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A theoretical model describing diffusion of a mixture of different types of ions in pore solution of concrete coupled to moisture transport

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Abstract

A theoretical model is established for diffusion of different types of ions in pore solution of concrete and the coupling to moisture flow and moisture content. Mass exchanges between ions in pore solution and solid hydration products in the concrete are also considered. The basic concepts behind the so-called mixture theory are used. The development of a mass balance principle for ions in pore solution is established. This principle accounts for (i) diffusion caused by concentration gradients of ions and gradients of the so-called internal electrical potential, (ii) convection, i.e. the effect on the motion of ions due to a motion of the pore solution in concrete, (iii) the effect on the concentration due to changes in the moisture content, and finally, (iv) the effect of mass exchange of ions between solid hydration products and the pore solution phase. The model is general in the sense that all different types of ions appearing in pore solution phase can be included and computed for during quite arbitrary boundary conditions.

Keywords: Diffusion; Ions; Pore solution; Moisture transport

1. Introduction

Most concrete constructions subjected to harmful ions such as chlorides, sulfates, and carbonic acid are also exposed to variations in moisture content. Phenomena such as capillary suction and drying will affect the diffusion of different types of ions dissolved in a pore solution. A stringent model of this problem should result in one equation for each type of ion appearing in a pore solution, one equation describing the moisture transport, and one equation for each solid component being formed from ions in the pore solution or being dissolved into the pore solution from solid components.

The need for knowledge about how the pore solution of concrete is changed due to different environmental conditions is crucial since most of the degradation mechanisms are dependent on the pore solution composition. Examples of such degradation mechanisms are chloride-induced reinforcement corrosion (see, e.g., Refs. [1–3]), carbonation (see, e.g., Ref. [4]), sulfate attack (see, e.g., Ref.[5]), salt frost scaling (see, e.g., Ref.[6]), and leaching of hydroxide from pore solution (see e.g., Ref. [7]).

A quite general model is established by considering mass balance equations for constituents building up two phases, a pore solution phase and a solid phase. The mass balance principles obtained for the different types of ions in pore water phase are supplemented with constitutive assumptions making the equation system complete.

2. Diffusion of a mixture of different types of ions coupled to moisture transport in concrete

The basic concept behind the so-called mixture theory will be used (see e.g., Ref. [8]) in order to establish a model describing diffusion of a mixture of different types of ions in a pore solution of concrete and its couplings to the moisture condition and moisture flow. Each constituent is assigned a mass density concentration. The mass density concentration of the $i=1,\ldots,\mathfrak{R}$ dissolved ions considered in pore solution will be denoted ρ_i^{p} (kg/m^3) and the $s=1,\ldots,\mathfrak{F}$ solid precipitated combinations of ions in pore solution will be denoted ρ_s^{p}. The $h=1,\ldots,\aleph$ solid components of the concrete will be denoted ρ_h^{c} and the mass density concentration of

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liquid water in the material volume will be denoted ρ_w^p. The total mass density of the mixture ρ is the sum of all constituents. Two phases will be considered, the pore solution phase p and the solid phase of the concrete c. Reactions within and between the phases will be considered in the general case. The only balance principles that will be considered are the mass balance equations for the constituents, the two phases, and the whole mixture, i.e. the momentum balance equation, energy balance equation, and the second axiom of thermodynamics are ignored in this presentation.

It will be seen that the complexity of the problem considered grows drastically as compared to, for example, the isothermal moisture transport problem that only includes one mass balance principle and one constitutive equation.

The mass density concentration of solid component phase ρ^c, i.e. the 'dry' concrete density, is the sum of the $\aleph$ number of individual solid constituents, i.e.

$$\rho^c = \sum_{h=1}^{\aleph} \rho_h^c \tag{1}$$

where ρ_h^c is the mass density concentration of the h-th solid component.

The mass density concentration of the pore solution phase ρ^p is the sum of the $\Re$ number of dissolved ion constituents, the sum of the $\mathfrak{F}$ number of solid precipitated combinations of ions and the water itself, i.e.

$$\rho^p = \sum_{i=1}^{\Re} \rho_i^p + \sum_{s=1}^{\Im} \rho_s^p + \rho_w^p \tag{2}$$

where ρ_i^p is the mass density concentration of the i-th dissolved ion constituent, ρ_s^p is the mass density concentration of the s-th precipitated constituent in pore water phase, and ρ_w^p is the mass density concentration of the 'pure' water in material. The total mass density concentration of the mixture ρ is

$$\rho = \rho^c + \rho^p = \sum_{h=1}^{\aleph} \rho_h^c + \sum_{i=1}^{\Re} \rho_i^p + \sum_{s=1}^{\Im} \rho_s^p + \rho_w^p \tag{3}$$

The mean velocity of the pore solution phase $\dot{\mathbf{x}}^p$ is defined as the mass weighted average of individual constituent velocities $\acute{\mathbf{x}}_i^p$, $\acute{\mathbf{x}}_s^p$ and $\acute{\mathbf{x}}_w^p$ (m/s), i.e.

$$\dot{\mathbf{x}}^p = \frac{1}{\rho^p} \sum_{i=1}^{\Re} \rho_i^p \acute{\mathbf{x}}_i^p + \frac{1}{\rho^p} \sum_{s=1}^{\Im} \rho_s^p \acute{\mathbf{x}}_s^p + \frac{\rho_w^p \acute{\mathbf{x}}_w^p}{\rho^p} \tag{4}$$

The mixture velocity of the solid phase $\dot{\mathbf{x}}^c$ is the mass-weighted average of individual solid-constituent velocity $\acute{\mathbf{x}}_h^c$, i.e.

$$\dot{\mathbf{x}}^c = \frac{1}{\rho^c} \sum_{h=1}^{\aleph} \rho_h^c \acute{\mathbf{x}}_h^c \tag{5}$$

The velocity of the whole mixture $\dot{\mathbf{x}}$ is defined to be the sum of $\dot{\mathbf{x}}^p$ and $\dot{\mathbf{x}}^c$, that is

$$\dot{\mathbf{x}} = \frac{1}{\rho} \sum_{i=1}^{\Re} \rho_i^p \acute{\mathbf{x}}_i^p + \frac{1}{\rho} \sum_{s=1}^{\Im} \rho_s^p \acute{\mathbf{x}}_s^p + \frac{\rho_w^p \acute{\mathbf{x}}_w^p}{\rho} + \frac{1}{\rho} \sum_{h=1}^{\aleph} \rho_h^c \acute{\mathbf{x}}_h^c \tag{6}$$

In a general case where $\acute{\mathbf{x}}_h^c$ is different from zero, the mass balance principle for the $\aleph$ number of solid constituents of the concrete phase c can be written as

$$\frac{B\rho_h^c}{Bt} = -\mathrm{div}(\rho_h^c \acute{\mathbf{x}}_h^c) + \hat{c}_h^c + \hat{r}_h^c; \quad h = 1, \ldots, \aleph \tag{7}$$

where $\hat{c}_h^c$ is the gain of mass from all $\aleph - 1$ number of solid constituents present in phase c. The term $\hat{r}_h^c$ is the gain of mass to the h-th constituent from the $\Re + \mathfrak{F} + 1$ number of constituents building up the pore solution phase p.

The postulate for the mass balance for the solid phase c is

$$\frac{B\rho^c}{Bt} = -\mathrm{div}(\rho^c \dot{\mathbf{x}}^c) + \hat{r}^c \tag{8}$$

where $\hat{r}^c$ is the total gain of mass to the solid concrete phase from the pore solution phase, i.e. $\hat{r}^c$ is related to $\hat{r}_h^c$, as

$$\hat{r}^c = \sum_{h=1}^{\aleph} \hat{r}_h^c \tag{9}$$

In mixture theory, it is postulated that the sum of the constituent balance principles in a phase should be equal to the mass balance equation for the whole phase. Summing the $\aleph$ number of balance principles in Eq. (7), therefore, results in

$$\sum_{h=1}^{\aleph} \hat{c}_h^c = 0 \tag{10}$$

where Eqs. (6)–(9) are used.

The mass balance for the pure water w in the pore solution phase p is the postulate

$$\frac{B\rho_w^p}{Bt} = -\mathrm{div}(\rho_w^p \acute{\mathbf{x}}_w^p) + \hat{c}_w^p + \hat{r}_w^p \tag{11}$$

where $\hat{c}_w^p$ and $\hat{r}_w^p$ are the gain of mass to the w constituents from constituents within phase p and from phase c, respectively.

The mass balance principle for the different types of dissolved ions in pore solution is

$$\frac{B\rho_i^p}{Bt} = -\mathrm{div}(\rho_i^p \acute{\mathbf{x}}_i^p) + \hat{c}_i^p + \hat{r}_i^p; \quad i = 1, \ldots, \Re \tag{12}$$

where $\hat{c}_i^p$ is the mass gain to the dissolved ion constituent i from all constituents in the pore solution, i.e. in phase p. The property $\hat{r}_i^p$ is the mass gain to the dissolved ion constituent i from the solid phase c.

The mass balance principle for the solid precipitated neutral combinations of ions in pore solution is

$$\frac{B\rho_s^p}{Bt} = -\mathrm{div}(\rho_s^p \acute{\mathbf{x}}_s^p) + \hat{c}_s^p + \hat{r}_s^p; \quad s = 1, \ldots, \mathfrak{I} \tag{13}$$

where $\hat{c}_s^p$ is the mass gain to the solid constituent s in the pore solution from the i number of dissolved ions also present in the pore solution. The term $\hat{r}_s^p$ is the mass gain to the solid constituent s in the pore solution, i.e. in phase p, from the solid phase c.

The mass balance for the whole pore solution phase p is the postulate

$$\frac{B\rho^p}{Bt} = -\mathrm{div}(\rho^p \dot{\mathbf{x}}^p) + \hat{r}^p \tag{14}$$

where $\hat{r}^p$ is the total gain of mass to the pore solution phase p from the solid phase c, i.e.

$$\hat{r}^p = \sum_{i=1}^{\mathfrak{R}} \hat{r}_i^p + \sum_{s=1}^{\mathfrak{I}} \hat{r}_s^p + \hat{r}_w^p \tag{15}$$

The sum of Eq. (11), the $\mathfrak{R}$ number of equations in Eq. (12), and the $\mathfrak{F}$ number of equations in Eq. (13) should result in satisfying the condition

$$\sum_{i=1}^{\mathfrak{R}} \hat{c}_i^p + \sum_{s=1}^{\mathfrak{I}} \hat{c}_s^p + \hat{c}_w = 0 \tag{16}$$

since it is postulated that Eq. (14) is the sum of the constituent equations in phase p.

The postulated mass balance for the whole mixture, including both the pore solution phase p and the solid phase c, is

$$\frac{B\rho}{Bt} = -\mathrm{div}(\rho \dot{\mathbf{x}}) \tag{17}$$

Summation of the mass balance equations for the c and p phases, i.e. Eqs. (7) and (14), results in the relation

$$\hat{r}^p + \hat{r}^c = 0 \tag{18}$$

where Eqs. (4)–(6) are used.

Yet another balance principle will be invoked for the pore solution phase p, the continuity equation for the charge, which is

$$\mathrm{div}(\mathbf{d}^p) = q^p \tag{19}$$

where the electrical displacement field is denoted by $\mathbf{d}^p$ (C/m^2) and the charge density by q^p (C/m^3). This equation will control the condition of the pore solution in terms of an electrical potential φ^p. The reason for obtaining an electrical potential in a pore solution is a momentarily unbalancing number of positive and negatively charged dissolved ions in a representative volume being much larger than the size of the ions themselves.

In this application, it is convenient to introduce the so-called diffusion velocity $\mathbf{u}$, which is the velocity of a constituent in relation to the phase mixture velocity.

$$\mathbf{u}_i^p = \acute{\mathbf{x}}_i^p - \dot{\mathbf{x}}^p \tag{20}$$

$$\mathbf{u}_h^c = \acute{\mathbf{x}}_h^c - \dot{\mathbf{x}}^c \tag{21}$$

It will be explicitly assumed that different dissolved ions in a pore solution cannot react with each other, i.e. the problem will be restricted to a case where precipitation of combinations of ions cannot occur. This means that the mass exchange terms $\hat{c}_i^p(\mathbf{x},t)$, $i = 1,\ldots,\mathfrak{R}$ are set to zero. The unknown quantities for the $\mathfrak{R}$ number of different types of ions dissolved in the pore solution, therefore, are

$$\rho_i^p(\mathbf{x},t);\ \mathbf{u}_i^p(\mathbf{x},t);\ r_i^p(\mathbf{x},t); \quad i = 1, \ldots, \mathfrak{R} \tag{22}$$

where ρ_i^p is the mass density concentration of an arbitrary type of ion dissolved in the pore solution, $\mathbf{u}_i^p$ is the corresponding diffusion velocity, i.e. the velocity of the ion type i in relation to the velocity of the phase mixture, i.e. in relation to $\dot{\mathbf{x}}^p$.

For the 'pure' water in a pore solution, it will be explicitly assumed that $\hat{c}_w^p(\mathbf{x},t) = 0$. Furthermore, it will be assumed that $r_w^p(\mathbf{x},t) = 0$, i.e. effects such as loss of water due to hydration or gain of water due to carbonation, will not be included in the model. The unknown properties left for the 'pure' water in the pore solution are

$$\rho_w^p(\mathbf{x},t) \text{ and } \acute{\mathbf{x}}_w^p(\mathbf{x},t) \tag{23}$$

For the $\mathfrak{F}$ number of solid components in the pore solution phase p, denoted by a subscript s, it will be assumed that the velocities $s = 1,\ldots,\mathfrak{F}$ are zero, i.e. $\acute{\mathbf{x}}_s^p(\mathbf{x},t) = 0$, and that no mass exchanges take place within the phase or between the two phases, i.e. $\hat{c}_s^p(\mathbf{x},t) = 0$ and $r_s^p(\mathbf{x},t) = 0$ for all $s = 1,\ldots,\mathfrak{F}$ constituents. This means that the mass densities for the precipitated combinations of ions in a pore solution will be entirely given by its initial values. For simplicity, these initial values will be set to zero.

The properties of the solid constituents in concrete will be restricted in the sense that the velocities for $\aleph$ number of constituents are set to zero, i.e. $\acute{\mathbf{x}}_h^c(\mathbf{x},t) = 0$. Further, no reactions between the $\aleph$ number of solid constituents within phase c will be included, i.e. $\hat{c}_h^c(\mathbf{x},t) = 0$. The unknown properties of the solid constituents in phase c, therefore, are

$$\rho_h^c(\mathbf{x},t) \text{ and } r_h^c(\mathbf{x},t); \quad h = 1, \ldots, \aleph \tag{24}$$

The unknown properties for the whole mixture, including both phases p and c, are

$$\rho(\mathbf{x},t) \text{ and } \dot{\mathbf{x}}(x,t) \tag{25}$$

where ρ and $\dot{\mathbf{x}}$ are defined in Eqs. (3) and (6).

In order to study the influence of the charge of the different kinds of ions in the pore solution phase on the diffusion behavior, the electrical potential φ^{p} (V), the electrical displacement field $\mathbf{d}^{\mathrm{p}}$ (C/m^2), and the charge density q^{p} (C/m^3) must be added to the list of unknown properties in the problem studied.

$$\varphi^{\mathrm{p}}(\mathbf{x},t),\ \mathbf{d}^{\mathrm{p}}(\mathbf{x},t),\ q^{\mathrm{p}}(\mathbf{x},t) \tag{26}$$

The number of unknown properties in the reduced problem is $7+3\Re + 2\mathfrak{F}$.

With the above assumptions, the balance principles for the constituents are simplified. For the solid components in the phase c, one obtains the mass balance equations

$$\frac{B\rho_h^{\mathrm{c}}}{Bt} = \hat{r}_h^{\mathrm{c}}; \quad h = 1,\ldots,\aleph \tag{27}$$

The simplified mass balance equation for the pure water constituent becomes

$$\frac{B\rho_{\mathrm{w}}^{\mathrm{p}}}{Bt} = -\mathrm{div}(\rho_{\mathrm{w}}^{\mathrm{p}}\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}) \tag{28}$$

The mass balance for the $\Re$ number of dissolved ions in the pore solution is

$$\frac{B\rho_i^{\mathrm{p}}}{Bt} = -\mathrm{div}(\rho_i^{\mathrm{p}}\acute{\mathbf{x}}_i^{\mathrm{p}}) + \hat{r}_i^{\mathrm{p}}; \quad i = 1,\ldots,\Re \tag{29}$$

The conditions imposed by the mass balance for the whole mixture imply that no net production of mass can take place during mass exchange between the two phases. That is, the mass balance condition

$$\sum_{i=1}^{\Re}\hat{r}_i^{\mathrm{p}} + \sum_{h=1}^{\aleph}\hat{r}_h^{\mathrm{c}} = 0 \tag{30}$$

must hold.

The last balance principle considered is the condition for the electrical potential, which is

$$\mathrm{div}(\mathbf{d}^{\mathrm{p}}) = q^{\mathrm{p}} \tag{31}$$

In the application to be presented, it will be of interest to use a mole density concentration definition of the ion constituents dissolved in pore water, instead of the mass density concentration definition. The relation between the mass density concentration ρ_{a} and the mole density concentration n_i^{p} (mol/m^3) is

$$\rho_i^{\mathrm{p}} = n_i^{\mathrm{p}} m_i \tag{32}$$

where m_i (kg/mol) is the mass of 1 mol of the i-th constituent that is a constant property. By definition, Eq. (32), the mass balance equation for the ion constituents (Eq. (29)), can be written

$$m_i\frac{Bn_i^{\mathrm{p}}}{Bt} = -m_i\mathrm{div}(n_i^{\mathrm{p}}\acute{\mathbf{x}}_i^{\mathrm{p}}) + m_i\hat{n}_i^{\mathrm{p}}; \quad i = 1,\ldots,\Re, \tag{33}$$

where the mass gain density to the i-th constituent $\hat{r}_i^{\mathrm{p}}$ is related to the mole gain density $\hat{n}_{\mathrm{a}}$ (mol/(m^{3}s)) as $\hat{n}_i^{\mathrm{p}} = \hat{r}_i^{\mathrm{p}}/m_i$. That is, the mass balance principle for the ion constituents (Eq. (33)) can be written as

$$\frac{Bn_i^{\mathrm{p}}}{Bt} = -\mathrm{div}(n_i^{\mathrm{p}}\acute{\mathbf{x}}_i^{\mathrm{p}}) + \hat{n}_i^{\mathrm{p}}; \quad i = 1,\ldots,\Re, \tag{34}$$

This equation will be rewritten in yet another way in order to facilitate the description of the diffusion velocities of the different types of dissolved ions. Consider the concentration c_i^{p} (−) of the ion constituents, defined as

$$c_i^{\mathrm{p}} = \rho_i^{\mathrm{p}}/\rho^{\mathrm{p}} = n_i^{\mathrm{p}} m_i/\rho^{\mathrm{p}} \tag{35}$$

This definition together with Eqs. (20) and (29) can be combined to yield

$$\frac{B(c_i^{\mathrm{p}}\rho^{\mathrm{p}})}{Bt} = -\mathrm{div}(\rho_i^{\mathrm{p}}\overset{\mathrm{p}}{\underset{i}{\mathbf{u}}}) - \mathrm{div}(c_i^{\mathrm{p}}\rho^{\mathrm{p}}\dot{\mathbf{x}}^{\mathrm{p}}) + \hat{r}_i^{\mathrm{p}};$$
$$i = 1,\ldots,\Re \tag{36}$$

Partial differentiation of the terms

$$\frac{B(c_i^{\mathrm{p}}\rho^{\mathrm{p}})}{Bt} = c_i^{\mathrm{p}}\frac{B\rho^{\mathrm{p}}}{Bt} + \rho^{\mathrm{p}}\frac{Bc_i^{\mathrm{p}}}{Bt} \tag{37}$$

and

$$\mathrm{div}(c_i^{\mathrm{p}}\rho^{\mathrm{p}}\dot{\mathbf{x}}^{\mathrm{p}}) = c_i^{\mathrm{p}}\mathrm{div}(\rho^{\mathrm{p}}\dot{\mathbf{x}}^{\mathrm{p}}) + \rho^{\mathrm{p}}\dot{\mathbf{x}}^{\mathrm{p}}\cdot\mathrm{grad}c_i^{\mathrm{p}} \tag{38}$$

makes it possible to write Eq. (36) as

$$c_i^{\mathrm{p}}\left(\frac{B\rho^{\mathrm{p}}}{Bt} + \mathrm{div}(\rho^{\mathrm{p}}\dot{\mathbf{x}}^{\mathrm{p}})\right) + \rho^{\mathrm{p}}\frac{Bc_i^{\mathrm{p}}}{Bt}$$
$$= -\mathrm{div}(\rho_i^{\mathrm{p}}\mathbf{u}_i^{\mathrm{p}}) - \rho^{\mathrm{p}}\dot{\mathbf{x}}^{\mathrm{p}}\cdot\mathrm{grad}c_i^{\mathrm{p}} + \hat{r}_i^{\mathrm{p}};$$
$$i = 1,\ldots,\Re \tag{39}$$

The first term on the left-hand side of Eq. (39) can be identified with the aid of the mass balance equation for the phase p, i.e. Eq. (14), as

$$c_i^{\mathrm{p}}\left(\frac{B\rho^{\mathrm{p}}}{Bt} + \mathrm{div}(\rho^{\mathrm{p}}\dot{\mathbf{x}}^{\mathrm{p}})\right) = c_i^{\mathrm{p}}\hat{r}^{\mathrm{p}} = c_i^{\mathrm{p}}\sum_{i=1}^{\Re}\hat{r}_i^{\mathrm{p}} \tag{40}$$

where Eq. (14) with $\hat{r}_s^{\mathrm{p}}=0$, for $s=1,\ldots,\mathfrak{F}$, and $\hat{r}_{\mathrm{w}}^{\mathrm{p}}=0$ are used. Eqs. (39) and (40) combine to yield

$$\rho^{\mathrm{p}}\frac{Bc_i^{\mathrm{p}}}{Bt} = -\mathrm{div}(\rho_i^{\mathrm{p}}\mathbf{u}_i^{\mathrm{p}}) - \rho^{\mathrm{p}}\dot{\mathbf{x}}^{\mathrm{p}}\cdot\mathrm{grad}c_i^{\mathrm{p}} + \hat{r}_i^{\mathrm{p}} - \frac{\rho_i^{\mathrm{p}}\sum_{i=1}^{\Re}\hat{r}_i^{\mathrm{p}}}{\rho^{p}};$$
$$i = 1,\ldots,\Re \tag{41}$$

Using the mole density concentration, as defined in Eq. (32), instead of the concentration c_{a}, the Eq. (41) takes the form

$$\rho^{\mathrm{p}}m_i\frac{B(n_i^{\mathrm{p}}/\rho^{\mathrm{p}})}{Bt} = -\mathrm{div}(\rho_i^{\mathrm{p}}\mathbf{u}_i^{\mathrm{p}}) - \rho^{\mathrm{p}}m_i\dot{\mathbf{x}}^{\mathrm{p}}\cdot\mathrm{grad}(n_i^{\mathrm{p}}/\rho^{\mathrm{p}})$$
$$+ \hat{r}_i^{\mathrm{p}} - \frac{n_i^{\mathrm{p}}\sum_{i=1}^{\Re}m_i\hat{r}_i^{\mathrm{p}}}{\rho^{\mathrm{p}}}; \quad i = 1,\ldots,\Re \tag{42}$$

Partial differentiation of the term

$$\mathrm{grad}(n_i^{\mathrm{p}}/\rho^{\mathrm{p}}) = \frac{1}{\rho^{\mathrm{p}}}\mathrm{grad}n_i^{\mathrm{p}} - \frac{n_i^{\mathrm{p}}}{(\rho^{\mathrm{p}})^2}\mathrm{grad}\rho^{\mathrm{p}} \tag{43}$$

and

$$\frac{B(n_i^{\mathrm{p}}/\rho^{\mathrm{p}})}{Bt} = \frac{1}{\rho^{\mathrm{p}}}\frac{Bn_i^{\mathrm{p}}}{Bt} - \frac{n_i^{\mathrm{p}}}{(\rho^{\mathrm{p}})^2}\frac{B\rho^{\mathrm{p}}}{Bt} \tag{44}$$

in Eq. (42) means that the mass balance equation for the $i=1,\ldots,\Re$ types of ions dissolved in pore water can be written as

$$\frac{Bn_i^{\mathrm{p}}}{Bt} - \frac{n_i^{\mathrm{p}}}{\rho^{\mathrm{p}}}\frac{B\rho^{\mathrm{p}}}{Bt} = -\frac{1}{m_i}\mathrm{div}(\rho_i^{\mathrm{p}}\mathbf{u}_i^{\mathrm{p}}) - \dot{\mathbf{x}}^{\mathrm{p}}\cdot\mathrm{grad}n_i^{\mathrm{p}} + \frac{n_i^{\mathrm{p}}\dot{\mathbf{x}}^{\mathrm{p}}}{\rho^{\mathrm{p}}}\cdot\mathrm{grad}\rho^{\mathrm{p}} + \hat{n}_i^{\mathrm{p}} - \frac{n_i^{\mathrm{p}}\sum_{i=1}^{\Re}\hat{r}_i^{\mathrm{p}}}{\rho^{\mathrm{p}}} \tag{45}$$

The assumption that the mass density concentration for the pure water phase is much greater than any of the mass density concentrations of the dissolved ions will be used, i.e.

$$\rho_{\mathrm{w}}^{\mathrm{p}} \gg \rho_{i=1,\ldots\Re}^{\mathrm{p}}; \tag{46}$$

This results in the mean velocity of the pore solution phase $\dot{\mathbf{x}}^{\mathrm{p}}$ being approximately equal to the velocity $\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}$ of the pore solution, i.e. compare with Eq. (4). Furthermore, the mass density of the pore solution phase is approximately equal to the mass density of pure water, i.e. the approximation in Eq. (46) results in

$$\dot{\mathbf{x}}^{\mathrm{p}} \approx \acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}} \text{ and } \rho^{\mathrm{p}} \approx \rho_{\mathrm{w}}^{\mathrm{p}} \tag{47}$$

The approximative version of the balance principle for the ion constituents in pore solution becomes with Eq. (47)

$$\frac{Bn_i^{\mathrm{p}}}{Bt} - \frac{n_i^{\mathrm{p}}}{\rho_{\mathrm{w}}^{\mathrm{p}}}\frac{B\rho_{\mathrm{w}}^{\mathrm{p}}}{Bt} = -\frac{1}{m_i}\mathrm{div}(\rho_i^{\mathrm{p}}\mathbf{u}_{\mathrm{i}}^{\mathrm{p}}) - \acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}\cdot\mathrm{gradn}_{\mathrm{i}}^{\mathrm{p}} + \frac{\mathrm{n}_{\mathrm{i}}^{\mathrm{p}}\dot{\mathbf{x}}^{\mathrm{p}}}{\rho_{\mathrm{w}}^{\mathrm{p}}}\cdot\mathrm{grad}\rho_{\mathrm{w}}^{\mathrm{p}} + \hat{n}_i^{\mathrm{p}};\quad i=1,\ldots,\Re \tag{48}$$

for all $\Re$ considered ions. It is noted that the term

$$\frac{n_i^{\mathrm{p}}\sum_{i=1}^{\Re}\hat{r}_i^{\mathrm{p}}}{\rho_{\mathrm{w}}^{\mathrm{p}}} = \frac{\rho_i^{\mathrm{p}}\sum_{i=1}^{\Re}\hat{r}_i^{\mathrm{p}}}{m_i\rho_{\mathrm{w}}^{\mathrm{p}}} \approx 0 \tag{49}$$

in Eq. (45) is approximately zero due to the conditions in Eq. (47).

Consider the mass balance equation for the pure water constituent, i.e. Eq. (28), written as

$$\frac{n_i^{\mathrm{p}}}{\rho_{\mathrm{w}}^{\mathrm{p}}}\frac{B\rho_{\mathrm{w}}^{\mathrm{p}}}{Bt} = -\frac{n_i^{\mathrm{p}}}{\rho_{\mathrm{w}}^{\mathrm{p}}}\mathrm{div}(\rho_{\mathrm{w}}^{\mathrm{p}}\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}) \tag{50}$$

i.e.

$$\frac{n_i^{\mathrm{p}}}{\rho_{\mathrm{w}}^{\mathrm{p}}}\frac{B\rho_{\mathrm{w}}^{\mathrm{p}}}{Bt} = -\frac{n_i^{\mathrm{p}}\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}}{\rho_{\mathrm{w}}^{\mathrm{p}}}\cdot\mathrm{grad}\rho_{\mathrm{w}}^{\mathrm{p}} - n_i^{\mathrm{p}}\mathrm{div}\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}} \tag{51}$$

This means that the $\Re$ equations in Eq. (48) can be written as

$$\frac{Bn_i^{\mathrm{p}}}{Bt} = -\frac{1}{m_i}\mathrm{div}(\rho_i^{\mathrm{p}}\mathbf{u}_i^{\mathrm{p}}) - \acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}\cdot\mathrm{grad}n_i^{\mathrm{p}} - n_i^{\mathrm{p}}\mathrm{div}\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}} + \hat{n}_i^{\mathrm{p}};\quad i=1,\ldots,\Re \tag{52}$$

The term $n_i^{\mathrm{p}}\mathrm{div}\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}$, in Eq. (52), represents the change in the mass density concentration of ion $\boldsymbol{i}$ in a pore solution due to a change in the mass density concentration of the pore solution caused by drying or capillary suction. The mass balance Eq. (52) for the mole density concentration of the ion type i dissolved in the pore solution is a generalization of the standard diffusion–convection equation (e.g., see Ref. [9]) in the sense that the change of the reference volume, i.e. the volume change of pore water phase, and the mass exchanges between phases are included.

To show the meaning of the term $n_i^{\mathrm{p}}\mathrm{div}\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}$, consider again the mass balance for the 'pure' water in the pore solution phase, i.e.

$$\frac{B\rho_{\mathrm{w}}^{\mathrm{p}}}{Bt} = -\mathrm{div}(\rho_{\mathrm{w}}^{\mathrm{p}}\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}) = -\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}\cdot\mathrm{grad}\rho_{\mathrm{w}}^{\mathrm{p}} - \rho_{\mathrm{w}}^{\mathrm{p}}\mathrm{div}\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}} \tag{53}$$

Note that the material derivative of $\rho_{\mathrm{w}}^{\mathrm{p}}$, denoted $(\rho_{\mathrm{w}}^{\mathrm{p}})'$, is the change in mass density concentration related to the motion $\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}$ given as

$$(\rho_{\mathrm{w}}^{\mathrm{p}})' = \frac{B\rho_{\mathrm{w}}^{\mathrm{p}}}{Bt} + \acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}\cdot\mathrm{grad}\rho_{\mathrm{w}}^{\mathrm{p}} \tag{54}$$

That is, by combining Eqs. (53) and (54), the mass balance equation using the material description becomes

$$(\rho_{\mathrm{w}}^{\mathrm{p}})' = -\rho_{\mathrm{w}}^{\mathrm{p}}\mathrm{div}\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}} \tag{55}$$

This means that the ratio between the change in mass density concentration of the pore water, following its own motion, and the actual mass density concentration, in this case, is proportional to $\mathrm{div}\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}$, i.e.

$$\frac{(\rho_{\mathrm{w}}^{\mathrm{p}})'}{\rho_{\mathrm{w}}^{\mathrm{p}}} = -\mathrm{div}\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}} \tag{56}$$

Hence, the term $n_i^{\mathrm{p}}\mathrm{div}\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}} = n_i^{\mathrm{p}}(\rho_{\mathrm{w}}^{\mathrm{p}})'/\rho_{\mathrm{w}}$, in Eq. (52), is the absolute change of the mass concentration of ion i dissolved in a pore solution, due to changes in mass concentration of pore water ρ_{w} only, following the motion of the pore water.

3. Constitutive relations

Next, consider the constitutive relations for the constituents. The velocity of the pore water in material is the assumption

$$\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}} = -\frac{D_{\mathrm{w}}^{\mathrm{p}}(\rho_{\mathrm{w}}^{\mathrm{p}})}{\rho_{\mathrm{w}}^{\mathrm{p}}}\mathrm{grad}\rho_{\mathrm{w}}^{\mathrm{p}} \tag{57}$$

where $D_{\mathrm{w}}^{\mathrm{p}}(\rho_{\mathrm{w}}^{\mathrm{p}})$ is the nonlinear material parameter relating the gradient of the mass density concentration of water in pores with the velocity $\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}$. Methods to evaluate $D_{\mathrm{w}}^{\mathrm{p}}(\rho_{\mathrm{w}}^{\mathrm{p}})$ from capillary suction experiments have been proposed (e.g., see Refs. [10,11]); further, methods using steady-state conditions to evaluate $D_{\mathrm{w}}^{\mathrm{p}}(\rho_{\mathrm{w}}^{\mathrm{p}})$ have been developed (see Ref. [12]). The effect on $\acute{\mathbf{x}}_{\mathrm{w}}^{\mathrm{p}}$ caused by an external applied pressure is not included in the present model.

The assumptions for the diffusion velocity flows for the $\Re$ considered types of ions in a pore solution are

$$\rho_i^{\mathrm{p}}\mathbf{u}_i^{\mathrm{p}} = -\tilde{D}_i^{\mathrm{p}}(\rho_{\mathrm{w}}^{\mathrm{p}})m_i\mathrm{grad}n_i^{\mathrm{p}} - \tilde{A}_i^{\mathrm{p}}(\rho_{\mathrm{w}}^{\mathrm{p}})m_i v_i n_i^{\mathrm{p}}\mathrm{grad}\varphi^{\mathrm{p}};\quad i = 1,\ldots,\Re \tag{58}$$

where $\tilde{D}_i^{\mathrm{p}}(\rho_{\mathrm{w}})$ (m^2/s) is the diffusion parameter for ion type i, dissolved in the pore solution, which is assumed to be dependent on the moisture condition ρ_{w}. The property $\tilde{A}_i^{\mathrm{p}}(\rho_{\mathrm{w}}^{\mathrm{p}})$ (m^2/(V s)) is the ion mobility parameter for ion type i in pore solution. The valence number for ion type i (to be used with the correct sign) is denoted by v_i (−), and φ^{p} (V) denotes the electrical potential in the pore solution. If effects caused by corrosion of reinforcement bars embedded in concrete are also included, an extra term must be added in Eq. (58), since an electrical potential (which is different from φ^{p}) will develop in the domain surrounding the anodic and cathodic area, i.e. in the corrosion zone. The gradient of the electric potential caused by reinforcement corrosion will affect the diffusion of all ions dissolved in pore solution near the corrosion zone. This phenomenon has been theoretically studied in Ref. [13].

The constitutive assumption for the mass flow of ions in water-filled pore system in concrete has been used by, for example, Refs. [14–16]. In Ref. [14], the gradient of the chemical activity is also included in the constitutive function for the mass density flow. The chemical activity is assumed to be a function of the concentration and temperature, i.e. the so-called Debye–Hückel model. The extended Debye–Hückel model also considers the radius of the various ions in solution.

The mass exchange rate for the ion type i with solid constituents can, in a somewhat general case, be described as functions of all $\Re$ number of mole density concentrations of the different types of ions in phase p and all $\aleph$ number of mass densities of solid components in phase c. The mole density gain of mass to the i-th ion constituent dissolved in a pore solution from the solid phase is written, in a general fashion, as

$$\hat{n}_i^{\mathrm{p}} = f_i(n_{i=1,\ldots\Re}^{\mathrm{p}},\ \rho_{h=1,\ldots\Im}^{\mathrm{c}}) \tag{59}$$

And the mole density gain of mass to the h-th constituent in solid phase from ions in the pore solution is written as

$$\hat{n}_h = f_h(n_{i=1,\ldots\Re}^{\mathrm{p}},\ \rho_{h=1,\ldots\Im}^{\mathrm{c}}) \tag{60}$$

where it should be noted that the function f_i is related to f_h through the chemical reaction assumed to be taking place. Typical mass exchanges to be described with the constitutive functions in Eqs. (59) and (60), for the studied case, are binding and leaching of chloride, hydroxide, and calcium ions. Explicit assumptions for this kind of reactions can be found in Ref. [17]. Properties related to chloride binding and its equilibrium conditions in concrete can be studied in, for example, Ref. [18].

The assumption for the electric displacement field $\mathbf{d}^{\mathrm{p}}$ in a pore solution is

$$\mathbf{d}^{\mathrm{p}} = -\tilde{\varepsilon}\varepsilon_o\mathrm{grad}\varphi^{\mathrm{p}} \tag{61}$$

where ε_o (C/V) is the coefficient of dielectricity or permittivity of vacuum, $\varepsilon_o = 8.854\times10^{-12}$, and $\tilde{\varepsilon}$ (−) is the relative coefficient of dielectricity that varies among different dielectrics. For water at 25 °C, $\tilde{\varepsilon} = 78.54$.

The charge density in the pore solution is the global imbalance of charge in a representative material volume given as

$$\mathbf{q}^{\mathrm{p}} = F\sum_{i=1}^{\Re} n_i^{\mathrm{p}} v_i \tag{62}$$

where $F = 96{,}490$ C/mol is a physical constant describing the charge of 1 mol of an ion having a valence number equal to 1.

4. Governing equations

Combining the mass balance equation (28) and the constitutive relation (57) for the mass density flow of the water phase, one obtains

$$\frac{B\rho_{\mathrm{w}}^{\mathrm{p}}}{Bt} = \mathrm{div}(D_{\mathrm{w}}^{\mathrm{p}}(\rho_{\mathrm{w}}^{\mathrm{p}})\mathrm{grad}\rho_{\mathrm{w}}) \tag{63}$$

which is the governing equation determining $\rho_{\mathrm{w}}^{\mathrm{p}}(\mathbf{x},t)$.

Combining the constitutive relation (58), for the diffusion velocity for the ion type i, and the assumption (57) with the mass balance (52) for the same ion type, one obtains for all $i = 1,\ldots,\Re$ ion types considered.

$$\begin{aligned}\frac{Bn_i^{\mathrm{p}}}{Bt} &= \mathrm{div}(\tilde{D}_i^{\mathrm{p}}(\rho_{\mathrm{w}}^{\mathrm{p}})\mathrm{grad}n_i^{\mathrm{p}}) + \mathrm{div}(\tilde{A}_i^{\mathrm{p}}(\rho_{\mathrm{w}}^{\mathrm{p}})v_i n_i^{\mathrm{p}}\mathrm{grad}\varphi)\\ &\quad + \frac{D_{\mathrm{w}}^{\mathrm{p}}(\rho_{\mathrm{w}}^{\mathrm{p}})}{\rho_{\mathrm{w}}^{\mathrm{p}}}\mathrm{grad}\rho_{\mathrm{w}}^{\mathrm{p}}\cdot\mathrm{grad}n_i^{\mathrm{p}} + n_i^{\mathrm{p}}\mathrm{div}\left(\frac{D_{\mathrm{w}}^{\mathrm{p}}(\rho_{\mathrm{w}}^{\mathrm{p}})}{\rho_{\mathrm{w}}^{\mathrm{p}}}\mathrm{grad}\rho_{\mathrm{w}}^{\mathrm{p}}\right)\\ &\quad + f_i(n_{i=1,\ldots\Re}^{\mathrm{p}},\ \rho_{h=1,\ldots\Im}^{\mathrm{c}})\end{aligned} \tag{64}$$

which is the governing equation determining $n_i^{\mathrm{p}}(\mathbf{x},t)$.

The first term on right-hand side of Eq. (64) describes the effect of normal diffusion, the second term describes the effect on diffusion caused by the internally induced electrical imbalance among positively and negatively charged ions in pore solution phase, the third term gives the change of concentration of ion type i due to a motion of the pore solution phase in the concrete pore structure, the fourth term models the effect of the change in concentration of ions in pore solution due to drying (or an increase in water content) of the pore water and, finally, the last term on the right-hand side of Eq. (64) is the loss or gain of ions due to mass exchanges between pore solution and solid hydration product of concrete.

The equation determining the mass density field $\rho_h^c(\mathbf{x},t)$, i.e. the mass density concentration of solid component h in concrete, is obtained by combining the mass balance (27) and the constitutive assumption (60), i.e.

$$\frac{B\rho_h^c}{Bt} = \xi_h(n^p_{i=1,\ldots\Re},\ \rho_{h=1,\ldots\Im}); \quad h = 1, \ldots, \aleph \tag{65}$$

where the function ξ_h is related to f_h, in Eq. (60), by the mole weight involved in the reaction. Examples of reactions are binding of chlorides and leaching of hydroxide.

The governing equation for the electric potential $\varphi^p(\mathbf{x},t)$ is obtained by inserting the two constitutive assumptions (61) and (62) into the continuity Eq. (31), i.e.

$$-\mathrm{div}(\tilde{\varepsilon}\varepsilon_o \mathrm{grad}\varphi^p) = F\sum_{i=1}^{\Re} n_i^p v_i \tag{66}$$

According to the mass balance principle for the local mass exchanges between pore solution phase and solid phase, i.e. Eq. (30), the following should also hold

$$\sum_{i=1}^{\Re} f_i(n^p_{i=1,\ldots\Re},\ \rho^c_{h=1,\ldots\Im}) = \sum_{b=1}^{\Im} f_h(n^p_{i=1,\ldots\Re},\ \rho^c_{h=1,\ldots\Im}) \tag{67}$$

One of the main ideas behind this method of treating multicomponent ion diffusion in concrete pore solutions is that the diffusion parameters $\tilde{D}_i^p(\rho_w)$ and ion mobility parameters $\tilde{A}_i^p$ for all i-th types of ions considered can be scaled with the same tortuosity factor t, which is assumed to be a function of the pore structure and moisture content ρ_w. That is,

$$\tilde{D}_i^p = t(\rho_w)D_i \text{ and } \tilde{A}_i^p = t(\rho_w)A_i; \quad i = 1, \ldots, \Re \tag{68}$$

where D_i and A_i are the bulk diffusion and ion mobility coefficient in water, respectively. The values of these bulk coefficients for different types of ions can be found in, for example, Ref. [19]. The experimental work concerning the diffusion characteristics, therefore, consists of determining only one parameter, i.e. $t(\rho_w)$ for the material in question. The main experimental and theoretical work, due to this choice of approach, is directed more toward describing the mass exchanges between ions in pore solution and the solid components of concrete, i.e. the description of f_i and f_h.

Solutions to the presented equation system have been reported for cases where the concrete is saturated, i.e. the convection is excluded (e.g., see Refs. [14,16,17,20]). Solutions for cases considering only concentration gradient-driven chloride diffusion and convection due to motion of the pore water phase in concrete have been studied in Refs. [21,22].

Studies conducted in Ref. [17] reveal that the dielectric effects in the pore solution phase play a significant rule in describing the chloride ion diffusion in the water-filled pore system of concrete, especially in cases where the concrete samples were dried and re-wetted in tap water before exposure to a chloride solution. The obtained tortuosity factors from this study were in the range of 0.006–0.009, in saturated conditions, for water-to-binder ratios of 0.35–0.55. Chloride profiles reported in Ref. [23] were used together with the model described in this work, to obtain these tortuosity factors. These results are in accordance with tortuosity factors determined by a gas diffusion technique [24]. The tortuosity factors obtained for concrete with the cement content 400 kg/m^3 having water-to-cement ratios of 0.40 and 0.55 were 0.007 and 0.011, respectively.

5. Conclusions

A theoretical model describing penetration and leaching of different types of ions in pore solution of concrete was established. The model accounts for (i) diffusion of different types of ions caused by its concentration gradient, (ii) diffusion caused by the gradient of the electrical potential that is determined from the momentarily developed imbalance of charge among positive and negative ions in pore solution, (iii) mass exchange between ions in pore solution and hydration products in concrete, e.g., binding and leaching of chloride, hydroxide, carbonic acid, sulfate, and calcium ions, (iv) convective flows caused by a motion of the pore solution phase, e.g., motion of ions dissolved in pore solution caused by capillary suction, and (v) the effect on the ion concentration due to a change in the mass concentration of pore water in the concrete, i.e. when drying of pore solution occurs the concentration of ions in the water phase increases and when the water content increase the solution becomes more dissolute. The derived mass balance principle for the different types of ions appearing in the pore solution phase, i.e. Eq. (52), includes all these important phenomena. The mass balance equation for the ion constituents dissolved in the pore solution was established by considering two phases, i.e. the pore solution phase and the solid phase using the basic assumptions defined in mixture theory as described in Ref. [8].

It is assumed that the different types of ions in pore solution are affected by the pore system in an identical manner with regard to diffusion caused by concentration and electric potential gradients. This way of simplifying the problem very much turns the problem toward describing the correct equilibrium and kinetic conditions for the mass exchange processes occurring between ions in pore solution and solid components of the concrete.

The convection of ions was introduced by using the so-called diffusion velocities, that is, the velocity relative to the velocity of the mixture (in this reduced problem the velocity of pore solution phase) together with the use of a proper equation for the mass balance for the ion constituents dissolved in pore water. The method for calculating the velocity of pore phase (see Eqs. (57) and (63)) may be criticized, since at relatively low moisture contents in concrete the distribution of moisture is mainly due to vapor diffusion in air-filled space in pore system not contributing to a motion of pore water phase. That is, the convection of ions in pore solution phase is most likely overestimated at medium and low water contents in pore system, for concrete exposed to drying or wetting, in the model described.

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