Computational modelling of chloride ion transport in reinforced concrete

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Exposure to a saline environment is a major threat with respect 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. They can eventually trigger a pitting corrosion process. The assessment of a corrosion-free service life of concrete structures is of paramount economic interest. However, the modelling of the ingress of chloride ions is complicated due to various influencing factors and transport mechanisms. Here a computational model for chloride ion transport through a porous material is presented. Chloride ion transport in reinforced concrete is modelled by focusing on centimeter-level and setting up three coupled equations for heat, moisture and chloride ion transport respectively. Three quasi-homogeneous components are distinguished: mortar, aggregates and interfacial transition zones. The model is handled computationally by discretising in space according to the finite element method and discretising in time according to the finite difference method. Stationary and transient, linear and non-linear, homogeneous or heterogeneous calculations can be performed. By applying the model a number of examples have been elaborated; one of these is presented. This example focuses on the coupling between chloride ion and moisture flow.

Key words: **chloride penetration, reinforced concrete, corrosion, coupled transport, porous media**

1. Introduction

The design of concrete structures involves mainly the evaluation of strength, stability and durability. A major threat to concrete durability is chloride. As chlorides are present in salty water and de-icing salts, special care has to be taken in the design of off-shore structures, bridges and parking garages. Also buildings in coastal areas are subjected to chloride ion ingress. The deterioration mechanism is the following: chloride ions penetrate the concrete to the level of the reinforcement, when they are in a sufficient quantity they depassivate the rebars, pitting corrosion starts if also oxygen is available, the effective cross section of the rebars decreases and cracks appear due to the expansion of rust products. The cracks and the decrease of the effective cross section of the reinforcing steel bars imply a strength loss, while the cracks also enhance the deterioration process.

Chloride ion ingress in reinforced concrete has been subject of research for many decades and tra-

ditionally this process has been modelled by Fick's second law. The only material parameter in this model is the effective chloride diffusion coefficient. The adjective "effective" already suggests that many effects are hidden in this coefficient. Very few attempts have been made to substantially refine the modelling, e.g. by [Saetta 1993]. With the aid of current computing techniques, complex problems can be solved which could not be handled in the time the effective diffusion approach was proposed. Here a refined approach is presented based on the interaction of three simultaneous processes: chloride ion transport, moisture migration and heat flow. The model also takes into account the inhomogeneous character of concrete on the meso-level. Three components are distinguished: mortar, aggregates and interfacial transition zones.

2. Model structure

The distance from the concrete surface to the reinforcement bars amounts to a few centimeters approximately. This is the distance which the chloride ions have to travel before they can depassivate the rebars. A certain threshold concentration of chloride ions at the reinforcement is required for the pitting corrosion process to start. Although the precise value of this threshold concentration is subject of debate, 0.3 % by mass of cement is commonly adopted as a safe value.

2.1 Heterogeneity on cm-level

The space domain of the chloride ingress problem is thus in the order of a few centimeters. At this level of observation three components of concrete are distinguished: mortar, aggregates and interfacial transition zones (ITZ). The interfacial transition zones form the interfaces between aggregates and mortar. As the width of these zones is about 30 μm, they do not really belong to the cm-level. In a very fine FEM-mesh, however, they could be taken into account. Mortar is a mixture of water, cement and sand particles and therefore in fact mortar also contains aggregates. Still, on the cm-level mortar is considered to be homogeneous. The aggregates in the model are then gravel particles, with dimensions of 3 mm and bigger[1]. This subdivision of concrete is illustrated in figure 1.
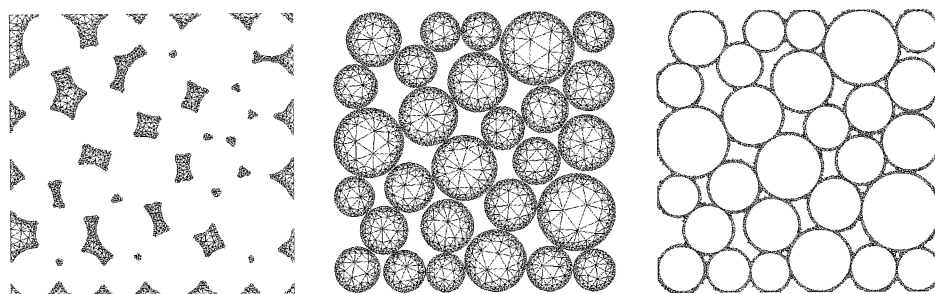

Figure 1. Subdivision of concrete into three components: mortar, aggregates and interfacial transition zones (from left to right). Putting the three figures on top of each other gives one FEM-mesh [Stroeven 1999]. The width of the ITZ is over-dimensioned.

The purpose of this explicit heterogeneity is to be able to attribute 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, 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.

Although the choice of the cm-level seems logical, a lower-level approach could have been followed. But 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 cm-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 mm-level, this would require very specialised equipment.

2.2 *Three coupled balances*

Chloride ion transport is closely related to moisture migration, and both of them have relations with heat flow. Among the various processes that occur in reinforced concrete after it has been cast, these three are selected for the model, thereby excluding cement hydration, oxygen flow and the corrosion process. Since only the corrosion initiation phase is considered and the latter two processes are relevant just for the corrosion propagation phase, they are not taken into account. Cement may still be hydrating, even years after casting. However, if calculations are to be performed for the service life of concrete structures, periods of 50 to 100 years are of interest. Then the effect of cement hydration may as well be summed up in the initial conditions for such a calculation and the actual process can be disregarded.

The processes of heat flow, moisture migration and chloride ion transport are based on the same principles in the model. 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 heat, moisture or chlorides. Furthermore, there are three potentials: temperature, moisture potential en chloride content. Usually temperature is associated with the heat balance, moisture potential with the moisture balance and chloride content with the chloride balance. But also cross-links are possible [Grunewald 1997, Roelfstra 1989, Groenevelt and Bolt 1969]. 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. Finally 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 2.

The moisture potential 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. The gradient of the macroscopic pore humidity drives – according to the definition of a potential – a moisture flow. From a thermodynamic point of view the choice of capillary pressure for the moisture potential and osmotic pressure instead of chloride content would have been preferable [Groenevelt and Bolt 1969]. However, as in most of the available data for concrete the macroscopic pore humidity and chloride content are used, these choices appear to be the most practical ones.
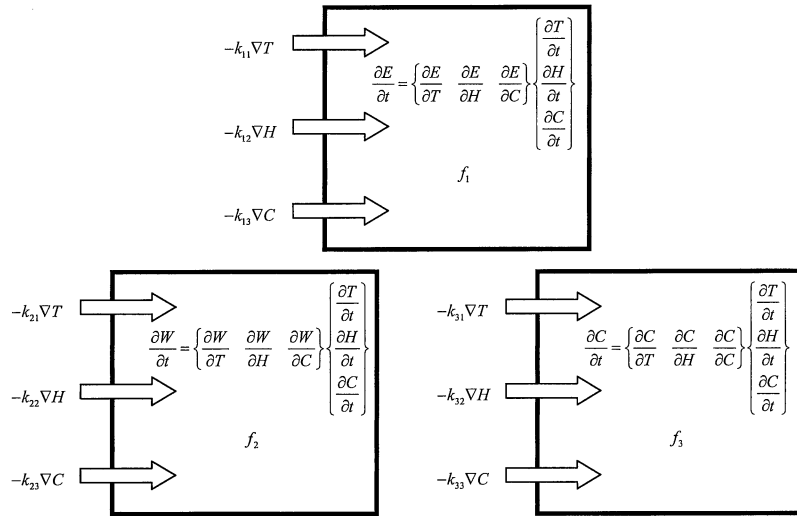

Figure 2. *Three coupled balances for heat (E), moisture (W) and chloride-ion (C) transport. In each balance it holds that the change of a quantity over time equals the net-influx from outside plus the inner generation of that quantity (f_1, f_2, or f_3)*

2.3 Mathematical representation

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

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix} \begin{Bmatrix} \dfrac{\partial T}{\partial t} \\ \dfrac{\partial H}{\partial t} \\ \dfrac{\partial C}{\partial t} \end{Bmatrix} = \nabla \cdot \left(\begin{bmatrix} k_{11} & k_{12} & k_{13} \\ k_{21} & k_{22} & k_{23} \\ k_{31} & k_{32} & k_{33} \end{bmatrix} \begin{Bmatrix} \nabla T \\ \nabla H \\ \nabla C \end{Bmatrix} \right) + \begin{Bmatrix} f_1 \\ f_2 \\ f_3 \end{Bmatrix} \qquad (1)$$

in which the derivates 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}), conductivities (k_{ij}) and sources (f_i) are in principle functions of the potentials, and – due to the explicit heterogeneity – functions of the spatial co-ordinates as well. This makes set of equations a set of coupled non-linear second order partial differential equations, or coupled non-linear diffusion equations.

The terms on the diagonal of the conductance matrix (kii) are the traditional transport properties for heat (Fourier), moisture[2] and chloride ions (Fick). The cross-terms in this matrix provide couplings between the three balances: osmosis, reversed osmosis, thermo-osmosis, thermo-filtration, Soret- and Dufour-effect [Grunewald 1997, Groenevelt and Bolt 1969]. The significance of some of the latter processes in concrete is questionable. Couplings between the balances also arise as a result of the dependencies of the diagonal terms on the potentials. Since chloride ions are particles bearing an electrical charge, the set of equations could have been completed with a fourth balance for electrical charge. Here electrical neutrality is assumed.

3. FEM implementation

Following the finite element method (FEM) the set of coupled non-linear diffusion equations (eqn. 1) is transformed into a set of non-linear algebraic equations [Zienkiewicz and Taylor 1997]. The set of differential equations is rewritten as follows using indicial notation and the Einstein convention:

$$c_{ij}\frac{\partial u_j}{\partial t} - \frac{\partial}{\partial s_l}\left(k_{ij}\frac{\partial u_j}{\partial s_l}\right) - f_i = 0 \tag{2}$$

in which u_j replaces T, H and C, and s_l denotes a spatial co-ordinate. The essential boundary condition is located on boundary Γ_{i1}:

$$u_i - \overline{u}_i = 0 \tag{3}$$

and the natural boundary condition on boundary Γ_{i2}:

$$-k_{ij}\frac{\partial u_j}{\partial s_l}n_l - \overline{q}_i = 0 \tag{4}$$

in which the overbar denotes prescribed values and nl is the component in l-direction of the (outward pointing) normal vector of boundary Γ_{i2}. The first step is to multiply eqn. 2 with weighting functions v_i and to integrate them over a reference surface area Ω (in case of two dimensions). Together with the integral over boundary Γ_{i2} of the product eqn. 4 and weighting functions w_i, they are required to be equal to zero:

$$\int_\Omega v_i\left[c_{ij}\frac{\partial u_j}{\partial t} - \frac{\partial}{\partial s_l}\left(k_{ij}\frac{\partial u_j}{\partial s_l}\right) - f_i\right]d\Omega + \int_{\Gamma_{i2}} w_i\left[k_{ij}\frac{\partial u_j}{\partial s_l}n_l + \overline{q}_i\right]d\Gamma = 0 \tag{5}$$

This implies that the three coupled balances are incorporated in a single finite element. Consequently, the solution procedure for temperature, moisture potential and chloride content becomes simultaneous; an alternative would have been a staggered scheme.

3.1 Non-linearity
After some standard elaborations [Zienkiewicz and Taylor 1997] and using Euler backward time stepping, the residual vector **r** at iteration i of time t+Δt is found:

$$\mathbf{r}_i^{t+\Delta t} = \frac{1}{\Delta t}\mathbf{C}_i^{t+\Delta t}\left(\mathbf{u}_i^{t+\Delta t} - \mathbf{u}^t\right) + \mathbf{K}_i^{t+\Delta t}\mathbf{u}_i^{t+\Delta t} - \mathbf{f}_i^{t+\Delta t} \tag{6}$$

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with $C_i^{t+\Delta t}$ the capacitance matrix and $K_i^{t+\Delta t}$ the conductance matrix. In a converged state the residual equals zero within some tolerance. In order to solve for the potential vector **u** at time $t+\Delta t$, the tangent matrix **S** is computed:

$$S_i^{t+\Delta t} = -\left(\frac{d\mathbf{r}}{d\mathbf{u}}\right)_i^{t+\Delta t}$$

(7)

The potential vector increment $d\mathbf{u}$ follows then from:

$$S_i^{t+\Delta t} d\mathbf{u}_i = \mathbf{r}_i^{t+\Delta t}$$

(8)

Finally, the potential vector is updated according to:

$$\mathbf{u}_{i+1}^{t+\Delta t} = \mathbf{u}_i^{t+\Delta t} + d\mathbf{u}_i$$

(9)

Because of the non-linearity of the problem, some iterations are needed to reach convergence within the preset tolerance.

3.2 Simultaneous solution

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. Adimensionalisation of the balances cannot cure this. As the fastest process determines the maximum timestep in the simultaneous solution procedure, the consequence is that simultaneously calculations are performed for the fastest and the two slower processes using the same timestep. The extra calculations for the two slower processes are superfluous, unless the couplings (both in diagonal and off-diagonal terms) are strong enough to affect these processes below their characteristic time scales. If the tightness of the couplings is not known a priori, the simultaneous solution strategy is a safe approach.

4. Results

The model has been implemented in the finite element code FEAP (R.L. Taylor) and several calculations have been performed. For every calculation the following choices can be made: stationary or transient, linear or (partly) non-linear, homogeneous or heterogeneous, (partly) coupled or uncoupled. All kinds of combinations are possible, ranging from simple stationary, linear, homogeneous, uncoupled calculations to complex transient, non-linear, heterogeneous, coupled ones. Here, a transient, partly non-linear, homogeneous, partly coupled problem is presented. Obviously, in order to be able to see some clear effects, the level of complexity should not be too high.

This example shows a piece of concrete which is exposed to a chloride solution on the left side; the other sides are impermeable for chlorides. Simultaneously, a moisture potential field is developing in vertical direction. This direction has been chosen perpendicular to the direction of chloride ingress to visualise the effect of coupling between the two flows. The moisture potentials are prescribed on the top and bottom side; the moisture cannot escape through the other sides. The tempe-

rature has been kept constant in this example. The non-linear moisture flow is governed by the following diffusion coefficient [Bazant and Najjar 1972]:

$$D(H) = \left(\frac{k_{22}}{c_{22}}\right)_H = a_1\left(a_2 + \frac{1-a_2}{1+\left(\dfrac{1-H}{1-a_3}\right)^{a_4}}\right) \tag{10}$$

and the following moisture content [Roelfstra 1989]:

$$W(H,T) = a_5 + a_6 H + a_7 T + a_8 HT + a_9 H^2 + a_{10} H^2 T \tag{11}$$

The coupling between moisture and chloride transport is achieved by putting:

$$k_{32}(T,H,C) = a_{11} C k_{22} \tag{12}$$

It can be shown that the consequence of this definition of k_{32} is chloride ion convection. An overview of the input is given in tables 1 to 3.

The calculation involved 400 quadrilateral elements and 40 timesteps. The chloride profile after these 40 timesteps is shown in figure 3. The dimension of the chloride content [C] is:

$$[C] = \frac{kg \quad Cl^-}{kg \quad cement} 100\,\% \tag{13}$$

The computed moisture potential field is depicted in figure 4.

Table 1. Inserted values of the capacities, conductivities and sources. The material functions c_{22}, k_{22} and k_{32}
are parametrised.

capacities	conductivities	sources
c_{11}=2.50.10^6 J/m^{3}K	k_{11}=2.40 W/mK	f_1=0.00
c_{12}=0.00	k_{12}=0.00	f_2=0.00
c_{13}=0.00	k_{13}=0.00	f_3=0.00
c_{21}=0.00	k_{21}=0.00	
c_{22}=(a_6,a_8,a_9,a_{10})	k_{22}=(a_1,a_2,a_3,a_4,a_6,a_8,a_9,a_{10})	
c_{23}=0.00	k_{23}=0.	
c_{31}=0.00	k_{31}=0.	
c_{32}=0.00	k_{32}=(a_1,a_2,a_3,a_4,a_6,a_8,a_9,a_{10},a_{11})	
c_{33}=1.00	k_{33}=1.00.10^{-12} m^2/s	

Table 2. Applied initial and boundary conditions, mesh size and timestep. The indices l, t and b denote left, top and bottom respectively. On boundaries where the potentials have not been prescribed, the corresponding flux is defined to be zero.

initial	boundary	mesh	timestep
T=283 K	T_l=283 K	l=0.01 m	Δt=86400 s
H=0.90	H_t=0.36	w=0.01 m	
C=0.00	H_b=1.00		
	C_l=2.00 %		

Table 3. Inserted values of the parameters for c_{22}, k_{22} and k_{32}. The parameters a_5 to a_{10} are applicable for a degree of hydration of 0.95 and a water to cement ratio of 0.50 [Roelfstra 1989].

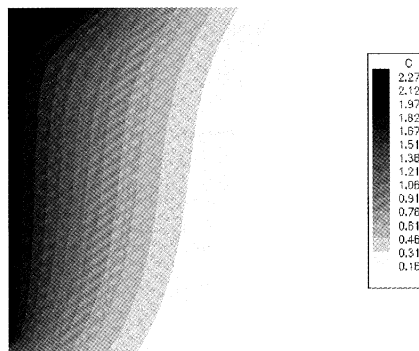|	parameters	
	0.35<H<0.85	0.85≤H≤1.00
a_1=1.00 ·10^{-10} m²/s	a_5=0.12	a_5=5.31
a_2=0.05	a_6=4.96	a_6=-7.28
a_3=0.70	a_7=0.00 K^{-1}	a_7=-0.02 K^{-1}
a_4=4.00	a_8=-0.02 K^{-1}	a_8=0.03 K^{-1}
a_{11}=0.50	a_9=-4.31	a_9=2.92
	a_{10}=0.01 K^{-1}	a_{10}=-0.01 K^{-1}

Fig. 3. Chloride profile as a result of coupling between chloride and moisture transport (after 40 days of exposure).
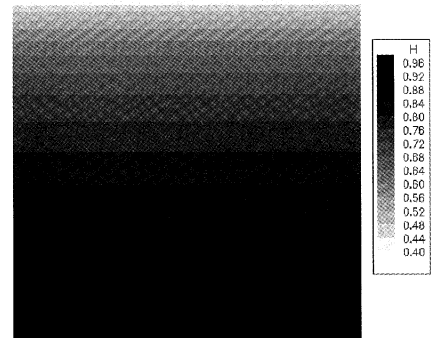

Fig. 4. Non-linear moisture potential field influencing the chloride ingress (after 40 days of exposure).

To assess the influence of material function k_{32}, this calculation has been repeated with $k_{32}=0$. The result is shown in figure 5. When comparing figure 5 and 3 the building up of chlorides in the upper left corner becomes apparent. Clearly the upward moisture flow drags the chloride ions in the same direction and together with the continuous supply of chloride ions from the left, this leads to an excess of chlorides in the upper left corner (note that the chloride content in that area is higher than the boundary and initial condition).
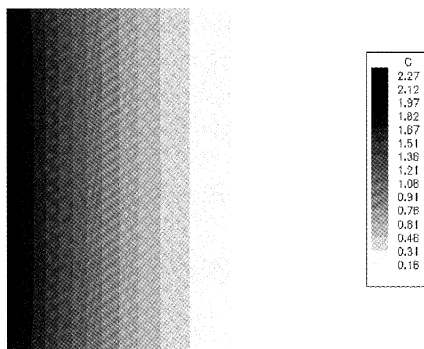

C
2.27
2.12
1.97
1.82
1.67
1.51
1.36
1.21
1.06
0.91
0.76
0.61
0.46
0.31
0.16

Figure 5. Chloride profile as a result of uncoupled chloride and moisture flow (after 40 days of exposure).

5.   Conclusion

Since chloride ingress in concrete is closely related to moisture migration, while both of them are temperature-dependent, it is essential to involve all three processes in calculations. Currently, the implemented finite element routine is able to deal with stationary and transient, linear and non-linear, homogeneous and heterogeneous, and coupled and uncoupled problems. However, not all relevant material functions have been implemented yet, in particular chloride ion adsorption on the hydrated cement. It is planned to extend the implementation of material functions and to perform further verifications. Finally, some service life predictions will be elaborated.

Acknowledgements

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Notes

[1] The transition point from sand to gravel particles is chosen at 3 mm.

[2] If H would have been interpreted as a hydraulic pressure head, then k_{22} would have represented Darcy's law.