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# A Coupled Chemical and Mass Transport Model for Concrete Durability

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### Abstract

In this paper a reactive mass transport model was developed for service life prediction of concrete structures. The model formulation is based on a continuum approach and solved by a non-linear finite element scheme. The model is an extended version of the Poisson-Nernst-Planck equation system, including a sorption hysteresis model and a chemical equilibrium module to model the chemical degradation part of the problem. The sorption hysteresis is modeled as a history depended equilibrium function between the liquid and vapor phase. A simple test case shows the improved result from the sorption hysteresis modelling and a chemical model shows the chemical degradation of cement paste.

**Keywords:** mass transport, chemical coupling, sorption hysteresis, continuum theory, finite element method.

# **1** Introduction

Service life modeling of concrete is a general framework that includes a range of different areas. For this study focus will be on multi-species mass transport coupled to a chemical module capable of predicting the chemical degradation of the solid matrix. Mass transport modeling of concrete is a diffusion process in a electrolytic pore solution, which is described in various papers by the Nernst-Planck equation e.g. see [1] and different extended versions of the Poisson-Nernst-Planck equation (PNP) e.g. see [2, 3, 4, 5]. The movement of ions in concrete is strongly coupled to the convection of water in the system, this is coupled on a continuum basis to the diffusion equation, see [6, 7]. A continuum system of this type is refered to as mixture theory, see [8]. Furthermore, unsaturated concrete exhibit sorption hysteresis e.g. see [9, 10]. In this context chemical equilibrium modeling consist of two main parts, the hydration process and the degradation of the solid matrix, see [11, 12, 13]. The topics studied here have related fields within groundwater chemistry, see [14], and nuclear waste disposal, see [15, 16], from which experiences can be drawn. Coupling of a mass transport model and a chemical model into a reactive transport model has been investigated in different papers, in terms of different mass transport equations and chemical equilibrium codes for cement based materials, see [17, 18, 19].

For this work the PNP equation system is used as basis for the description of an extended reactive mass transport model. The aim is to include, a water/vapor coupling in terms of a sorption hysteresis effects, including the advection of dissolved ionic species which constitute the novelty of this work. Furthermore, it is important to keep the model in a general formulation, especially for the chemical module, which give the possibility of working with different chemical models without limitations in the number of state variables adopted. A simple test case is evaluated in order to show the effect of sorption hysteresis modeling and chemical degradation of the solid matrix.

### 2 Model description

### 2.1 General formulation of the model

The mass transport model described in this work is based on the Poisson-Nernst-Planck equations for ionic species with addition of a advection term coupled with vapor diffusion by a sorption hysteresis model. The sorption hysteresis model will improve the ability to describe non-saturated system e.g caused by time depended boundary conditions. Furthermore, a chemical module is added to the mass transport equation as a source/sink term, for establishing chemical equilibrium between the solid matrix and pore solution. The governing equation is solved by a non-linear finite element (FEM) scheme, where the chemical module is running as a separate routine on each node in the discrete system. By using the separate approach, it is assumed that complete chemical equilibrium is established instantaneously in each time step considered.

### 2.2 Mass transport modeling

#### 2.2.1 Extended Possion-Nernst-Planck

The extended Nernst-Planck part of the problem including for chemical reactions and advection can according to [8, 19] be expressed as

$$\varepsilon^{l} \frac{\partial c_{i}^{l}}{\partial t} + c_{i}^{l} \frac{\partial \varepsilon^{l}}{\partial t} = \nabla \cdot \left( D_{i}^{l} \varepsilon^{l} \nabla c_{i}^{l} + D_{i}^{l} c_{i}^{l} \nabla \varepsilon^{l} - A_{i}^{l} c_{i}^{l} z_{i} \varepsilon^{l} \nabla \Phi \right) +$$

$$v^{l,s} \varepsilon^{l} \nabla c_{i}^{l} + v^{l,s} c_{i}^{l} \nabla \varepsilon^{l} + q_{i}; \qquad i = 1, 2.., m$$

$$(1)$$

where  $\varepsilon^l$  is the volume concentration of the liquid phase l,  $c_i^l$  is the concentration of the *i*'th aquas specie which is dissolved in the liquid phase l, t is time,  $D_i^l$  is the diffusion

coefficient,  $A_i^l$  is the ion mobility,  $z_i$  is the valence,  $\Phi$  is the electrostatic potential of the bulk solution,  $v^{l,s}$  is the liquid velocity with respect to the solid matrix s and  $q_i$  is generation/dissolution of species from establishment of chemical equilibrium. In partial saturated systems, the diffusion coefficient, ion mobility and liquid velocity are assumed to be functions of the liquid volume fraction  $\varepsilon^l$ .

The charge balance of the solution is based on Gauss law which in this case is reduce to a Poisson type of equation.

$$\xi_d \xi_0 \nabla^2 \Phi = F \sum_{i=1}^n c_i z_i \tag{2}$$

where  $\xi_d$  is the relative dielectricity coefficient,  $\xi_0$  is the dielectricity coefficient of vacuum and F is the Faraday's constant.

The change in volume concentration of liquid  $\varepsilon^l$  is described by a mass balance equation including a source/sink term, coupling the vapor/liquid transport and establish phase equilibrium in terms of a history depended function, see [9, 10].

$$\rho_w \frac{\partial \varepsilon^l}{\partial t} = \nabla \cdot \left( D_{\varepsilon^l} \nabla \varepsilon^l \right) + R \left( \varepsilon^{l,eq} - \varepsilon^l \right)$$
(3)

where  $\rho_w$  is the density of water,  $D_{\varepsilon^l}$  is the diffusion coefficient of the liquid, which is a function of  $\varepsilon^l$ , R is the rate constant for sorption and  $\varepsilon^{l,eq}$  is the equilibrium volume concentration of water .  $\varepsilon^{l,eq}$  is a function of relative humidity  $\phi_v$  and sorption history. A more detailed description of a sorption hysteresis model, including scanning between the two boundary curves, will be given in Section (2.2.3).

A mass balance equation similar to Equation (3) describes the change in vapor volume concentration  $\varepsilon^v$ . To simplify the coupling a non-deformable matrix is considered and a relation between  $\varepsilon^v$ ,  $\varepsilon^l$  and  $\varepsilon_p$  is utilized  $\varepsilon^v + \varepsilon^l = \varepsilon_p$  where  $\varepsilon_p$  is the porosity. Furthermore, it is convenient to work with relative humidity as driving potential for the vapor phase. Relative humidity is related to the vapor density concentration  $\rho_v$  by  $\phi_v = \rho_v / \rho_{vs}$  where  $\rho_{vs}$  is the mass density concentration of vapor at saturation at a given temperature. The governing equation for vapor transport is given in Equation (4).

$$\rho_{vs}\left(\varepsilon_p - \varepsilon^l\right) \frac{\partial \phi_v}{\partial t} - \rho_{vs}\phi_v \frac{\partial \varepsilon^l}{\partial t} = \nabla \cdot \left(D_\phi \nabla \phi_v\right) - R\left(\varepsilon^{l,eq} - \varepsilon^l\right) \tag{4}$$

where  $D_{\phi}$  is the vapor diffusion coefficient, which is a function of  $\varepsilon^{l}$ . Note different sign in the source/sink terms from Equation (3) to (4).

#### 2.2.2 Finite element formulation

The complete set of coupled Equations (1), (2), (3) and (4), is solved by a non-linear finite element scheme. A weak formulation of the system is established by multiplying the governing equations with an arbitrary function w and W for the spatial and time

domain respectively. Using the Green-Gauss theorem and integrate over time and spatial domain, give

$$\int_{t_{1}}^{t_{2}} W \int_{V} w \varepsilon^{l} \frac{\partial c_{i}^{l}}{\partial t} dV dt + \int_{t_{1}}^{t_{2}} W \int_{V} w c_{i}^{l} \frac{\partial \varepsilon^{l}}{\partial t} dV dt = -\int_{t_{1}}^{t_{2}} W \int_{V} (\nabla w)^{\mathsf{T}} \left( D_{i}^{l} \varepsilon^{l} \nabla c_{i}^{l} + D_{i}^{l} c_{i}^{l} \nabla \varepsilon^{l} - A_{i}^{l} c_{i}^{l} z_{i} \varepsilon^{l} \nabla \Phi \right) dV dt + \int_{t_{1}}^{t_{2}} W \oint_{S} \mathbf{j}_{i} \mathbf{n} \, dS \, dt + \int_{t_{1}}^{t_{2}} W \int_{V} W v^{l,s} \varepsilon^{l} \nabla c_{i}^{l} \, dV dt + \int_{t_{1}}^{t_{2}} W \oint_{V} \mathbf{w} \, v^{l,s} c_{i}^{l} \nabla \varepsilon^{l} \, dV dt \quad (5)$$

where  $\mathbf{j}$  is the flux vector from the surface S and  $\mathbf{n}$  is the normal to the surface.

For the Poisson equation (2), it is used that the arbitrary function w(x, y, z) = 0 for  $(x, y, z) \in S$ , after integration by parts. It is seen that the function is independent of time and therefore only integrated in the spatial domain, as

$$\int_{V} (\nabla w)^{\mathsf{T}} \xi_d \xi_0 \nabla \Phi \, dV = \int_{V} w \, F \sum_{i=1}^n c_i z_i \, dV \tag{6}$$

, The weak form of the liquid flow described in Equation (3) is given by the same approach as in Equation (5), i.e

$$\int_{t_1}^{t_2} W \int_{V} w \,\rho_w \frac{\partial \varepsilon^l}{\partial t} \, dV dt = -\int_{t_1}^{t_2} W \int_{V} (\nabla w)^{\mathsf{T}} \left( D_{\varepsilon^l} \nabla \varepsilon^l \right) dV dt + \int_{t_1}^{t_2} W \oint_{S} \mathbf{j}^l \mathbf{n} \, dS dt + \int_{t_1}^{t_2} W \int_{V} w R \left( \varepsilon^{l, \mathsf{eq}} - \varepsilon^l \right) dV dt \quad (7)$$

The weak form of the governing vapor transport equation (4) is

$$\int_{t_{1}}^{t_{2}} W \int_{V} w \rho_{vs} \left(\varepsilon_{p} - \varepsilon^{l}\right) \frac{\partial \phi_{v}}{\partial t} dV dt - \int_{t_{1}}^{t_{2}} W \int_{V} w \rho_{vs} \phi_{v} \frac{\partial \varepsilon^{l}}{\partial t} dV dt = -\int_{t_{1}}^{t_{2}} W \int_{V} (\nabla w)^{\mathsf{T}} \left(D_{\phi} \nabla \phi_{v}\right) dV dT + \int_{t_{1}}^{t_{2}} W \oint_{S} \mathbf{j}^{v} \mathbf{n} \, dS dt - \int_{t_{1}}^{t_{2}} W \int_{V} w \, R \left(\varepsilon^{l, \mathsf{eq}} - \varepsilon^{l}\right) \, dV dt$$

$$\tag{8}$$

The state variables of the model are approximated with the shape function N and from the Galerkin's method, the arbitrary spatial weight function w is approximated with the same shape function.

$$c_i^l = \mathbf{N}\mathbf{a}_i; \qquad \varepsilon^l = \mathbf{N}\mathbf{a}_l; \qquad \Phi = \mathbf{N}\mathbf{a}_{\Phi}; \qquad \phi_v = \mathbf{N}\mathbf{a}_{\phi}; \qquad w = \mathbf{c}^{\mathsf{T}}\mathbf{N}^{\mathsf{T}}$$
(9)

Note that the property  $w = w^{T}$  for the arbitrary function is used, so  $Nc = c^{T}N^{T}$ . The gradient of the shape function is denoted  $B = \nabla N$ , which results in the approximation of the gradient of the state variables and the spatial weight functions as

$$\nabla c_i^l = \mathbf{B} \mathbf{a}_i; \qquad \nabla \varepsilon^l = \mathbf{B} \mathbf{a}_l; \qquad \nabla \Phi = \mathbf{B} \mathbf{a}_{\Phi}; \qquad \nabla \phi_v = \mathbf{B} \mathbf{a}_{\phi}; \qquad \nabla w = \mathbf{B} \mathbf{c}$$
(10)

The general global matrix formulation of the system can be written as

$$\mathbf{C}\dot{\mathbf{a}} = -\mathbf{K}\mathbf{a} + \mathbf{f} \tag{11}$$

where C is the global damping matrix, K is the global stiffness matrix and f is the global load vector. The global matrices can be established in terms of local matrices as  $\begin{bmatrix} c \\ c \end{bmatrix} = \begin{bmatrix} c \\ c \end{bmatrix}$ 

$$\mathbf{C}\dot{\mathbf{a}} = \begin{bmatrix} \mathbf{C}^{1} & 0 & 0 & 0 & \mathbf{W}^{1} & 0 \\ 0 & \mathbf{C}^{2} & 0 & 0 & \mathbf{W}^{2} & 0 \\ 0 & 0 & \ddots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \mathbf{C}^{i} & 0 & \mathbf{W}^{i} & 0 \\ 0 & 0 & 0 & 0 & 0 & \mathbf{C}^{\varepsilon} & 0 \\ 0 & 0 & 0 & 0 & \mathbf{C}^{\varepsilon} & 0 \\ 0 & 0 & 0 & 0 & \mathbf{O} & -\mathbf{M} & \mathbf{C}^{\phi} \end{bmatrix} \begin{bmatrix} \dot{\mathbf{a}}_{1} \\ \dot{\mathbf{a}}_{2} \\ \vdots \\ \dot{\mathbf{a}}_{i} \\ 0 \\ \dot{\mathbf{a}}_{\varepsilon} \\ \dot{\mathbf{a}}_{\phi} \end{bmatrix}$$
(12)

where the local matrices in  $\mathbb{C}$  is obtained by inserting the assumptions from equation (9) and (10) in the weak formulations given in equation (5), (7) and (8). The following is used

$$\mathbf{C}^{i} = \int_{V} \mathbf{N}^{\mathrm{T}} \varepsilon^{l} \mathbf{N} \, dV; \quad \mathbf{W}^{i} = \int_{V} \mathbf{N}^{\mathrm{T}} c_{i}^{l} \mathbf{N} \, dV; \quad \mathbf{C}^{\varepsilon} = \int_{V} \mathbf{N}^{\mathrm{T}} \rho_{w} \mathbf{N} \, dV$$
$$\mathbf{C}^{\phi} = \int_{V} \mathbf{N}^{\mathrm{T}} \rho_{vs} \left( \varepsilon_{p} - \varepsilon^{l} \right) \mathbf{N} \, dV; \quad \mathbf{M} = \int_{V} \mathbf{N}^{\mathrm{T}} \rho_{vs} \phi_{v} \mathbf{N} \, dV$$

and for the global stiffness matrix

$$\mathbf{K}\mathbf{a} = \begin{bmatrix} \mathbf{K}^{1} + \tilde{\mathbf{K}}^{1} & 0 & 0 & 0 & \mathbf{V}^{1} & \mathbf{P}^{1} + \tilde{\mathbf{P}}^{1} & 0 \\ 0 & \mathbf{K}^{2} + \tilde{\mathbf{K}}^{2} & 0 & 0 & \mathbf{V}^{2} & \mathbf{P}^{2} + \tilde{\mathbf{P}}^{2} & 0 \\ & & \ddots & \vdots & \vdots & & \\ 0 & 0 & 0 & \mathbf{K}^{i} + \tilde{\mathbf{K}}^{i} & \mathbf{V}^{i} & \mathbf{P}^{i} + \tilde{\mathbf{P}}^{i} & 0 \\ \mathbf{E}^{1} & \mathbf{E}^{2} & \cdots & \mathbf{E}^{i} & \mathbf{K}^{\Phi} & 0 & 0 \\ 0 & 0 & 0 & 0 & \mathbf{K}^{\varepsilon} + \mathbf{R}^{\varepsilon} & \mathbf{R}^{eq}_{\varepsilon} \\ 0 & 0 & 0 & 0 & 0 & \mathbf{R}^{eq}_{\varepsilon} & \mathbf{K}^{\phi} - \mathbf{R}^{\varepsilon} \end{bmatrix} \begin{bmatrix} \mathbf{a}_{1} \\ \mathbf{a}_{2} \\ \vdots \\ \mathbf{a}_{i} \\ \mathbf{a}_{\phi} \\ \mathbf{a}_{\varphi} \\ \mathbf{a}_{\phi} \end{bmatrix}$$
(13)

where the local matrices are obtained by inserting the assumptions from equation (9) and (10) into the weak formulation given in equation (5), (6), (7) and (8).

$$\begin{split} \mathbf{K}^{i} &= \int_{V} \mathbf{B}^{\mathrm{T}} D_{i}^{l} \varepsilon^{l} \mathbf{B} \, dV; \quad \tilde{\mathbf{K}}^{i} = \int_{V} \mathbf{B}^{\mathrm{T}} D_{i}^{l} c_{i}^{l} \mathbf{B} \, dV; \quad \mathbf{V}^{\varepsilon} = \int_{V} \mathbf{B}^{\mathrm{T}} A_{i}^{l} c_{i}^{l} z_{i} \varepsilon^{l} \mathbf{B} \, dV \\ \mathbf{K}^{\Phi} &= \int_{V} \mathbf{B}^{\mathrm{T}} \xi_{d} \xi_{0} \mathbf{B} \, dV; \quad \mathbf{E}^{i} = \int_{V} \mathbf{N}^{\mathrm{T}} F z_{i} \mathbf{N} \, dV; \quad \mathbf{P}^{i} = \int_{V} \mathbf{N}^{\mathrm{T}} v^{l,s} \varepsilon^{l} \mathbf{B} \, dV \\ \tilde{\mathbf{P}}^{i} &= \int_{V} \mathbf{N}^{\mathrm{T}} v^{l,s} c_{i}^{l} \mathbf{B} \, dV; \quad \mathbf{K}^{\varepsilon} = \int_{V} \mathbf{B}^{\mathrm{T}} D_{\varepsilon^{l}} \mathbf{B} \, dV; \quad \mathbf{R}^{\varepsilon} = \int_{V} \mathbf{B}^{\mathrm{T}} R \mathbf{B} \, dV \\ \mathbf{R}^{\mathrm{eq}}_{\varepsilon} &= \int_{V} \mathbf{B}^{\mathrm{T}} R \varepsilon^{l} (\phi) \mathbf{B} \, dV; \quad \mathbf{K}^{\phi} = \int_{V} \mathbf{B}^{\mathrm{T}} D_{\phi} \mathbf{B} \, dV \end{split}$$

The problem is considered as a boundary value problem where the boundary conditions are prescribed as Dirichlet boundary conditions.

The time domain is considered as an initial value problem, where a single parameter time stepping procedure is used in the form

$$\left(\mathbf{C} + \Delta t \theta \mathbf{K}\right) \mathbf{a}_{n+1} = \left(\mathbf{C} + \Delta t \left(1 - \theta\right) \mathbf{K}\right) \mathbf{a}_n + \Delta \theta \mathbf{f}_{n+1} + \Delta t \left(1 - \theta\right) \mathbf{f}_n \qquad (14)$$

where the time integration parameter  $\theta$  is restricted to  $0 < \theta < 1$ . For this case it is convenient to use  $\theta = 1$  (the forward Euler method) and the Newton-Raphson scheme, due to the non-linearity of the system. n is at the time t and n+1 is at the time  $t + \Delta t$ .

The finite element formulation is implemented in a Matlab code and solved in one dimension for this work. The calculation is computational expensive as all the non-linear parts are constructed in every time-step in every Newton-Raphson iteration. A great effort for vectorization of the code have been conducted in order to perform long term simulations within reasonable computational time.

#### 2.2.3 Sorption hysteresis model

The extension of the PNP equations, to include moisture transport in the porous media and to account for sorption hysteresis is crucial for describing long term behavior of concrete materials. It should be emphasized that this formulation of the problem is not compared against any thermodynamic restrictions, but a way of reproduce experimental observations in a numerical model. The method is described in general terms in [9, 20, 10] and proven to be valid for cement based materials in [20]. These papers describe a two phase model, analogue to Equation (7) and (8) in this paper, describing only the moisture flow in the material.

The key property of this method is the definition of the water equilibrium function  $\varepsilon_l^{\text{eq}}(\phi)$ , which is a function of the relative humidity in the porous media and established from the sorption history in terms of  $\phi_{n-1}$ . It is concluded from experiments

that concrete and other porous materials have an upper boundary desorption curve and lower boundary absorption curve and scanning curves in between, see Figure 1. In this work, third order polynomials are used to describe all types of sorption state and a set of criteria is used to establish the description for the change between desorption $\leftrightarrow$ absorption states. The equilibrium function is described by

$$\varepsilon_l^{\text{eq},i}(\phi) = b_{i,1}\phi + b_{i,2}\phi^2 + b_{i,3}\phi^3; \qquad \varepsilon_l^{\text{eq},i}, \phi \in [0,1]$$
 (15)

where *i* denote the soprtion state of the inner scanning curve, which is restricted by the boundary curves, given as i = a, where *a* denoteabsorption or i = d, where *d* denote desorption. The criteria for establishing an inner scanning curve can be formulated in a general form, where *c* denote the current sorption state and  $\tilde{c}$  is the opposite state of *c* 

$$\frac{\mathrm{d}\varepsilon_{l}^{\mathrm{eq},i}}{\mathrm{d}\phi}\Big|_{\phi=\phi_{n-1}} = K_{i}\frac{\mathrm{d}\varepsilon_{l}^{\mathrm{eq},c}}{\mathrm{d}\phi}\Big|_{\phi=\phi_{n-1}}; \qquad 0 \le K_{i} \le 1$$
(16)

$$\varepsilon_l^{\mathrm{eq},i}(\phi_{n-1}) = \varepsilon_l^{\mathrm{eq},c}(\phi_{n-1}) \tag{17}$$

$$\frac{\mathrm{d}\varepsilon_{l}^{\mathrm{eq,e}}}{\mathrm{d}\phi}\Big|_{\phi=\phi^{intsec}} = \frac{\mathrm{d}\varepsilon_{l}^{\mathrm{eq,e}}}{\mathrm{d}\phi}\Big|_{\phi=\phi^{intsec}}$$
(18)

$$\varepsilon_l^{\text{eq},i}(\phi^{intsec}) = \varepsilon_l^{\text{eq},\tilde{c}}(\phi^{intsec}); \qquad 0 \le \varepsilon_l^{\text{eq},i}, \varepsilon_l^{\text{eq},\tilde{c}}, \phi^{intsec} \le 1$$
(19)

In Equation (16), the angle of the inner scanning curve is set by adjusting  $K_i$ . It should be noticed, however, that  $K_i$  can have different values, depending on the direction of the sorption state change. Furthermore, it is set that the angle is in the point given by Equation (17), where *n* denote the current time-step in the FE formulation. The inner scanning curve should have a tangent to the boundary curve, for which this is heading, this is given in equation (18). The tangent point is  $\phi^{intsec}$  which is restricted in an interval given in equation (19). Figure (1) shows an illustration of the two points considered in order to establish an inner sorption curve. The figure show an example of state change from absorption to desorption.

In addition to the general formulation of the state change, there is a set of direction depended restriction that must be fulfilled, that is

$$a \to d \Rightarrow \phi_{n-1} > \phi^{intsec}; \qquad d \to a \Rightarrow \phi_{n-1} < \phi^{intsec}$$
 (20)

and the inner scanning is valid in the interval

$$\phi \subset \left[\phi_{n-1}, \phi^{intsec}\right] \tag{21}$$

where sorption will follow the boundary curve outside the above given interval.

The computational scheme for the sorption hysteresis model involves the determination of the current sorption state in terms of sorption history and to establish an inner sorption curve in terms of the criteria listed above. The history dependency is included by comparing the time steps n and n-1, in all FE node points considered. This means that all nodes in the spatial domain follow individual sorption isotherms and can be at different sorption states at the same time. The establishment of the inner sorption polynomial is based on a general solution from a symbolic solver. It is remarked that vectorization of this part is crucial to keep the computational time reasonable.



Figure 1: Illustration showing an absorption from  $\phi = 0$ , following the absorption boundary curve to the state  $\phi_{n-1}$ . A state change occur and a new inner sorption curve is constructed based on the criteria in equation (16) to (19).

### 2.3 Chemical modeling

The chemical modeling is treated as a source/sink term  $q_i$  in the governing equation (1). In general this mean that all ionic constituents of the pore solution i evaluated in a chemical model, considering both solid-liquid and liquid-liquid reactions. It is assumed that the chemical reactions are sufficient fast, so chemical equilibrium is obtained for all constituents in all time steps. The chemical code IPHREEQC is used in this work to solve the chemical system, see [21] for manual and documentation.

#### 2.3.1 Chemical equilibrium calculation

The chemical code IPHREEQC is based on the principles of mass action laws, this is derived from the first and second thermodynamic law with Gibbs potential as constitutive dependent. The solubility product  $K_p$  is introduced in the mass action law, for each reaction p described in the system. The mass action law is

$$K_p = \prod_i (\gamma_i c_i)^{n_{i,p}} \tag{22}$$

where  $\gamma_i$  is the activity coefficient of the ion *i* and *n* is the stoichiometric coefficient of ion *i* in reaction *p*. The product  $\gamma_i c_i$  determines the activity of the ion *i*, where the activity coefficient is determined from two different equations, the Davies equation

$$\log \gamma_i = -Az_i^2 \left( \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \right) \tag{23}$$

or a version of the WATEQ Debye-H?ckel equation

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{\mu}}{1 + Ba_i \sqrt{\mu}} + b_i \mu \quad \begin{cases} b_i = 0; & \text{WATEQ Debye-H?ckel} \\ b_i \neq 0 & \text{extended WATEQDebye-H?ckel} \end{cases}$$
(24)

where A and B are constants depended on the temperature,  $z_i$  is the valence and  $\mu$  is the ionic strength. For the WATEQ Debye-H?ckel,  $a_i$  is an ion size parameter and for the extended WATEQ Debye-H?ckel  $a_i$  and  $b_i$  are fitted values based on mean salt activity coefficient[22, 19]. The different methods are set by the database file in IPHREEQC, in this case Phreeqc.dat is used, see [21]. The ionic strength  $\mu$  of a solution, see [22], is defined as

$$\mu = \frac{1}{2} \sum_{i}^{m} c_i z_i^2 \tag{25}$$

It is seen that activity coefficient is a function of the concentration, which lead to an iterative solving method. PHREEQC solve this, by simultaneously solve a mass balance equation for each constituent and a charge balance equation [22], the mass balance is described as

$$c_i^{tot} = m_i + \sum_j c_j n_{j,i} \tag{26}$$

where  $c_i^{tot}$  is the total concentration of the *i*'th constituent,  $m_i$  is the concentration of the *i*'th free ion,  $c_j$  is the concentration of *j*'th complex or mineral and  $n_{j,i}$  is the stoichiometric coefficient of the *i*'th constituent in the *j*'th mineral or complex. The charge balance is defined as

$$\sum_{j} c_j z_j + \sum_{i} m_i z_i = 0 \tag{27}$$

where  $z_j$  and  $z_i$  is the valence of *i* and *j*.

The law of mass action Equation (22) is for pure phases only, but this type is not sufficient in many cases to chemically describe the solid matrix of cement paste. Different types methods like solid solution and surface complexation models is often used for the major constituents like C-S-H and Afm phases. Solid solution theory will be explained shortly and used in the test modeling. The mass action law for a solid solution is

$$K_{p_{ss}} = \prod_{i} (\gamma_i c_i)^{n_{i,p_{ss}}} / \lambda_{p_{ss}} x_{p_{ss}}$$
(28)

where the solubility product  $K_{p_{ss}}$  is for the pure phase p in the solid solution  $ss. n_{i,p_{ss}}$  is the stoichiometric coefficient,  $\lambda_{p_{ss}}$  is the activity coefficient, which is 1 for ideal solutions and  $x_{p_{ss}}$  is the mole fraction of the pure phase in the solid solution, see equation (29).

$$x_{p_{ss}} = n_{p_{ss}} / \sum_{p_{ss}}^{N_{ss}} n_{p_{ss}}$$
(29)

where  $N_{ss}$  is the total number of pure phases in the solid solution.

#### 2.3.2 Chemical models for cement paste

With the chemical equilibrium module described in Section 2.3.1, it is possible to test various chemical models, describing cement paste and combine these with a mass transport model described in Section 2.2.1. The cement paste composition described in Table 1 is based on data from various papers. The main focus for this model composition is to describe the chemical degradation of the cement paste, mainly in terms of the CSH described by a solid solution, see [12].

Notation	Phase	Reaction	$\log K_p$
СН	Portlandite	$\mathrm{Ca(OH)_2} + 2\mathrm{H^-} \leftrightarrow \mathrm{Ca^{2+}} + 2\mathrm{H_2O}$	
CC	Calcite	$\rm CaCO_3 + H^+ {\leftrightarrow} \rm Ca^{2+} + \rm HCO_3^-$	1.849
Br	Brucite	$\rm Mg(OH)_2 + 2H^+ {\leftrightarrow} Mg^{2+} + 2H_2O$	16.84
Ett	Ettringite	$\rm Ca_6Al_2(SO_4)_3(OH)_{12} \cdot _{26}H_2O \leftrightarrow _2Al(OH)_4^- + 6 Ca^{2+} + 26 H_2O + 4 OH^{-}3 SO_4^{2-}$	-45.09
AFm(s)	Monosulfate	$\mathrm{Ca_4Al_2O_6(SO_4)} \cdot_{12}\mathrm{H_2O} {\leftrightarrow_4}\mathrm{Ca^{2+}} + 2\mathrm{Al}(\mathrm{OH})_4^- + \mathrm{SO_4^{2-}} + 4\mathrm{OH^-} + 6\mathrm{H_2O}$	-29.4
AFm(Cl)	Friedel's salt	$({\rm CaO})_3({\rm Al_2O_3}){\rm CaCl_2} \cdot_{10}{\rm H_2O} + 12{\rm H^+} {\leftrightarrow}_4{\rm Ca^{2+}} + 2{\rm Al^{3+}} + 2{\rm Cl^-} + 16{\rm H_2O}$	-73.2
Am.Si	Amourphous silicate	$\mathrm{SiO}_2 + 2\mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{H}_4\mathrm{SiO}_4$	-2.71
	Tobermorite H	$({\rm CaO})_{0.66}({\rm SiO}_2)({\rm H}_2{\rm O})_{1.5} + 1.32{\rm H}^+ \leftrightarrow 0.66{\rm Ca}^{2+} + {\rm H}_4{\rm SiO}_4 + 0.16{\rm H}_2{\rm O}$	8.27
$CSH_{(ss)}$	Tobermorite D	$({\rm CaO})_{0.83}({\rm SiO}_2)_{0.66}({\rm H}_2{\rm O})_{1.83} + 1.66{\rm H}^+ \leftrightarrow 0.83{\rm Ca}^{2+} + 0.66{\rm H}_4{\rm SiO}_4 + 1.34{\rm H}_2{\rm O}$	13.62
	Jennite H	$({\rm CaO})_{1.33}({\rm SiO}_2)({\rm H_2O})_{2.16} + 2.66{\rm H^+} \leftrightarrow 1.33{\rm Ca^{2+}} + {\rm H_4SiO_4} + 1.49{\rm H_2O}$	22.17
	Jennite D	$({\rm CaO})_{1.5} ({\rm SiO}_2)_{0.66}  ({\rm H_2O})_{2.5} + 3.00 {\rm H^+} \leftrightarrow 1.50 {\rm Ca^{2+}} + 0.66 {\rm H_4SiO_4} + 2.68 {\rm H_2O}$	28.71

Table 1: Chemical model with pure phases and a solid solution describing the cement paste composition, the data is found in [12, 11, 19]

## **3** Calculations

The calculations will emphasize the addition of the sorption hysteresis model, described in Section 2.2.3 and the chemical model described in Section 2.3.1 to the PNP equation. The system of equations is solved as a 1D problem.

### 3.1 Sorption hysteresis

The sorption hysteresis problem is a boundary value problem, modeled with Dirichlet boundary condition, where the relative humidity is prescribed at the boundary node. The total number of spatial elements for the sorption model is 999 and in total 200 time steps. The diffusion coefficients  $D_{\varepsilon^l}$  and  $D_{\phi}$  are assumed constant in this case, although these have shown to be functions of the water content. The porosity is assumed to be  $\varepsilon_p = 0.15$  and the vapor density is assumed to be  $\rho_{vs} = 0.07 \, [\text{kg/m}^3]$ . The boundary curves in all plots in Figure 3 are generic, for use of this method, sorption isotherms should be determined for each cement paste type and composition. The factor for change in sorption is assumed to be  $K_i = \frac{1}{10}$  for both directions, adsorption—desorption and desorption—adsorption.

The result from the simulation is given in Figure 2 and 3. Figure 2 show the volume concentration of water and the relative humidity in the spatial domain, with the time depended boundary variation. The spatial profiles are shown at four different time steps



Figure 2: Top left plot, volume concentration of water as a function of the depth in the sample, represented as node number from the finite element formulation. Top right plot, relative humidity as a function depth in sample, represented as node number from the finite element formulation. Lower left plot, relative humidity as a function of the time-step, this is prescribed as RH in the boundary node of the FE formulation.

The sorption history for each node is only shown for four time step, in Figure 2. Four different spatial positions are plotted as a function of time, showing the volume concentration of water as a function of the relative humidity,  $\varepsilon_l^{\text{eq}}(\phi(t), t)$ , see Figure 3



Figure 3: The plots show volume concentration of water as a function of relative humidity and time, in a depth from the loaded surface. The boundary curves are generic examples of adsorption and desorption curves.

It is seen that each node plotted in Figure (2), have different sorption history, depending on the boundary condition. The plot shown in Figure 3a corresponds to the variation of the boundary condition, it is seen that the adsorption follow the boundary curve until  $\phi_v = 0.8$  and change to desorption and a inner scanning curve. The scanning curve move towards the desorption boundary curve and change direction. A new inner scanning curve is established, moving towards the adsorption boundary. The scanning curve ends in the tangential point with the adsorption boundary and the adsorption follow the boundary curve until  $\phi_v = 1$ . In Figures 3b, 3c and 3d the same type of profile in different spatial depth of the sample are shown. It is seen that the water intrusion varies and the inner scanning curves change direction before reaching the desorption boundary. The results presented in Figure 3c and 3d show that second adsorption phase have not reach the adsorption boundary yet.

### 3.2 Chemical equilibrium model

The chemical module is shown here by the cement paste model described in Table 1. The initial amount of solid phases and pore solution composition is determined by adding 2 mole portlandite and 1 mole etteringite, monosulfate and calcite to the model and determine the equilibrium state with IPHREEQC. The ionic species used in the chemical equilibrium calculation is also considered in the transport calculation. In this case 29 ionic state variables are considered in the system, these are given in Table 2. The diffusion coefficient is multiplied with a general tortuosity factor  $\delta = 0.01$ 

The porous system is assumed fully saturated to emphasize the chemical term in the governing equation and the 1D FEM system is discretized into 29 elements, the total time of 10 years in 500 time steps and a total spatial length of 0.03 m.

	$OH^-$	$\mathrm{H}^+$	$Al(OH)_4^-$	$\mathrm{Al(OH)}_{3}^{*a}$	$\mathrm{Al}(\mathrm{OH})_2^{+*a}$	$AlOH^{2+*a}$
$\frac{D_{i}^{l} \cdot 10^{-8}}{A_{i}^{l} \cdot 10^{-6}}$	0.5300 0.2253	0.9311 0.3958	0.1040 0.2142	0.1040 0	0.1040 0	0.1040 0
	$Al^{3+*}$	$AlSO_4^{+*a}$	$Al(SO_4)_2^{-*a}$	$\mathrm{Ca}^{2+}$	$CaOH^+$	${\rm CaSO}_4$
$\frac{D_i^l \cdot 10^{-8}}{A_i^l \cdot 10^{-7}}$	0.0541 0	0.1040 0	0.1040 0	0.0792 0.3367	0.0792 0.3367	0.0471 0
	$CaHSO_4^{+*e}$	$\mathrm{SO}_4^{2-}$	$\mathrm{HSO}_4^{-*}$	$\mathrm{H_2SiO_4^{2-}}$	$\mathrm{H_{3}SiO_{4}}{-^{d}}$	$\mathrm{H}_4\mathrm{SiO}_4^d$
$\frac{D_i^l \cdot 10^{-8}}{A_i^l \cdot 10^{-7}}$	0.0471 0	0.1070 0.4548	0.1385 0	0.1100 0.4676	0.1100 0.4676	0.1100 0
	$\mathrm{Cl}^-$	$Na^+$	NaOH <sup>b</sup>	$\operatorname{NaSO}_4^-$	$CaCO_3$	$\mathrm{CO}_3^{2-}$
$\frac{D_i^l \cdot 10^{-8}}{A_i^l \cdot 10^{-7}}$	0.2030 0.8629	0.1330 0.5653	0.1330 0	0.0618 0.2627	0.4460 0	0.9550 0.4059
	$\mathrm{HCO}_3^-$	$\mathrm{CaHCO}_3^{+e}$	$\mathrm{H}_{3}\mathrm{CaSiO}_{4}^{+e}$	$MgOH^{+c}$	$\mathrm{Mg}_2^+$	
$\frac{D_{i}^{l}\cdot 10^{-8}}{A_{i}^{l}\cdot 10^{-7}}$	0.1180 0.5016	0.0471 0.5016	0.0471 0.2002	0.0705 0.2997	0.0705 0.2627	

\*Ion mobility assumed 0;  $D_i^l \text{ is } [\text{m}^2/\text{s}] \text{ and } A_i^l \text{is } [\text{m}^2/\text{s}/\text{V}];$  All non-assumed values are found in [19]  $a,b,c,d,eD_i^l \text{ is assumed from Al}(OH)_4^-, \text{Na}^+, \text{Mg}_2^+, \text{H}_2\text{SiO}_4^{-2}, \text{CaSO}_4, \text{respectively.}$ 

#### Table 2: Ion's included in the coupled mass transport and chemical model

The results of the chemical degradation of the solid phases is shown in Figure 4. It is seen that portlandite is dissolved first and then the components in the solid solution starts to change. The degradation of portlandite, amourphias silica and C-S-H(ss) corresponds well to the results in [12], where amourphous silicate is formed when tobermoriteH and tobermoriteD is the only constituent left in the solid solution, at low Ca/Si ration . Etteringite is formed and monosulfate and calcite is dissolved in different amounts and to different depths. The formation of solids due to intrusion of external ions is friedel's salt and brucite, which is found in different depths of the sample.



Figure 4: Chemical degradation of cement paste components, in a 10 year simulation. The sample is assumed complete water saturated.

In total 15000 chemical equilibrium calculations was conducted with IPHREEQC for the simulation and less than 0.1% did not meet the residual requirements. The non-converging nodes was replaced by the average concentration from the two neighbor nodes. It is believed that convergence problems was caused by a small charge imbalances in the input data for the chemical module.

## **4** Discussion

The general model presented in Section 2.2, is an attempt to increase the accuracy of concrete deterioration modeling and in greater perspective to model service life of concrete structures. The theory for the model is very consistent, but numerical problems are experienced, especially the large difference in ionic concentration of the different constituent in the pore solution. The chemical module based on IPHREEQC have to some extent numerical problems in terms of convergence for determine the chemical equilibrium state. In general numerical stability for the whole model should be improved in order to work as general service life model.

The sorption hysteresis model is not a direct consequence of the thermodynamic formulation of the problem but a direct way to express the phase balance between liquid water and vapor. The phase balance equations in this paper described by 3'rd order polynomials, which could be extended to higher order polynomials for better approximation of the experimental data needed for setting the boundary isotherms. The hysteresis module is of great importance in the model as the ionic concentration is in mol/l and the thereby vary with the volume concentration of water and, further, affect the degradation process of the solid matrix. The great advance with this model is the direct implementation into the FEM scheme and each node in the discrete system have their own sorption history.

The chemical module is added to the system as a source/sink term in the transport equation for ionic and non-ionic dissolved species. So that chemical equilibrium is established between the solid material and pore solution in each node and each time step. Chemical equilibrium is established in every time step in the model, which explicit neglect the reaction kinetics. The reaction kinetics is in general difficult to work with by classic thermodynamics .. Chemical reactions kinetics in cement chemistry is often at nano-scale and difficult to combine with service life modeling with a time scale in years. The results from the relative simple chemical model setup, show that the chemical reactions cannot be neglected in modeling of cement paste degradation. If the problem was considered as a diffusion problem only, then a fixed amount ions were present in the solution and equilibrium with the boundary conditions would occur much faster than the model including chemical equilibrium, just to mention a few implications.

## 5 Conclusion

A transient mass transport model coupled with a chemical equilibrium module was established. The mass transport equation system is solved by a non-linear finite element scheme and the chemical module is based on the geochemical code IPHREEQC. The mass transport is described by the Poisson-Nernst-Planck equations, with an extension for describing the moisture transport. The liquid and vapor phases is coupled by a phase equilibrium term, describing the sorption hysteresis.

The coupled model presented here is a quite general formulation, for which it is possible to use different chemical models in combination with a mass transport model. A simple chemical cement paste model is used for illustration of a long term simulation, showing the importance of a chemical model in relation to chemical degradation.

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