range – become equal to the zero vector. The Newton-Raphson scheme always exhibits a quadratic asymptotic convergence rate.

Elaboration of the derivative of vector \( \mathbf{r}^e \) with respect to vector \( \mathbf{u}^e \) (pertaining to a single element \( e \)) yields:

\[
\frac{d \mathbf{r}^e(u_1,u_2,\ldots,u_n)}{d \mathbf{u}^e} = \begin{bmatrix}
\frac{\partial r_1}{\partial u_1} & \frac{\partial r_1}{\partial u_2} & \cdots & \frac{\partial r_1}{\partial u_n} \\
\frac{\partial r_2}{\partial u_1} & \frac{\partial r_2}{\partial u_2} & \cdots & \frac{\partial r_2}{\partial u_n} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial r_n}{\partial u_1} & \frac{\partial r_n}{\partial u_2} & \cdots & \frac{\partial r_n}{\partial u_n}
\end{bmatrix}
\]

(4.60)

with \( n \) as the product of the number of DOFs and the number of nodes on the element. Clearly, the dimension of the element tangent matrix \( \mathbf{S}^e \) is \( n \times n \). The derivative of the element conductance vector \( \mathbf{K}^e(u_1,u_2,\ldots,u_n)\mathbf{u}^e \) with respect to vector \( \mathbf{u}^e \) can be split up into two components according to the product rule:

\[
\frac{d}{d \mathbf{u}^e} (\mathbf{K}^e(u_1,u_2,\ldots,u_n)\mathbf{u}^e) = \mathbf{K}^e(u_1,u_2,\ldots,u_n) I + \frac{d \mathbf{K}^e(u_1,u_2,\ldots,u_n)}{d \mathbf{u}^e} \mathbf{U}^e
\]

(4.61)

in which \( I \) symbolises the identity matrix and \( \mathbf{U}^e \) the matrix extension of \( \mathbf{u}^e \). Matrix \( \mathbf{U}^e \) is defined as follows:
\[ \mathbf{U}^e = \begin{bmatrix} u_1 & 0 & \cdots & 0 \\ 0 & u_1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & u_1 \\ u_2 & 0 & \cdots & 0 \\ 0 & u_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & u_2 \\ \vdots & \vdots & \ddots & \vdots \\ u_n & 0 & \cdots & 0 \\ 0 & u_n & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & u_n \end{bmatrix} \]

So, the size of \( \mathbf{U}^e \) is \( n^2 \times n \). The derivative of matrix \( \mathbf{K}^e(u_1, u_2, \ldots, u_n) \) with respect to vector \( \mathbf{u}^e \) is of size \( n \times n^2 \):

\[
\frac{d\mathbf{K}^e(u_1, u_2, \ldots, u_n)}{d\mathbf{u}^e} = 
\begin{bmatrix}
\frac{\partial k_{11}}{\partial u_1} & \frac{\partial k_{11}}{\partial u_2} & \cdots & \frac{\partial k_{11}}{\partial u_n} \\
\frac{\partial k_{12}}{\partial u_1} & \frac{\partial k_{12}}{\partial u_2} & \cdots & \frac{\partial k_{12}}{\partial u_n} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial k_{1n}}{\partial u_1} & \frac{\partial k_{1n}}{\partial u_2} & \cdots & \frac{\partial k_{1n}}{\partial u_n}
\end{bmatrix}
\]

(4.63) Analogous to the element conductance vector, the derivative of the element capacitance vector \( \mathbf{C}^e(u_1, u_2, \ldots, u_n) \dot{\mathbf{u}}^e \) with respect to \( \mathbf{u}^e \) can be written as:

\[
\frac{d}{d\mathbf{u}^e} \left( \mathbf{C}^e(u_1, u_2, \ldots, u_n) \dot{\mathbf{u}}^e \right) = \mathbf{C}^e(u_1, u_2, \ldots, u_n) \frac{d\dot{\mathbf{u}}^e}{d\mathbf{u}^e} + \mathbf{C}^e(u_1, u_2, \ldots, u_n) \frac{d\mathbf{u}^e}{d\mathbf{u}^e} \dot{\mathbf{u}}^e
\]

(4.64)

From equation 4.51 it follows that:

\[
\frac{d\dot{\mathbf{u}}^e}{d\mathbf{u}^e} = \frac{1}{\Delta t} \mathbf{I}
\]

(4.65)

Then the element tangent matrix \( \mathbf{S}^e \) (at time \( t + \Delta t \)) can be written as follows:
\[ S^c = \left[ \frac{1}{\Delta t} C^c \left( u_1, u_2, \ldots, u_n \right) + K^c \left( u_1, u_2, \ldots, u_n \right) \right]_{\text{linear}} + \]
\[ + \left[ \frac{dC^c}{du^c} \left( u_1, u_2, \ldots, u_n \right) u^c \frac{dK^c}{du^c} \left( u_1, u_2, \ldots, u_n \right) u^c - \frac{df^c}{du^c} \left( u_1, u_2, \ldots, u_n \right) \right]_{\text{non-linear}} \]  (4.66)

If the analysis is linear, then only the first two terms on the right-hand-side of the last equation appear. However, if the analysis is non-linear, also the last three terms of the last equation have to be taken into account. The capacities and conductivities, as defined in section 3.4, yield an unsymmetric element tangent matrix \( S^e \). The element tangent matrix is already unsymmetric, if only the diagonal terms \( c_{ii} \) and \( k_{ii} \) are non-zero, \( c_{ii} \) and \( k_{ii} \) and \( f_i \) are constants (excepting \( c_{22} \)), and \( k_{22} \) is e.g. a linear function of \( H \) (which is an uncoupled non-linear system); this observation is confirmed in [ZIE97].

The derivatives of the entries in element matrices \( C^e \), \( K^e \) and element vector \( f^e \) with respect to the entries of element vector \( u^e \), which contribute to the non-linear part of the element tangent matrix \( S^e \), are defined by (in two spatial dimensions)\(^4\):

\[ \frac{\partial c_{pq}^e}{\partial u_{qv}^e} = \int c_{pq}^e N_q^e N_s^e d\Omega = \int \int \frac{\partial c_{pq}^e}{\partial u_{av}^e} N_r^e N_s^e |J| \; d\xi \; d\eta \]
\[ \frac{\partial k_{pq}^e}{\partial u_{qv}^e} = \int k_{pq}^e \left( \frac{\partial N_r^e}{\partial x} k_r^e \frac{\partial N_s^e}{\partial x} + \frac{\partial N_r^e}{\partial y} k_r^e \frac{\partial N_s^e}{\partial y} \right) d\Omega = \]
\[ \int \int \frac{\partial k_{pq}^e}{\partial u_{av}^e} \left( \frac{\partial N_r^e}{\partial x} \frac{\partial N_s^e}{\partial x} + \frac{\partial N_r^e}{\partial y} \frac{\partial N_s^e}{\partial y} \right) |J| \; d\xi \; d\eta \]
\[ \frac{\partial f_{pq}^e}{\partial u_{qv}^e} = \int f_{pq}^e \; d\Omega = \int \int \frac{\partial f_{pq}^e}{\partial u_{av}^e} N_r^e |J| \; d\xi \; d\eta \]

with element node numbers \( p, q \) and \( v \), and DOFs \( r, s \) and \( w \). According to the chain rule the differentiation of capacity \( c_{pq}^e \), conductivity \( k_{pq}^e \) and source \( f_{pq}^e \), with respect to nodal DOF \( u_{qv}^e \) can be written as:

\[ \frac{\partial c_{pq}^e}{\partial u_{qv}^e} = \frac{\partial c_{pq}^e}{\partial N_q^e} \quad , \quad \frac{\partial k_{pq}^e}{\partial u_{qv}^e} = \frac{\partial k_{pq}^e}{\partial N_q^e} \quad , \quad \frac{\partial f_{pq}^e}{\partial u_{qv}^e} = \frac{\partial f_{pq}^e}{\partial N_q^e} \]  (4.68)

since

\[ \frac{\partial u_{qv}^e}{\partial u_{qv}^e} = N_q^e \]  (4.69)

meaning that the capacities, conductivities and sources as defined in section 3.4 can be differentiated with respect to temperature \( T \) (\( w=1 \)), moisture potential \( H \) (\( w=2 \))

---

\(^4\) without summation over repeated indices
and chloride content C (w=3), and next multiplied with the appropriate shape function \(N_{w,n}\) in order to calculate their derivative with respect to the nodal DOF \(u_i\).

A straightforward way to assemble the first two (matrix) terms of the non-linear part of the element tangent matrix \(S^e\) (see equation 4.66), is to literally perform the given matrix multiplications. An algorithm for this task, with matrix \(U^e\) and its time derivative according to equation 4.62, is shown in figure 4.5. However, a large number of zero-multiplications are involved in this algorithm. These zero-multiplications, the result of which is of course known in advance, have been avoided in the algorithm shown in figure 4.6. Both algorithms have been tested and

```
loop l = 1, lint (Gauss points)
  • determine shape functions shp(3,a) corresponding to every element node a, derivatives of the shape functions with respect to x shp(1,a) and y shp(2,a), Jacobian determinant xsj and weight w at Gauss point l
  • determine derivatives of capacity \(c_n\) and conductivity \(k_n\) with respect to DOF w at Gauss point l: dc(r,s,w) and dk(r,s,w)

loop p4 = 1, nel (element nodes)
  loop p3 = 1, ndf (DOFs)
    s1 = (p4-1)*ndf+p3
    loop q4 = 1, nel
      loop q3 = 1, ndf
        loop q2 = 1, nel
          loop q1 = 1, ndf
            s2 = (((q4-1)*ndf+q3-1)*nel*ndf+(q2-1)*ndf+q1
            knl(s1,s2) = dk(p3,q3,q1)* (shp(1,p4)*shp(1,q4)
            +shp(2,p4)*shp(2,q4))* shp(3,q2)*xsj*wf
            cnl(s1,s2) = dc(p3,q3,q1)*shp(3,p4)*shp(3,q4)
            *shp(3,q2)*xsj*wf

loop p4 = 1, nst (with nst = nel*ndf)
  loop q4 = 1, nst
    loop r4 = 1, nst*nst
      snl(p4,q4) = snl(p4,q4)+knl(p4,r4)*umat(r4,q4)+
      cnl(p4,r4)*umat(r4,q4)
```

Figure 4.5: algorithm for the assembly of the non-linear part of tangent matrix \(S^e\) (with entries snl), related to the products \((dC/du^e)\)\(U^e\) (with entries cnl and umat respectively) and \((dK/du^e)\)\(U^e\) (with entries knl and umat respectively; see also equation 4.66). Although a large number of zero-multiplications are involved in the computation of these products, this algorithm seems to be faster than the one in figure 4.6.
it seems that despite its extra computational effort regarding the zero-multiplications, the former algorithm (in figure 4.5) is faster than the latter.

Figure 4.6: alternative algorithm for the assembly of the non-linear part of tangent matrix $S^*$ (with entries $snl$), related to the products $(dC/du^i)\tilde{U}$ and $(dK^e/du^i)\tilde{U}$ (see equation 4.66). Zero-multiplications are avoided by multiplying $knl$ (from matrix $dK^e/du^i$) and $cnl$ (from matrix $dC/du^i$) directly with $u(i,j,1)$ (DOF i at node j in vector $u^i$) and $u(i,j,4)$ (DOF i at node j in vector $\tilde{u}^i$) respectively. Still, this algorithm seems to be slower than the algorithm in figure 4.5.
4.4 Dimensional analysis and scaling

The values of diagonal terms of the capacitance and conductance matrices are roughly:

\[
\begin{bmatrix}
2.40 \cdot 10^8 \frac{J}{m^3K} & * & * \\
* & 1 & * \\
* & * & 1
\end{bmatrix}
\begin{bmatrix}
\frac{\partial T}{\partial t} \\
\frac{\partial H}{\partial t} \\
\frac{\partial C}{\partial t}
\end{bmatrix}
= \nabla \cdot
\begin{bmatrix}
2.40 \frac{J}{smK} & * & * \\
* & 1.00 \cdot 10^{-10} \frac{m^2}{s} & * \\
* & * & 1.00 \cdot 10^{-12} \frac{m^2}{s}
\end{bmatrix}
\begin{bmatrix}
\nabla T \\
\nabla H \\
\nabla C
\end{bmatrix}
\]

(4.70) The sources \( f \), and off-diagonal terms \( c_{ij} \) and \( k_{ij} \) (with \( i \neq j \)) have been omitted in the last set of coupled balances. These off-diagonal terms are zero or of a lower order of magnitude than the diagonal terms, except in the chloride balance (the third row of the last equation), where they can reach the same order of magnitude as \( c_{33} \) and \( k_{33} \). The timescales of the individual processes can then be characterised by their diffusion coefficients \( D_i = k_i/c_i \), which are in fact the diffusion coefficients of the uncoupled linear diffusion processes. So, the diffusion coefficient of the heat flow process (the first row in the last equation) is in the order of \( 10^{-6} \) m²/s, the one of the moisture migration process (the second row in the last equation) in the order of \( 10^{-10} \) m²/s and the one of the chloride transport process in the order of \( 10^{-12} \) m²/s. Clearly, heat flow is the fastest process, followed consecutively by moisture migration and chloride transport. Due to these different timescales of the three coupled processes, the capacitance and conductance matrices are in principle ill-conditioned. Oscillations arise, in particular in the chloride-DOF, if the element size is too big for the time step. The conditioning of these matrices can be improved by modifying the equations such that the diagonal terms are all close to unity [TRU00]. As a first step the units mm and day can be used instead of m and s respectively, which leads to \( c_{11} = 2.40 \cdot 10^{-3} \text{J mm}^{-3} \text{K}^{-1} \), \( c_{22} = 1 \), \( c_{33} = 1 \), \( k_{11} = 207 \cdot 10^3 \text{J day}^{-1} \text{mm}^{-1} \text{K}^{-1} \), \( k_{22} = 8.64 \text{mm}^2 \text{day}^{-1} \), and \( k_{33} = 8.64 \cdot 10^{-2} \text{mm}^2 \text{day}^{-1} \). The (internal) units mm and day have been used in all the computations presented in chapter 5 and 6.

For a single balance both its capacity and conductivity can be transformed to unity by adimensionalisation. However, due to the incorporation of the three coupled balances into a single finite element, this cannot be achieved for the other two balances, which is explained below. The dimensionless potentials \( \Psi \), time \( \tau \) and space \( \varphi \), are defined as [SMI73][HO091]:

\[
\Psi_i = \frac{u_i}{a_i}, \quad \tau = \frac{t}{t_{ref}}, \quad \varphi_i = \frac{x_i}{x_{ref}}
\]

(4.71)
in which $a_i$, $t_{ref}$, and $x_{ref}$ are constants. Upon substitution of these dimensionless quantities the original set of equations (equation 4.1) transforms into:

$$
\frac{\partial^2 \psi_j}{\partial \tau^2} - \frac{\partial}{\partial \phi_i} \left( k_{ij} \frac{\partial \psi_j}{\partial \phi_i} \right) - \frac{a_i}{t_{ref}} f_i = 0
$$

(4.72)

To obtain a dimensionless equivalent this set of equations can be divided by its diagonal capacitance terms (which ensures that there is no division by zero):\(^5\)

$$
\hat{c}_{ij} \frac{a_i}{t_{ref}}
$$

(4.73)

in which the hat ($\hat{\cdot}$) over $c_{ij}$ indicates that a constant (typical value of $c_{ij}$ and with its dimension) is meant. The result is the following set of dimensionless coupled balances:

$$
\frac{c_{ij}}{\hat{c}_{ij}} \frac{a_j}{t_{ref}} \frac{\partial \psi_j}{\partial \tau} - \frac{\partial}{\partial \phi_i} \left( k_{ij} \frac{a_j}{t_{ref}} \frac{\partial \psi_j}{\partial \phi_i} \right) - \frac{f_i}{t_{ref}} = 0
$$

(4.74)

The new variables are also substituted into the natural (convective) boundary conditions:

$$
-k_y \frac{a_j}{x_{ref}} \frac{\partial \psi_j}{\partial \phi_i} n_i - \chi_{ij} a_j \psi_j - \bar{q}_i = 0
$$

(4.75)

To adimensionalise this set of equations, it is divided by:

$$
\hat{c}_{ij} \frac{a_i x_{ref}}{t_{ref}}
$$

(4.76)

which yields:

$$
\frac{k_{ij}}{\hat{c}_{ij}} \frac{a_j t_{ref}}{x_{ref}^2} \frac{\partial \psi_j}{\partial \phi_i} n_i - \frac{\chi_{ij}}{\hat{c}_{ij}} \frac{a_j t_{ref}}{x_{ref}} \psi_j - \frac{\bar{q}_i}{\hat{c}_{ij} a_i x_{ref}} = 0
$$

(4.77)

In table 4.2 both the old dimensional and new dimensionless variables, material functions and boundary conditions are listed. Note that for each balance and potential the value of $\hat{c}_{ij}$ and $a_i$ respectively can be chosen freely: they are scaling factors. However, the values of $t_{ref}$ and $x_{ref}$ have to be the same in each balance, since all three balances are incorporated in a single finite element.

With $t_{ref} = 2.50 \times 10^3$ s, $x_{ref} = 5.00 \times 10^3$ m, $\hat{c}_{11} = 2.40 \times 10^6$ Jm$^{-3}$K, $\hat{c}_{22} = 1.00 \times 10^4$ and $\hat{c}_{33} = 1.00 \times 10^6$ equation 4.70 transforms into the following dimensionless equivalent\(^6\):

---

\(^5\) without summation over repeated $i$

\(^6\) Note that the choice of $a_i$ is irrelevant for the diagonal terms of the dimensionless capacitance and conductance matrices.
\[
\begin{bmatrix}
1 & \cdots & \frac{\partial \Psi_1}{\partial \tau} \\
10^6 & \cdots & \frac{\partial \Psi_2}{\partial \tau} \\
\cdots & 10^6 & \frac{\partial \Psi_3}{\partial \tau}
\end{bmatrix} = \nabla \cdot \begin{bmatrix}
1 & \cdots & \nabla \Psi_1 \\
1 & \cdots & \nabla \Psi_2 \\
\cdots & 1 & \nabla \Psi_3
\end{bmatrix}
\] 

(4.78)

Now that both the heat capacity and conductivity (on the diagonals) are unity, as well as the conductivities of the moisture and chloride balance (on the diagonal), it must be noted that the differences between the time scales (i.e. the orders of magnitude of the diffusion coefficients) of the respective processes are still the same.

Table 4.2: dimensional (*) and dimensionless (.) variables, material functions and boundary conditions.

<table>
<thead>
<tr>
<th>variables</th>
<th>material functions</th>
<th>boundary conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t )</td>
<td>( \tau )</td>
<td>( \Psi )</td>
</tr>
<tr>
<td>( x )</td>
<td>( \phi )</td>
<td>( \Psi )</td>
</tr>
<tr>
<td>( u )</td>
<td>( f )</td>
<td>( \psi )</td>
</tr>
<tr>
<td>( k )</td>
<td>( \beta )</td>
<td>( \chi )</td>
</tr>
<tr>
<td>( q )</td>
<td>( q )</td>
<td>( q )</td>
</tr>
</tbody>
</table>

The off-diagonal terms in the matrices have been disregarded so far. In order to preserve a possible symmetry in the capacitance and conductance matrices (which is favourable from a computational point of view), the following scaling method can be used [BOR02]. Each row in the original set of equations (equation 3.12), in which \( c_i = c_{ij} \) or \( k_i = k_{ij} \) for any \( j \), is divided by the square root of its diagonal entry. This can be either the square root of \( c_i \) or the square root of \( k_i \); in case of non-linearity some typical value (constant, indicated by a hat) is taken. The result of this operation is:

\[
\begin{bmatrix}
\frac{c_{11}}{\sqrt{k_{11}}} & \frac{c_{12}}{\sqrt{k_{12}}} & \frac{c_{13}}{\sqrt{k_{13}}} \\
\frac{c_{21}}{\sqrt{k_{22}}} & \frac{c_{22}}{\sqrt{k_{22}}} & \frac{c_{23}}{\sqrt{k_{23}}} \\
\frac{c_{31}}{\sqrt{k_{33}}} & \frac{c_{32}}{\sqrt{k_{33}}} & \frac{c_{33}}{\sqrt{k_{33}}}
\end{bmatrix}
\frac{\partial T}{\partial \tau} = \nabla \cdot \begin{bmatrix}
\frac{k_{11}}{\sqrt{k_{11}}} & \frac{k_{12}}{\sqrt{k_{12}}} & \frac{k_{13}}{\sqrt{k_{13}}} \\
\frac{k_{21}}{\sqrt{k_{22}}} & \frac{k_{22}}{\sqrt{k_{22}}} & \frac{k_{23}}{\sqrt{k_{23}}} \\
\frac{k_{31}}{\sqrt{k_{33}}} & \frac{k_{32}}{\sqrt{k_{33}}} & \frac{k_{33}}{\sqrt{k_{33}}}
\end{bmatrix}
\begin{bmatrix}
\nabla T \\
\nabla H \\
\nabla C
\end{bmatrix}
+ \begin{bmatrix}
\frac{f_1}{\sqrt{k_{11}}} \\
\frac{f_2}{\sqrt{k_{22}}} \\
\frac{f_3}{\sqrt{k_{33}}}
\end{bmatrix}
\] 

(4.79)
Note that generally symmetry is lost at this point. In order to restore the symmetry the following new potentials are introduced:

\[
\begin{bmatrix}
\mathbf{T} \\
\mathbf{H} \\
\mathbf{C}
\end{bmatrix} = \begin{bmatrix}
\sqrt{k_{11}} T \\
\sqrt{k_{22}} H \\
\sqrt{k_{33}} C
\end{bmatrix}
\]  

which are combined with equation 4.79 to yield:

\[
\begin{bmatrix}
\frac{c_{11}}{k_{11}} & \frac{c_{12}}{\sqrt{k_{11}k_{22}}} & \frac{c_{13}}{\sqrt{k_{11}k_{33}}} \\
\frac{c_{21}}{\sqrt{k_{22}k_{11}}} & \frac{c_{22}}{k_{22}} & \frac{c_{23}}{\sqrt{k_{22}k_{33}}} \\
\frac{c_{31}}{\sqrt{k_{33}k_{11}}} & \frac{c_{32}}{\sqrt{k_{33}k_{22}}} & \frac{c_{33}}{k_{33}}
\end{bmatrix}
\begin{bmatrix}
\frac{\partial \mathbf{T}}{\partial t} \\
\frac{\partial \mathbf{H}}{\partial t} \\
\frac{\partial \mathbf{C}}{\partial t}
\end{bmatrix} = \nabla \cdot \begin{bmatrix}
\frac{k_{11}}{k_{11}} & \frac{k_{12}}{\sqrt{k_{11}k_{22}}} & \frac{k_{13}}{\sqrt{k_{11}k_{33}}} \\
\frac{k_{21}}{\sqrt{k_{22}k_{11}}} & \frac{k_{22}}{k_{22}} & \frac{k_{23}}{\sqrt{k_{22}k_{33}}} \\
\frac{k_{31}}{\sqrt{k_{33}k_{11}}} & \frac{k_{32}}{\sqrt{k_{33}k_{22}}} & \frac{k_{33}}{k_{33}}
\end{bmatrix}
\begin{bmatrix}
\mathbf{T} \\
\mathbf{H} \\
\mathbf{C}
\end{bmatrix} + \begin{bmatrix}
\frac{f_1}{\sqrt{k_{11}}} \\
\frac{f_2}{\sqrt{k_{22}}} \\
\frac{f_3}{\sqrt{k_{33}}}
\end{bmatrix}
\]

(4.81) Clearly, both matrices in the last equation are symmetrical, if \(c_i = c_j\) and \(k_i = k_j\) for \(i \neq j\). Moreover, scaling of the set of equations is achieved, if \(\hat{k}_{ii}\) is chosen such that the ratio of \(k_i\) and \(\hat{k}_{ii}\) is close to unity. The old material functions \(c_i, k_i\) and \(f_i\) are generally functions of the old potentials \(T, H\) and \(C\). For the computation of the element residual vector \(\mathbf{r}\) these old potentials must be used in the new material functions (as in the last equation). Then for the computation of the element tangent matrix \(\mathbf{S}\), being the derivative of the residual with respect to the new (nodal) potentials, the individual derivatives of the new material functions with respect to the old potentials must be multiplied with the corresponding derivatives of the old potentials with respect to the new potentials. This scaling method has been implemented and preliminary tests pointed out that the improvement of the numerical solution process was marginal.
Chapter 5
APPLICATION OF THE MODEL

In this chapter the application of the computational model for chloride ingress into reinforced concrete is demonstrated in a number of cases. Practical cases which enable comparison of experimental and numerical results, have been chosen for this purpose. Since in general most of the chloride data are one-dimensional chloride profiles and in the cases in this chapter two-dimensional effects are not probable, a one-dimensional routine has been deployed for most of these cases. As compared to the two-dimensional version the calculation speed was considerably higher. The translation of practical environmental conditions to boundary conditions in the model is explained in section 1. In the next section simple cases, which serve as benchmarks, are discussed. The last section deals with a complicated case.

5.1 Boundary conditions

The environmental conditions near the concrete surface during the entire simulated period have to be translated into either a prescribed potential, a prescribed flux or a combination of these. The corresponding boundary conditions are of the Dirichlet-, Neumann- and Robbins-type respectively. They are successively represented by the following mathematical expressions:

\[ u_i = \bar{u}_i \]

\[ -k_o \frac{\partial u_i}{\partial x_i} n_i = \bar{q}_i \]

\[ -k_o \frac{\partial u_j}{\partial x_i} n_i = \chi_{ij} (u_j - \psi_j) \]

(5.1)
In the present work the off-diagonal terms of transfer matrix $\chi_{ij}$ are assumed to be zero and hence the last equation (Robbins boundary condition) reduces to:

$$-k_{ij} \frac{\partial u_i}{\partial x_j} \cdot n_i = \chi_{ii}(u_i - \psi_i)$$  \hspace{1cm} (5.2)

Boundary conditions have to be defined for the outer nodes of the finite element mesh in order to obtain a solution. As the mesh represents a piece of concrete, also these outer nodes exhibit the characteristics of concrete. The boundary conditions can be merged with the respective heat, moisture and chloride models. However, the possible combinations and the underlying assumptions need further explanation.

The respective heat, moisture and chloride models use different potentials. What is referred to as ‘potential’ in a physical context, is equivalent to a degree-of-freedom (DOF) in a numerical context. It is clear that the potential or DOF in the heat balance is temperature ($T$), both for heat model 0 and 1. In the moisture models there are two alternative potentials: the moisture potential ($H$) and the moisture content ($W$). Only in moisture model 0 these two alternatives are available; in moisture models 1 to 4 the DOF is always the moisture potential. In the chloride balance there are two possible DOFs: the total chloride content $C_{\text{total}}$ and the free chloride concentration $C_{\text{free}}$. While in chloride model 0 both alternatives can be used, in chloride model 1 it is $C_{\text{total}}$ and in chloride models 2 and 3 $C_{\text{free}}$.

Application of a Dirichlet boundary condition means in case of heat model 0 and 1 prescription of the temperature of the boundary nodes, i.e. the temperature of the concrete surface. It is then assumed that an instantaneous equilibrium exists between the environmental temperature and the temperature of the concrete surface. If the moisture potential is the DOF in the used moisture model, a Dirichlet boundary condition implies that the moisture potential at the boundary nodes is prescribed. It is then assumed firstly that the environmental relative humidity is equal to the boundary moisture potential, and secondly that the two of them are instantaneously in equilibrium. If the moisture content is used as potential in moisture model 0, this moisture content is prescribed at the outer nodes by a Dirichlet boundary condition.

The Dirichlet boundary condition in combination with chloride model 2 and 3 implies that the free chloride concentration on the concrete surface is prescribed. Strictly speaking this is the free chloride concentration in the pores of the concrete skin, and not the chloride concentration in water on the concrete surface. However, it is assumed that an instantaneous equilibrium exists between the chloride concentration in the water on the concrete surface and the free chloride concentration in the pores of the concrete skin. If the Dirichlet boundary condition is applied in combination with chloride model 1, then the total chloride content of the concrete surface is prescribed. This implies generally that not only the free chloride concentration in the
pores of the concrete skin are prescribed, but also the bound chloride content. It is further assumed then that also at the boundary the chloride binding is instantaneous and that the free chloride concentration in the pores of the concrete skin is still equal to the chloride concentration in the water on the concrete surface. For chloride model 0, used with either \( C_{\text{free}} \) or \( C_{\text{total}} \) as DOF, the same assumptions are applicable.

The Neumann boundary condition combined with the heat models implies a prescribed boundary heat flux (in \( \text{Jm}^{-2}\text{s}^{-1} \)). If the moisture potential is the DOF in the used moisture model, then a Neumann boundary condition leads to a prescribed boundary pseudo-moisture flux (in \( \text{ms}^{-1} \)). This is not a real moisture flux because of the division of the moisture balance by \( \partial W/\partial H \) (see section 3.4.2). However, if this pseudo-moisture flux is prescribed to be zero, the difference with the real moisture flux (in \( \text{kgm}^{-2}\text{s}^{-1} \)) disappears from a computational point of view. This zero boundary moisture flux will often be applied and it represents insulation or symmetry. Combination of the moisture content as a DOF in moisture model 0 with a Neumann boundary condition yields a prescribed real boundary moisture flux (in \( \text{kgm}^{-2}\text{s}^{-1} \)) at the boundary.

If the Neumann boundary condition is combined with the chloride models, the result is a prescribed boundary chloride flux (in \( \text{kgm}^{-2}\text{s}^{-1} \)). A chloride flux caused by a gradient of the total chloride content (as in chloride model 1) may seem strange, because bound chlorides (included in the total chloride content) cannot move. However, in chloride model 1 the free chlorides are selected by the definition of conductivities \( k_{3j} \). If the boundary chloride flux is prescribed, it is usually put equal to zero, which models insulation or symmetry. In that case also the distinction between free and bound chlorides with respect to the boundary chloride flow is not relevant anymore, as both free and bound chlorides cannot pass the boundary then for all chloride models (0 to 3). Since in chloride models 1, 2 and 3 more than one conductivity \( k_{3j} \) is non-zero, a zero boundary flux implies that the sum of the respective fluxes equals zero. So, these respective fluxes must annihilate each other, and in the case of two fluxes they must have opposite signs at the boundary.

The Robbins boundary condition can be combined with the heat and moisture models. In case the Robbins boundary condition is combined with the heat models, a heat transfer coefficient \( \chi_1 \) and an environmental temperature \( \psi_1 \) must be specified. Neither the temperature at the boundary is then prescribed, nor the heat flux, but a heat flux which is proportional to the difference between the environmental temperature and the temperature of the concrete surface (the outer nodes). Similarly, a moisture transfer coefficient \( \chi_2 \) and an environmental relative humidity \( \psi_2 \) must be specified for the combination of a Robbins boundary condition with moisture models.
1 to 4. A moisture flux at the boundary is prescribed which is proportional to the difference between the environmental relative humidity and the moisture potential of the concrete surface (the outer nodes). If the moisture potential is the DOF of moisture model 0, a Robbins boundary condition can be used together with this model as well. In addition to the linear (convective) boundary condition as shown in equation 5.2, for the heat balance a non-linear (radiation) boundary condition can be used:

\[-k_{1i} \frac{\partial T}{\partial x_i} = \chi_1 \left(T^4 - \psi^4\right)\]  

(5.3)

### 5.2 Benchmark cases

Two relatively simple cases have been elaborated in order to verify that both input and output of the computational model correspond to experimental results. The low level of complexity is achieved by constant boundary conditions and by a small amount of involved parameters. The transparency of the calculations then allows for straight comparisons of experimental and numerical data, which are considered to be benchmarks. To further enhance the validation first a separate moisture case is discussed. The second case deals with chloride ingress in combination with little moisture movement.

#### 5.2.1 Moisture

As chloride transport in concrete is strongly related to moisture migration in concrete, it is beneficial to first get an insight in the behaviour of moisture migration separately. Here one experiment from the work of [BIS02] is simulated. In this experiment small cement paste prisms were dried at 30 °C and 30 % relative humidity during 150 days. After mixing the specimens were in a mould for 1 day, next they were demoulded and put under water for 6 days. Then exposure started at the age of 7 days. During exposure evaporation could occur from only one side of the prism; all other sides were insulated. The exposed surface was 160·40=6400 mm². The specification of the cement paste experiment and some measured quantities are given in table 5.1.

The cement content \(\zeta_2\) and the cement density can be calculated with a mass and volume balance at demoulding respectively, inserting the water-cement ratio \(\zeta_1\), the mass at demoulding and the specimen dimensions (while neglecting the air content). The result is that the cement content equals 1309 kg/m³ and the cement density 3193 kg/m³. In the implemented moisture models the degree of hydration \(\alpha\) does
not change in time. Moreover, the moisture data fit in [ROE89] allows for \(\alpha\) in the range [0.7... 0.9]. It is acknowledged, however, that in this experiment the degree of hydration varies over time and that at the start of the experiment (age 7 days) it is lower than 0.7. From the moisture data in [ROE89] it follows that for the parameter-set \((\alpha, \zeta_1, \zeta_2) = (0.7, 0.45, 1309 \text{ kg/m}^3)\) and variable-set \((T, H) = (303 \text{ K}, 1)\) the corresponding (saturated) moisture content is 417 kg/m\(^3\). As can be seen in table 5.1, the measured maximum moisture content was 452 kg/m\(^3\); this is 8% more.

<table>
<thead>
<tr>
<th>cement type</th>
<th>Portland CEM I 52.5 R</th>
</tr>
</thead>
<tbody>
<tr>
<td>water-cement ratio</td>
<td>0.45</td>
</tr>
<tr>
<td>specimen dimensions</td>
<td>160-40-40 mm(^3)</td>
</tr>
<tr>
<td>mass at demoulding</td>
<td>0.486 kg</td>
</tr>
<tr>
<td>moisture content at exposure start</td>
<td>433 kg/m(^3)</td>
</tr>
<tr>
<td>maximum moisture content</td>
<td>452 kg/m(^3)</td>
</tr>
</tbody>
</table>

The initial moisture potential for the computations has been derived in the following way. The ratio between the measured moisture content at the start of the exposure and the measured maximum moisture content is 433/452 = 0.958. If the same ratio is applied to the computed moisture contents, then it follows that the (computed) moisture content at the exposure start is 0.958 \times 417 = 399 kg/m\(^3\). For \((\alpha, \zeta_1, \zeta_2) = (0.7, 0.45, 1309 \text{ kg/m}^3)\) and \(T = 303 \text{ K}\) (the same as above), this moisture content corresponds to a moisture potential of approximately 0.99. If \(\alpha = 0.45\) (in principle outside the allowable range) was inserted instead of \(\alpha = 0.7\), the resulting moisture potential would have been the same.

The experiment has been simulated with moisture model 1 (computation A and B), moisture model 0 (computation C), moisture model 0 in combination with the interface element (computation D) and moisture model 1 in combination with the interface element (computation E). In all computations the moisture conductivity \((k_{x2} \text{ and } \theta_1)\) respectively has been chosen such to approach the measured data as close as possible (visually). The values of the remaining moisture parameters \(\theta_2, \theta_3\) and \(\theta_4\) have been obtained from [BAZ72]. The moisture model and solution parameters for these computations are shown in tables 5.2 to 5.4. Furthermore, the measured data are compared to an analytical solution from [CRA75] for linear diffusion into a semi-infinite medium.
Table 5.2: moisture model parameters for the computations (A, B, C, D and E). Parameter lists (in parentheses) indicate the dependency on the parameters in the list. In computation B $k_{22}$ is constant due to $\theta_2=1$. For computations A, B and C the interface element (with parameters $\chi_2$ and $\psi_2$) has not been used.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>model</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$c_{22}$</td>
<td>0.65, 0.85</td>
<td>0.85, 0.85</td>
<td>3.47 $10^{-4}$</td>
<td>1.00 $10^{-3}$</td>
</tr>
<tr>
<td>$k_{22}$</td>
<td>(aE, c_{22})</td>
<td>(a_{22}, c_{22})</td>
<td>452</td>
<td>452</td>
</tr>
<tr>
<td>$W_{max}$</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>$\zeta_1$</td>
<td>1309</td>
<td>1309</td>
<td>1309</td>
<td>1309</td>
</tr>
<tr>
<td>$\theta_1$</td>
<td>3.47 $10^{-4}$</td>
<td>1.91 $10^{-4}$</td>
<td>4.91 $10^{-4}$</td>
<td>4.91 $10^{-4}$</td>
</tr>
<tr>
<td>$\theta_2$</td>
<td>0.05</td>
<td>1.00</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>$\theta_3$</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>$\theta_4$</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$\chi_2$</td>
<td>1.00 $10^{-7}$</td>
<td>1.00 $10^{-7}$</td>
<td>1.00 $10^{-7}$</td>
<td>1.00 $10^{-7}$</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 5.3: intermediate moisture model parameters in computations A, B and E derived with $\alpha$ and $\zeta_1$ from table 5.2.

<table>
<thead>
<tr>
<th>$H$</th>
<th>0.35</th>
<th>0.35 &lt; $H$ &lt; 0.89</th>
<th>0.89 &lt; $H$ &lt; 1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_1$</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>$\eta_2$</td>
<td>3.51 $10^{-2}$</td>
<td>3.51 $10^{-2}$</td>
<td>3.51 $10^{-2}$</td>
</tr>
<tr>
<td>$\eta_3$</td>
<td>1.21 $10^{-2}$</td>
<td>1.21 $10^{-2}$</td>
<td>1.21 $10^{-2}$</td>
</tr>
<tr>
<td>$\eta_4$</td>
<td>1.21 $10^{-2}$</td>
<td>1.21 $10^{-2}$</td>
<td>1.21 $10^{-2}$</td>
</tr>
<tr>
<td>$\eta_5$</td>
<td>3.89</td>
<td>3.89</td>
<td>3.89</td>
</tr>
<tr>
<td>$\eta_6$</td>
<td>1.10 $10^{-2}$</td>
<td>1.10 $10^{-2}$</td>
<td>1.10 $10^{-2}$</td>
</tr>
</tbody>
</table>

Table 5.4: solution parameters in the simulation of the experiments. In the case of computations C and D the flux through left boundary is a function of H, $\chi_2$ and $\psi_2$.

<table>
<thead>
<tr>
<th>space</th>
<th>time</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimension</td>
<td>40·1 mm$^2$</td>
</tr>
<tr>
<td>element-size</td>
<td>1·1 mm$^2$</td>
</tr>
<tr>
<td>elements</td>
<td>40</td>
</tr>
<tr>
<td>element-type</td>
<td>2-dimensional</td>
</tr>
</tbody>
</table>

initial conditions

<table>
<thead>
<tr>
<th>space</th>
<th>boundary conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>left</td>
<td>right, top and bottom</td>
</tr>
<tr>
<td>$T=303$ K</td>
<td>$T=303$ K</td>
</tr>
<tr>
<td>$H=0.99$</td>
<td>$H=0.3$ (A, B, E), $q_{in}=(H, \chi_2, \psi_2)$ ms$^{-1}$ (C, D)</td>
</tr>
<tr>
<td>iterations</td>
<td></td>
</tr>
<tr>
<td>tolerance</td>
<td>$10^{-14}$</td>
</tr>
<tr>
<td>scheme</td>
<td>Newton-Raphson</td>
</tr>
</tbody>
</table>
Results and discussion

The comparison of the (gravimetrically) measured moisture data and the results of computation A is shown in figure 5.1. During the first 90 days of exposure the agreement between experimental and computational data is good. In the period from 90 until 150 days the computed moisture loss becomes increasingly smaller than the measured moisture loss.

Figure 5.1: comparison of measured moisture data and computations A (left) and B (right). The results of computation A start to deviate from the measured data after 90 days of exposure. The results of computation B slightly deviate between 60 and 120 days of exposure.

The computed (A) moisture potential and moisture content profiles are depicted in figure 5.2. The moisture potential profiles are in the case of computation A the result of non-linear diffusion; the moisture content is a quadratic function of the moisture potential (and hence the bumps in the moisture content curves).

Figure 5.2: computed (A) moisture potential (left) and moisture content (right) profiles at time 0, 1, 30, 60, 90, 120 and 150 days. Lower lines correspond to later points in time. The basis of these results is non-linear diffusion and a non-linear dependence of the moisture content on the moisture potential.
Figure 5.1 also shows the comparison of measured moisture loss and the results of computation B. This computation is basically linear diffusion of the moisture potential H (since $\theta_2$ equals 1), but for the calculation of moisture contents the quadratic relation is used. The agreement between experimental and computational data is good, excepting a slight deviation in the time interval [60 ... 120] days. The moisture potential and moisture content profiles in computation B are depicted in figure 5.3.

![Diagram](image)

*Figure 5.3: computed (B) moisture potential and moisture content profiles at time 0, 1, 30, 60, 90, 120 and 150 days. Lower lines correspond to later points in time. The basis of these results is linear diffusion and a non-linear dependence of the moisture content on the moisture potential.*

Computation C is fully linear: linear diffusion of the moisture potential and a linear relation between moisture content W and moisture potential H. This relation is defined as $W = W_{max} - H$. Despite the simplicity of this computation, the agreement between the measured moisture loss and the computational results is surprisingly good, as can be observed in figure 5.4. Figure 5.5 shows the corresponding moisture potential and moisture content profiles.

An analytical solution for 1-dimensional linear diffusion in a semi-infinite medium is given in [CRA75]. Suppose that in this case moisture migration through concrete can be described by 1-dimensional linear diffusion of the moisture content W:

$$\frac{\partial W}{\partial t} = D \frac{\partial^2 W}{\partial x^2}$$

(5.4)

in which D (in m$^2$/s) is the moisture diffusion coefficient. Then for $x$ ranging from 0 m to infinity, a uniform initial moisture content $W_{max}$ and a constant boundary moisture content $W_{out}$ at $x=0$ m, the moisture content W (in kg/m$^3$) as a function of time t and space x is:
5.2 benchmark cases

Figure 5.4: comparison of measured moisture data and computations C (left) and an analytical expression by [CRA75] (right). The results of the fully linear computation (C) are fairly good for this case. The analytical expression was derived from linear diffusion into a semi-infinite medium.

\[ W(t,x) = (W_{\text{int}} - W_{\text{bou}}) \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) + W_{\text{bou}} \quad (5.5) \]

The moisture flux (in kg m^{-2} s^{-1}) through the boundary (x=0 m) is then:

\[ q_w|_{x=0} (t) = -D \frac{\partial W}{\partial x} \bigg|_{x=0} = (W_{\text{bou}} - W_{\text{int}}) \frac{D}{\sqrt{\pi t}} \quad (5.6) \]

Suppose that exposure starts at time \( t=0 \) s. An analytical expression for the moisture loss in the specimen \( L \) (in kg) at time \( t' \) is obtained by integrating this moisture flux over the time range \([0 \ldots t']\) s and multiplying the result with the exposed surface area \( A \) (in m^2):

\[ L(t') = A \int_0^{t'} q_w|_{x=0} (t) \, dt = a\sqrt{t'} \quad (5.7) \]

with:

\[ a = 2A(W_{\text{bou}} - W_{\text{int}}) \frac{D}{\sqrt{\pi}} \quad (5.8) \]

Equation 5.7 is the well-known square-root-of-time relation for moisture loss and uptake in porous materials [HAL86][GRT93]. As can be seen in figure 5.4, the experimental results follow this analytical expression almost exactly, despite the fact that the specimen dimensions were not semi-infinite at all. The matching factor is \( a=3.85\times10^{-3} \) kg/\( \text{day} \). In the moisture models used for computations A to E the moisture potential \( H \) is the main variable in the (uncoupled, 1-dimensional) moisture diffusion equation:
5 APPLICATION OF THE MODEL

Figure 5.5: moisture potential and moisture content profiles at time 0, 1, 30, 60, 90, 120 and 150 days in computation C (left) and D (right). Lower lines correspond to later points in time. Both computations C and D are fully linear, however in computation D the interface element has been deployed.

\[
c_{22} \frac{\partial H}{\partial t} = \frac{\partial}{\partial x} \left( k_{22} \frac{\partial H}{\partial x} \right)
\]  

(5.9)

The diffusion coefficient D in equation 5.4 and \( k_{22} \) (or \( \theta_i \)) in the last equation can be compared, if \( c_{22} = 1 \) and if \( W \) is a linear function of \( H \). The value of \( D \) can be calculated from equation 5.8 (with \( A = 6400 \) mm²). There are two alternative sets of values for \( W_{\text{bou}} \) and \( W_{\text{in}} \) in this calculation. For direct comparison to computation C the set \( (W_{\text{bou}}, W_{\text{in}}) = (136, 447) \) kg/m³ is most suitable, since this corresponds to the relation \( W = W_{\text{max}} - H \) with \( W_{\text{max}} = 452 \) kg/m³. The resulting diffusion coefficient is \( D = 3.38 \times 10^{-11} \) m²/s; the difference with \( k_{22} \) in computation C \( (3.47 \times 10^{-11} \) m²/s) is 3 %. Note that the solution in computation C has been obtained for finite space, whereas the analytical solution was derived for semi-infinite space. Alternatively, the measured initial moisture content of 433 kg/m³ can be used together with an estimate of the boundary moisture content. Although the specimens were stored in a climate room with constant relative humidity (30 %), in reality the boundary moisture content was not constant due to the increasing degree of hydration. However, the analytical solution has been derived for a constant boundary condition. So, some 'effective' boundary moisture content must be selected here. If this effective boundary moisture content is estimated at 125 kg/m³, it follows that \( D = 3.47 \times 10^{-11} \) m²/s.

Finally, some computations have been performed with the interface element: one with linear diffusion (D) and one with non-linear diffusion (E). In both computations the parameters for the interface element were the same: a moisture transfer coefficient \( \chi \) of \( 1.00 \times 10^{-9} \) m/s [JAC99] and an environmental relative humidity \( \psi_i \) of 0.3. The results of both computations differ significantly from the measured moisture.
data, as can be observed in figure 5.6. The computed moisture potential and moisture content profiles are shown in figure 5.5 (computation D) and 5.7 (computation E). As opposed to computation A, B and C, the boundary moisture potential and boundary moisture content gradually decrease. This is characteristic for the interface element, which models a certain resistance (with respect to moisture flow) between the concrete surface and its environment. A sensitivity analysis for the moisture transfer coefficient, based on computation C, is carried out in section 6.1.1. The moisture conductivities in computation D and E ($k_{22}$ and $\theta_1$ respectively) are considerably higher than the ones in computations A, B and C.

![Figure 5.6: comparison of measured moisture data and computation D (left) and E (right). In both computations the interface element has been deployed. Both the results of computation D (linear) and E (non-linear) deviate from the measurements.](image)

![Figure 5.7: computed (E) moisture potential (left) and moisture content (right) profiles at time 0, 1, 30, 60, 90, 120 and 150 days. Lower lines correspond to later points in time. In this computation the interface element has been used, combined with non-linear diffusion.](image)
In spite of the good results of moisture model 0 (linear), further moisture computations are performed with moisture model 1 (non-linear), since the latter model relates moisture storage in concrete not only to the macroscopic pore humidity $H$, but also to temperature and to the usual concrete properties, viz. degree of hydration, water to cement ratio and cement content. Moreover, the difference between cement paste and concrete may favour moisture model 1. The poor results with the moisture interface element caused it not to be used any further.

### 5.2.2 CHLORIDE

An investigation of chloride ingress into concrete slabs submerged at different depths in the North Sea was conducted by the Dutch institutes SMOZ and CUR [LAN84] [POL95] [CUR96]. Chloride profiles in the slabs were obtained by chemical analysis (Volhard's method) after 2, 8 and 16 years of exposure. Three different types of concrete, three different curing conditions and three different geometrical configurations were studied; these are specified in tables 5.5 to 5.7.

#### Table 5.5: respective concrete compositions in the experiments.

<table>
<thead>
<tr>
<th>code</th>
<th>cement type</th>
<th>w/c ratio</th>
<th>cement content [kg/m$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>ordinary Portland cement (CEM I 32.5 R)</td>
<td>0.400</td>
<td>420</td>
</tr>
<tr>
<td>II</td>
<td>blast furnace slag cement (CEM II/B 42.5)</td>
<td>0.415</td>
<td>420</td>
</tr>
<tr>
<td>III</td>
<td>ordinary Portland cement (CEM I 32.5 R)</td>
<td>0.540</td>
<td>300</td>
</tr>
</tbody>
</table>

#### Table 5.6: respective curing conditions in the experiments. Only the experiments with code 1 are simulated here.

<table>
<thead>
<tr>
<th>code</th>
<th>duration [weeks]</th>
<th>details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>20 °C and 65 % relative humidity</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>20 °C and 65 % relative humidity</td>
</tr>
<tr>
<td>14</td>
<td>14</td>
<td>1 week in a fog room and 13 weeks at 20 °C and 65 % relative humidity</td>
</tr>
</tbody>
</table>

#### Table 5.7: respective geometrical configurations in the experiments. The diameter of the reinforcement bars was 8 mm. Only the experiments with code a and e are simulated here.

<table>
<thead>
<tr>
<th>code</th>
<th>dimensions [mm$^3$]</th>
<th>reinforcement position (depth) [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, b</td>
<td>300·100·100</td>
<td>none</td>
</tr>
<tr>
<td>c, d</td>
<td>500·100·100</td>
<td>15, 30, 46</td>
</tr>
<tr>
<td>e</td>
<td>600·150·150</td>
<td>20, 40, 71</td>
</tr>
</tbody>
</table>

Simulations have been performed for experiments 11e (composition I, curing 1 and configuration e), 11e (composition II, curing 1 and configuration e) and IIIa.
(composition III, curing 1 and configuration a). However, no experimental data seem to be available for IIe and IIIe after 2 years of exposure; instead, the data for I1a and IIIa have been used. Furthermore, experimental data are missing for IIe after 8 years of exposure at a depth of 5 m; there are data for 100 m depth. Up to 8 years the specimens were placed at a depth of both 5 and 100 m in the North Sea. Then the specimens at 100 m depth were moved to a depth of 40 m and exposed for another 8 years. So, the data after 16 years of exposure are not representative for a single depth, but for a combination of 100 and 40 m. Thus the simulations comprise of all concrete compositions, only 1 week curing and configurations a and e.

The curing conditions have caused drying of the surface layer of the specimens. According to [CUR96] the evaporation depth of composition I, II and III is 2.2, 1.6 and 2.8 mm respectively for curing code 1. A sharp evaporation front was assumed in [CUR96], meaning that from the surface to the evaporation front the concrete is dried out and behind the evaporation front fully saturated. This dried surface layer causes some capillary sea-water uptake in the beginning of the experiments. Moreover, the surface layer is not only dried out, but also carbonated as a result of the curing conditions. The consequence of this carbonation will be addressed for IIIe.

Moisture model 1 and chloride model 1 have been deployed in the computations for IIe and IIIa. Although both models are in principle non-linear, they quickly reduce to linear models. This is due to the constant boundary conditions for moisture and chloride and due to the initial moisture condition. The 1-dimensional finite element mesh is initially for the major part moisture saturated, except a few elements at the ends. When these outer elements have become moisture saturated as well, the chloride conductivity is constant all over the mesh and moisture migration has stopped. The experiments IIIe have at first been simulated with moisture model 1 and chloride model 2. Also in this case the computations quickly became linear for the same reasons as mentioned in the previous paragraph. Next, for the carbonation analysis of IIIe moisture model 1 has been combined with chloride model 3, and finally moisture model 4 with chloride model 3.

The temperature is assumed to be constant at 293 K in the computations. This temperature is somewhat high for the North Sea, but it is the lowest admissible temperature in the moisture data [ROE89]. Due to the constant temperature in these computations, the Arrhenius function in the definition of \( k_c \) (see equation 3.131) reduces to a constant as well. Therefore, the latter constant must be considered to be included in the value of \( k_1 \) and \( k_2 \). The degree of hydration \( \alpha \) is a constant in the analysis and it has been assumed that for the period of 16 years an average of 0.7 can be used [SOU98]. The value of the saturated moisture conductivity \( \Theta_1 \) is based on
the remaining moisture parameters $\theta_2$, $\theta_3$ and $\theta_4$ have been obtained from [BAZ72]. The input for the computations for IIe, IIIe (without carbonation effects) and IIIa has been summarised in tables 5.8 to 5.11. Figure 5.8 shows the approximation of the initial moisture state in the specimens used in the computations.

Table 5.8: moisture model parameters in the computations for IIe, IIIe and IIIa.

<table>
<thead>
<tr>
<th></th>
<th>IIe</th>
<th>IIIe</th>
<th>IIIa</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>$\zeta_1$</td>
<td>0.400</td>
<td>0.415</td>
<td>0.440</td>
</tr>
<tr>
<td>$\zeta_2$</td>
<td>420</td>
<td>420</td>
<td>300</td>
</tr>
<tr>
<td>$\theta_1$</td>
<td>$1.00 \times 10^{-6}$</td>
<td>$1.00 \times 10^{-6}$</td>
<td>$1.00 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\theta_2$</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>$\theta_3$</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>$\theta_4$</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 5.9: chloride model parameters in the computations for IIe, IIIe and IIIa. The values of $\kappa_1$ and $\kappa_2$ apply to $T=293 \, K$.

<table>
<thead>
<tr>
<th></th>
<th>IIe</th>
<th>IIIe</th>
<th>IIIa</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa_1$</td>
<td>0.745</td>
<td>0.745</td>
<td>0.745</td>
</tr>
<tr>
<td>$\kappa_2$</td>
<td>490</td>
<td>490</td>
<td>490</td>
</tr>
<tr>
<td>$\xi_1$</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
</tr>
<tr>
<td>$\zeta_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\zeta_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.10: intermediate moisture model parameters derived with $\alpha$ and $\zeta_1$ from table 5.8.

<table>
<thead>
<tr>
<th></th>
<th>IIe</th>
<th>IIIe</th>
<th>IIIa</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_1$</td>
<td>$8.75 \times 10^2$</td>
<td>$-6.23 \times 10^2$</td>
<td>$2.34 \times 10^3$</td>
</tr>
<tr>
<td>$\eta_2$</td>
<td>0</td>
<td>$6.94 \times 10^2$</td>
<td>$1.91 \times 10^3$</td>
</tr>
<tr>
<td>$\eta_3$</td>
<td>3.66</td>
<td>3.99</td>
<td>$-1.43 \times 10^2$</td>
</tr>
<tr>
<td>$\eta_4$</td>
<td>$-1.21 \times 10^2$</td>
<td>$-2.77 \times 10^2$</td>
<td>$-1.64 \times 10^2$</td>
</tr>
<tr>
<td>$\eta_5$</td>
<td>3.17</td>
<td>$-3.36 \times 10^2$</td>
<td>$3.19 \times 10^1$</td>
</tr>
<tr>
<td>$\eta_6$</td>
<td>$1.10 \times 10^2$</td>
<td>$1.98 \times 10^2$</td>
<td>$1.34 \times 10^2$</td>
</tr>
</tbody>
</table>

$0.35 < H < 0.89 \quad 0.89 < H \leq 1.00$
5.2 benchmark cases

Table 5.11: solution parameters in the simulation of experiments Ile, llle (without carbonation effects) and IIIla.

<table>
<thead>
<tr>
<th></th>
<th>Ile</th>
<th>llle</th>
<th>IIIla</th>
</tr>
</thead>
<tbody>
<tr>
<td>space</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>length</td>
<td>150</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>element-size</td>
<td>0.33</td>
<td>0.33</td>
<td>0.25</td>
</tr>
<tr>
<td>elements</td>
<td>450</td>
<td>450</td>
<td>400</td>
</tr>
<tr>
<td>element-type</td>
<td>1-dimensional</td>
<td>1-dimensional</td>
<td>1-dimensional</td>
</tr>
<tr>
<td>time</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>span</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>step-size</td>
<td>0.5, 1, 73</td>
<td>1, 10, 73</td>
<td>0.5, 1, 73</td>
</tr>
<tr>
<td>steps</td>
<td>30, 350, 75</td>
<td>15, 35, 75</td>
<td>30, 350, 75</td>
</tr>
<tr>
<td>scheme</td>
<td>Euler backward</td>
<td>Euler backward</td>
<td>Euler backward</td>
</tr>
<tr>
<td>initial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>heat</td>
<td>$T=293$</td>
<td>$T=293$</td>
<td>$T=293$</td>
</tr>
<tr>
<td>moisture</td>
<td>$0.65 \leq H \leq 1.00$</td>
<td>$0.65 \leq H \leq 1.00$</td>
<td>$0.65 \leq H \leq 1.00$</td>
</tr>
<tr>
<td>chloride</td>
<td>$C_{\text{sat}}=0$</td>
<td>$C_{\text{sat}}=0$</td>
<td>$C_{\text{sat}}=0$</td>
</tr>
<tr>
<td>boundaries</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>heat</td>
<td>$q_t=0$</td>
<td>$q_t=0$</td>
<td>$q_t=0$</td>
</tr>
<tr>
<td>moisture</td>
<td>$H=1.00$</td>
<td>$H=1.00$</td>
<td>$H=1.00$</td>
</tr>
<tr>
<td>chloride</td>
<td>$C_{\text{sat}}=15.5$</td>
<td>$C_{\text{sat}}=20$</td>
<td>$C_{\text{sat}}=13.2$</td>
</tr>
<tr>
<td>iterations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tolerance</td>
<td>$10^{-16}$</td>
<td>$10^{-16}$</td>
<td>$10^{-16}$</td>
</tr>
<tr>
<td>scheme</td>
<td>Newton-Raphson</td>
<td>Newton-Raphson</td>
<td>Newton-Raphson</td>
</tr>
</tbody>
</table>

The chloride concentration in the North Sea has been assumed as 20 g/l (CUR96). If it is further assumed that the free chloride concentration in the pores at the concrete surface equals this concentration, then the chloride boundary condition in conjunction with chloride model 2 is also 20 kgm$^{-3}$ (specimens IIle). For chloride model 1, this free chloride concentration must be converted to a total chloride content, assuming immediate binding. This can be calculated with formula 3.125, in which the moisture content at the concrete surface (118 and 126 kg/m$^3$ for IIle and IIIla respectively), the maximum moisture content (119 and 127 kg/m$^3$ for IIle and IIIla respectively)
and the binding ratio (0.746 and 0.612 for 11e and III1a respectively) must be inserted. With respect to the computations for specimen 11e the parameter set \((\xi_1, \xi_2, \xi_3) = (368 \text{ kgm}^{-3}, 699 \text{ kgm}^{-3}, 0)\) in chloride model 2 is equivalent to parameter set \((\xi_1, \xi_2) = (125 \text{ kgm}^{-3}, 0.601)\) in chloride model 1 (see equations 3.34 and 3.151). Linear chloride binding has been assumed in the simulation of all three experiments. The binding ratio \(\xi_2\) has been chosen such to yield a total chloride content at the boundary which agreed best (visually) with the measurements. The diffusion coefficient at saturation \(\kappa_1\) has been selected to (visually) fit the measurements behind the concrete surface after 2, 8 and 16 years respectively. As the influence of moisture migration on the chloride ingress is marginal in this case, the computed chloride profiles are mainly determined by \(\xi_2\) and \(\kappa_1\): \(\xi_2\) for the surface chloride content and \(\kappa_1\) for the internal chloride contents.

Results and discussion

A comparison of the experimental data and the computational results for 11e, III1e and III1a is shown in figure 5.9, 5.10 and 5.11 respectively. The agreement between experimental and numerical data is good for 11e. In the case of III1e there are some deviations with respect to the curves at 2 and 16 years: after 2 years of exposure the real chloride ingress seems to have proceeded farther and after 16 years the chloride content near the surface appears to be higher. The deviation of the chloride contents near the concrete surface after 16 years cannot be simulated with linear diffusion. In order to investigate whether carbonation could have caused this deviation, the carbonation model is deployed for the simulation of III1e later in this section. The agreement between experimental and numerical data is also good for III1a,

![Figure 5.9: comparison of experimental and computational data for 11e. For the measurements after 2 years of exposure the 11a data (indicated with an 'a' in the legend) have been depicted, since data for 11e are missing.](image-url)
excepting chloride contents near the surface after 2 and 8 years of exposure, and the measurements after 8 years for the specimens which were placed at a depth of 100 m. The difference between the 5 m and 100 m measurements after 8 years is striking; the 100 m measurements even more or less coincide with the 16 year measurements. This shift of the 100 m measurements with respect to the 5 m measurements indicates a significant increase of the binding ratio $\xi_2$ after 2 years of exposure.

Figure 5.10: comparison of experimental and computational data for IIIe. For the measurements after 2 years of exposure the IIIa data (indicated with an ‘a’ in the legend) have been depicted, since data for IIIe are missing. In this computation the initial moisture conditions as shown in figure 5.8 have been used (denoted with ‘initial A’ in the legend).

Figure 5.11: comparison of experimental and computational data for III1a.
In [CUR96] effective chloride diffusion coefficients have been determined from the 16-year measurements for IIle, IIle and IIIla: 3.5·10^{-12}, 3.3·10^{-13} and 2.7·10^{-12} m²/s respectively. The basis of this analysis was probably linear diffusion of total chlorides (as % on cement mass). Realising that in general care should be taken in comparing parameters of different models, in this case a comparison between the calculated effective diffusion coefficients in [CUR96] and the values of $\kappa_i$ in the present analyses is possible. The first reason for this is that in the calculation of [CUR96] total chlorides are treated computationally as free chlorides. Secondly, the dimensional difference between free chloride content in [CUR96] (% on cement mass) and in the present analyses (kg Cl⁻ per m³ water) does not affect the value of the chloride diffusion coefficient, if the cement is uniformly distributed in the concrete and if the concrete is fully water saturated. Both conditions are not completely satisfied, but this deviation can be neglected. Then, a comparison between the chloride diffusion coefficients in [CUR96] and the values of $\kappa_i$ in the present analyses yields that in the case of specimens IIle and IIIla the former values are lower than the latter and that in the case of specimen IIle the two values are identical. The explanation for the results of this comparison must be sought in chloride binding. Chloride binding slows down the ingress of free chloride ions, but the amount of (instantaneously) bound chloride adds up to the total chloride content. If – hypothetically – the amount of bound chloride would not add up to the total chloride content, then the effective diffusion coefficients in [CUR96] had to be lower than the values of $\kappa_i$. But, of course, the total chloride content is the sum of free and bound chlorides, so then the relative influence of chloride conductivity and binding parameters determines the total chloride profile (see equation 6.1). In view of the concrete composition (see table 5.5) it is strange that the effective chloride diffusion coefficient in [CUR96] for IIIla is lower than the one for IIle. This is not the case for the saturated chloride conductivities $\kappa_i$ in the present computations.

Curing period

Some advanced computations have been performed for experiments IIle. To investigate the effect of the curing conditions, the internal moisture conditions at the moment of submersion have been computed rather than assumed from [CUR96]. However, the curing conditions have been exaggerated in order to be able to observe significant effects: curing at 20 °C and 40 % relative humidity during 4 weeks. The initial moisture condition for the 4-week curing period was a uniform distribution of $H=0.9$. Then, at the end of the curing period, the initial moisture condition for the actual exposure to sea-water is established. The results of the computation for IIle with this initial condition is shown in figure 5.12. This computation will be a reference for 2 carbonation analyses (carbonation A and B), to
be explained in the following paragraphs. The used models and additional model parameters will already be mentioned in table 5.12. Some solution parameters are different from the ones in table 5.11; they are given in table 5.13.

Table 5.12: deployed moisture and chloride models for further analysis of IIIe.

<table>
<thead>
<tr>
<th>moisture model</th>
<th>reference</th>
<th>carbonation A</th>
<th>carbonation B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>additional parameters</td>
<td>none</td>
<td>$\varphi_3=0.7$, $\varphi_4=20$</td>
<td>$\varphi_3=0.7$, $\varphi_4=1.5$, $\varphi_5=0.7$, $\varphi_6=20$</td>
</tr>
</tbody>
</table>

Table 5.13: modified solution parameters in the additional simulations of experiments IIIe. The other parameters are equal to the ones listed in table 5.11. The time span is 16 years plus 28 days.

<table>
<thead>
<tr>
<th></th>
<th>reference</th>
<th>carbonation A</th>
<th>carbonation B</th>
</tr>
</thead>
<tbody>
<tr>
<td>time span</td>
<td>5868</td>
<td>5868, 5868</td>
<td>5868</td>
</tr>
<tr>
<td>step-size</td>
<td>1, 10, 73</td>
<td>1, 10, 73, 10, 73</td>
<td>0.10, 1, 0.33, 1, 10, 73</td>
</tr>
<tr>
<td>steps</td>
<td>43, 35, 75</td>
<td>43, 35, 75, 30, 25, 6, 13, 35, 75</td>
<td></td>
</tr>
<tr>
<td>initial</td>
<td>H=0.2</td>
<td>H=0.9</td>
<td>H=0.9</td>
</tr>
<tr>
<td>boundaries until 28 days</td>
<td>H=0.4</td>
<td>H=0.4</td>
<td>H=0.4</td>
</tr>
<tr>
<td>moisture chloride</td>
<td>$C_{\text{con}}=0$</td>
<td>$C_{\text{con}}=0$</td>
<td>$C_{\text{con}}=0$</td>
</tr>
<tr>
<td>boundaries from 28 days</td>
<td>H=1.00</td>
<td>H=1.00</td>
<td>H=1.00</td>
</tr>
<tr>
<td>moisture chloride</td>
<td>$C_{\text{con}}=20$</td>
<td>$C_{\text{con}}=20$</td>
<td>$C_{\text{con}}=20$</td>
</tr>
</tbody>
</table>

The chloride penetration is clearly deeper after 2 years due to the enhanced suction, but this effect gradually disappears after 8 and 16 years. Although the deviation with respect to the 2 year measurements has become less, the 16 year measurements near the surface are still not matched. Next, the effect of the release of bound chloride ions due to carbonation is investigated with chloride model 3. During the 4-week curing period the outer 10 elements carbonate; this corresponds to a carbonation depth of 3.3 mm. So, from the start of the submersion on, there cannot be any bound chlorides in this carbonated zone. Consequently, both diffusion and convection of chlorides (due to the suction) are more effective, since binding damps the chloride gradients which drive the diffusive chloride flow and no free chlorides are taken out of the convective flow to become bound chlorides in this zone. But, as can be observed in figure 5.13, the effect of this enhanced diffusion and convection is relatively small, at least after 2 years of exposure. Characteristic is the drop of the total chloride content in the carbonated zone; this confirms experimental findings by
With a saturated moisture content of 124 kg/m³, a free chloride concentration of 20 kg/m³ and a cement content of 420 kg/m³, the surface chloride content becomes 0.6 % on cement mass. The solution parameters in this computation (in the tables referred to as ‘carbonation A’) are identical to the ones used in the previous (reference) computation, just chloride model 3 (with additional parameters $\varphi_3=0.7$ and $\varphi_4=20$) has been used instead of chloride model 2.

**Figure 5.12:** comparison of experimental and computational data for l11e. The initial conditions for this computation have been obtained by computing the moisture potential distribution after a 4 week exposure to 293 K and 40 % relative humidity (denoted with ‘initial B’ in the legend).

**Figure 5.13:** effect of absence of chloride binding in the carbonated zone (3.3 mm). Due to the absence of chloride binding in the carbonated zone chloride diffusion and convection are slightly increased.
Finally, an analysis is performed with the two carbonation models: moisture model 4 and chloride model 3 ("carbonation B"). It is assumed that in the carbonated zone the moisture content decreases 30%, while the moisture conductivity increases 50% [NGA97][BIU96]. When the moisture content decreases, then also the chloride conductivity is reduced, since the latter is scaled linearly with the moisture content (see equation 3.131). The consequence of the greater moisture conductivity after carbonation is firstly that during the 28-day curing period the carbonation depth becomes greater: the outer 13½ elements have been carbonated now, corresponding to a carbonation depth of 4.5 mm. Secondly, the suction at first contact with sea-water is increased due to this higher moisture conductivity. Figure 5.14 shows that differences with the 'carbonation A' analysis mainly appear at the surfaces (near 0 and 150 mm). The moisture content at the surface is reduced to 87 kg/m³, which makes the total chloride content 0.4% on cement mass. The greater difference between diffusion and convection of chloride ions probably causes the more pronounced growth of the peaks over time in case of carbonation analysis B. Although the peaks after 16 years are higher in analysis A than in B, it must be noted that also the surface chloride content is higher in analysis A than in B. The overall match between experimental and computational data is good, however the computed curves do not capture the measured total chloride contents near the surface at 16 years.

Figure 5.14: resulting chloride profiles from a full carbonation analysis. In the carbonated zone (4.5 mm) the moisture content and the chloride ion conductivity are less than in the uncarbonated zone, while the reverse applies for the moisture conductivity. Moreover, there are no bound chlorides in the carbonated zone.

---

1 The predefined carbonation threshold has been surpassed in the outer Gauss point of the 14th element.
5.3 Drying-wetting case

In the experimental work of Taheri [TAH98] concrete beams and cubes were exposed to chlorides, while the ambient temperature and humidity varied. As temperature and humidity (wet and dry) were controlled during the experiments, and the total chloride content was determined afterwards, this experimental work is suitable for comparison with the results of the computational model [MEI02b].

The concrete beams (6 m long, 0.75 m high and 0.4 m wide) and cubes (0.15 m edge) were subjected to 87 exposure cycles in total. Every cycle lasted 48 hours. Two different concrete mixtures were used: one with Portland cement and one with blastfurnace slag cement. Only the experiments with the Portland cement concrete are simulated here, the composition of which is given in table 5.14. The concrete beams and cubes were dried during the first 42 hours of a cycle and next wetted with salty water during the remaining 6 hours. The concentration of NaCl in the water was 50 g/l, corresponding to a 3% chloride solution. In set 1 of the experiments the ambient temperature varied sinusoidally between 293 and 333 K during the drying period, while in set 3 the temperature remained constant at 293 K. The periodical time of the sine was 12 hours. It is well-known that these drying-wetting cycles can
lead to rapid chloride penetration in practice. Taheri showed that the imposed temperature variation during the drying period even enhanced the chloride ingress rate (by comparing set 3 to set 1)\(^2\).

**Table 5.14: concrete composition in the experiments of [TAH98].**

<table>
<thead>
<tr>
<th>amount</th>
<th>unit</th>
<th>component</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>kg/m(^3)</td>
<td>ordinary Portland cement (CEM I 32.5 R)</td>
</tr>
<tr>
<td>189</td>
<td>kg/m(^3)</td>
<td>water</td>
</tr>
<tr>
<td>826</td>
<td>kg/m(^3)</td>
<td>fine aggregates</td>
</tr>
<tr>
<td>1068</td>
<td>kg/m(^3)</td>
<td>coarse aggregates</td>
</tr>
</tbody>
</table>

The ambient relative humidity \(h\) was controlled only to the extent that during the first 42 hours of an exposure cycle it was lower than 100 \%, and during the last 6 hours of an exposure cycle (the wetting phase) equal to 100 \%. Unfortunately, no measurements have been performed to determine the exact values of the ambient relative humidity during the drying phase. In the case of set 3 of the experiments (with constant temperature during the drying phase) the ambient relative humidity is estimated at 65 \%. In the case of set 1 the temperature variation will have caused a variation of ambient relative humidity, which may have fluctuated from 65 \% down to 9 \%. The corresponding calculations are shown in table 5.15. In these calculations the starting point is the environmental condition: 65 \% relative humidity at 293 K. At this temperature the saturation pressure is 2.34·10\(^3\) Pa, which gives a partial pressure of 1.52·10\(^3\) Pa and hence, with the law of Boyle-Gay-Lussac, a molar density of 0.624 mol/m\(^3\). This molar density (or absolute humidity) is assumed to be constant for other temperatures.

**Table 5.15: calculation of humidity variation due to temperature variation**

<table>
<thead>
<tr>
<th>(T) [K]</th>
<th>(p_r) [Pa]</th>
<th>(p) [Pa]</th>
<th>(h) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>2.34·10(^3)</td>
<td>1.52·10(^3)</td>
<td>65</td>
</tr>
<tr>
<td>303</td>
<td>4.24·10(^3)</td>
<td>1.57·10(^3)</td>
<td>37</td>
</tr>
<tr>
<td>313</td>
<td>7.38·10(^3)</td>
<td>1.62·10(^3)</td>
<td>22</td>
</tr>
<tr>
<td>323</td>
<td>1.23·10(^4)</td>
<td>1.68·10(^3)</td>
<td>14</td>
</tr>
<tr>
<td>333</td>
<td>1.99·10(^4)</td>
<td>1.73·10(^3)</td>
<td>9</td>
</tr>
</tbody>
</table>

For the computations the temperature variation in set 1 has been limited to the range 293 – 323 K, instead of 293 – 333 K. The reason for this deviation is the presence of asymptotes in material function \(c_{21}\) for the combination of elevated temperatures and low humidities. The asymptotes can be calculated by putting the denominator of equation 3.117 equal to zero and next transcribing to an explicit form for either \(T\) or

\(^2\) In set 2 of the experiments the cement type was blast furnace slag cement. This set is not simulated here.
H. With $H_{\text{asym}}$ and $T_{\text{asym}}$ as the moisture potential and temperature respectively that create an asymptote in $c_{21}$, the explicit form for $T_{\text{asym}}$ is:

$$T_{\text{asym}} = -\frac{\eta_3 + 2\eta_1 H_{\text{asym}}}{\eta_4 + 2\eta_6 H_{\text{asym}}}$$

(5.10)

For this case (with $\alpha=0.7$ and $\zeta_1=0.59$) the above formula has been depicted in figure 5.16 (for $\eta_3$ to $\eta_6$ see table 5.18). It appears that asymptotes only occur at moisture potentials lower than 0.46 and at temperatures higher than 326 K. It should be noted that moisture potentials lower than 0.36 and temperatures higher than 343 K are outside the ranges defined in [ROE89]. It can be observed in figure 5.16 that for $T=333$ K asymptotes would be encountered at $H=0.30$ and at $H=0.38$. These encounters would surely happen with the humidity variation in set 1 as calculated in table 5.15. Obviously, asymptotes are undesirable from a computational point of view.

The temperature boundary condition for set 1 has been defined as a linear variation between 293 and 323 K for the first 36 hours of a cycle (see figure 5.17). During the following 6 hours the boundary temperature rises linearly from 293 to 313 K and back, and remains constant at 293 K during the wetting phase (also 6 hours). For the computations of this set the moisture potential at the exposed surface varies linearly between 1 and 0.14. In set 3 the transition from the drying to the wetting phase and vice versa has been given a 1.5 hour allowance numerically, i.e. the boundary moisture potential changes (linearly) in 1.5 hour from 0.65 to 1.0 before a wetting period and from 1.0 to 0.65 after a wetting period. The model input for the estimated experimental moisture conditions at the concrete surface are shown in figure 5.18.

It is assumed that at the exposed surface of the concrete the free chloride concentration (in kg Cl$\text{^{-1}}$ per m$^3$ of pure water) equals the chloride concentration in the water which this surface is in contact with. As the latter concentration is 50 NaCl g/l, the free chloride concentration becomes 30.3 kg Cl$\text{^{-1}}$ per m$^3$ of pure water. Furthermore, as already explained in section 3.4.3, instantaneous binding is assumed. Consequently, an amount of bound chlorides is present at the surface from the beginning of the computations. The degree of hydration $\alpha$ of the samples is
estimated at 0.7, since the age of the concrete at the beginning of the experiments was 56 days. With a cement content $\zeta_2$ of 320 kg/m³ and equation 3.34 it follows then that $\xi_1 = 280$ kg/m³.

![Graph 5.17: experimental temperature variation at the concrete surface in set 1 and the applied temperature boundary condition (numerical).](image)

![Graph 5.18: moisture boundary conditions used in the computations for set 1 and set 3.](image)

The chloride adsorption measurements of [TAN93] can be roughly approximated with a fixed ratio between bound and free chlorides. With such linear binding and $\xi_2 = 956$ kg/m³ ($\xi_3 = 0$ in the case of linear binding) the amount of bound chloride is 0.0317 kg Cl⁻ per kg cement gel. The bound chloride content as a percentage of the cement mass is 2.8%. Since the free chloride ion concentration is fixed during the wetting phase and $\xi_2$ is a constant, this amount of bound chlorides remains constant at the boundary during the wetting phase. The free chloride content at the surface as a percentage of the cement mass, also remains constant during the wetting phase due to the prescribed constant moisture potential. As the value of this potential is 1, which corresponds in this case at 293 K to a moisture content $W$ of 151 kg/m³, the free chloride content then equals 1.4%.

It is essential to recognise that during the drying phase the chloride flux through the surface equals 0. Otherwise, some kind of leaching would occur, which is impossible in the case of drying. This implies that at the transition from wetting phase to drying phase the boundary condition for the chloride balance changes from prescribed potential to prescribed flux. It would be a mistake to put the chloride potential equal to 0 at the boundary during the drying phase, since this obviously reduces the surface chloride content to 0, but also creates an outflux of chlorides due to the
imposed chloride gradient. It has to be acknowledged that even the outermost node on the mesh represents a piece of concrete and not its environment.

The activation energy of the diffusion process $\lambda_1$ and the corresponding reference temperature $\lambda_2$ have been obtained from [SAE93], and moisture model parameters $\theta_2$, $\theta_3$ and $\theta_4$ from [BAZ72]. The ensemble of parameters $\theta_1$ (saturated moisture conductivity), $\kappa_1$ (saturated chloride conductivity) and $\xi_2$ (ratio between free and bound chloride ions) has been chosen such to provide a best (visual) fit of the measured total chloride profiles after both 18 and 87 exposure cycles, both for the case of constant and varying temperature. It is emphasized that the heat and moisture boundary conditions are different in the constant temperature and varying temperature case respectively (see table 5.19), while all material parameters are the same in the two cases (see tables 5.16 to 5.18). Both the experiments with set 1 and set 3 have been analysed with heat model 0, moisture model 1 and chloride model 2.

Results and discussion

First, the numerical solutions for set 3 (constant temperature) are presented. Figure 5.19 shows the gradual build-up of the chloride content during the first 3 exposure cycles. During the wetting phase chloride is sucked into the concrete and next, during the drying phase, it is redistributed. In the latter phase the chloride ions cannot leave the concrete. On the one hand the chloride ions are forced to diffuse inwards, but on the other hand the outward moisture movement due to the drying drags the chloride ions back to the surface (see also [NIL00]). So, diffusive and convective forces are in competition during the drying phase. However, at the left boundary, where the total chloride flux is prescribed to be zero, the diffusive and convective chloride flux must balance each other. This explains the small negative slope of the free chloride graph at $x=0$ mm: the resulting inward diffusive flux is fully compensated by an outward convective flux at this point. This outward convective flux obviously exists, since both a positive moisture potential gradient and a certain free chloride concentration are present at $x=0$ mm during the drying phase (excepting the first drying phase, when the chlorides have not been introduced yet). It can also be observed in figure 5.19 that at the end of the second wetting phase ($t=4$ days) the free chloride concentration slightly increases just behind $x=0$ mm. This seems strange since a fixed boundary free chloride concentration has been applied during the preceding wetting phase. Indeed, this observation cannot be explained by pure diffusion, neither by pure convection. However, the definition of the convective flux leads to this behaviour. This issue will be addressed for the simulation of set 1, in which the effect is more pronounced (see figure 5.23).
Table 5.16: values of capacities, conductivities and sources in the computations. Lists of parameters enclosed in parentheses indicate that the value of the material function depends on these parameters (see section 3.4 and tables 5.17 and 5.18).

<table>
<thead>
<tr>
<th>Capacities</th>
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<tbody>
<tr>
<td>( c_{11} )</td>
<td>( 2.40 \times 10^6 )</td>
<td>Jm(^{-3})K(^{-1})</td>
</tr>
<tr>
<td>( c_{12} )</td>
<td>0</td>
<td>Jm(^{-3})</td>
</tr>
<tr>
<td>( c_{13} )</td>
<td>0</td>
<td>Jkg(^{-1})</td>
</tr>
<tr>
<td>( c_{21} )</td>
<td>((\eta_{1}, \eta_{2}, \eta_{3}, \eta_{4}, \eta_{5}))</td>
<td>K(^{-1})</td>
</tr>
<tr>
<td>( c_{22} )</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>( c_{23} )</td>
<td>0</td>
<td>m(^{3})kg(^{-1})</td>
</tr>
<tr>
<td>( c_{31} )</td>
<td>((\alpha_{1}, \alpha_{2}, \alpha_{3}))</td>
<td>kgm(^{-3})K (^{1})</td>
</tr>
<tr>
<td>( c_{32} )</td>
<td>((\alpha_{1}, \alpha_{2}, \alpha_{3}, \theta_{1}, \theta_{2}, \theta_{3}, \theta_{4}))</td>
<td>kgm(^{-3})</td>
</tr>
<tr>
<td>( c_{33} )</td>
<td>((\alpha_{1}, \alpha_{2}, \alpha_{3}, \theta_{1}, \theta_{2}, \theta_{3}, \theta_{4}, \lambda_{1}, \lambda_{2}))</td>
<td></td>
</tr>
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<table>
<thead>
<tr>
<th>Conductivities</th>
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</thead>
<tbody>
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<td>( k_{11} )</td>
<td>( 2.40 )</td>
<td>JK(^{-1})s(^{-1})m(^{-1})</td>
</tr>
<tr>
<td>( k_{12} )</td>
<td>0</td>
<td>Js(^{-1})m(^{-1})</td>
</tr>
<tr>
<td>( k_{13} )</td>
<td>0</td>
<td>Jm(^{2})s(^{-1})kg(^{-1})</td>
</tr>
<tr>
<td>( k_{21} )</td>
<td>0</td>
<td>m(^{3})K(^{-1})s(^{-1})</td>
</tr>
<tr>
<td>( k_{22} )</td>
<td>((\theta_{1}, \theta_{2}, \theta_{3}, \theta_{4}))</td>
<td>m(^{2})s(^{-1})</td>
</tr>
<tr>
<td>( k_{23} )</td>
<td>0</td>
<td>m(^{3})s(^{-1})kg(^{-1})</td>
</tr>
<tr>
<td>( k_{31} )</td>
<td>0</td>
<td>kgK(^{-1})s(^{-1})m(^{-1})</td>
</tr>
<tr>
<td>( k_{32} )</td>
<td>((\alpha_{1}, \alpha_{2}, \alpha_{3}, \theta_{1}, \theta_{2}, \theta_{3}, \theta_{4}))</td>
<td>kgs(^{-1})m(^{-1})</td>
</tr>
<tr>
<td>( k_{33} )</td>
<td>((\alpha_{1}, \alpha_{2}, \alpha_{3}, \theta_{1}, \theta_{2}, \theta_{3}, \theta_{4}, \lambda_{1}, \lambda_{2}))</td>
<td>m(^{2})s(^{-1})</td>
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<table>
<thead>
<tr>
<th>Sources</th>
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<tbody>
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<td>( f_{1} )</td>
<td>0</td>
<td>Jm(^{-3})s(^{-1})</td>
</tr>
<tr>
<td>( f_{2} )</td>
<td>0</td>
<td>s(^{-1})</td>
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<tr>
<td>( f_{3} )</td>
<td>0</td>
<td>kgm(^{-3})s(^{-1})</td>
</tr>
</tbody>
</table>

Table 5.17: parameters of the moisture and chloride model. Moisture model 1 and chloride model 2 have been deployed.

<table>
<thead>
<tr>
<th>Moisture</th>
<th>Chloride</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>0.7</td>
<td>( \kappa_{1} )</td>
<td>1.00 \times 10^{-11}</td>
</tr>
<tr>
<td>( \zeta_{1} )</td>
<td>0.59</td>
<td>( \kappa_{2} )</td>
<td>0</td>
</tr>
<tr>
<td>( \zeta_{2} )</td>
<td>320</td>
<td>( \lambda_{1} )</td>
<td>32.0 \times 10^{3}</td>
</tr>
<tr>
<td>( \theta_{1} )</td>
<td>5.00 \times 10^{-11}</td>
<td>( \lambda_{2} )</td>
<td>296</td>
</tr>
<tr>
<td>( \theta_{2} )</td>
<td>0.05</td>
<td>( \xi_{1} )</td>
<td>280</td>
</tr>
<tr>
<td>( \theta_{3} )</td>
<td>0.7</td>
<td>( \xi_{2} )</td>
<td>956</td>
</tr>
<tr>
<td>( \theta_{4} )</td>
<td>4</td>
<td>( \xi_{3} )</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 5.18: intermediate moisture model parameters derived with $\alpha$ and $\xi_i$ from Table 5.17.

<table>
<thead>
<tr>
<th>$\eta_1$</th>
<th>$\eta_2$</th>
<th>$\eta_3$</th>
<th>$\eta_4$</th>
<th>$\eta_5$</th>
<th>$\eta_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0 \leq H \leq 0.35$</td>
<td>$0.35 &lt; H &lt; 0.89$</td>
<td>$0.89 \leq H \leq 1.00$</td>
<td>$K^{-1}$</td>
<td>$K^{-1}$</td>
<td>$K^{-1}$</td>
</tr>
</tbody>
</table>

Table 5.19: solution parameters in the simulation of the experiments. The left chloride boundary condition alternates between a prescribed flux ($q_c=0 \text{ kgm}^2\text{s}^{-1}$) during the drying phase and a prescribed free chloride concentration ($C_{\text{free}}=30.3 \text{ kgm}^3$) during the wetting phase.

<table>
<thead>
<tr>
<th>space</th>
<th>time</th>
</tr>
</thead>
<tbody>
<tr>
<td>length</td>
<td>span</td>
</tr>
<tr>
<td>element-size</td>
<td>step-size</td>
</tr>
<tr>
<td>elements</td>
<td>steps per cycle</td>
</tr>
<tr>
<td>element-type</td>
<td>scheme</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>initial conditions</th>
<th>boundary conditions</th>
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</thead>
<tbody>
<tr>
<td>left</td>
<td>right</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>iterations</th>
<th>tolerance</th>
<th>scheme</th>
</tr>
</thead>
</table>

After 87 cycles a full comparison between experimental and numerical data can be made; this is shown in Figure 5.20. The agreement between the measured and computed chloride profiles is fairly good, except for the measurements at a depth of 3 mm (36 days). Maybe this can be explained by the effect of carbonation. The outer zone will be carbonated during the drying period. Carbonation decreases the binding capacity of the cement stone substantially. This causes a peak in the chloride profile as shown in [TUU82].

Another cause of the lower surface chloride contents can be the so-called skin-effect: a relatively high cement content in the outer layer of concrete due to the wall effect. The consequences of the skin-effect are twofold. Firstly, as chloride ions migrate exclusively through the hardened cement paste phase in concrete, the transport medium for chloride ions is heterogeneous in the sense that transport of chlorides is more efficient in the surface layer than deeper inside the concrete due to the higher cement content. Secondly, as the mass of chlorides is expressed with respect to the
mass of cement, the same amount of chloride ions in the surface layer and deeper inside the concrete yields lower total chloride contents in the surface layer than behind that layer. The two consequences of the skin-effect together may yield lower total chloride contents in the surface zone. The moisture profiles during the first three cycles are depicted in figure 5.21.

![Diagram](image1.png)

Figure 5.19: gradual build-up of total chloride content (left) and free chloride ion concentration (right) in the simulation of set 3 (constant temperature). The even days are just at the end of a wetting period, while the odd days are approximately in the middle of a drying period. Clearly, the chloride ions are redistributed in the drying period.

![Diagram](image2.png)

Figure 5.20: comparison of the numerical solution to experimental data of Tahei for set 3 (constant temperature) [TAH98]. The numerical data at 37 and 175 days are displayed instead of the ones at 36 and 174 days to allow for some redistribution of chloride ions after the last wetting period. The chloride measurements have probably not been performed directly after the last wetting period either.
Chloride binding can also be expressed as the ratio between the second and first term on the right-hand-side of equation 3.139. This ratio is called here macroscopic binding ratio $b_m$:

$$b_m = \frac{\rho \cdot \xi \cdot C_{\text{bound}}}{W \cdot C_{\text{free}}}$$  \hspace{1cm} (5.11)

The adjective ‘macroscopic’ refers to the fact that bound and free chloride contents are in this way expressed with respect to the volume of concrete (instead of mass of cement gel and volume of pore water respectively). Note that this binding ratio is not fixed (as opposed to $\xi_c$) because of the dependence on the moisture content $W$. The values of the macroscopic binding ratio at three different times are shown in figure 5.22. It appears that this ratio between bound and free chlorides is initially around 3; while the overall drying progresses, it increases to a maximum of around 5.

Next, the analysis of set 1 of the experiments (varying temperature) is presented. The build-up of chloride content during the first three cycles is shown in figure 5.23. The slopes of the free chloride concentration graphs at $x=0$ mm are now positive for $t=3$ and $t=5$ days (in the drying phase). This seems to cause an outflow of chloride ions. However, the applied boundary condition ($q_c=0$ kgm$^{-2}$s$^{-1}$ at $x=0$ mm during the drying phase) is satisfied by an additional inward convective flux. The moisture potential gradient that causes this inward convective flux can be read from figure 5.24. The peaks near the surface reveal the severe drying conditions: the strong suction after the drying period leads to accumulation of chlorides in the outer
millimetre (during the wetting period). However, the mechanism behind this phenomenon and the free chloride concentrations higher than the applied boundary condition during the wetting phase ($C_{\text{free}} = 30.3 \text{ kgm}^{-3}$) need further explanation, as already mentioned earlier.

![Graphs showing total chloride content and free chloride ion concentration over time.](image)

*Figure 5.23: Gradual build-up of total chloride content (left) and free chloride ion concentration (right) in the simulation of set 1 (varying temperature). The even days are just at the end of a wetting period, while the odd days are approximately in the middle of a drying period. Clearly, the chloride ions are redistributed in the drying period.*

Accumulation of chlorides can only happen if the influx of free chloride ions into a reference volume is greater than the outflux out of that volume. There are two possible chloride ion fluxes: a diffusive and a convective flux. As the contribution of diffusive fluxes to this accumulation is probably negligible, attention is now paid to the convective fluxes in the surface zone. In figure 5.23 it can be seen that the peak in the free chloride concentration profile occurs within the outer mm at $t=2$ and $t=4$ days. Figure 5.24 shows that at these points in time the moisture potential gradient is rather constant in the outer mm. So, this would suggest that there cannot be a greater convective influx than outflux of chloride ions. However, there is another factor in the definition of the convective chloride ion flux: the derivative of the moisture content $W$ with respect to the moisture potential $H$. This factor converts (by approximation) the pseudo-moisture flux in ms$^{-1}$ to a real moisture flux in kgm$^{-2}$s$^{-1}$ and also selects (again by approximation) the liquid-component of the moisture flow (as opposed to the vapour-component, which does not transport chloride ions). The value of this factor changes drastically around $H=0.9$, as can be read from figure 5.25. This turning point is located at approximately $x=0.4$ mm for $t=2$ and $t=4$ days, so that the unbalance of convective chloride ion fluxes must take place there. Moreover, the slope $\partial W/\partial H$ is more positive for $H>0.9$ than for $H<0.9$, so that
indeed the convective flux up to a depth of 0.4 mm is greater than the one beyond that point. This completes the explanation of the peaks in the free chloride ion concentration profiles. Note that this mechanism is much less strong for $H<0.9$.

**Figure 5.24**: computed moisture potential profiles during the first days of exposure in the simulation of set 1. The negative slopes at $x=0$ mm cause inward convective chloride ion flows.

**Figure 5.25**: moisture desorption isotherm for $\alpha=0.7$, $C_1=0.59$, $C_2=320$ kg/m$^3$ and $T=293$ K. The drastic change of slope around $H=0.9$ causes a significant change of the convective chloride ion flux for a constant moisture potential gradient.

Figure 5.26 shows the comparison between experimental and numerical data after 18 and 87 exposure cycles. The match here is less good than for constant temperature. The computed curves lie somewhat behind the experimental data; carbonation (not included in the analysis so far) may be the cause of this. Again, the wall effect may be held responsible for the relatively low measured chloride contents at a depth of 3 mm (36 days). Some moisture profiles during the first three cycles are plotted in figure 5.27. The moisture fluctuations near the surface are clearly larger than in the case of constant temperature. Also the drying deeper inside proceeds more rapidly. Due to this relatively quick drying the average macroscopic binding ratio rises rapidly from 3 to 8 approximately, as shown in figure 5.28. In figure 5.29 several moisture profiles are depicted for both set 1 and 3.

The numerical and experimental results at constant and variable temperature are compared in figures 5.30 and 5.31. After 18 exposure cycles the temperature effect is hardly noticeable in both simulation and experiments. However, after 87 cycles the experiments show that in case of variable (and elevated) temperature the chloride penetration is considerably deeper than in case of constant temperature, whereas this difference is much smaller in the simulation. Probably the imposed drying conditions in the simulation of the drying-wetting case at variable temperature (between $h_a=14$
% at 323 K and \( h_r = 65 \% \) at 293 K) were too severe and counteracted chloride ingress to a large extend.

![Graph showing chloride content vs depth](image)

**Figure 5.26:** comparison of the numerical solution to experimental data of Taheiri for set 1 (varying temperature) [TAH98]. The numerical data at 37 and 175 days are displayed instead of the ones at 36 and 174 days to allow for some redistribution of chloride ions after the last wetting period. The chloride measurements have probably not been performed directly after the last wetting period either.

![Graph showing moisture content vs depth](image)

**Figure 5.27:** development of the moisture profile in the simulation of set 1 (varying temperature). There are large moisture fluctuations at the exposed surface; deeper inside the concrete the moisture content decreases gradually.

![Graph showing macroscopic binding ratio vs depth](image)

**Figure 5.28:** macroscopic binding ratio in the simulation of set 1 (varying temperature). While the sample dries out, this ratio increases quickly.
Figure 5.29: computed moisture profiles in the simulation of set 1 (varying temperature, right) and 3 (constant temperature, left). The drying in the simulation of set 1 is much faster than in the simulation of set 3.

Figure 5.30: comparison of the computed total chloride profiles at constant and variable temperature. Elevated and variable temperatures enhance chloride ingress only slightly, probably due to the severe drying conditions.

The accumulation of chloride in the mesh proceeds step-wise. During the wetting phase a certain amount of chlorides comes into the system and this amount remains constant during the next drying phase. Then, in the following wetting phase, an additional dose of chloride is taken in, which is conserved again in the mesh. This behaviour can be read from figure 5.32. Actually, this figure shows that the total chloride content in the mesh slightly decreases during the drying phase. The cause of
this deviation is numerical accuracy. Figure 5.32 also shows the moisture loss. During the drying phase an amount of moisture leaves the mesh and during the wetting phase an other amount of moisture enters the mesh. The latter amount is generally smaller than the former, so that there is a net moisture loss over time.

\[ \begin{align*}
18 \text{ cycles, } T &= 293 \, \text{K} \\
18 \text{ cycles, } 293 < T < 333 \, \text{K} \\
87 \text{ cycles, } T &= 293 \, \text{K} \\
87 \text{ cycles, } 293 < T < 333 \, \text{K}
\end{align*} \]

Figure 5.31: comparison of measured total chloride profiles at constant and variable temperature [TAH98]. A clear temperature effect can be observed after 87 exposure cycles.

\[ \begin{align*}
\text{total chloride content [g/m}^3\text{]} &
\begin{array}{c}
\text{T = 293 K} \\
293 < T < 323 \, \text{K}
\end{array}
\end{align*} \]

\[ \begin{align*}
\text{total moisture content [g/m}^3\text{]} &
\begin{array}{c}
\text{T = 293 K} \\
293 < T < 323 \, \text{K}
\end{array}
\end{align*} \]

Figure 5.32: computed accumulation of chloride (left) and moisture loss (right) in the samples during the first 10 days of exposure. The left figure clearly reflects the step-wise character of the chloride exposure. The right figure shows the moisture loss during the long drying period (42 hours) followed by a small water uptake in the short wetting period (6 hours).
It can be observed in figure 5.33 that the temperature variation causes a bigger chloride uptake combined with a faster drying process. Moreover, a quasi-stationary moisture state is reached after approximately 50 days in the simulation of set 1 (varying temperature). Clearly, this phenomenon is related to the mesh size (75 mm). While the mesh size is correct for the simulation of the concrete cubes (with 150 mm edges and symmetrical conditions), it should probably be increased for the simulation of the beams (with a depth of 750 mm).

![Graph showing chloride and moisture content over time with varying temperatures](image)

*Figure 5.33: computed accumulation of chloride and moisture loss in the samples. The temperature variation causes a higher accumulation of chloride and severe drying. A quasi-stationary moisture state is reached after approximately 50 days for the analysis with varying temperature.*

**Carbonation**

In addition, the experiments with constant temperature (set 3) have been analysed with the carbonation models (moisture model 4 and chloride model 3). The pore structure of concrete changes due to carbonation, and in the case of Portland cement the pores become wider. Consequently, the moisture capacity and conductivity decrease [HOU92][KRP93][REL99][CLA99]. It is assumed that this decrease is 20%, which leads to the carbonation parameters $\varphi_1 = 0.8$ and $\varphi_2 = 0.8$. Note that as a consequence of the scaling of the chloride ion conductivity with the moisture content, this conductivity decreases in the case of carbonation, and that due to the coupling of the convective chloride ion flux to the moisture flux, the former flux is reduced in the carbonated zone. A more aggressive drying situation has been created in order to surpass the carbonation threshold ($H = 0.6$) in some elements: the moisture boundary condition has therefore been lowered to $H = 0.4$. Furthermore, the mesh and time marching were refined in order to capture the imposed changes. The
saturated moisture conductivity $\theta_1$ and chloride conductivity $\kappa_1$ have been adjusted with the explicit intention to provide a good (visual) fit of the measured data in carbonation analysis A. Carbonation analyses B and C demonstrate the partial effects of the release of bound chloride ions and changed moisture properties respectively. Additional and modified parameters are listed in tables 5.20 and 5.21. Figure 5.34 shows the comparison between the measured total chloride contents and the results of these carbonation analyses (A, B and C). In this figure also a reference curve is plotted, which represents a non-carbonation analysis with for the rest parameters equal to the ones in carbonation analyses A, B and C.

**Table 5.20: moisture and chloride model combinations and additional parameters for carbonation analyses A, B and C of the experiments with constant temperature.**

<table>
<thead>
<tr>
<th>moisture model</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>chloride model</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\phi_1$</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>$\phi_2$</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>$\phi_3$</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>$\phi_4$</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

**Table 5.21: modified parameters for carbonation analyses A, B and C, as well as for the carbonation reference curve. The mesh was refined in the outer 10 mm.**

<table>
<thead>
<tr>
<th></th>
<th>$3.47.10^{-12}$ m²/s</th>
<th>$3.79.10^{-12}$ m²/s</th>
<th>0.4</th>
<th>100-325 mm</th>
<th>15, 90, 15 minutes</th>
<th>6, 25, 30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\kappa_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H$ at left boundary (drying phase)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>element-size</td>
<td>0.1, 0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>elements</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>timestep-size</td>
<td>15, 90, 15 minutes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>time steps per cycle</td>
<td>6, 25, 30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The peak in carbonation analysis A corresponds well to experimental observations by [TUU82] and model results of [AND95]. Carbonation progresses during exposure and eventually, after 175 days, the computed carbonated zone is 1.0 mm deep. Note that the peak in curve A, at a depth of 5.5 mm, is located behind the carbonation front. In carbonation analysis B only the effect of the release of bound chloride ions in the carbonated zone has been studied. The shape of curve B is similar to the one of curve A, however the peak is higher and located deeper (at 6.3 mm). As opposed to carbonation analysis A, the moisture capacity and conductivity are not reduced in carbonation analysis B, which yields a slight increase of the carbonated zone to 1.1 mm. Consequently, suction of the salt solution proceeds more rapidly in analysis B.
than in analysis A, which explains the horizontal and vertical shift of the peak. By comparing curves A and B to the reference curve, the impact of the small carbonated zone on the chloride profile becomes evident. The absence of chloride binding in the carbonated zone leads to relatively low total chloride contents in that zone. Moreover, as pointed out in section 5.2.2, diffusion and convection of chloride ions reach maximum efficiency there. This causes a steeper chloride front than in the reference curve, which can be observed in figure 5.34.

![Graph showing total chloride content vs. depth](image)

*Figure 5.34: comparison of measured total chloride contents in the experiments with constant temperature (set 3) and the results of carbonation analyses A, B and C. The release of bound chloride ions in the carbonated zone leads to the peaks in curves A and B.*

In carbonation analysis C the effect of the modified moisture storage and conductance has been investigated. The computed carbonated zone in analysis C after 175 days extends to a depth of 1.0 mm again. The reduced moisture conductivity decreases also the convective chloride ion flux during the wetting phase, as a consequence of which curve B lies under the reference curve. Figure 5.35 shows the total and free chloride profiles during the first days of exposure for carbonation analysis A. Clearly, the free chloride ion distribution is smooth, whereas in the total chloride profiles sharp transitions occur at the carbonation front at the end of the wetting phase ($t=2$ and $t=4$ days). The progress of the carbonation front can also be followed in figure 5.35: at $t=2$ days the carbonation depth is 0.3 mm and at $t=4$ days it has reached 0.4 mm. Although the outcome of the implemented carbonation models appears to correspond well to experimental results, their numerical stability needs further testing.
Figure 5.35: computed total (left) and free (right) chloride profiles during the first days of exposure in carbonation analysis A. The free chloride profiles are smooth, whereas the hooks in the total chloride profiles (at t=2 and t=4 days) indicate roughly the position of the carbonation front.
Chapter 6

SENSITIVITY AND CHLORIDE-MOISTURE COUPLINGS

The sensitivity of the model to various parameters is shown in this chapter. The computed results as presented in the previous chapter, have been subjected to these sensitivity analyses. The drying-wetting case further serves in a comparison between the developed model in this work and conventional pure diffusion approaches to chloride ingress into concrete, which enables an evaluation of the chloride-moisture couplings in the model as described in chapter 3.

6.1 Sensitivity analyses

The case studies from chapter 5 are subjected to sensitivity analyses in this section. In the moisture case a variation of the moisture transfer coefficient \( \chi_2 \) has been investigated. The saturated chloride ion conductivity \( \kappa_1 \) has been varied in the chloride case. In the drying-wetting case the influence has been tested of the degree of hydration \( \alpha \) in conjunction to chloride binding parameter \( \xi_1 \), the saturated moisture conductivity \( \Theta_1 \), the saturated chloride ion conductivity \( \kappa_1 \) and chloride binding parameters \( \xi_2 \) and \( \xi_3 \). The material parameters which were not involved in the sensitivity analyses, and the solution parameters were generally the same as in chapter 5; a deviation from the parameters in chapter 5 is mentioned explicitly.
6.1.1 Moisture transfer coefficient

The sensitivity analysis of the moisture transfer coefficient $\chi_2$ has been based on computation C from section 5.2.1. This was a fully linear computation with a Dirichlet boundary condition, which agreed well with measurements in [BIS02]. The moisture transfer coefficient is involved in the application of a Robbins boundary condition. The value of $\chi_2$ varied between $10^{-10}$ and $10^{-7}$ m/s [JAC99], while the environmental humidity $\psi_2$ was constant at 30%. The moisture conductivity $k_{22}$ in the computations was constant at $3.47 \times 10^{-11}$ m²/s, as in computation C in section 5.2.1. The resulting curves for the respective values of $\chi_2$ are shown in figure 6.1. For comparison the curve corresponding to the Dirichlet boundary condition is plotted as well; it can be considered to represent the moisture measurements.

![Figure 6.1: moisture loss curves for $\chi_2=1\times10^{-10}, 5\times10^{-10}$, $1\times10^{-9}, 5\times10^{-9}, 5\times10^{-8}$ and $1\times10^{-7}$ m/s (in grey from bottom to top). The upper curve (in black) corresponds to computation C in section 5.2.1, in which a Dirichlet boundary condition was applied. The moisture conductivity is the same for all curves.](image)

It appears that for $\chi_2=10^{-10}$ m/s there is hardly any moisture loss and that the curve corresponding to $\chi_2=10^{-7}$ m/s almost coincides with the curve corresponding to the Dirichlet boundary condition. In fact, curves corresponding to values of $\chi_2$ larger than $10^{-7}$ m/s would only further approach the curve corresponding to the Dirichlet boundary condition, so that the Robbins boundary condition transforms into a Dirichlet boundary condition.
6.1 sensitivity analyses

Data about the moisture transfer coefficient for concrete are often applicable to moisture models in which the potentials are different from the macroscopic pore humidity \([SBR69][JON94]\). Translation of these values to moisture transfer coefficients that can be used in the present work is not straightforward. From figure 6.1 it can then at least be concluded that the validity of values for \(\chi_2\) smaller than \(10^{-10}\) m/s and greater than \(10^{-7}\) m/s is questionable.

6.1.2 MOISTURE DIFFUSION

The influence of the value of the saturated moisture conductivity \(\theta_1\) on the results of the drying-wetting case for constant temperature as described in section 5.3, has been investigated. The finite element mesh has been refined from 5 to 10 elements per mm. In section 5.3 the value of \(\theta_1\) was \(5 \cdot 10^{-11}\) m²/s; here the results for the values \(1 \cdot 10^{-11}\) and \(1 \cdot 10^{-10}\) m²/s are presented. Figure 6.2 shows the three curves at 175 days, as well as the corresponding moisture profiles.

![Figure 6.2: total chloride (left) and moisture (right) profiles in the drying-wetting case for constant temperature (see section 5.3) at 175 days corresponding to three different values of the saturated moisture conductivity \(\theta_1\). For the legend of the measurements (solid squares and triangles), see figure 5.20.](image)

It appears that a higher value of the saturated moisture conductivity causes lower moisture contents. Although the exposure condition consisted of cycles of a drying and wetting period, it must be noted that the drying period lasted 42 hours, whereas the wetting period 6 hours. So, the drying phase dominated the exposure which explains the lower moisture contents at higher values of the saturated moisture conductivity.
The stronger suction in the case of higher values of the saturated moisture conductivity, causes a greater inward convection of chloride ions during the wetting phases. During the drying phases higher values of the saturated moisture conductivity lead to quicker drying and thus to lower moisture potentials. The moisture potential gradients, the value of the moisture conductivity $k_{22}$ and the derivative of the moisture content with respect to the moisture potential $\partial W/\partial H$ play a role in chloride convection. The moisture conductivity $k_{22}$ is determined by parameter $\theta_1$ (and $\theta_2$, $\theta_3$ and $\theta_4$) and the value of the moisture potential $H$ (see equation 3.102). Apparently, the sum of all these effects is that the global ratio of chloride diffusion and convection is unaffected by the value of the saturated moisture conductivity, since the chloride penetration depth is the same for the three values of $\theta_1$. Still, more chloride ions accumulate near the surface in the case of higher values of the saturated moisture conductivity.

6.1.3 Degree of Hydration

The drying-wetting case for constant temperature has also been used to investigate the influence of the degree of hydration $\alpha$. In section 5.3 the computation was performed with $\alpha=0.7$; here the values 0.8 and 0.9 are tested. Higher degrees of hydration lead to higher moisture contents, except at high values of the moisture potential, where the reverse applies [ROE89]. As the degree of hydration, together with the water to cement ratio, is a fundamental characterisation of concrete as a porous medium, strictly speaking all parameters in the model depend on it. However, not so many of these dependencies are well-defined. The influence of the degree of hydration on the cement gel content $\xi_1$ is given by equation 3.34. Only this parameter has been varied with $\alpha$, thereby neglecting the influence of $\alpha$ on e.g. the saturated moisture conductivity $\theta_1$ and the saturated chloride conductivity $\kappa_1$. With a cement content of 320 kg/m$^3$ the values of $\xi_1$ corresponding to $\alpha$ equal to 0.7, 0.8 and 0.9 are 280, 320 and 360 kg/m$^3$ respectively.

The total chloride profiles as well as the moisture profiles after 175 days of exposure have been plotted in figure 6.3. While the moisture contents are higher for higher degrees of hydration, the total chloride contents are rather unaffected by a change of the degree of hydration. This seems to indicate that the total chloride profile is almost insensitive to a change of the degree of hydration. In order to investigate what the contribution was of the simultaneous change of parameter $\xi_1$ with parameter $\alpha$, the computations were repeated with a constant value of $\xi_1$ of 280 kg/m$^3$. It can be observed in figure 6.4 that then three distinct curves appear, which leads to the conclusion that the individual influence of $\alpha$ and $\xi_1$ on the total chloride profile is
such that the combined influence of the two (with $\xi_1$ according to equation 3.34) yields approximately coinciding total chloride profiles.

Figure 6.3: total chloride (left) and moisture (right) profiles in the drying-wetting case for constant temperature (see section 5.3) at 175 days corresponding to three different values of the degree of hydration $\alpha$. The influence of $\alpha$ on the cement gel content $\xi_1$ has been taken into account.

Figure 6.4: total chloride profiles in the drying-wetting case for constant temperature (see section 5.3) at 175 days corresponding to three different values of the degree of hydration $\alpha$ and a constant cement gel content $\xi_1$ of 280 kg/m$^3$. 

6.1.4 CHLORIDE DIFFUSION

The sensitivity of results from chapter 5 to the saturated chloride conductivity $\kappa_1$ is demonstrated in this section. Both the chloride case and the drying-wetting case have been analysed. Although the set of equations was initially non-linear in the chloride case, it quickly reduced to linear diffusion of chloride ions with a diffusion coefficient $D_c$ of $k_1/k_w$. This (constant) diffusion coefficient varies linearly with $\kappa_1$. In section 5.2.2 the values of $\kappa_1$ for the simulation of experiments IIe and IIIIa were $3.50 \times 10^{-12}$ and $4.56 \times 10^{-12}$ m$^2$/s respectively. In this section a variation of $\kappa_1$ of $\pm 1.00 \times 10^{-12}$ m$^2$/s has been investigated for both experiments IIe and IIIIa. The diffusion coefficient $D_c$ changes then by $\pm 1.29 \times 10^{-12}$ m$^2$/s in the case of experiments IIe and by $\pm 1.51 \times 10^{-12}$ m$^2$/s in the case of experiments IIIIa. This difference is of course caused by the different adsorption function $f_\kappa$ for experiments IIe and IIIIa respectively. The results are depicted in figures 6.5 and 6.6.

![Graphs showing chloride profiles](image-url)

**Figure 6.5:** Total chloride profiles related to experiment IIe (see section 5.2.2) for $\kappa_1 = 2.50 \times 10^{-12}$ (lower line), $3.50 \times 10^{-12}$ (middle line) and $4.50 \times 10^{-12}$ m$^2$/s (upper line).

**Figure 6.6:** Total chloride profiles related to experiment IIIIa (see section 5.2.2) for $\kappa_1 = 3.56 \times 10^{-12}$ (lower line), $4.56 \times 10^{-12}$ (middle line) and $5.56 \times 10^{-12}$ m$^2$/s (upper line).

As can be observed in figure 6.5, the variation of $\kappa_1$ of $\pm 1.00 \times 10^{-12}$ m$^2$/s causes a difference between the upper and lower curve in the middle of samples IIe (at 75 mm) of 0.048 % (on cement mass) after 2 years, 0.747 % after 8 years and 0.992 % after 16 years. The same variation of $\kappa_1$ leads to a difference between the upper and lower curve in the middle of samples IIIIa (at 50 mm) of 0.593 % (on cement mass).
mass) after 2 years, 0.770 % after 8 years and 0.305 % after 16 years. From figure 6.5 it follows that the sensitivity of the total chloride profiles to $\kappa_i$ is different before and after the two chloride fronts have met in the middle of the sample. Figure 6.6 shows that after 16 years the differences between the curves are considerably smaller than after 2 and 8 years, which is obviously due to the approximate chloride saturation of samples III1a after 16 years of exposure for all three values of $\kappa_i$.

The sensitivity of the results of the drying-wetting case for constant temperature to the saturated chloride ion conductivity $\kappa_i$ has also been investigated. While in section 5.3 the computation was performed with $\kappa_i = 1.00 \times 10^{-11}$ m$^2$/s, here the values $1.00 \times 10^{-12}$, $5.00 \times 10^{-12}$ and $5.00 \times 10^{-11}$ m$^2$/s are tested. The mesh was refined from 5 to 10 elements per mm. The results at 37 and 175 days are shown in figure 6.7.

![Figure 6.7: total chloride profiles in the drying-wetting case for constant temperature (see section 5.3) at 37 (left) and 175 days (right) corresponding to different values of the saturated chloride ion conductivity $\kappa_i$. For the legend of the measurements (solid squares and triangles), see figure 5.20.](image)

Since the drying phase was 7 times longer than the wetting phase (42 and 6 hours respectively) and chloride ion convection dominates the wetting phase, the drying phase is of primary interest in the sensitivity analysis of $\kappa_i$. In section 5.3 it was already mentioned that during the drying phase chloride ion diffusion and convection are in competition. A decrease of the saturated chloride ion conductivity $\kappa_i$ implies a decrease of chloride ion diffusion and hence chloride ion convection is then relatively stronger in the drying phase. Since chloride diffusion and convection take place globally in opposite directions during the drying phase (inward diffusion and outward convection), stronger convection inevitably leads to increased accumulation of chlorides near the surface\(^1\) and a reduced penetration depth, which can be observed.

\(^1\) The exposed surface is located at 0 mm.
in figure 6.7. In case of $\kappa_1 = 1.00 \times 10^{-12}$ m²/s this (computed) accumulation was so tremendous, that the solubility of NaCl (218 kg Cl⁻ per m³ of water at 298 K [BIN86]) was exceeded after 36 days of exposure; figure 6.7 (on the left side) shows that the peak of the corresponding total chloride curve is far above the other curves. It must be concluded that with $\kappa_1 = 1.00 \times 10^{-12}$ m²/s the application limits of the model have been surpassed in the drying-wetting case. Still, the computation with $\kappa_1 = 1.00 \times 10^{-12}$ m²/s seems to indicate that if chloride diffusion is weak enough compared to chloride convection, the chloride ions can be locked in the surface zone of concrete in case of drying-wetting cycles. This ‘chloride locking’ manifests itself by an extreme accumulation of chloride ions in a small zone under the exposed surface of concrete; it may explain the observations reported in [BU00].

Noteworthy is further that the curves corresponding to the different values of $\kappa_1$ intersect at approximately the same point. These intersection points are different at 37 and 175 days, as can be observed in figure 6.7. While at 37 days the curve corresponding to $\kappa_1 = 1.00 \times 10^{-11}$ m²/s is closer to the measured points than the curve corresponding to $\kappa_1 = 5.00 \times 10^{-12}$ m²/s, at 175 days the reverse seems to apply. This may indicate that the saturated chloride ion conductivity has decreased in time, which is also suggested by [BAM97].

6.1.5 Chloride Adsorption

The drying-wetting case for constant temperature, as described in section 5.3, has been subjected to a sensitivity analysis with respect to the chloride binding parameters $\xi_2$ and $\xi_3$. The sensitivity to chloride binding parameter $\xi_1$ (the cement gel content in chloride model 2) has already been addressed in section 6.1.3. In the deployed chloride model 2 the chloride binding parameters $\xi_2$ and $\xi_3$ are contained in a Longmuir-type relation between bound chloride ions $C_{\text{bound}}$ (in kg Cl⁻ per kg cement gel) and free chloride ions $C_{\text{free}}$ (in kg Cl⁻ per m³ water); see equation 3.140. For $\xi_3 = 0$ the relation between $C_{\text{bound}}$ and $C_{\text{free}}$ reduces to a linear one with the reciprocity of $\xi_2$ as the constant of proportionality. Both results with linear and Langmuir-type adsorption are presented here. The parameters $\xi_2$ and $\xi_3$ have been chosen to approximate the measurements shown in figure 3.23. In section 5.3 linear chloride adsorption was used with $\xi_2 = 956$ kg/m³ (and $\xi_3 = 0$). The additional values of $\xi_2$ and $\xi_3$ that have been investigated, are shown in figures 6.8 and 6.9. The computed results at 175 days of exposure are depicted in figure 6.10.

It appears that in case of linear chloride adsorption lower values of the chloride binding parameter $\xi_2$, and thus more binding, lead to more accumulation of (total) chloride ions in the surface zone and a reduced penetration depth. Because of the
6.1 sensitivity analyses

Figure 6.8: tested values of chloride binding parameter $\xi_2$ with $\xi_3=0$ (linear chloride adsorption) in comparison with measurements from [TRI89][TAN93]. For the legend of the measurements (squares, triangles and circles) see figure 3.23.

Figure 6.9: tested values of chloride binding parameters $\xi_2$ and $\xi_3$ (Langmuir-type chloride adsorption) in comparison with measurements from [TRI89][TAN93]. For the legend of the measurements (squares, triangles and circles) see figure 3.23.

Instantaneous binding (see chapter 3) more chloride ions can be taken in during the wetting phase in case of lower values of $\xi_2$ (see figure 6.11); this explains the greater accumulation of chlorides at small depths in figure 6.10. In section 5.2.2 it has
already been mentioned that chloride binding reduces the efficiency of chloride diffusion and convection. It follows from equation 3.141 that the same increase of the total chloride content in time $\partial C_{\text{total}}/\partial t$ leads to a smaller increase of the free chloride concentration in time $\partial C_{\text{free}}/\partial t$ in case of lower values of $\xi_2$. So, if in a certain volume the total chloride content increases due to a net diffusive and convective chloride influx, less chloride ions are free and available for further transport in case of lower values of $\xi_2$. This explains why lower values of $\xi_2$, and thus more chloride binding, reduce the penetration depth. Note that the curves for the different values of $\xi_2$ intersect at approximately the same point.

![Graphs showing total chloride profiles](image)

*Figure 6.10: total chloride profiles in the drying-wetting case for constant temperature (see section 5.3) at 175 days in case of linear chloride adsorption (left, with variable $\xi_2$ and $\xi_3=0$) and Langmuir-type chloride adsorption (right, with variable $\xi_2$ and $\xi_3$). For the legend of the measurements (solid squares and triangles), see figure 5.20.*

Langmuir-type adsorption leads to total chloride profiles that deviate considerably from the measurements in [TAH98], as shown in figure 6.10. Still, the same observation is made as in the case of linear binding: weak chloride binding ($\xi_2=824$ kg/m$^3$, $\xi_3=71$) leads to lower total chloride contents near the surface and to a greater penetration depth compared to strong chloride binding ($\xi_2=150$ kg/m$^3$, $\xi_3=65$). Also the curves corresponding to Langmuir-type chloride binding intersect at approximately the same point.
6.2 Evaluation of the chloride-moisture couplings

The simultaneous moisture migration in concrete influences the chloride transport. The extent of this influence is investigated in this section, firstly by eliminating the convective chloride ion flux and the scaling of the chloride ion conductivity with the moisture content, and secondly by comparing chloride diffusion properties corresponding to chloride ingress in (water-) saturated and unsaturated concrete. The drying-wetting case at constant temperature (see section 5.3) serves as basis for this evaluation. Best fits (visually) of these data after 87 exposure cycles (at 175 days) have been created with the developed model and the analytical (error-function) solution of the linear diffusion equation for semi-infinite media (see section 2.2) [MEI02c].

Three analyses have been performed with the model developed in this work: one with moisture fluctuations (referred to as A ‘full model’), one with saturated and stable moisture conditions and exposure to chlorides in the wetting phase only (referred to as B ‘without convection’), and one with saturated and stable moisture conditions and permanent exposure to chlorides, so also in the drying phase (referred to as C ‘permanent diffusion’). The last two analyses are in fact simulations of the solution of the linear diffusion equation with periodical and constant boundary conditions respectively. Analysis A is identical to the solution for $\kappa_i=5\cdot10^{-12}$ m$^2$/s in section...
6.1.4. The convective chloride ion flux in analysis A has been removed for analysis B by imposing H=1 (water saturation) throughout the mesh during the entire time span; all other input parameters are the same in A and B, except the mesh fineness (10 and 5 elements per mm respectively). Comparison of analyses A and B therefore shows the influence of chloride ion convection and the reduced chloride diffusion in drier zones. In analysis C the chloride binding parameter $\xi_2$ and the (saturated) chloride ion conductivity $\kappa_1$ have been adjusted, so as to provide a (visually) best fit of the data in case of permanent (during the wetting and drying phase) exposure to chlorides. The resulting diffusion coefficient $D_c$ can be calculated as:

$$D_c = \frac{\kappa_1^*}{W_x + \frac{\xi_2}{\rho_w}}$$

with:

$$\kappa_1^* = \kappa_1 e^{\frac{\lambda_2}{R(T_x - T)}}$$

(6.1) (6.2)

for chloride model 2, $W=W_x$ and $\xi_3=0$ (linear chloride binding). Since the simulated experiments were performed at a constant temperature of 293 K, it follows with $\lambda_1=32\cdot10^3$ Jmol$^{-1}$ and $\lambda_2=296$ K that $\kappa_1^*=0.875\kappa_1$. Note that chloride binding (represented by $\xi_1$ and $\xi_2$ in equation 6.1) affects the chloride diffusion coefficient $D_c$. This diffusion coefficient in analysis C equals the diffusion coefficient that provides a best fit of the curve corresponding to the analytical solution of the linear diffusion equation.

The analytical solution of the linear diffusion equation for semi-infinite media has been adopted by e.g. DuraCrete [DUR99]. The surface chloride content ('left boundary' in table 6.1) and the chloride diffusion coefficient in this analytical solution have been chosen such, that the resulting chloride profile at 175 days (referred to as D ‘DuraCrete’) agreed well with the measurements. In [DUR99] the formulation has been extended with a time-dependent chloride diffusion coefficient (see section 2.2). This time-dependency, however, has been omitted in analysis D. Note that application of this analytical solution to the drying-wetting case implies that the concrete is exposed to chlorides also during the drying phase, which is not true from a physical point of view.

Summarising, in analyses A and B the chloride (left) boundary condition varies periodically, while in analyses C and D this boundary condition is constant over time. Analysis A is non-linear, while analyses B, C and D are linear. Curves A, C and D have been explicitly fitted on the measured data, while curve B is intended to be compared with curve A. The relevant input parameters are listed in table 6.1; the remaining parameters of analyses A, B and C can be found in tables 5.16 to 5.19.
Table 6.1: input parameters in the analyses with the developed model (A, B and C) and in the analysis with the analytical solution of the linear diffusion equation for semi-infinite media (D). The remaining parameters in analyses A, B and C are listed in tables 5.16 to 5.19. The diffusion coefficients $D_e$ in analyses B and C follow from equation 6.1 with $W_e=151 \text{ kg/m}^3$, $\rho_e=998 \text{ kg/m}^3$ and $\xi_e=280 \text{ kg/m}^3$. The diffusion coefficient in analysis A is obviously variable, since the moisture content $W$ fluctuates. The percentage of chlorides in the last column is related to the cement mass.

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| $\kappa_1$    | $4.38 \times 10^{-12} \text{ m}^2/\text{s}$ | $4.38 \times 10^{-12} \text{ m}^2/\text{s}$ | $3.76 \times 10^{-12} \text{ m}^2/\text{s}$ | $5.00 \times 10^{-12} \text{ m}^2/\text{s}$ |
| $\xi_2$       | 956 kg/m$^3$                             | 956 kg/m$^3$                           | 476 kg/m$^3$                           |                                        |
| $D_c$          | variable                                | $9.85 \times 10^{-12} \text{ m}^2/\text{s}$ | $3.00 \times 10^{-12} \text{ m}^2/\text{s}$ | $5.00 \times 10^{-12} \text{ m}^2/\text{s}$ |

As can be observed in figure 6.12 by comparing curve ‘without convection’ to curve ‘full model’, the elimination of the convective chloride ion flux and the moisture dependence of the chloride ion conductivity $k_1$ leads to lower total chloride contents near the surface and a deeper penetration. From figure 6.14 it follows that less chlorides have accumulated in the mesh in case of analysis B (‘without convection’) than in case of analysis A (‘full model’). This can clearly be explained by the absence of suction in analysis B. It also explains the lower chloride contents near the surface in analysis B, as in this analysis chloride uptake during the wetting phase is by diffusion only. The moisture content in analysis A fluctuates between 59 (at $H=0.65$) and 151 kg/m$^3$ (at $H=1.00$) and consequently the chloride ion conductivity $k_c$ varies between $1.71 \times 10^{-12}$ and $4.38 \times 10^{-12} \text{ m}^2/\text{s}$ (according to equation 3.131). For analysis B it holds that $k_c=k_1$ ($=4.38 \times 10^{-12} \text{ m}^2/\text{s}$) during the entire simulation period. The net reduction of $k_c$ in analysis A yields a smaller penetration depth.
Figure 6.12: fitted curves at 175 days ('full model', 'permanent diffusion' and 'DuraCrete') on measurements from [TAH98]. The measurements, after 87 exposure cycles, are related to the drying-wetting case at constant temperature (see section 5.3). The curves 'permanent diffusion' and 'DuraCrete' coincide. In curve 'without convection' the convective chloride ion flux and the moisture content dependency of the chloride ion conductivity have been eliminated from the 'full model' curve.

Figure 6.13: development of the total chloride profile during the first days of exposure in the 'full model' (A, left) and 'DuraCrete' (D, right) analysis. In spite of the cyclic exposure to chlorides the total chloride content at the surface (at a depth of 0 mm) is maintained at 7% in case of the 'DuraCrete' analysis.
The curves ‘permanent diffusion’ and ‘DuraCrete’ coincide in figure 6.12. Since both analyses are based on the same linear diffusion problem, the mesh-size of 75 mm in analysis C (‘permanent diffusion’) can apparently, up to 175 days, be considered as semi-infinite. It should be noted that both analyses are strictly speaking unrealistic, since exposure to chlorides is permanent, i.e. during both the wetting and drying phase. However, supposing permanent exposure is the only option for application of the analytical solution as adopted in [DUR99]. Chloride binding has been made stronger in analysis C by lowering $\xi_2$ from 956 down to 476 kg/m$^3$. Consequently, with a moisture content $W$ of 151 kg/m$^3$ ($=W_1$), a cement gel content $\xi_1$ of 280 kg/m$^3$ (and $\xi_3=0$, linear chloride binding) and a cement content $\zeta_2$ of 320 kg/m$^3$, the total chloride content at the surface (at a depth of 0 mm) equals 7 % (on cement mass). Lowering of the chloride ion conductivity $\kappa_1^-$ from $4.38 \cdot 10^{-12}$ down to $3.70 \cdot 10^{-12}$ m$^2$/s then yields a chloride ion diffusion coefficient $D_c$ of $5.00 \cdot 10^{-12}$ m$^2$/s. The result of analysis C is in principle a free chloride ion profile, which is proportional to a total chloride profile, since the total chloride content $C_{tot}$ (in kg/m$^3$) is in this case a linear function of the free chloride concentration $C_{free}$:

$$C_{tot} = \left( \frac{W}{\rho_v} + \frac{\xi_1}{\xi_2} \right) C_{free}$$  \hspace{1cm} (6.3)

according to equation 3.139 and 3.140, with $W=W_1$ and $\xi_3=0$. If the unit of $C_{tot}$ is % on cement mass, the righthand-side of the last equation must be multiplied by $100/\xi_2$. From the comparison of analyses C and D it is concluded, that the diffusion coefficient $D_c$ in analysis D (‘DuraCrete’) can be considered to contain a factor (the denominator in equation 6.1) which accounts for the fact (at least by convention) that only free chloride ions can diffuse. This diffusion coefficient is therefore rightly called ‘apparent’ diffusion coefficient, as it does not relate the free chloride ion flux and the free chloride ion concentration gradient, but the free chloride ion flux and the gradient of the total chloride content. In both analyses this chloride ion flux $q_c$ is the same:

$$q_c = -D_c \nabla C_{tot} = -\kappa_1^- \nabla C_{free}$$  \hspace{1cm} (6.4)

in spite of the different values of $D_c$ and $\kappa_1^-$ ($5.00 \cdot 10^{-12}$ and $3.70 \cdot 10^{-12}$ m$^2$/s respectively). The last equation can be verified by substitution of equations 6.1 and 6.3. The benefit of the equivalence of analyses C and D is that the ‘DuraCrete’ (D) analysis can be compared to the ‘full model’ (A) analysis via C. This comparison of analyses A and D via C is necessary, since a diffusion coefficient in analysis A cannot be defined in a straightforward way due to the varying moisture content and thus the non-linearity.

The ‘full model’ (A) curve in figure 6.12 nearly coincides with the ‘DuraCrete’ (D, and ‘permanent diffusion’ C) curve at 175 days. The total chloride content at the surface is 6.7 % (on cement mass) in analysis A versus 7.0 % in analysis D. Also at
greater depths curve A is slightly below curve D. In figure 6.14 it can be observed that the calculated amount of chlorides inside the concrete is smaller in analysis A than in analysis D (being equivalent to the ‘permanent diffusion’ analysis) during the entire simulation period. While the total chloride profiles at 175 days are approximately the same in both analyses, it must be noted, however, that the development of these profiles is completely different. Figure 6.13 shows that during the first days of exposure the total chloride content at the surface varies between 4.2 and 2.0 % in analysis A, while it is fixed at 7.0 % in analysis D. In analysis A the total chloride content at the surface is fixed at 4.2 % during the wetting phase and it sinks during the subsequent drying phase. The total chloride profiles just after the wetting phase (at 2 and 4 days) globally straighten out during the subsequent drying phase (at 3 and 5 days). Figure 6.13 clearly shows that the development of the total chloride profile is much simpler in analysis D.

![Graph showing chloride content over time](image)

*Figure 6.14: accumulation of chloride ions in the (1-dimensional) mesh. This accumulation proceeds step-wise in case of the ‘full model’ and ‘without convection’ analysis, while it is continuous in case of the ‘permanent diffusion’ analysis.*

Moreover, in analysis A chloride ions are sucked into the concrete by convection during the wetting phases, while these convective forces also drag the chloride ions back in the direction of the exposed surface during the drying phases. It has already been mentioned that the chloride ion conductivity \( k_c \) varies between \( 1.71 \times 10^{-12} \) and \( 4.38 \times 10^{-12} \) m\(^2\)/s in analysis A. Now that the differences between analyses A and D have been elucidated, their input parameters can be compared via analysis C (see the darker shaded cells in table 6.1). The (constant) total chloride content at the surface of 7 % and the (constant) chloride diffusion coefficient \( D_c \) of \( 5.00 \times 10^{-12} \) m\(^2\)/s
in D are equivalent to a (constant) free chloride ion concentration at the surface of 30.3 kg/m³, a chloride ion conductivity \( \kappa_1 \) of \( 3.7 \times 10^{-12} \) m²/s and a chloride binding factor \( \xi_2 \) of 476 kg/m³ in C. In order to obtain an approximately equal prediction of the total chloride profile at 175 days with the 'full model' \( \text{A} \), the (saturated) chloride ion conductivity \( \kappa_1 \) can be set to \( 4.38 \times 10^{-12} \) m²/s (an 18% increase) and the chloride binding factor \( \xi_2 \) to 956 kg/m³ (a 101% increase). So, the diffusion of chloride ions in water-saturated zones is slightly greater in A than in D, and the chloride binding is much less in A than in D.

**General discussion**

Prediction of chloride ingress in reinforced concrete is usually associated with chloride diffusion coefficients and surface chloride contents. These diffusion coefficients can be obtained in various ways and therefore a broad range of values exists. In many cases the diffusion coefficient and the surface chloride content follow from curve-fitting of a linear diffusion equation (Fick's second law) on an experimentally determined chloride profile. The surface chloride content is thereby just a parameter in the solution of the diffusion equation and usually deviates from the measured chloride content at the concrete surface. The diffusion coefficients resulting from this curve-fitting procedure include chloride binding effects, and in case the chloride profile comes from a concrete structure the derived diffusion coefficient even includes the chloride exposure history and moisture effects (such as capillary suction and evaporation of pore liquid). Such a quantity can therefore hardly be called a material property and it is referred to as the apparent or effective (expressing its global and averaged nature) diffusion coefficient.

The negative product of the diffusion coefficient and the gradient of the total chloride content (the total amount of chloride ions per volume of concrete) gives the flow of free chloride ions through a unit area of concrete per unit time. The negative product of the diffusion coefficient and the gradient of the free chloride concentration (the amount of free chloride ions per volume pore water) equals, in some models, the flow of free chloride ions through a unit area of concrete per unit time, but in other models the flow of free chloride ions through a unit area of pore water per unit time. In the latter case the diffusion coefficient is called intrinsic diffusion coefficient, as it characterises the diffusivity of chloride ions in a purely liquid substance. Clearly, when modelling transport phenomena in a porous medium like concrete, it is of major importance to mention not only the units of quantities, but also the phases which these units refer to. Diffusion in a porous medium differs from diffusion in a purely liquid substance in the sense that diffusion in the porous medium is restricted...
to paths of pore liquid. The values of all apparent and effective chloride diffusion coefficients are therefore dependent on the water content in concrete.

For diffusion-based models which are more complicated than linear diffusion, like the developed model, the chloride diffusion coefficient can generally be defined as the ratio of conductivity and capacity. The conductivity is then the multiplier of the spatial derivative (gradient) of the chloride potential and the capacity the multiplier of the time derivative of the chloride potential (its rate). However, the definition of this ratio between conductivity and capacity is difficult, if the capacity is a function of the spatial co-ordinates. This is the case if the capacity depends e.g. on the water content in concrete. The conductivities and capacities in the developed model must be considered to replace the traditional diffusion coefficient (and surface chloride content) and regarded as a better approximation of the material properties involved in chloride transport in concrete.
Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Performance of the model

From comparisons between experimental and numerical results it followed that the developed model is able to simulate the transport of chloride ions inside concrete under variable external conditions, viz. variable environmental temperature, humidity and chloride exposure. As opposed to linear chloride binding, Langmuir chloride binding has led to results that did not correspond well with experimental data. The carbonation model, which is part of the global chloride model, effectively reproduces the experimentally observed chloride peak at some depth in carbonated concrete subjected to chloride loading.

Sensitivity of the model

The sensitivity of the model to variations of some of its parameters has been evaluated, viz. the moisture transfer coefficient, the saturated moisture conductivity, the degree of hydration, the saturated chloride conductivity and the chloride binding parameters. In the case of drying-wetting exposure an increase of the saturated moisture conductivity does not affect the chloride penetration depth, but leads to higher surface chloride contents. The computed chloride profiles, as opposed to the computed moisture profiles, are not affected by a change of the degree of hydration in case of drying-wetting exposure, if only the conjunct change of the cement gel
content is taken into account and other dependencies are disregarded. An increase of the saturated chloride conductivity yields greater chloride penetration depths, both in case of permanent chloride loading and drying-wetting exposure. In case of drying-wetting exposure higher surface chloride contents can arise as a consequence of a lower saturated chloride conductivity or stronger chloride binding; moreover, stronger chloride binding reduces the chloride penetration depth. The release of bound chloride ions in case of carbonation has a considerable effect on the computed total chloride profile, even for small carbonation depths.

Special findings

In case of drying-wetting exposure chloride ions are forced into the concrete by capillary suction during the wetting phase. During the subsequent drying phase further ingress of the chlorides which are already inside the concrete, is driven by diffusion. However, this process is counteracted by convection of chlorides in the opposite direction, as drying is accompanied by a moisture flow towards the drying surface. In the simulation of drying-wetting exposure it has been observed that the balance between chloride ion diffusion and convection during the drying phase is so delicate that chlorides can be locked in the surface zone. In this phenomenon not only the ratio of the parameters saturated chloride ion and saturated moisture conductivity play a role, but also the moisture desorption isotherm corresponding to the actual concrete, the environmental relative humidity during the drying period and the ratio of the durations of the drying and wetting period.

Modelling advances

As opposed to chloride ingress models based on the error-function solution of Fick's second law (with constant diffusivity), the present model can handle drying-wetting exposure. Application of the error-function solution to drying-wetting exposure implies the assumption of a constant chloride loading and uniform moisture contents throughout time, which is physically unrealistic. Good correspondence between experimental and computed results at certain points in time can still be obtained with the error-function solution in such exposure mainly by overestimating the chloride binding capacity. The two parameters in the error-function solution, viz. the surface chloride content and the chloride diffusivity, are then merely regression parameters.

In some models for chloride ingress in concrete reported in literature the moisture balance appears twice and the two formulations per model do not seem to be identical. This introduces an inconsistency in these models. A balance for the total
chloride content (the total amount of chloride ions per volume of concrete) offers the best possibilities for the modelling of chloride transport in concrete. This does not necessarily mean that the total chloride content must be the chloride potential; also the free chloride concentration (the amount of free chloride ions per volume pore water) can serve as chloride potential in a balance for the total chloride content. Such a balance allows for fluctuating moisture contents in concrete. This would be troublesome in case of a balance for free chloride ions in the pore water.

Numerical analysis

The heat, moisture and chloride balance of the developed model are solved according to a monolithic scheme. It is probably the first chloride ingress model that deploys such a scheme, since in literature only staggered schemes have been encountered. The benefit of the monolithic scheme is that in every iteration the entire set of balances including the couplings is dealt with, whereas in a staggered scheme, apart from iterations due to non-linearity, additional iterations between the individual balances are needed in order to assure that the effect of the couplings has been involved. The monolithic scheme, however, leads to larger system matrices, which increase the computation time, and enforces a timestep which is identical for the individual balances. This timestep must then be determined by the fastest process.

The more complicated chloride ingress models rely on numerical methods, such as the finite difference and finite element method, to provide solutions resulting from the model. There are, however, various pitfalls in the field of numerical analysis and these numerical solutions should therefore be produced and presented with due care. While the correctness of analytical solutions can easily be evaluated, numerical solutions can be incorrect without an easy way to prove that. The cause of any peculiar numerical results ought first to be attributed to the numerical solution procedure, before a physical explanation is attempted. Moreover, for more accurate simulations the level of complexity of the chloride models will increase, which not only makes numerical procedures dealing with them more time-consuming, but also endangers the stability of these numerical procedures.
7.2 Recommendations

Use of the model

The developed model and computer program offer a tool to improve the understanding of the chloride ingress process, however it cannot yet be used for quantitative predictions. It appears that prediction of the duration of the corrosion initiation period, related to the total chloride content or free chloride concentration at the depth of the reinforcement bars at a certain point in time, is rather ambitious. To reach that goal on the basis of the present computer program at least the following four requirements must be met. Firstly, more test cases must be analysed with the program, so that the underlying model can be refined. Secondly, for predictions there should be absolute certainty about the values of the input parameters for the various types of concrete, which necessitates standardised experimental procedures related to the model to determine these values. Thirdly, a corrosion prediction tool is useless without a clear definition of the corrosion criterium. In that sense the currently broad range of values for the threshold chloride content is an obstacle and this criterium should therefore be refined. Fourthly, stochastic effects due to the heterogeneity of concrete, the construction phase of the concrete structure and the variability of environmental conditions during its designed lifetime, must be assessed. Satisfaction of these requirements can ultimately lead to durability design of reinforced concrete structures on the basis of, firstly, standardised tests for the determination of the chloride transport properties of a certain type of concrete and, secondly, a classification of concrete types for certain durability classes related to the outcome of these tests. And yet, the accessibility for inspection and the repair possibilities of spots that are clearly vulnerable to corrosion damage, should still be considered in the design stage of a reinforced concrete structure.

Further development of the model

Continuation of the development of the present model and computer program should start with further testing of the computational stability of the carbonation model and an examination of the moisture-heat couplings. In particular, the heat balance ought to be extended with terms accounting for heat of evaporation and condensation. Next, the effect of non-instantaneous chloride binding can be investigated. The effect of heterogeneity on chloride transport properties can be studied by means of 2-dimensional heterogeneous meshes. Also hygroscopic effects can be incorporated and evaluated in the model. Elaboration of the dependencies of the conductivities on the degree of hydration and the water to cement ratio is
desirable. Computational improvements may be achieved by the programming of
infinity elements to reduce the mesh size and by the application of a space-time
formulation, instead of the finite element method for the spatial discretisation and the
finite difference method for the time discretisation.
REFERENCES


The error-function

\[
erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt, \quad \text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt, \quad \text{erfc}(x) = 1 - \text{erf}(x)
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| 1.61 | 0.977  | 1.81 | 0.990  | 2.01 | 0.996  | 2.21 | 0.998  | 2.41 | 0.999  |
| 1.62 | 0.978  | 1.82 | 0.990  | 2.02 | 0.996  | 2.22 | 0.998  | 2.42 | 0.999  |
| 1.63 | 0.979  | 1.83 | 0.990  | 2.03 | 0.996  | 2.23 | 0.998  | 2.43 | 0.999  |
| 1.64 | 0.980  | 1.84 | 0.991  | 2.04 | 0.996  | 2.24 | 0.998  | 2.44 | 0.999  |
| 1.65 | 0.980  | 1.85 | 0.991  | 2.05 | 0.996  | 2.25 | 0.999  | 2.45 | 0.999  |
| 1.66 | 0.981  | 1.86 | 0.991  | 2.06 | 0.996  | 2.26 | 0.999  | 2.46 | 0.999  |
| 1.67 | 0.982  | 1.87 | 0.992  | 2.07 | 0.997  | 2.27 | 0.999  | 2.47 | 1.000  |
| 1.68 | 0.982  | 1.88 | 0.992  | 2.08 | 0.997  | 2.28 | 0.999  | 2.48 | 1.000  |
| 1.69 | 0.983  | 1.89 | 0.992  | 2.09 | 0.997  | 2.29 | 0.999  | 2.49 | 1.000  |
| 1.70 | 0.984  | 1.90 | 0.993  | 2.10 | 0.997  | 2.30 | 0.999  | 2.50 | 1.000  |
| 1.71 | 0.984  | 1.91 | 0.993  | 2.11 | 0.997  | 2.31 | 0.999  | 2.51 | 1.000  |
| 1.72 | 0.985  | 1.92 | 0.993  | 2.12 | 0.997  | 2.32 | 0.999  | 2.52 | 1.000  |
| 1.73 | 0.986  | 1.93 | 0.994  | 2.13 | 0.997  | 2.33 | 0.999  | 2.53 | 1.000  |
| 1.74 | 0.986  | 1.94 | 0.994  | 2.14 | 0.998  | 2.34 | 0.999  | 2.54 | 1.000  |
| 1.75 | 0.987  | 1.95 | 0.994  | 2.15 | 0.998  | 2.35 | 0.999  | 2.55 | 1.000  |
| 1.76 | 0.987  | 1.96 | 0.994  | 2.16 | 0.998  | 2.36 | 0.999  | 2.56 | 1.000  |
| 1.77 | 0.988  | 1.97 | 0.995  | 2.17 | 0.998  | 2.37 | 0.999  | 2.57 | 1.000  |
| 1.78 | 0.988  | 1.98 | 0.995  | 2.18 | 0.998  | 2.38 | 0.999  | 2.58 | 1.000  |
| 1.79 | 0.989  | 1.99 | 0.995  | 2.19 | 0.998  | 2.39 | 0.999  | 2.59 | 1.000  |
| 1.80 | 0.989  | 2.00 | 0.995  | 2.20 | 0.998  | 2.40 | 0.999  | 2.60 | 1.000  |
APPENDIX B

Experiments hygroscopic effects

---

volume cylinder $1.20 \times 10^{-5} \text{m}^3$

height cylinder 29 mm

cement content 450 kg/m$^3$

diameter cylinder 23 mm
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
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<tr>
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<td></td>
<td>85 % h&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>NaCl  (on cement)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>chloride (on cement)</td>
<td>%</td>
<td>kg/m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>g</td>
</tr>
<tr>
<td>chloride (on mortar)</td>
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<td></td>
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<tr>
<td>chloride (on mortar)</td>
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<td></td>
</tr>
<tr>
<td>chloride (on cement)</td>
<td></td>
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<td></td>
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<tr>
<td>chloride (on mortar)</td>
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</tr>
<tr>
<td>moisture (on cement)</td>
<td>%</td>
<td>kg/m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>g</td>
</tr>
<tr>
<td>moisture (on mortar)</td>
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<td>moisture (on mortar)</td>
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</tr>
<tr>
<td>moisture (on cement)</td>
<td>%</td>
<td>kg/m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>g</td>
</tr>
<tr>
<td>moisture (on mortar)</td>
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<td></td>
</tr>
<tr>
<td>moisture (on mortar)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| blast furnace slag cement     |                 |                               |                               |
|                               | 50 % h<sub>2</sub>|                               | 85 % h<sub>2</sub>            |
| NoCl  (on cement)             |                 |                               |                               |
| chloride (on cement)          | %               | kg/m<sup>3</sup>              | g                             |
| chloride (on mortar)          |                 |                               |                               |
| chloride (on mortar)          |                 |                               |                               |
| chloride (on cement)          |                 |                               |                               |
| chloride (on mortar)          |                 |                               |                               |
| moisture (on cement)          | %               | kg/m<sup>3</sup>              | g                             |
| moisture (on mortar)          |                 |                               |                               |
| moisture (on mortar)          |                 |                               |                               |
| moisture (on cement)          | %               | kg/m<sup>3</sup>              | g                             |
| moisture (on mortar)          |                 |                               |                               |
| moisture (on mortar)          |                 |                               |                               |

| chloride midpoints (on mortar) | c<sub>23</sub> | c<sub>23</sub>          | c<sub>23</sub>          |
| chloride midpoints (on mortar) | weighted average | weighted average | weighted average |
| [kg/m<sup>3</sup>]             | []              | []                      | []                      |

| chloride midpoints (on mortar) | c<sub>23</sub> | c<sub>23</sub>          | c<sub>23</sub>          |
| chloride midpoints (on mortar) | weighted average | weighted average | weighted average |
| [kg/m<sup>3</sup>]             | []              | []                      | []                      |
APPENDIX C

Heat conductivity

Suppose a series of pores and solid matrix with lengths $l_{p1}$ and $l_s$, respectively. The heat conductivity of the pores is $\gamma_p$ and the one of the solid matrix $\gamma_s$.

\[
\begin{array}{cccccccc}
\gamma_p & \gamma_s & \gamma_p & \gamma_s & \gamma_p & \gamma_s & \gamma_p \\
 l_{p1} & l_1 & l_{p2} & l_2 & l_{p3} & l_3 & l_{p4} & \end{array}
\]

In case of linear heat conduction this can be simplified into:

\[
T_A \quad \gamma_s \quad T_B \quad \gamma_p \quad T_C
\]

\[
l_s \quad l_p
\]

with:

\[
\sum l_{p} = l_p \quad \sum l_s = l_s
\]

(C.1)

and temperatures $T_A$, $T_B$ and $T_C$. In steady state it holds that:

\[
T_A - T_B = q \frac{l_s}{\gamma_s} \quad T_B - T_C = q \frac{l_p}{\gamma_p}
\]

(C.2)

with heat flux $q$. Addition of the last two equations yields:

\[
T_A - T_C = q \left( \frac{l_s + l_p}{\gamma_s \gamma_p} \right)
\]

(C.3)

The overall heat conductivity $\gamma_o$ can then be determined from the last equation and:

\[
T_A - T_C = q \frac{l_s + l_p}{\gamma_o}
\]

(C.4)

with the following result:

\[
\gamma_o = \frac{l_s + l_p}{l_s + l_p}
\]

(C.5)

If the concrete is water-saturated, it follows then, with $\gamma_o=0.60 \text{Wm}^{-1}\text{K}^{-1}$ (water), $\gamma_o=2.40 \text{Wm}^{-1}\text{K}^{-1}$ (concrete), $l_p=0.13$ m and $l_s=0.87$ m, that $\gamma_s=4.35 \text{Wm}^{-1}\text{K}^{-1}$. Using the last equation again with $\gamma_s=4.35 \text{Wm}^{-1}\text{K}^{-1}$ (solid matrix), $\gamma_p=0.024 \text{Wm}^{-1}\text{K}^{-1}$ (air), $l_p=0.13$ m and $l_s=0.87$ m, yields $\gamma_o=0.178 \text{Wm}^{-1}\text{K}^{-1}$. 
Freundlich adsorption

Freundlich adsorption is defined as:

$$C_{\text{bound}} = aC_{\text{free}}^b$$  \hspace{1cm} (C.6)

with $a$ and $b$ constants. The consequence of substitution in a balance for total chlorides $C_{\text{tot}}$ is that the time derivative of $C_{\text{bound}}$ must be determined, which can be written as:

$$\frac{\partial C_{\text{bound}}}{\partial t} = abC_{\text{free}}^{b-1} \frac{\partial C_{\text{free}}}{\partial t}$$  \hspace{1cm} (C.7)

The value of $b$ is usually in the range $[0 \ldots 1]$ and e.g. for $b=0.5$ it follows that:

$$\frac{\partial C_{\text{bound}}}{\partial t} = \frac{1}{2} \frac{a}{C_{\text{free}}} \frac{\partial C_{\text{free}}}{\partial t}$$  \hspace{1cm} (C.8)

Clearly, division by zero occurs in the initial situation when $C_{\text{free}}=0$ kg/m$^3$.

Weak monolithic formulation

$$\int_{\Omega} \left( V_{e_{11}} \frac{\partial T}{\partial t} + V_{e_{12}} \frac{\partial H}{\partial t} + V_{e_{13}} \frac{\partial C}{\partial t} + \frac{\partial V_1}{\partial x} k_{11} \frac{\partial T}{\partial x} + \frac{\partial V_1}{\partial y} k_{11} \frac{\partial T}{\partial y} + \frac{\partial V_1}{\partial x} k_{12} \frac{\partial H}{\partial x} + \frac{\partial V_1}{\partial y} k_{12} \frac{\partial H}{\partial y} + \frac{\partial V_1}{\partial x} k_{13} \frac{\partial C}{\partial x} + \frac{\partial V_1}{\partial y} k_{13} \frac{\partial C}{\partial y} - v_1 f_1 \right) d\Omega + \int_{r_{12}} (V_1 \chi_{11} T + V_1 \chi_{12} H + V_1 \chi_{13} C + v_1 \tilde{q}_1) d\Gamma +$$

$$+ \int_{\Omega} \left( V_{e_{21}} \frac{\partial T}{\partial t} + V_{e_{22}} \frac{\partial H}{\partial t} + V_{e_{23}} \frac{\partial C}{\partial t} + \frac{\partial V_2}{\partial x} k_{21} \frac{\partial T}{\partial x} + \frac{\partial V_2}{\partial y} k_{21} \frac{\partial T}{\partial y} + \frac{\partial V_2}{\partial x} k_{22} \frac{\partial H}{\partial x} + \frac{\partial V_2}{\partial y} k_{22} \frac{\partial H}{\partial y} + \frac{\partial V_2}{\partial x} k_{23} \frac{\partial C}{\partial x} + \frac{\partial V_2}{\partial y} k_{23} \frac{\partial C}{\partial y} - v_2 f_2 \right) d\Omega + \int_{r_{12}} (V_2 \chi_{21} T + V_2 \chi_{22} H + V_2 \chi_{23} C + v_2 \tilde{q}_2) d\Gamma +$$

$$+ \int_{\Omega} \left( V_{e_{31}} \frac{\partial T}{\partial t} + V_{e_{32}} \frac{\partial H}{\partial t} + V_{e_{33}} \frac{\partial C}{\partial t} + \frac{\partial V_3}{\partial x} k_{31} \frac{\partial T}{\partial x} + \frac{\partial V_3}{\partial y} k_{31} \frac{\partial T}{\partial y} + \frac{\partial V_3}{\partial x} k_{32} \frac{\partial H}{\partial x} + \frac{\partial V_3}{\partial y} k_{32} \frac{\partial H}{\partial y} + \frac{\partial V_3}{\partial x} k_{33} \frac{\partial C}{\partial x} + \frac{\partial V_3}{\partial y} k_{33} \frac{\partial C}{\partial y} - v_3 f_3 \right) d\Omega + \int_{r_{12}} (V_3 \chi_{31} T + V_3 \chi_{32} H + V_3 \chi_{33} C + v_3 \tilde{q}_3) d\Gamma = 0$$
### APPENDIX D

**Chloride adsorption**

mixed-in chloride, $\zeta_1$=0.6, $\alpha$=0.7 [TR89]

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<tr>
<th>C_{tot}</th>
<th>C_{free}</th>
<th>C_{tot}</th>
<th>C_{free}</th>
<th>C_{free}</th>
<th>C_{bound}</th>
<th>C_{bound}</th>
<th>C_{bound}</th>
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<td>ppm</td>
<td>kg/m^3 c</td>
<td>kg/m^3 w</td>
<td>kg/m^3 c</td>
<td>kg/m^3 c</td>
<td>kg/kg_gel</td>
<td>mg/g gel</td>
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mixed-in chloride, $\zeta_1$=1 % [TR89]

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<th>$\alpha$</th>
<th>$V_{ri}$</th>
<th>$V_{pore}$</th>
<th>$m_w$</th>
<th>$V_w$</th>
<th>$W$</th>
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<tr>
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<td>m^3</td>
<td>kg</td>
<td>m^3 w/m^3 c</td>
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<tr>
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<th>C_{free}</th>
<th>C_{free}</th>
<th>C_{bound}</th>
<th>C_{bound}</th>
<th>C_{bound}</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg/m^3</td>
<td>ppm</td>
<td>kg/m^3 c</td>
<td>kg/m^3 w</td>
<td>kg/m^3 c</td>
<td>kg/kg_gel</td>
<td>mg/g gel</td>
<td></td>
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</table>
### Appendix D

\( \zeta_2 \) \( \frac{1222 \text{ kg/m}^3}{\text{saturated moisture content}} \) \( \frac{0.461 \text{ m}^3 \_w/\text{m}^3 \_c}{\zeta_1} \) \( 993 \text{ kg/m}^3 \)

<table>
<thead>
<tr>
<th>% cem</th>
<th>ppm</th>
<th>( \text{kg/m}^3 _c )</th>
<th>( \text{kg/m}^3 _w )</th>
<th>( \text{kg/m}^3 _c )</th>
<th>( \text{kg/m}^3 _c )</th>
<th>( \text{kg/kg gel} )</th>
<th>mg/g gel</th>
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SUMMARY

Chloride ions can locally destroy the passivating gamma ferric oxide film, which surrounds the steel in concrete. If oxygen is present, this depassivation leads to reinforcement corrosion, which endangers the durability of the concrete structure. The objective of the present work was to develop a computational model for chloride ingress in reinforced concrete, which is based on the coherent processes of chloride ion transport and moisture migration. Particularly, the model was supposed to be able to deal with varying external conditions, i.e. varying environmental temperature, humidity and chloride loading. As carbonation is coupled with drying of concrete and is known to influence chloride ingress, it was to be included in the modelling as well. The performance of the computational model was to be tested by comparing both its input and output to experimental data from literature.

Moisture and salt transport in concrete resembles such transport in soil. For these porous media moisture migration is commonly modelled by one or two diffusion equations, the variables and parameters of which have different definitions among authors. In case of two diffusion equations the one is related to moisture migration and the other to heat flow, while various couplings in the two balances account for the interaction of these processes. Models for chloride transport in concrete essentially predict the chloride content at the level of the reinforcement steel at a certain point in time, which is to be compared to the threshold chloride content for corrosion. Those models can be divided into models which do not consider simultaneous moisture movements and models which do. A well-known representative of the first category is the error-function solution of the diffusion equation with basically two parameters: the diffusion coefficient and the surface chloride content. The overall nature of that diffusion coefficient is expressed by the adjective 'effective' or 'apparent'. The error-function model has been extended with a decrease of the diffusion coefficient over time and by distinguishing between a skin layer and bulk concrete. Other models in this category are also based on the diffusion equation and incorporate chloride binding. The second category of models for chloride ion transport in concrete allows for simultaneous moisture transport. Movement of pore liquid containing dissolved ions implies convective transport of these ions. Some of these models include heat flow as well. The complexity of the combined models necessitates numerical solution strategies.

Chloride ingress in concrete has been modelled at centimetre-level, since the distance between the concrete surface and the location of the reinforcement steel amounts to a few centimetres. At this level of observation concrete has been
considered to be homogeneous. The developed chloride ingress model basically consists of three coupled balances for heat flow, moisture migration and chloride transport. The model is represented mathematically by three coupled second order partial differential equations. Convection of chloride ions has been established by one of the couplings between the chloride and moisture balance. The parabolic partial differential equations can be linear or non-linear, depending on the types of submodels. Non-linearity arises as a consequence of the dependence of the capacities, conductivities and sources on the potentials.

One non-linear heat model, four non-linear moisture models and three non-linear chloride models have been implemented. The overall model is then the combination of the selected heat, moisture and chloride model. In the non-linear heat model the heat capacity and conductivity are a function of the moisture content. The non-linear moisture models are based on an s-shaped relation between moisture conductivity and moisture potential. The moisture potential has been chosen as the macroscopic pore humidity. The moisture content is a function of the degree of hydration, the water to cement ratio, the cement content, the temperature and the moisture potential. In one moisture model carbonation effects have been included, i.e. irreversible changes of the desorption isotherms and moisture conductivity in the carbonated zone. The criterium for carbonation has been chosen as a threshold moisture potential and thus a dynamic boundary exists between the carbonated and uncarbonated zone. In the non-linear chloride models a distinction is made between free and bound chloride ions. Free chloride ions are dissolved in the pore water inside concrete, while bound chloride ions are adsorbed to (parts of) the solid matrix. Linear and Langmuir-type chloride binding has been implemented. The total chloride content is the weighted sum of free and bound chloride ions. Generally chloride ions are transported both by a diffusive and convective flux. The diffusive chloride ion flux is proportional to the moisture content and the gradient of the free chloride concentration in the pore water. The convective chloride ion flux is proportional to the free chloride ion concentration and the gradient of the moisture potential. The chloride models have been formulated with either the total chloride content or the free chloride concentration as the chloride potential. In one chloride model the effect of carbonation on chloride binding has been taken into account by irreversibly annihilating the chloride binding capacity in the carbonated zone.

A 1- and 2-dimensional element for the three coupled balances and a 1-dimensional element for surface resistance have been implemented according to the finite element method. The weak formulation has been set up according to a monolithic scheme and consequently each finite element deals with heat flow, moisture migration and chloride transport simultaneously. Time marching has been performed with the Euler backward algorithm and the full Newton-Raphson
algorithm has been used to deal with the non-linearity. Due to the different
timescales of the three coupled processes, the capacitance and conductance
matrices are in principle ill-conditioned. A scaling method has been implemented to
improve the conditioning of the matrices.

The computational model has been tested in a moisture case, a chloride case and a
drying-wetting case. The linear and one non-linear moisture model, both with and
without surface transfer element, have been used to simulate the drying of cement
paste without chloride loading. Comparison with experimental data of moisture loss
over time yielded that the linear model without the surface transfer element
performed best. The chloride case describes the comparison of the computational
model with experimental data of concrete slabs submerged in sea-water. Ingress of
chloride ions was mainly by diffusion; only in the beginning of the exposure some
convective chloride uptake occurred due to the curing conditions. The chloride
boundary condition was obtained by assuming that the free chloride concentration in
the pore water at the concrete surface equals the chloride concentration in the sea-
water. Generally, the simulations reflected the measurements after 2, 8 and 16 years
of exposure well; deviations appeared mostly in the surface zone. Also the input of
the computations corresponded well to value ranges in literature. The effect of the
curing conditions on the eventual chloride profile has been investigated by means of
the carbonation models. The loss of chloride binding in the carbonated zone caused
a peak in the computed total chloride profile.

In the drying-wetting case the capacity of the computational model to deal with
varying environmental temperature, environmental humidity and chloride loading has
been demonstrated. Experiments with cyclic exposure to chlorides have been
simulated. During the drying phases the temperature remained constant in one set of
the experiments and varied sinusoidally in another set. The environmental humidity
variation during the drying phases was assumed opposite to the environmental
temperature variation. The material parameters were the same in the simulation of
the set with constant temperature and the one with varying temperature; the heat and
moisture boundary conditions were different though. A best fit of the measurements
corresponding to both sets has been attempted with plausible material parameters.
In the simulations an amount of salty water was absorbed during the wetting phases,
while the chloride ions were redistributed during the drying phases. It appeared that
during the drying phases inward chloride ion diffusion and outward chloride ion
convection are in competition. Comparison between measured and computed total
chloride profiles yielded that, while match was good for the set with constant
temperature, the computed chloride contents were smaller than the measured ones
for the set with varying temperature. The simulations confirmed the experimental
finding that compared to the constant temperature, the temperature variation
induced generally greater total chloride contents. Also the carbonation models could capture the experimental findings for the set with constant temperature, while a peak in the computed total chloride profile indicated the absence of chloride binding in the carbonated zone.

The sensitivity of the developed model to several parameters has been investigated: the moisture transfer coefficient, the saturated moisture conductivity, the degree of hydration, the saturated chloride conductivity and the chloride binding parameters. For the drying-wetting case with constant temperature it appeared that a higher value of the saturated moisture conductivity caused higher total chloride contents near the surface and overall lower moisture contents, while the chloride penetration depth was unaffected. The computed total chloride profile was insensitive to a change of the degree of hydration, if only the conjunct change of the cement gel content is taken into account and other dependencies are disregarded. Lower values of the saturated chloride conductivity led to increased accumulation of chlorides near the surface and a reduced penetration depth, which seems to indicate that chloride ions can be locked in the surface zone of concrete in case of drying-wetting cycles. Also stronger linear chloride binding yielded higher total chloride contents in the surface zone and a reduced penetration depth. Langmuir-type adsorption led to total chloride profiles that deviated considerably from the measurements.

The contribution of moisture migration to the eventual total chloride profile has been investigated by comparing results of the drying-wetting case with constant temperature to computations based on water-saturation and to a fitting of the error-function. It followed that in the absence of chloride convection and with optimal chloride diffusion, the surface chloride content was reduced and the chloride penetration depth increased. Comparison of the developed model to the error-function analysis yielded that the development of the total chloride profile over time is completely different and that disregarding moisture movements due to drying-wetting exposure mainly leads to an overestimation of chloride binding.

The developed model and computer program offer a tool to improve the understanding of the chloride ingress process in concrete. Before quantitative predictions for the purpose of durability analysis can be made, firstly more test cases must be analysed with the program, secondly the input parameters must be uniquely related to the various types of concrete by means of standardised experiments, thirdly the threshold chloride content as a corrosion criterium must be specified more precisely, and fourthly stochastic effects due to the heterogeneity of concrete, the construction phase of the concrete structure and due to the variability of environmental conditions during its designed lifetime, must be assessed.
SAMENVATTING

Chloride-ionen zijn in staat om lokaal de gamma-ferrische oxide-film, die het staal in beton omhult, te vernietigen. In de aanwezigheid van zuurstof leidt deze depassivatie tot wapeningscorrosie, die de duurzaamheid van de betonconstructie in gevaar brengt. De doelstelling van het onderhavige werk was een numeriek model te ontwikkelen voor chloride-indringing in gewapend beton, dat gebaseerd is op de samenhangende processen van chloride-ionentransport en vochtmigratie. Het was in het bijzonder de bedoeling dat het model variabele externe condities, d.w.z. variabele omgevingstemperatuur, -vochtigheid en chloridebelasting, kon hanteren. Omdat carbonatatie gekoppeld is aan het drogen van beton en het de chloride-indringing beïnvloedt, moest ook carbonatatie in de modellering opgenomen worden. De prestaties van het numeriek model moesten getest worden aan de hand van vergelijkingen van zowel input als output met experimentele gegevens in de literatuur.

Vocht- en zouttransport in beton heeft overeenkomsten met zodanig transport in grond. Voor deze poreuze media wordt vochtmigratie gewoonlijk gemoduleerd d.m.v. een of twee diffusievergelijkingen, waarvan de variabelen en parameters verschillend gedefinieerd worden onder auteurs. In geval van twee diffusievergelijkingen is de ene gerelateerd aan vochtmigratie en de andere aan warmtestroming, terwijl verscheidene koppelingen in de twee balansen de interactie van deze processen in rekening brengen. In essentie voorspellen modellen voor chloridetransport in beton het chloridegehalte ter plaatse van het wapeningsstaal op een bepaald tijdstip, dat vergeleken moet worden met het kritische chloridegehalte voor corrosie. Die modellen kunnen onderscheiden worden in modellen die wel en niet simultane vochtbewegingen in beschouwing nemen. Een bekende vertegenwoordiger van de eerste categorie is de ‘error-functie’ oplossing van de diffusievergelijking met standaard twee parameters: de diffusiecoëfficiënt en het oppervlakte-chloridegehalte. Het globale karakter van die diffusiecoëfficiënt komt tot uitdrukking in het bijvoeglijk naamwoord ‘effectief’ of ‘schihtbaar’. Het error-functie model is uitgebreid met een afname van de diffusiecoëfficiënt over de tijd en met het onderscheid tussen de oppervlakte della van het beton en het dieper gelegen beton. Andere modellen in deze categorie zijn ook gebaseerd op de diffusievergelijking en bevatten chloridebinding. De tweede categorie modellen voor chloride-ionentransport in beton erkennen een simultaan vochttransport. Beweging van het opgeloste ionen bevattende poriewater impliceert convectief transport van deze
SAMENVATTING

Ionen. Enige van deze modellen bevatten ook warmtestroming. De complexiteit van deze gecombineerde modellen maakt numerieke oplossingsstrategieën noodzakelijk.


Een niet-lineair warmtestmodel, vier niet-lineaire vochtmodellen en drie niet-lineaire chloridemodellen zijn geïmplementeerd. Het globale model is dan de combinatie van het geselecteerde warmte-, vocht- en chloridemodel. In het niet-lineaire warmtestmodel zijn de warmtecapaciteit en -conductiviteit een functie van het vochtgehalte. De niet-lineaire vochtmodellen zijn gebaseerd op een s-vormige relatie tussen vochtcondensaties en vochtpotential. De vochtpotential is gekozen als de macroscopische porievochtigheid. Het vochtgehalte is een functie van de hydratatiegraad, de water-cementfactor, het cementgehalte, de temperatuur en de vochtpotential. In een van de vochtmodellen zijn carbonatatie-effecten opgenomen, d.w.z. irreversibele veranderingen van de desorptie-isothermen en de vochtcondensaties in de gecarbonaterte zême. Het criterium voor carbonatatie is gekozen als een kritische vochtpotential en zodoende bestaat er een dynamische grens tussen de gecarbonaterte en ongecarbonaterte zôme. In de niet-lineaire chloridemodellen is onderscheid gemaakt tussen vrije en gebonden chloride-ionen. Vrije chloride-ionen zijn opgelost in het poriewater in het beton, terwijl gebonden chloride ionen geadsorbeerde zijn aan (delen van) de vaste-stof matrix. Lineaire en Langmuir-achtige chloride-binding is geïmplementeerd. Het totale chloridegehalte is de gewogen som van de vrije en gebonden chloride-ionen. Chloride ionen worden in het algemeen getransporteerd zowel door een diffusieve als convectieve stroom. De diffusieve chloride-ionenstroom is evenredig met het vochtgehalte en de gradiënt van de concentratie vrij chloride in het poriewater. De convectieve chloride-ionenstroom is evenredig met de concentratie vrij chloride en de gradiënt van de vochtpotential. De chloridemodellen zijn uitgewerkt met ofwel het totale chloridegehalte ofwel de concentratie vrij chloride als de chloridepotential. In een van de chloridemodellen is het effect van carbonatatie op de chloridebinding in
rekening gebracht door de chloride-bindingscapaciteit in de gecarbonateerde zone irreversibel tot nul terug te brengen.


Het numeriek model is getest in een vocht-case, een chloride-case en een droging-benattingscase. Het lineaire en een niet-lineair vochtmodel, zowel met als zonder het overgangselement, zijn gebruikt om de droging van cementpasto zonder chloridebelasting te simuleren. Een vergelijking met experimentele data van het vochtverlies over de tijd leerde dat het lineaire model zonder het overgangselement het best presteerde. De chloride-case beschrijft de vergelijking van het numerieke model metexperimentele gegevens van in zee water ondergedompelde betonblokken. De indringing van chloride-ionen geschiedde hoofdzakelijk door diffusie; alleen in het begin van de expositie was er enige convective chloride-opname vanwege de nabehandeling van het beton. De chloride-randvoorwaarde is verkregen door aan te nemen dat de concentratie vrij chloride in het portierwater aan het betonoppervlak gelijk is aan de chloride-concentratie in het zee water. De simulaties kwamen in het algemeen goed overeen met de meetresultaten na 2, 8 en 16 jaar expositie; afwijkingen verschenen vooral in de oppervlaktezone. Ook de input van de berekeningen correspondeerde met waardebereiken in de literatuur. Het effect van de nabehandeling op het uiteindelijke chlora profiel is onderzocht d.m.v. de carbonatiemodellen. Het verloren gaan van de chloride-bindingscapaciteit leidde tot een piek in het berekende totaal-chlorideprofiel.

In de droging-benattingscase is de capaciteit van het numerieke model gedemonstreerd om met variabele omgevingstemperatuur, vochtigheid en chloridebelasting om te gaan. Experimenten met cyclische chloride-expositie zijn gesimuleerd. Gedurende de droogfases bleef de temperatuur constant in de ene set van de experimenten en varieerde volgens een sinus in de andere set. Het is aangenomen dat de variatie van de omgevingsvochtigheid gedurende de droogfases tegengesteld was aan de variatie van de omgevingstemperatuur. Identieke materiaalparameters zijn gebruikt in de simulatie van de set met constante
temperatuur en die met variabele temperatuur; de warmte- en
evochtrandvoorwaarden waren echter verschillend. Een ‘best fit’ van de
meetresultaten behorende bij beide sets is nagestreefd met plausibele
materiaalparameters. In de simulaties werd een hoeveelheid zout water
geabsorbeerd gedurende de benattingfasen, terwijl de chloride-ionen zich
herverdeelden gedurende de droogfasen. Het bleek dat tijdens de droogfasen
de inwaartse chloridediffusie en de naar het oppervlak gerichte chloride-ionenconvectie
in competitie zijn. Vergelijkingen tussen gemeten en berekende totaal-
chlorideprofielen lieten zien dat de overeenkomst goed was voor de set met
constante temperatuur, maar dat de berekende chloridegehalten kleiner waren dan
de gemeten chloridegehalten voor de set met variabele temperatuur. De simulaties
bevestigden de experimentele observatie dat in vergelijking met de constante
temperatuur, de temperatuurvariatie grotere totaal-chloridegehalten tot gevolg heeft.
Ook de carbonatatiemodellen leidden tot resultaten die in overeenstemming waren
met de experimentele gegevens voor de set met constante temperatuur. De
afwezigheid van gebonden chloride in de gecarbonateerde zöne veroorzaakte een
piek in het berekende totaal-chlorideprofiel.

De gevoeligheid van het ontwikkelde model voor verscheidene parameters is
onderzocht, namelijk: de vochtovergangscœfficiënt, de vochtconductiviteit bij
verzadiging, de hydratatiegraad, de chlorideconductiviteit bij verzadiging en de
chloride-bindingsparameters. In de droging-benattingscase met constante
temperatuur bleek dat een grotere waarde van verzadigings-vochtconductiviteit
grote totaal-chloridegehalten aan het oppervlak en glooai lagere vochtgehalten
veroorzaakte, terwijl de chloride-indringingsdiepte onveranderd bleef. Het berekende
totaal-chlorideprofiel was ongevoelig voor een verandering van de hydratatiegraad,
voorover alleen de gerelateerde verandering van het cementgel-gehalte in rekening
is gebracht en andere afhankelijkheden buiten beschouwing worden gelaten. Lagere
waarden van de verzadigings-chlorideconductiviteit leidden tot een toegenomen
accumulatie van chloriden aan het oppervlak en een gereduceerde
indringingsdiepte, hetgeen lijkt aan te geven dat chloride-ionen als het ware
opgesloten kunnen worden in de oppervlaktezone van beton bij droging-
benattingscycli. Ook sterkere lineaire chloridebinding leverde grotere totaal-
chloridegehalten in de oppervlaktezone en een gereduceerde indringingsdiepte op.
Langmuir-achtige adsorptie gaf totaal-chlorideprofielen die aanzienlijk afwijken van
de meetresultaten.

Het aandeel van vocht migratie in het uiteindelijke totaal-chlorideprofiel is onderzocht
door resultaten van de droging-benattingscase met constante temperatuur te
vergelijken met berekeningen gebaseerd op water-verzadiging en met een ‘fitting’
van de error-functie. Het bleek dat in afwezigheid van chloride-convectie en met
optimale chloride-diffusie, het oppervlakte-chloridegehalte afneemt en de chloride-indringingsdiepte toeneemt. De vergelijking van het ontwikkelde model met de error-functie analyse liet zien dat de ontwikkeling van het totaal-chlorideprofiel in de tijd geheel verschillend is en dat het buiten beschouwing laten van vochtbewegingen veroorzaakt door de droging-benattingsexpositie hoofdzakelijk leidt tot een overschatting van de chloride-binding.

Het ontwikkelde model en bijbehorende computer-programma bieden gereedschap om het begrip van het chloride-indringingsproces in beton te verbeteren. Voordat echter kwantitatieve voorspellingen t.b.v. duurzaamheidsanalyse gedaan kunnen worden, moeten ten eerste meer testcases geanalyseerd worden met het programma, ten tweede de input-parameters uniek gerelateerd worden aan de verscheidene betontypes d.m.v. gestandaardiseerde experimenten, ten derde het kritische chloridegehalte als corrosie-criterium preciezer gespecificeerd worden en ten vierde stochastische effecten door de heterogeniteit van beton, de bouwfase van de betonconstructie en door de wisselende omgevingscondities gedurende de ontwerp-levensduur, vastgesteld worden.
DANKWOORD

Een woord van dank wil ik ten eerste graag richten aan prof. Bijen voor de stimulerende wijze waarop hij mijn promotie-onderzoek begeleidde. Hij zorgde ervoor dat ik steeds goed op koers bleef. Ik dank hem voor zijn vertrouwen in mijn capaciteiten en voor de bescherming die hij bood. De inbreng van prof. de Borst is van groot belang geweest voor het welslagen van dit onderzoek. Zijn visie heeft me voor dwalingen behoed. Ik kon altijd rekenen op zijn begrip voor problemen in het onderzoek en op zijn toewijding bij de oplossing daarvan. Ik dank hem ook hartelijk voor de zes weken verlenging van mijn vierjarig aio-contract, die hij bekostigde. Alex zette zich allijt in om mij alle interessante aspecten van het onderzoeksgebied te doen zien. Zijn enthousiasme en aanmoediging waren een grote stimulans. Ik ben hem ook dankbaar voor zijn sociale bijstand toen dat nodig was. Peter Roelfstra was altijd bereid onderzoeksvragen met mij te bespreken. Ik dank hem voor zijn hulp en gastvrijheid.

I cordially thank Carmen Andrade for involving me in Rilem technical committee 178 ‘testing and modelling chloride ingress into concrete’. I thank ook Bert voor het ter beschikking stellen van computer-faciliteiten, Frank voor de ondersteuning daarvan, Harm en Garth voor hun hulp bij FEAP, en Plonia, Allard en Gerard voor hun hulp bij de experimenten. Mijn kamergenoten Hiroshi en Jan ben ik dankbaar voor de prettige sfeer waarin ik kon werken en mijn paranimfen Roel en Oğuzhan voor het aanvaarden van deze taak. Ik dank mijn huidige werkgever Intron voor de vrijheid die genoemd bedrijf mij gaf om dit proefschrift te voltooien.

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Sander Meijers
januari 2003
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1985 - 1991 diploma Gymnasium β cum laude, Serviam Lyceum Sittard


2002 - heden projectingenieur Intrion BV Culemborg
The analysis of chloride ingress is an important part of the durability design of concrete structures. A computational model based on the finite element method is presented here, which links chloride transport to moisture migration and heat flow in concrete. Model simulations are compared to experimental data.