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A MODEL DESCRIBING WATER AND CHLORIDE MIGRATION IN CONCRETE DURING WETTING/DRYING CYCLES

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Abstract

In order to predict the life span of concrete structures, models describing the migration of chloride are needed. In this paper, a model describing water and chloride transport in concrete is presented. Water transport is considered with Fick’s second law of diffusion, which describes the time-evolution of water content. Chloride transport is described with a combination of advection and diffusion, with interdiffusion, which describes the migration of chloride. Furthermore, chloride can be bound to the surface of the pore walls. This bound chloride is immobile, thus unavailable for transport. The result is a partial differential equation for the time-evolution of the chloride concentration, coupled to the partial differential equation for water transport. This partial differential equation is solved using the Crank-Nicolson implicit method for a situation in which chloride enters, and in a certain extent also leaves the sample. Because the goal is to describe the migration behavior in the sample during wetting and drying cycles, the sample gets wet during one half of a day and dries during the other half.

Key Words: Concrete, Modeling, Water transport, Chloride transport, Wetting/drying cycles

1. INTRODUCTION

Corrosion due to the presence of chloride is a large threat for the service life of a reinforced concrete structure in a marine environment. It is therefore very important to accurately describe water and chloride migration in concrete.

In the literature, models often describe chloride transport in a porous medium by means of a chloride diffusion coefficient [1–4]. These models are frequently based on the error function. However, Meijers et al. [5] and Wang et al. [6] concluded that a model which also considers advection of chloride with water, describes chloride transport better than a model which considers pure diffusion of chloride solely. A model which includes the effects of water transport on chloride ingress, as well as chloride binding, is presented by Oh and Yang [7]. The results are in good agreement with experimental data. The present model describes chloride transport as a sum of chloride advection with water and chloride diffusion due to differences in the chloride concentration of the pore solution.

Besides entering a concrete sample, chloride can, to a certain extent, be washed out of concrete with water, as found by Hong and Hooton [8]. This situation is studied in this paper. It is, however, expected, as described in [8], that the mass of chloride entering the sample is much larger than the mass of chloride leaving, resulting in an accumulation of chloride in the sample.

2. WATER TRANSPORT

In the present study, it is assumed that the one-dimensional water volume flux in a partially saturated concrete is, according to Fick’s first law, proportional to the water content gradient,

\[ n_{w} = -D \frac{\partial \theta}{\partial x} \]  \hspace{1cm} (1)

where \( D \) is the diffusion coefficient of water in concrete, \( \theta \) the water content in concrete [m³/m³] and \( x \) the position coordinate.

Using a micro mass balance and Eq. (1) results in Fick’s second law, which is a partial differential equation describing the time-evolution of the water content as

\[ \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial \theta}{\partial x} \right) \]  \hspace{1cm} (2)

where \( t \) is time. This equation will be applied on a concrete sample between \( x=0 \), where the surface is exposed to water transport, and \( x=L \), where the sample is isolated against water transport.

Two boundary conditions arise in describing the water transport. The first is a prescribed water content at the exposed surface of the sample. In this model, a wetting/drying cycle is considered. Corresponding to a tidal cycle, the sample gets wet during one half of the day and dries during the other half. During wetting, i.e. during the first half of a cycle, the water saturation at the surface is 1. During drying, the saturation is 0.1. In conclusion, the boundary condition for water transport is

\[ s_{x=0} = \begin{cases} 1 & \text{during wetting} \\ 0.1 & \text{during drying} \end{cases} \]  \hspace{1cm} (3)

with the saturation

\[ s = \frac{\theta}{\theta_{sat}} \]  \hspace{1cm} (4)

where \( \theta_{sat} \) is the saturated water content of the studied concrete. It is assumed that the porosity is not dependent on \( x \), therefore \( \theta_{sat} \) is constant. In a later section, the properties of the studied concrete are discussed.

The second boundary condition states that no water transport occurs at the isolated surface of the sample, i.e.
\[ \frac{\partial \theta}{\partial x} \bigg|_{x=L} = 0. \]  

At the start of the process, the water content in the concrete sample is prescribed.

### 3. CHLORIDE TRANSPORT

It is assumed that two types of chloride are present in the medium: dissolved free chloride in the pore solution and chloride bound to the surface of the pore walls. Whereas free chloride is available for transport, bound chloride is immobile. Furthermore, equilibrium between free and bound chloride is assumed. Also, a linear relation between the free and bound chloride is assumed. This linear relation is

\[ C_b = K_c c_f, \]  

where \( C_b \) is the concentration of bound chloride [kg/m\(^3\) concrete], \( c_f \) the concentration of free chloride [kg/m\(^3\) pore solution] and \( K_c \) an empirical constant. The total chloride concentration [kg/m\(^3\) concrete] is written as

\[ C_{\text{tot}} = c_f + K_c c_f = c_f (\theta + K_c). \]  

The chloride mass flux consists of an advective and a diffusive component. The advective component arises if the dissolved free chloride is transported through the concrete due to the bulk motion of the water. The advective chloride mass flux is

\[ n_{\text{advective}} = n_{\text{solution}} c_f = -D_m \frac{\partial c_f}{\partial x}. \]  

The diffusive component arises due to differences in the chloride concentration of the pore solution. The diffusive chloride mass flux in the pore solution is proportional to the chloride concentration gradient, written as

\[ n_{\text{solution}} = -D_m \frac{\partial c_f}{\partial x}, \]  

where \( D_m \) is the molecular diffusion coefficient of chloride in water, which has a value of 1.26\times10^{-9} \text{ m}^2/\text{s} \ [9]. The diffusive chloride mass flux in the concrete is

\[ n_{\text{diffusive}} = n_{\text{solution}} \frac{\theta}{\tau} = -D_m \frac{c_f}{\tau} \frac{\partial \theta}{\partial x}. \]  

with the tortuosity \( \tau \) has been added to the expression to incorporate deviations from the ideal situation. With Eqs. (8) and (10), the total chloride mass flux in concrete can be written as

\[ n_f = -D_m \frac{\partial c_f}{\partial x} - \frac{D_m}{\tau} \frac{\partial c_f}{\partial x} \frac{\partial \theta}{\partial x}. \]  

With the aid of a micro mass balance and Eq. (11), the result is a partial differential equation describing the time-evolution of the chloride concentration as

\[ \frac{\partial}{\partial t} \left( c_f (\theta + K_c) \right) = \frac{\partial}{\partial x} \left( D_m \frac{\partial c_f}{\partial x} + \frac{D_m c_f}{\tau} \frac{\partial \theta}{\partial x} \right). \]  

The boundary condition for the surface where the sample is isolated against water transport states that the chloride mass flux at \( x=L \) is zero. Because the advective chloride flux is zero, the diffusive chloride flux must be zero as well. This leads to the boundary condition

\[ \frac{\partial \theta}{\partial x} \bigg|_{x=L} = 0. \]  

At the exposed boundary of the sample, salt or fresh water can enter the sample during wetting and salt or fresh water can leave the sample during drying. In this study, the situation in which salt water, for instance seawater, enters the sample will be considered. When the sample dries, water with a certain amount of chloride leaves the sample.

During wetting, it is assumed that the surface of the concrete sample is in contact with external water having a chloride concentration \( c_{\text{outside}} \). There are two ways for chloride to enter the sample: by advection if external water containing chloride is adsorbed by the sample, and by diffusion, due to a difference in the chloride concentration of the external water and the pore solution at the surface. The boundary condition at \( x=0 \) is

\[ n_{\text{fuel}} \bigg|_{x=0} = D_m \left( c_{\text{outside}} - c_f \right) \bigg|_{x=0} = n_{\text{fuel}} \bigg|_{x=0}, \]  

which, with Eqs. (1) and (11), transforms into

\[ -D_m \frac{\partial c_f}{\partial x} \bigg|_{x=0} + D_m \left( c_{\text{outside}} - c_f \right) \bigg|_{x=0} = -D_m \frac{\partial c_f}{\partial x} \bigg|_{x=0} c_f - \frac{D_m}{\tau} \frac{\partial c_f}{\partial x} \bigg|_{x=0} \frac{\partial \theta}{\partial x}. \]  

The value for \( c_{\text{outside}} \) is chosen to be the value of the chloride concentration in seawater, which is approximately 19 kg/m\(^3\).

During drying, the chloride concentration of the water leaving the sample equals the chloride concentration of the pore solution at the surface, i.e., \( c_f \). The boundary condition during drying becomes

\[ n_{\text{fuel}} \bigg|_{x=0} = n_{\text{fuel}} \bigg|_{x=0} c_f, \]  

which, with Eqs. (1) and (11), transforms into

\[ -D_m \frac{\partial c_f}{\partial x} \bigg|_{x=0} c_f - \frac{D_m}{\tau} \frac{\partial c_f}{\partial x} \bigg|_{x=0} \frac{\partial \theta}{\partial x} = -D_m \frac{\partial c_f}{\partial x} \bigg|_{x=0} c_f, \]  

and thus the final form of this boundary condition is

\[ \frac{\partial c_f}{\partial x} \bigg|_{x=0} = 0. \]  

### 4. STUDIED CONCRETE

In order to simulate the water and chloride transport in concrete, a concrete with known diffusion coefficient and chloride binding capacity is needed. Since no such concrete is found in the literature, a combination of properties is used. Zibara [10] studied the chloride binding of various kinds of cement pastes. Samples were exposed to water with a chloride concentration of 0.5 M, which corresponds well to the chloride concentration of the external water used in the present model. The experimental data for cement paste were translated to a concrete with an evaporable water content of 8%. It is therefore assumed that the concrete in the present study has a saturated water content \( \theta_{\text{sat}} \) of 0.08 m\(^3\)/m\(^3\). The binding constant \( K_b \) then has a value of 0.19.  

Li et al. [11] used two experimentally determined diffusion coefficients in their model. These diffusion coefficients will be used in the present model. The diffusivity during wetting is given by the relation

\[ D^* = 10^{-10} \cdot e^{\theta}. \]  

The diffusivity coefficient during drying is described with
\[
D' = 10^{-10} \left( 0.025 + \frac{0.975}{1 + \left( \frac{1 - s}{0.208} \right)^3} \right)
\]  

(20)

In absence of a specific value, the tortuosity of the studied concrete is assumed to be 1.0.

5. RESULTS
The equations in the previous sections are discretized and numerically solved using MATLAB. In the computations, a sample length of 0.1 m is considered, with an equidistant grid of 0.5 mm. The numerical solution technique and the discretization are discussed in the Appendix.

Fig. 1 shows the water content profiles after 1, 5 and 10 cycles, where the sample was initially half-saturated, i.e. the water content at \( t=0 \) was 0.04 m\(^3\)/m\(^3\). Since the diffusivity during drying is much smaller than during wetting, the sample drains only a small amount of water during the drying period. It is therefore seen that water accumulates rapidly, and after 10 cycles, the sample is almost completely saturated in the bulk of the sample.

The free chloride concentration of the pore solution, i.e. \( c_f \), after 1, 5 and 10 cycles is illustrated in Fig. 2. The sample initially contained no chloride. It can be seen that the chloride concentration has the highest value at the surface of the sample. After 10 cycles, chloride is diffused towards the back of the sample. A more constant water content decreases the water transport, and therefore the influence of advection on chloride transport. Diffusion then dominates over advection.

Since the bound chloride concentration is the multiplication of the chloride concentration in Fig. 2 with the constant \( K_b \), the shape of the bound chloride profiles is equal to the shape presented in Fig. 2, only the values are different. Therefore, these graphs will not be illustrated in a figure.

In Fig. 3, the profiles of the total chloride concentration in concrete, i.e. \( C_{tot} \), are shown after 1, 5 and 10 cycles. These profiles illustrate that the total chloride concentration has the highest value just below the surface. Since the water content at the surface is small at the end of a cycle, the amount of free chloride per m\(^2\) concrete at the surface is small as well. A similar chloride concentration profile for a concrete sample subjected to a wetting/drying cycle is found by Polder and Peelen [12].

6. DISCUSSION
A simple model for water and chloride migration is presented in this paper. Water transport is modeled with Fick’s second law of diffusion and chloride transport is modeled as a combination of advection and diffusion.

However, some aspects have not been incorporated in the present study, although it is recognized that these aspects could have an influence on the water and chloride transport. First of all, the presence of salt and a gradient in salt concentration can influence water transport. In the study of Reuvers et al. [13], the salt concentration did not significantly influence the diffusivity of water in nylon 6 films. The influence of salt on the water transport in mortar or concrete is not well known.

Crystallization and its effects are not incorporated in this model. Although the solubility of chloride in water is not exceeded in the time considered in this study, crystallization could occur after a larger number of cycles. The solid
particles can then hinder water and chloride transport, for instance by pore blocking.

Whereas in this study one-dimensional water and chloride transport is considered, two- or even three-dimensional transport can occur in reality. During tidal cycles, the lower part of the structure is under water, whereas the higher part remains above water. Water can enter the structure in the lower part and can then be transported to the higher part due to a difference in capillary pressure. The transport of water and chloride during tidal cycles is therefore more complex than presented here.

In the assumptions on chloride binding, some phenomena are simplified. For instance, a linear binding isotherm is assumed. In the literature [14-16], other types of binding isotherms have been found that correspond well to experimental data. These other types (Langmuir, Freundlich) are considered as a better description of reality by many authors. Furthermore, equilibrium between free and bound chloride is assumed. Since the exposure period of chloride in concrete during a daily wetting/drying cycle is small due to the motion of chloride, it is expected that the application of a chloride mass transfer rate between free and bound chloride would describe the phenomenon of chloride binding more accurately.

APPENDIX: NUMERICAL SOLUTION TECHNIQUE

First, a dimensionless length scale is introduced as

\[ z = \frac{N x}{L} \]

where \( N \) is the number of grid points in the computations and \( L \) is the length of the sample. This means that \( z \) has an integer value on the grid points. Eq. (2) then becomes

\[ \frac{\partial \theta}{\partial t} = \frac{D}{N^2} \frac{\partial^2 \theta}{\partial z^2} \]

which equals

\[ \frac{L^2}{N^2} \frac{\partial \theta}{\partial t} = \frac{D}{\partial z^2} \frac{\partial \theta}{\partial z} + \frac{\partial^2 \theta}{\partial z^2} \]  

In order to numerically solve the partial differential equation, the Crank-Nicolson implicit method [17] will be applied, which approximates Eq. (23) with

\[ \frac{L^2}{N^2} \frac{\partial \theta}{\partial t} = \frac{D}{\partial z^2} \frac{\partial \theta}{\partial z} + \frac{\partial^2 \theta}{\partial z^2} \]

\[ \frac{1}{2} \left( \frac{D_i^{j+1} - D_i^j}{\Delta t} \theta_i^j - \theta_i^j + \frac{D_i^j}{2} \left( \theta_i^{j+1} - 2 \theta_i^j + \theta_i^{j-1} \right) + \right) \]

where \( j \) and \( j+1 \) represent the time rows and \( i \) represents a grid point. The terms of this discretized equation are rearranged to yield the following linear relation

\[ \theta_i^{j+1} = \left( \frac{1}{4} D_i^{j+1} - D_i^j \right) \theta_i^j + \theta_i^j - \frac{2L^2}{N^2 \Delta t} \theta_i^j \]

\[ \theta_i^{j+1} = \left( \frac{1}{4} D_i^{j+1} - D_i^j \right) \theta_i^j + \theta_i^j - \frac{2L^2}{N^2 \Delta t} \theta_i^j \]  

\[ \theta_i^{j+1} = \left( \frac{1}{4} D_i^{j+1} - D_i^j \right) \theta_i^j + \theta_i^j - \frac{2L^2}{N^2 \Delta t} \theta_i^j \]

where the horizontal lines represent the terms on the left side of Eq. (25).

For chloride transport, Eq. (12) and the boundary conditions in Eqs. (13) and (15/18) are discretized similarly using the Crank-Nicolson method and solved in matrix form. Although these equations are more extensive, the used technique remains equal.

REFERENCES