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Diffusion of a mixture of cations and anions dissolved in water

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Abstract

In service life modeling of concrete, the ion transport in the pore solution is crucial. The main deterioration phenomena associated with ions in the pore solution are (1) corrosion due to external chloride ions reaching the embedded reinforcement bars; (2) carbonation due to presence of dissolved carbon dioxide (which will form carbonic acid with water) supplied from the surrounding air; and (3) leaching of hydroxide ions from the pore solution to the surrounding environment. Models dealing with diffusion of ions are usually based on the mass balance equations for the individual diffusing ions together with constitutive relations for the mass density flows and for the mass exchange among the constituents. The important consequences of electroneutrality among the diffusing ions, however, is often omitted in models dealing with diffusion of ions in the pore solution of concrete. Here a method will be examined that allows diffusion of different ions in water, which satisfies both the electroneutrality requirement and the mass balance laws. For simplicity the effect of built-up electric double layers on the charged pore walls will not be treated.

Keywords: Diffusion; Carbonation; Leaching; Pore solution; Surface layer

1. Introduction

Transport of a mixture of ions in the pore solution in concrete is influenced by five main different mechanisms:

1. diffusion (i.e., gradient dependent mass flow of the individual ions)
2. forced convection (i.e., a mass flow of dissolved ions due to the motion of the pore solution induced by capillary suction or/and an external pressure gradient)
3. binding of ions onto the pore walls and leaching of ions from the solid (i.e., the effect of creation of so-called double layers on the pore walls and also due to chemical reactions with the solid hydration products in the cement)
4. motion of ions due to an external electrical field induced by reinforcement corrosion
5. motion of ions due to a momentarily induced internal electrical field among the ions present in the pore solution (i.e., the effect of the composition of the mixture on the mass flow among positive and negative charged ions in solution)

In this paper only the last mechanism (motion of ions due to a momentarily induced internal electrical field among the ions present in the pore solution) will be analyzed. The others can be studied elsewhere [1–15].

2. Mass balance

Mass balance of different constituents present in a mixture may be formulated as shown in Eq. (1) (compare to ref. [16]):

$$\rho\frac{\partial c_a}{\partial t} = -\operatorname{div}(\rho_a \mathbf{u}_a) - \rho\dot{\mathbf{x}}\operatorname{grad}c_a + \hat{c}_a; \qquad a = 1, \ldots, \Re \tag{1}$$

where $c_a(\mathbf{x}, t)$ is the mass concentration of an arbitrary constituent denoted a. The total number of constituents is denoted $\Re$. The mass concentration is defined as $c_a = \rho_a/\rho$ where $\rho_a(\mathbf{x}, t)$ is the mass density of the constituent and where $\rho(\mathbf{x}, t)$ is the mass density of the whole mixture (i.e., the sum of all ρ_a). The diffusion velocity $\mathbf{u}_a$ is defined as $\mathbf{u}_a = \dot{\mathbf{x}}_a - \dot{\mathbf{x}}$, where $\dot{\mathbf{x}}_a(\mathbf{x}, t)$ is the velocity of the a:th constituent and $\dot{\mathbf{x}}(\mathbf{x}, t)$ denotes the velocity of the whole mixture, which is the mass weighted sum of the individual velocities of the constituents. The mass exchange rate between the ath constituent and all other constituents is denoted $\hat{c}_a(\mathbf{x}, t)$. Due to the mass balance for the whole mixture, one must assure that there is no net production of mass in a material point: $\Sigma_{a=1}^{\Re}\,\hat{c}_a(\mathbf{x}, t) = 0$.

Here it will be assumed that ions appearing in solution are in weak concentration; therefore it will be assumed that

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$\rho(\mathbf{x}, t)$ is an approximately constant property and that the velocity of the mixture is approximately zero. These assumptions result in the diffusion velocities $\mathbf{u}_a(\mathbf{x}, t)$ for the constituents being approximately the same as their corresponding velocities $\dot{\mathbf{x}}_a(\mathbf{x}, t)$. Furthermore, it will be assumed that no net mass exchange takes place among the constituents in the mixture. A more simplified version of Eq. (1) can therefore be written as Eq. (2):

$$\frac{\partial n_a}{\partial t} = -\mathrm{div}(n_a\mathbf{u}_a); \qquad a = 1, \ldots, \Re \tag{2}$$

where n_a (mol/m^3) denotes the mol concentration of the ath constituent. In Eq. (2) it is assumed that $\dot{\rho} \approx 0$ and that $\dot{\mathbf{x}} \approx \mathbf{0}$.

3. Electroneutrality

Elecroneutrality in a solution with different ions is expressed with the mole concentrations $n_a(\mathbf{x}, t)$ and its corresponding valence number v_a as in Eq. (3).

$$\sum_{a=1}^{\Re} n_a(\mathbf{x}, t)v_a = 0 \tag{3}$$

Indeed, Eq. (3) may not be valid during extremely small scales of length and time. During such conditions the ion solution can be subjected to a static electrical field vector $\mathbf{e} = \mathrm{grad}\varphi$ where φ is the electrostatic potential. This potential is induced by a momentary small net difference between present positively and negatively charged ions in a certain material point $\mathbf{x}$ and at a certain time t. In the application to be presented it seems reasonable to always fulfill the restriction of electrical balance among the constituents in a representative volume of the pore solution, assuming explicitly that $\varphi(\mathbf{x}, t) = 0$. However, it is supposed that a more general consideration in which the possibility of having a present self-induced electrostatic field in the solution may improve the constitutive assumptions for the mass density flow of the ions in a mixture with different dissolved charged constituents. Furthermore, such quantitative considerations may be used in a simpler method where electroneutrality is assumed among the constituents [i.e., when always having Eq. (3) satisfied].

4. Static continuity equation for the charge

When dealing with diffusing charged constituents, Fick's second law type of equations, based on the mass balance and a constitutive relation for the flow, can be improved by also invoking the local statement of balance for the charge. This means that two physical balance principles can be used as a foundation when constituting the flow characteristics of ions in solution.

The local statement of the static continuity equation for the charge is one of Maxwell's equations, that is, Eq. (4)

$$\mathrm{div}(\mathbf{d}) = q \tag{4}$$

where $\mathbf{d}$ is the electric displacement field vector $\mathbf{d}$ (C/m^2) and q (C/m^3) is the space charge density scalar.

5. Constitutive relations—approach 1

This approach will be based on the mass balance equations for the individual charged constituents only. However, a state variable $\phi(\mathbf{x}, t)$ will be introduced, which determines the unbalance of charge at a certain material point $\mathbf{x}$ in the domain and at the time t. The mol concentration flow will be assumed to depend both on the mol concentration gradient and the gradient of the state variable ϕ.

The 2 $\Re$ + 1 introduced unknown properties are shown in Eq. (5).

$$\begin{aligned} &\Re \text{ number of: } n_a(\mathbf{x}, t) \\ &\Re \text{ number of: } \mathbf{u}_a(\mathbf{x}, t) \\ &\qquad\qquad\quad \phi(\mathbf{x}, t) \end{aligned} \tag{5}$$

where $\Re$ is the number of introduced charged constituents and n_a and $\mathbf{u}_a$ denote the mol concentration and diffusion velocity vector, respectively. The number of balance equations is $\Re$ (i.e., $\Re + 1$ constitutive relations are required to make the equation system closed).

The mass flow of the considered $\Re$ ions 1, . . ., $\Re$ are the assumption shown in Eq. (6):

$$n_a\mathbf{u}_a = -D_a\mathrm{grad}n_a - E_a v_a\mathrm{grad}\phi; \qquad a = 1, \ldots, \Re \tag{6}$$

where D_a (m^2/s) is the separate diffusion constant for the ath constituent and where E_a (mol/s/m) is a material constant describing the tendency of the ath ion diffusing towards opposite charged domains or being repelled from equally charged domains.

In this first approach the state variable ϕ will be defined as shown in Eq. (7)

$$\phi(\mathbf{x}, t) = \sum_{a=1}^{\Re} n_a(\mathbf{x}, t)v_a \tag{7}$$

This means that ϕ determines the charge unbalance in a certain material point in the domain of interest.

6. Governing equations—approach 1

By combining the mass balance law with the constitutive relations discussed in the previous section, a closed equations system will be obtain. Using these equations, concentration fields of different dissolved ions in a mixture may be calculated.

The $\Re$ equations describing the mol concentration fields $n_a(\mathbf{x}, t)$, using the constitutive assumption in approach 1, are shown in Eq. (8):

$$\frac{\partial n_a}{\partial t} = \mathrm{div}\left[D_a \mathrm{grad} n_a + E_a v_a \mathrm{grad}\left(\sum_{a=1}^{\Re} n_a v_a\right)\right]; \qquad a = 1, \ldots, \Re \tag{8}$$

This equation is obtained by combining the mass balance equations, Eq. (2), with the corresponding constitutive relation for the mol density flow, Eq. (6), and also by using the definition, Eq. (7).

The prescription of the mol concentration as a boundary condition to be used in Eq. (8) can be written as Eq. (9):

$$n_a(\mathbf{x}, t)|_{\mathrm{boundary}} = g_a^{\mathrm{Dirichlet}} \tag{9}$$

where $g_a^{\mathrm{Dirichlet}}$ is a prescribed value of the mol concentration at the boundary surface at the time *t*.

Alternatively, a Newman type of boundary condition can be adopted that is a prescription of the mol concentration flow through the boundary surface at the time *t*, as in Eq. (10)

$$n_a \mathbf{u}_a(\mathbf{x}, t) \cdot \mathbf{m}|_{\mathrm{boundary}} = h_a^{\mathrm{Newman}} \tag{10}$$

where **m** is the outdrawn normal vector located at the boundary surface and $\Re$ is the prescribed value of the flow $n_a \mathbf{u}_a(\mathbf{x}, t) \cdot \mathbf{m}|_{\mathrm{boundary}}$.

7. Constitutive relations—approach 2

In a mixture consisting of $\Re$ different types of dissolved ions there are a determined number of combinations of cations and anions that can form different salts or acids. The number of potential combinations of cations and anions will be denoted $\mathfrak{T}$, and the potentially formed salt or acid will be denoted with a subscript *b*.

In the method to be presented here it will be explicitly assumed that when ions are transported in the water, the electroneutrality $\phi(\mathbf{x}, t)$ will always be equal to zero (i.e., no net difference of charge is allowed under any circumstances). One way to arrange the equations is to combine the present ions in a material point at a certain time, forming potential salts and acids. These salts and acids are then only allowed to be transported in the solution as a neutrally charged "package." When only letting anions and cations be transported in pairs, the $2\,\mathfrak{T} + 1$ unknown properties must be solved for, as in Eq. (11):

$$\begin{aligned} &\Im \text{ number of: } n_b(\mathbf{x}, t) \\ &\Im \text{ number of: } \mathbf{u}_b(\mathbf{x}, t) \\ &\qquad\qquad \phi(\mathbf{x}, t) \end{aligned} \tag{11}$$

where subscript *b* denotes the $\mathfrak{T}$ number of potentially formed salts or acids.

The number of mass balance equations introduced for the neutrally charged package of anions and cations is $\mathfrak{T}$ (i.e., $\mathfrak{T} + 1$ number of constitutive relations are required).

It will be explicitly assumed that the charge is balanced at every material point **x** and at every time *t*, as seen in Eq. (12):

$$\phi(\mathbf{x}, t) = \sum_{a=1}^{\Re} n_a(\mathbf{x}, t) v_a = 0 \tag{12}$$

The assumption for the mol concentration flow of the $\mathfrak{T}$ number of a neutrally charged package of an anion and a cation is shown in Eq. (13).

$$\rho_b \mathbf{u}_b = -\tilde{D}_b \mathrm{grad} n_b; \qquad b = 1, \ldots, \Im \tag{13}$$

where $\tilde{D}_b$ is a weighted value of the separate diffusion constants for the cation and the anion, forming the neutrally charged substance *b*. It can be argued that the following weight of the individual diffusion constants is reasonable [17, see Eq. (14)]:

$$\tilde{D}_b = 2\left(\frac{1}{D^{(+)}} + \frac{1}{D^{(-)}}\right)^{-1} \tag{14}$$

Some values of weighted diffusion constants for different salts and acids are given in Table 1.

When using the method discussed in this section, a reasonable technique for distributing the separate ion concentrations among the potential neutral package *b* must be sought. One of the simplest methods for distributing the ions among salts or acids will be explained by an example. Consider a mixture of two anions and two cations dissolved in water. The ion with the lowest concentration denoted $n_{b\min}$ is, in this example, determined by Eq. (15):

$$n_{b\min} = \min(n^{(+)}_{a=1}, n^{(+)}_{a=2}, n^{(-)}_{a=3}, n^{(-)}_{a=4}) \tag{15}$$

The concentration *nb*min will be combined with its two oppositely charged ions (at the same proportions) so that all of the substance having the lowest mol concentration is consumed. The two missing constituents having neutral charge will in this simple example be given directly. If for example $n^{(-)}_{a=3}(\mathbf{x}, t)$ is the smallest number of $n^{(-)}_{a=1}$, $n^{(-)}_{a=2}$, $n^{(+)}_{a=3}$, and $n^{(+)}_{a=4}$ the composition will be [see Eq. (16)]

$$\begin{aligned} n_{b=13} &= 0.5 n^{(-)}_{a=3}(\mathbf{x}, t) \\ n_{b=23} &= 0.5 n^{(-)}_{a=3}(\mathbf{x}, t) \\ n_{b=14} &= n^{(+)}_{a=1}(\mathbf{x}, t) - 0.5 n^{(-)}_{a=3}(\mathbf{x}, t) \\ n_{b=24} &= n^{(+)}_{a=2}(\mathbf{x}, t) - 0.5 n^{(-)}_{a=3}(\mathbf{x}, t) \end{aligned} \tag{16}$$

For a case with a mixture of dissolved Na^+, K^+, Cl^-, and OH^- in water with the mol concentrations $n_{a=Na+}^{(+)} = 0.20 \cdot 10^{-3}$ (mol/m^3), $n_{a=K+}^{(+)} = 0.10 \cdot 10^{-3}$ (mol/m^3), $n_{a=Cl-}^{(-)} = 0.20 \cdot$

Table 1
Example of weighted material constants to be used in approach 2

Substance	Weighted diffusion coefficient (m^2/s)
NaCl	$1.67 \cdot 10^{-9}$
NaOH	$2.21 \cdot 10^{-9}$
KCl	$2.06 \cdot 10^{-9}$
KOH	$2.97 \cdot 10^{-9}$

10^{-3} (mol/m^3), and $n_{a=\mathrm{OH}-}^{(-)} = 0.10 \cdot 10^{-3}$ (mol/m^3) the mol concentration of the neutrally charged components will be: $n_{b=\mathrm{KCl}} = 0.05 \cdot 10^{-3}$ (mol/m^3), $n_{b=\mathrm{KOH}} = 0.05 \cdot 10^{-3}$ (mol/m^3), $n_{b=\mathrm{NaCl}} = 0.15 \cdot 10^{-3}$ (mol/m^3), and $n_{b=\mathrm{NaOH}} = 0.05 \cdot 10^{-3}$ (mol/m^3) when using the weighting method discussed above.

8. Governing equations—approach 2

For all $\mathfrak{T}$ number of neutrally charged combinations of ions in solution the following $\mathfrak{T}$ number of equations are obtained by the mass balance equation for the individual constituents [Eq. (2)] and the corresponding constitutive assumption for the mol concentration flow [Eq. (13)], as shown in Eq. (17).

$$\frac{\partial n_b}{\partial t} = \mathrm{div}(D_b \mathrm{grad} n_b); \qquad b = 1, \ldots, \mathfrak{I} \tag{17}$$

Boundary conditions that can be used in Eq. (17) are either the Dirichlet type of boundary condition, as in Eq. (18).

$$n_b(\mathbf{x}, t)\big|_{\mathrm{boundary}} = g_b^{\mathrm{Dirichlet}} \tag{18}$$

Eq. (18) is a prescription of the mol concentration $g_b^{\mathrm{Dirichlet}}$ of the neutrally charged substance b at the boundary surface, or the Newman boundary condition [see Eq. (19)]

$$n_b \mathbf{u}_b(\mathbf{x}, t) \cdot \mathbf{m}\big|_{\mathrm{boundary}} = h_b^{\mathrm{Newman}} \tag{19}$$

where h_b^{Newman} is a prescribed value of the mol concentration flow through the boundary surface having a direction determined by the outward drawn normal vector **m.**

It should be observed that ions supplied from external sources must be composed into potential salts or acids in the same manner as was proposed for the ions present within the domain of interest.

9. Constitutive relations—approach 3

This approach is based on both the mass balance equation for the individual constituents [Eq. (2)] and the balance of charge equation [Eq. (4)]. Constitutive relations to be used in these balance equations will be discussed in this section.

The 2 $\mathfrak{R} + 3$ unknown properties in this approach are shown in Eq. (20).

$$\begin{aligned} &\mathfrak{R} \text{ number of: } n_a(\mathbf{x}, t) \\ &\mathfrak{R} \text{ number of: } \mathbf{u}_a(\mathbf{x}, t) \\ &\qquad \mathbf{d}(\mathbf{x}, t) \\ &\qquad q(\mathbf{x}, t) \\ &\qquad \varphi(\mathbf{x}, t) \end{aligned} \tag{20}$$

The number of mass balance equation is $\mathfrak{R}$ and the continuity equation for the current density gives on extra equation (i.e., $\mathfrak{R} + 2$ constitutive relations are required to make the equation system closed).

The electric displacement field vector **d** will be related to the electric field vector **e** by the constitutive relation shown in Eq. (21):

$$\mathbf{d} = \varepsilon\varepsilon_0 \mathbf{e} \tag{21}$$

where the electric field vector **e** will be defined with the gradient of the electrostatic scalar potential φ(V), as shown in Eq. (22):

$$\mathbf{e} = -\mathrm{grad}\varphi \tag{22}$$

Eq. (21) and Eq. (22) combine to yield the assumption for **d,** as seen in Eq. (23)

$$\mathbf{d} = -\varepsilon\varepsilon_0 \mathrm{grad}\varphi \tag{23}$$

where ε_0 (C/V) is the coefficient of dielectricity or permittivity of vacuum, $\varepsilon_0 = 8.854 \cdot 10-12$, and ε (−) is the relative coefficient of dielectricity that varies among different dielectrics. For water at 25°C, $\varepsilon = 78.54$.

The charge density q can be related to the composition of the mixture of ions, written in the local form, as Eq. (24)

$$q = F \sum_{a=1}^{\mathfrak{R}} n_a(\mathbf{x}, t) v_a \tag{24}$$

where $F = 96490$ (C/mol) is a physical constant describing the charge of one mol of an ion having a valence number equal to one.

The constitutive relation for the mole density flows for the $\mathfrak{R}$ ions 1, . . ., $\mathfrak{R}$ is the assumption [see Eq. (25)]

$$n_a \mathbf{u}_a = -D_a \mathrm{grad} n_a - A_a v_a n_a \mathrm{grad}\varphi; \qquad a = 1, \ldots, \mathfrak{R} \tag{25}$$

where D_a (m^2/s) and A_a (m^2/s/V) are material constants. Some values of these material constants for different ions dissolved in water are shown in Table 2. It should be noted that the diffusion coefficients D_a are predicted values obtained by scaling the ionic mobilities A_a [17,18].

The assumption for the mol concentration flow [Eq. (25)] is in accordance with the phenomena where matter tends to be transported to regions having the lowest chemical potential. That is, the constitutive relation [Eq. (25)] can be obtained for the case when the chemical potential is assumed to be a function of both the mol concentration and the electrostatic potential.

It should be observed that the electroneutrality cannot be fulfilled in every material point at every time level t using this approach.

Table 2
Example of material constants to be used in approach 3

Substance	Diffusion coefficient (m^2/s)	Ionic mobility (m^2/s/V)	Dielectricity coefficient (C/V)
Cl^-	$2.03 \cdot 10^{-9}$	$7.91 \cdot 10^{-8}$	–
OH^-	$5.30 \cdot 10^{-9}$	$20.64 \cdot 10^{-8}$	–
CO_3^{2-}	$1.96 \cdot 10^{-9}$	$7.46 \cdot 10^{-8}$	–
Na^+	$1.33 \cdot 10^{-9}$	$5.19 \cdot 10^{-8}$	–
K^+	$1.96 \cdot 10^{-9}$	$7.62 \cdot 10^{-8}$	–
Ca^{2+}	$1.58 \cdot 10^{-9}$	$6.17 \cdot 10^{-8}$	–
H_2O	–	–	$695.4 \cdot 10^{-12}$

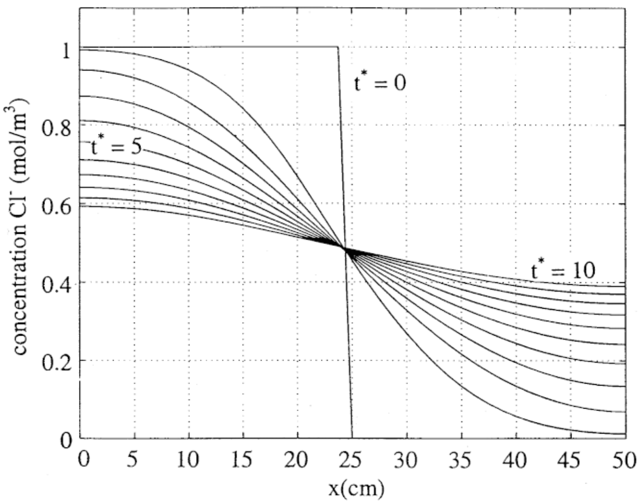

Fig. 1. Concentration of Cl^- at different times, calculated with approach 2. The total time is 1 year and the profiles shown in the figure are divided into 10 equally long time periods.

10. Governing equations—approach 3

The governing equations for the $\mathfrak{R}$ concentration fields $n_a(\mathbf{x}, t)$ are obtained by combining the mass balance equation [Eq. (2)] and the constitutive relation [Eq. (25)] [i.e., see Eq. (26)]:

$$\frac{\partial n_a}{\partial t} = \mathrm{div}(D_a \mathrm{grad} n_a + A_a v_a n_a \mathrm{grad}\varphi); \qquad a = 1, \ldots, \mathfrak{R} \tag{26}$$

A Dirichlet type of boundary condition to be used in Eq. (26) is a prescribed value of the concentration at the boundary surface, written as Eq. (27)

$$n_a(\mathbf{x}, t)|_{\mathrm{boundary}} = g_a^{\mathrm{Dirichlet}} \tag{27}$$

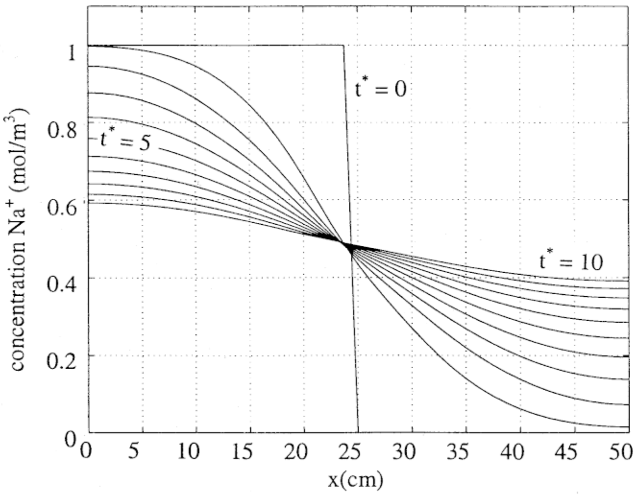

Fig. 2. Concentration of Na^+ at different times, calculated with approach 2. The total time is 1 year and the profiles shown in the figure are divided into 10 equally long time periods.

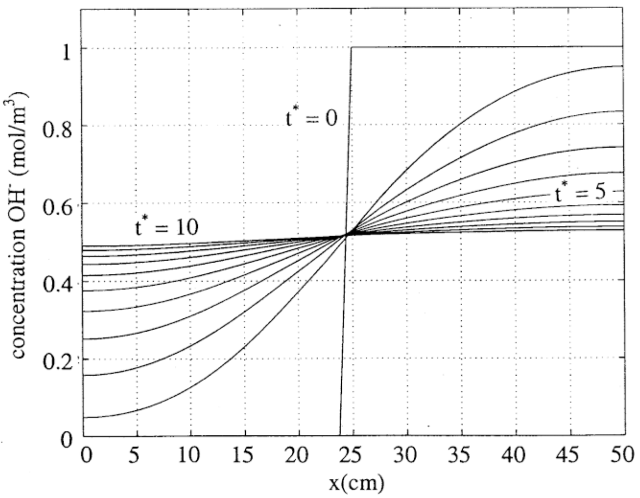

Fig. 3. Concentration of OH^- at different times, calculated with approach 2. The total time is 1 year and the profiles shown in the figure are divided into 10 equally long time periods.

The Newman boundary condition is a prescribed value of the mass flow $n_a\mathbf{u}_a$ through the boundary surface [see Eq. (28)],

$$n_a\mathbf{u}_a(\mathbf{x}, t) \cdot \mathbf{m}|_{\mathrm{boundary}} = h_a^{\mathrm{Newman}} \tag{28}$$

where $\mathbf{m}$ denotes a unit vector directed outwards from the boundary surface and where h_a^{Newmawn} (mol/s/m^2) is a prescribed normal value of the out or in flow of mol to the domain.

By using the static continuity equation for the charge [Eq. (4)] together with the constitutive relations for the electric displacement field vector $\mathbf{d}$ [Eq. (23)] and the charge density q [Eq. (24)], the governing equation for the static electro potential becomes Eq. (29):

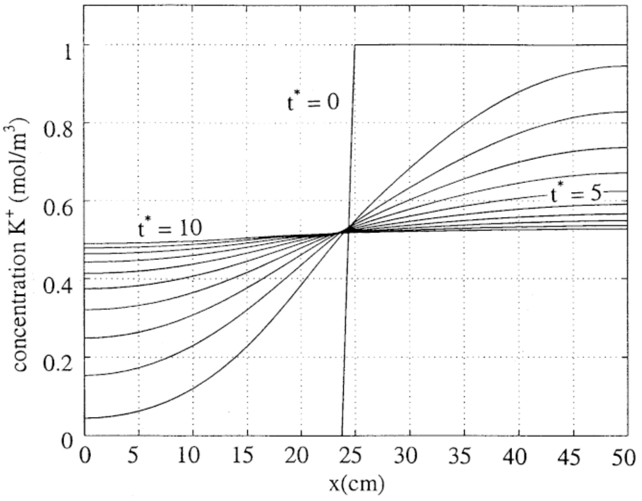

Fig. 4. Concentration of K^+ at different times, calculated with approach 2. The total time is 1 year and the profiles shown in the figure are divided into 10 equally long time periods.

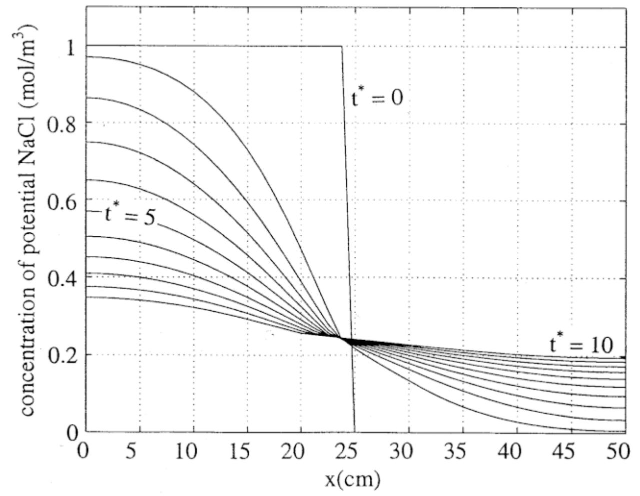

Fig. 5. Concentration at different times of neutrally charged package diffusing as NaCl, calculated with approach 2. The total time is 1 year and the profiles shown in the figure are divided into 10 equally long time periods.

$$-\mathrm{div}(\varepsilon\varepsilon_0 \mathrm{grad}\varphi) = F\sum_{a=1}^{\Re} n_a(\mathbf{x}, t)v_a \tag{29}$$

where it should be observed that this equation is coupled to the $\Re$ mass diffusion equations [Eq. (26)].

The boundary condition to be prescribed in Eq. (29) is a value of the net supply of charge through the boundary surface. This known value denoted r^{Newman} (C/s/m^2) is given from the $\Re$ mass diffusion equations [Eq. (26)], which means that Eq. (29) is coupled to the mass diffusion equations not only at the differential equation level but also at the boundaries. The net supply of charge through the boundary surface is given by Eq. (30):

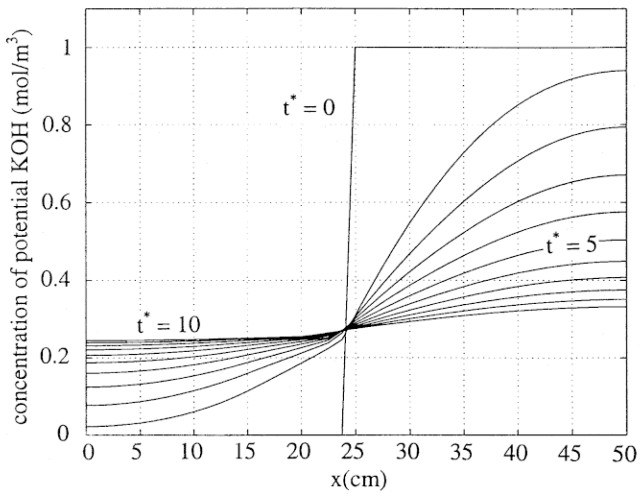

Fig. 6. Concentration at different times of neutrally charged package diffusing as KOH, calculated with approach 2. The total time is 1 year and the profiles shown in the figure are divided into 10 equally long time periods.

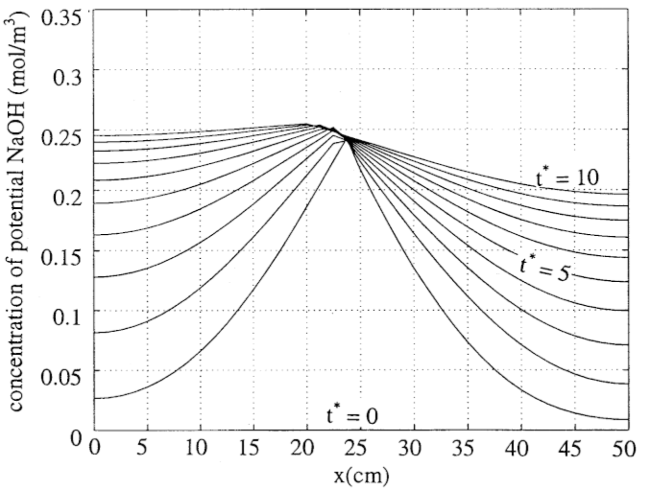

Fig. 7. Concentration at different times of neutrally charged package diffusing as NaOH, calculated with approach 2. The total time is 1 year and the profiles shown in the figure are divided into 10 equally long time periods.

$$r^{\mathrm{Newman}} = \int_\tau F\left(\sum_{a=1}^{\Re} v_a n_a \boldsymbol{u}_a(\mathbf{x}, t)\right)\cdot \mathbf{m}\,\mathrm{d}t\big|_{\mathrm{boundary}} \tag{30}$$

which is the Newman type of boundary condition to be used in Eq. (29). No Dirichlet boundary condition can be used in the application here because the potential φ is an unknown property in the whole domain and at the boundaries.

When using this method to calculate the $\Re$ concentration fields n_a the eletroneutrality will not be satisfied [i.e., Eq. (31)]:

$$\phi(\mathbf{x}, t) = \sum_{a=1}^{\Re} n_a(\mathbf{x}, t)v_a \neq 0 \tag{31}$$

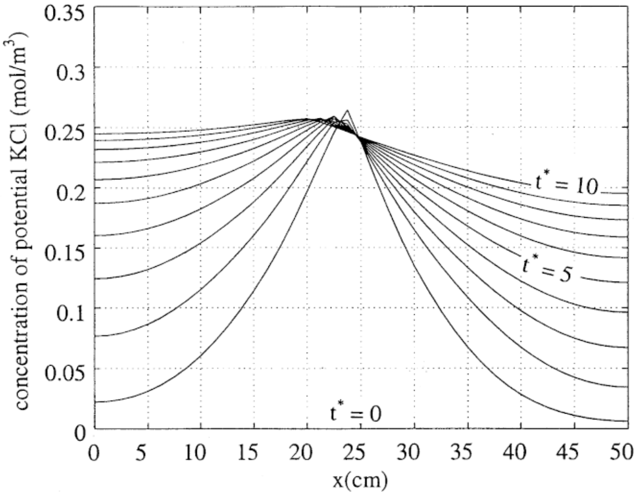

Fig. 8. Concentration at different times of neutrally charged package diffusing as KCl, calculated with approach 2. The total time is 1 year and the profiles shown in the figure are divided into 10 equally long time periods.

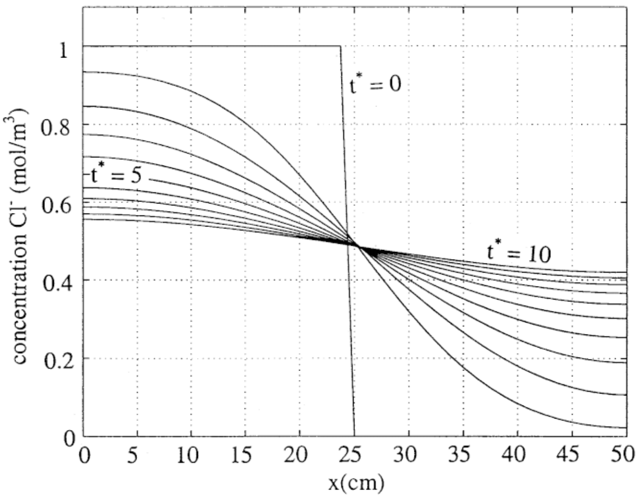

Fig. 9. Concentration of Cl^- at different times, calculated with approach 3. The total time is 1 year and the profiles shown in the figure are divided into 10 equally long time periods.

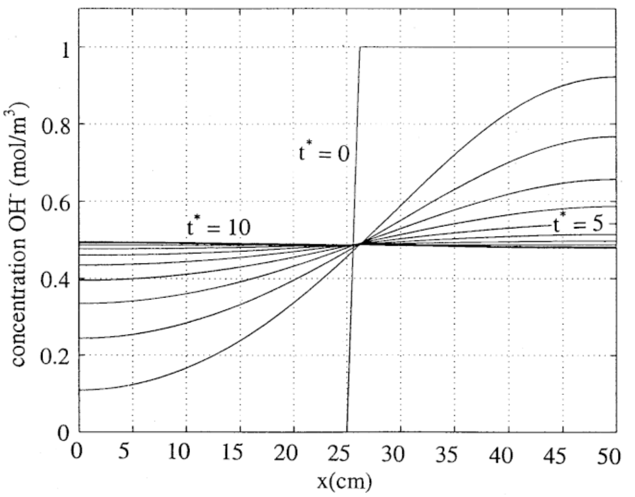

Fig. 11. Concentration of OH^- at different times, calculated with approach 3. The total time is 1 year and the profiles shown in the figure are divided into 10 equally long time periods.

However, due to the time scale in the problem the potential $\phi(\mathbf{x}, t)$ will be very close to the value zero.

11. Numerical solution strategy

In order to compare the different methods of treating diffusion of cations and anions dissolved in water with experiments, a solution strategy is needed. The calculation of the different concentration fields n_a and the electrostatic field φ involves a set of equations that is coupled at the differential equation level and at the boundaries; furthermore, the total equation system will become nonsymmetric and nonlinear. Therefore a numerical solution strategy will be outlined, which makes it possible to solve the equations. The finite element method will be adopted [19–22].

A finite time increment Δt will be considered, which is related to the time levels t_i and t_{i+1} as $t_{i+1} = t_i + \Delta t$, in order to obtain so-called recurrence relations. A time integration parameter Θ is introduced where $\Theta = 0$ is a truly explicit scheme, $\Theta = 1$ is a truly implicit scheme, $\Theta = 0.5$ is the Crank-Nicholson scheme, and $\Theta = 0.878$ is the Liniger scheme in which Θ is chosen to minimize the whole domain error. Values of Θ greater than or equal to 0.5 are shown to be unconditionally stable for equation systems that are symmetric and positive definite.

The total equation system can be written in the form seen in Eq. (32)

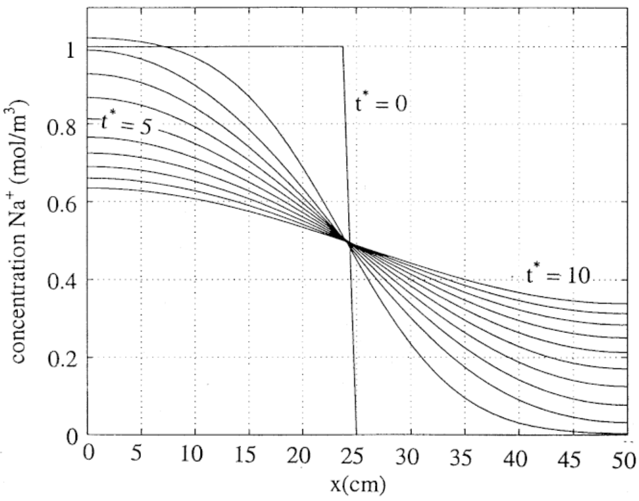

Fig. 10. Concentration of Na^+ at different times, calculated with the approach 3. The total time is 1 year and the profiles shown in the figure are divided into 10 equally long time periods.

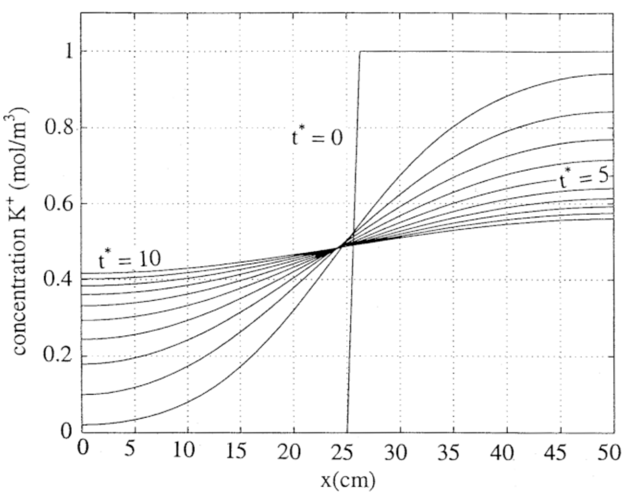

Fig. 12. Concentration of K^+ at different times, calculated with approach 3. The total time is 1 year and the profiles shown in the figure are divided into 10 equally long time periods.

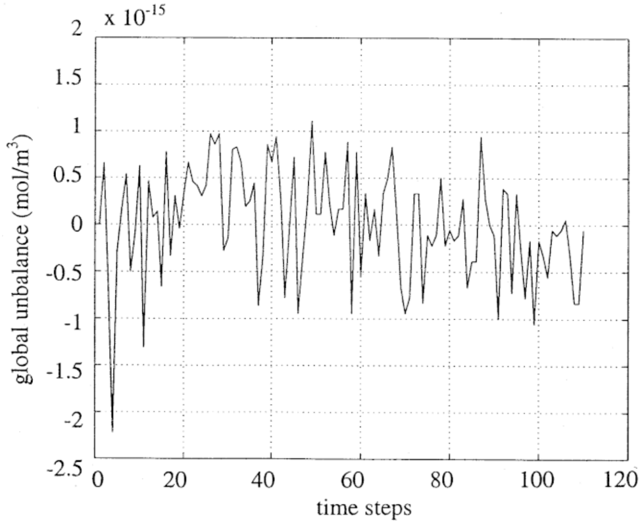

Fig. 13. The global error in terms of differences in the mol concentrations of anions and cations in the whole domain. Calculated with approach 3.

$$\mathbf{C}^{tot}\dot{\mathbf{a}}^{tot} + \mathbf{K}^{tot}\mathbf{a}^{tot} + \mathbf{f}^{tot} = \mathbf{0} \tag{32}$$

where $\mathbf{C}^{tot}$ is the damping matrix for the whole equation system, $\mathbf{K}^{tot}$ is the stiffness matrix for the whole system, and $\mathbf{f}^{tot}$ is the boundary and load vector in the problem. When using a single time-step algorithm, Eq. (32) takes the form shown in Eq. (33).

$$\mathbf{0} = \frac{\mathbf{C}^{tot}(\mathbf{a}_{i+1}^{tot} - \mathbf{a}_i^{tot})}{\Delta t} + \mathbf{K}^{tot}[\mathbf{a}_i^{tot} + \Theta(\mathbf{a}_{i+1}^{tot} - \mathbf{a}_i^{tot})]$$
$$+ \mathrm{f}_i^{tot} + \Theta(\mathbf{f}_{i+1}^{tot} - \mathbf{f}_i^{tot}) \tag{33}$$

This equation is used to solve the unknown vector $\mathbf{a}_{i+1}^{tot}$.

The total damping $\mathbf{C}^{tot}$ is formed by assembling the damping matrixes for the individual diffusion equations as block matrixes. As an example considering four different ions $a = 1, \ldots, 4$, and noting that only the mass diffusion equations involve damping, the matrix $\mathbf{C}^{tot}$ can be formed as [see Eq. (34)]

$$\mathbf{C}^{tot}\dot{\mathbf{a}}^{tot} = \begin{bmatrix} [\mathbf{C}_{n1}] & 0 & 0 & 0 & 0 \\ 0 & [\mathbf{C}_{n2}] & 0 & 0 & 0 \\ 0 & 0 & [\mathbf{C}_{n3}] & 0 & 0 \\ 0 & 0 & 0 & [\mathbf{C}_{n4}] & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} [\dot{\mathbf{a}}_{n1}] \\ [\dot{\mathbf{a}}_{n2}] \\ [\dot{\mathbf{a}}_{n3}] \\ [\dot{\mathbf{a}}_{n4}] \\ 0 \end{bmatrix} \tag{34}$$

where $[\mathbf{C}_{na}]$ is expressed with the shape function $\mathbf{N}(\mathbf{x})$ as $[\mathbf{C}_{na}] = \int_V \mathbf{N}^{\mathrm{T}}\mathbf{N}dV$ and where $\dot{\mathbf{a}}^{tot} = (\mathbf{a}_{i+1}^{tot} - \mathbf{a}_i^{tot})/\Delta t$.

The stiffness matrix for the concentration gradient-dependent diffusion is formed as $\mathbf{K}_{ca} = \int_V \mathbf{B}^{\mathrm{T}} D_a \mathbf{B} dV$ where $\mathbf{B}(\mathbf{x})$ is defined as the gradient of the shape function [i.e., $\mathbf{B}(\mathbf{x}) = \nabla\mathbf{N}(\mathbf{x})$]. The stiffness matrix for the electrical displacement field is formed as $\mathbf{K}_\varphi = \int_V \mathbf{B}^{\mathrm{T}}\varepsilon_o\varepsilon\mathbf{B}dV$. The stiffness matrix for the part of the mass flow, which is dependent on the gradient of the electrostatic potential φ is formed as $\mathbf{K}_{na\varphi}(\mathbf{a}_{na}) = \int_V \mathbf{B}^{\mathrm{T}} A_a v_a(\tilde{a}_{na})\mathbf{B}dV$, where the second term on the right-hand side of Eq. (26) is treated as a nonlinear parameter. The term related to the charge density q is $\mathbf{E}_{\varphi an} = \int_V \mathbf{N}^{\mathrm{T}} F v_a \mathbf{N} dV$.

The total stiffness $\mathbf{K}^{tot}$ can be written as seen in Eq. (35)

$$\mathbf{K}^{tot}\mathbf{a}^{tot} =$$
$$\begin{bmatrix} [\mathbf{K}_{n1}] & 0 & 0 & 0 & [\mathbf{K}_{n1\varphi}(\mathbf{a}_{n1})] \\ 0 & [\mathbf{K}_{n2}] & 0 & 0 & [\mathbf{K}_{n2\varphi}(\mathbf{a}_{n2})] \\ 0 & 0 & [\mathbf{K}_{n3}] & 0 & [\mathbf{K}_{n3\varphi}(\mathbf{a}_{n3})] \\ 0 & 0 & 0 & [\mathbf{K}_{n4}] & [\mathbf{K}_{n4\varphi}(\mathbf{a}_{n4})] \\ [\mathbf{E}_{\varphi 1n}] & [\mathbf{E}_{\varphi 1n}] & [\mathbf{E}_{\varphi 1n}] & [\mathbf{E}_{\varphi 1n}] & [\mathbf{K}_\varphi] \end{bmatrix} \begin{bmatrix} [\mathbf{a}_{n1}] \\ [\mathbf{a}_{n2}] \\ [\mathbf{a}_{n3}] \\ [\mathbf{a}_{n4}] \\ [\mathbf{a}_\varphi] \end{bmatrix} \tag{35}$$

where $\mathbf{a}^{tot} = [\mathbf{a}_i^{tot} + \Theta(\mathbf{a}_{i+1}^{tot} - \mathbf{a}_i^{tot})]$. The total load and boundary vector $\mathbf{f}_{tot}$ is expressed as shown in Eq. (36).

$$\mathbf{f}^{tot} = \begin{bmatrix} [\mathbf{f}_{n1}] \\ [\mathbf{f}_{n2}] \\ [\mathbf{f}_{n3}] \\ [\mathbf{f}_{n4}] \\ [\mathbf{f}_\varphi] \end{bmatrix} \tag{36}$$

The load and boundary vector for the diffusion equations is in general terms written as $\mathbf{f}_{na} = -\int_{S_h}\mathbf{N}^{\mathrm{T}} h_a dS - \int_{Sn=g} \mathbf{N}^{\mathrm{T}} q_a dS$ where h_a is a prescribed value of the normal flow of ions through the boundary surface S_h and q_a is the value of the flow through the boundary surface $S_n = g$ on which the concentration n_a has been prescribed. The values of q_a can be calculated whenever the concentration n_a is prescribed at the same material point.

The boundary vector for the electrical displacement field problem can be formulated as $\mathbf{f}_\varphi = -\int_{S_r}\mathbf{N}^{\mathrm{T}}(F(\sum_{a=1}^{\Re} v_a \mathrm{n}_a \mathbf{u}_a) \cdot \mathbf{m}\Delta t)dS$ (i.e., the boundary condition to be used in the part of the equation system calculating the electostatic potential vector $\mathbf{a}_\varphi$ is coupled to the mass diffusion equations).

Prescription of the value of the electrostatic potential φ at the boundaries is not relevant in this kind of physical problem due to φ being an unknown property both at the boundaries and in the domain of interest.

It is important to note that the matrix system [Eq. (33)] is nonlinear and nonsymmetric with serious timescale differences. Numerical oscillations may therefore be observed due to the system being inadequately scaled. It was, however, possible to obtain accurate solution results using the proposed numerical method for certain choices of time steps and element lengths. If the numerical approach presented here is to be used in problems where arbitrary element sizes and time steps are implemented, some improvements concerning stability conditions must be considered. One improvement is to extend the single time step scheme suggested here to a two time step scheme such as the Newmark algorithm [20]. Using a Newmark algorithm of the type called the Lees scheme, the nonlinear parameters may be evaluated at the current time step, which will decrease the error as compared to the simple Euler forward method that was used to tackle the nonlinearities in Eq. (35).

12. Test results from approaches 2 and 3

One test example will be studied using approaches 2 and 3. In this example a water solution of NaCl at the concentration 1 mol/m^3 is stored in a container with the length 0.25 m; a container with the NaCl solution is in contact with another container of the same size filled with a KOH dissolved in water at the concentration 1 mol/m^3. At the start of the simulation the Na^+ and Cl^- ions will be allowed to be transported into the KOH solution, and the K^+ and OH^- ions will be transported into the NaCl solution. By making this kind of simulation, the effect of the mixture on the separated diffusion processes for the individual ions can be analyzed in a quantitative manner. One example is that an ion having a large diffusion coefficient, such as OH^-, is suspected to increase the diffusion velocity for ions having a low diffusion coefficient, such as Na^+.

The numerical solution of the test example using approach 2 is performed with a standard staggered finite element method. The solution to the test example with approach 3 is performed with the numerical method outlined in the previous section.

Forty-one one-dimensional elements are used in the total domain and 110 time steps are used to divide the total time domain, which is 1 year. The Liniger time integration scheme is adopted in both approaches (i.e., $\Theta = 0.878$).

In Figs. 1 to 4, the result of the different mol concentration fields obtained for Cl^-, Na^+, OH^-, and K^+ are shown; approach 2 was used to obtain these results. The weighted material constants shown in Table 1 were used. In Figs. 5 to 8, results from the same simulation are presented. These results are illustrated in terms of mol concentration fields of the potentially diffusing neutral package (i.e., all the possible combinations of NaCl, KOH, NaOH, and KCl). The results presented in Figs. 1 through 4 are calculated from the results in Figs. 5 through 8.

Figs. 9 to 12 show results from a simulation using approach 3 with the material constants illustrated in Table 2. In Fig. 13 the total error in terms of the charge unbalance in the whole domain is shown at different time levels; these values should be zero in the example studied.

13. Conclusions

Approach 1 suffers from several drawbacks. One of them is the lack of knowledge of the material parameters E_a. Compared to approach 3, the first approach even seems to include doubtful physical assumptions.

The main advantage of approach 2 is that quite simple numerical solution procedures can be used to solve problems of diffusing cations and anions. Another advantage is that the assumption of electroneutrality is always fulfilled even during the flow. The main drawback using approach 2 is that a quite arbitrary method must be adopted when combining the different ions into charge-free salts or acids.

The main advantage of approach 3 is that physical sound assumptions are used. These assumptions lead to an equation system where the electrostatic potential controls the influence of the mixture on the flow of the individual constituents in an elegant manner. One of the drawbacks of approach 3 is, however, that the matrix equation system to be solved is very badly scaled, mainly due to the nonsymmetric properties and also due to the different timescales in the determination of the different mol concentration fields and the electrostatic field.

Approaches 2 and 3 give the same principle solution to the test example studied. It is observed that both methods give the expected nonsymmetric behavior in the mol concentration profiles. Furthermore, the influence of ions having a large diffusion coefficient affecting the ions with a low diffusion coefficient is observed.

Approach 2 overestimates the diffusion rates for K^+ and Na^+ ions and underestimates the rates for the Cl^- and OH^- ions as compared to approach 3; the effect is, however, quite small. This behavior is suspected to be caused by the somewhat arbitrary method used to combine ions into charge-free packages, which was the strategy adopted behind approach 2.

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