


Physico-Chemical Modelling of Chloride Migration in Cement-Based Materials Considering Electrode Processes [†]

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Abstract: A multispecies model for chloride migration in cementitious materials was proposed. The model is applied to simulate chloride migration in the concrete submitted to the chloride migration test, considering the electrode processes. These processes are very rarely integrated into the literature, despite their impact on the chloride migration and the electroneutrality in the pore solution of the material. The generation of OH^- in the cathode and H^+ in the anode allows for the monitoring of the electroneutrality. The modelling considers all the ions of the pore solution. Ion fluxes are calculated using Nernst–Planck equation. The Langmuir model is used to simulate the chloride isotherms. The thermodynamic equilibrium in the material is considered, which reflects the liquid–solid interactions during the migration. The ion profiles with and without considering the electrode processes are presented.

Keywords: durability; chloride migration; modelling; multispecies interactions; electrode processes

1. Introduction

The corrosion of steel in reinforced concrete (RC) structures in coastal zones is mainly induced by chloride ingress, which represents a permanent risk of degradation. Chlorides penetrate into the cover concrete under a concentration gradient between seawater and the concrete pore solution and/or liquid pressure gradient in partially saturated concrete when heat and moisture transfers occur (tidal areas or marine fogs). When chlorides reach the rebars with a threshold concentration, they generate rebar depassivation and corrosion [1]. Given the high cost of maintenance/repair, nowadays the durability of RC structures in their environments is one of the main challenges mentioned in the specifications of construction.

In the last decades, several experimental and numerical studies were developed to propose methods and tools for predicting chloride transport in cementitious materials. The standard migration test is used to determine the chloride diffusion coefficient in a steady state or non-steady state [2–8]. Moreover, single-species modelling was used to predict chloride transport in cementitious materials [2]. After that, many multispecies approaches were developed, considering several ions in the pore solution and more chemical and physical interactions during the transport [9–20]. Xia and Li [21] proposed numerical modelling of ion transport in saturated cementitious materials based on Poisson–Nernst–Planck (PNP) equations, considering the chemical interaction between the monovalent ions in the pore solution in order to monitor the impact of the interactions on the chloride ingress. Fenaux et al. [22] proposed a chloride transport modelling in saturated concrete taking into account monovalent and divalent ions of the pore solution: Cl^- , Na^+ , K^+ , OH^- and Ca^{2+} . The diffusion, migration and chemical activity were considered. The chemical activity was calculated using the Pitzer model. The numerical results highlighted the influence of the composition of the pore solution and the chemical activity on the chloride penetration.

Furthermore, recent research discussed the impact of the thermodynamic equilibria on the chloride reactive transport in cementitious materials [23–27]. Yu and Zhang [28]



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proposed a model to predict the leaching of cement paste in an ammonium nitrate solution taking into account ion transport, chemical kinetics and thermodynamic equilibria. The ion transport was calculated by the PNP equation, while, the chemical activity was calculated using the Davies model. Tran et al. [29,30] developed a coupling between chloride transport and thermodynamic equilibrium, considering kinetic control to predict chloride fixation in concrete. Jensen et al. [31,32] developed a multispecies approach for reactive mass transport in a saturated mortar exposed to chlorides for 180 days, including the chemical equilibria. Cherif et al. [33] proposed a coupling between multispecies transport and thermodynamic equilibria in cementitious materials containing mineral additions. The modelling considered all the ions of the pore solution, the portlandite dissolution and Friedel's and Kugel salt precipitation during chloride transport. Ion fluxes were calculated using Nernst–Planck equation, while the thermodynamic coupling was based on the low mass action and the rate of dissolution/precipitation of the solid phases.

The models mentioned above are generally based on the PNP equation with a limited number of ions in the pore solution, whose concentrations are considered significant. The other models consider all the multispecies interactions in the material, but they are based on Fick's law, which misdescribes the chloride ion transport. Researchers dealing with chloride migration, considering electrode processes remain very little in the literature.

Motivated by this need, multispecies modelling of chloride migration is proposed in this study, considering the electrode processes. The modelling is applied on Portland cement submitted to standard chloride migration test. The electrode processes reflect the generation of OH^- and H^+ in the cathode and anode, respectively. The electrode processes ensure the electroneutrality in the migration cell (sample and compartments). The concentrations of OH^- and H^+ are calculated from the current density measured during the test, using Faraday's law. The charge passed is deduced from the current density measured. Ion fluxes are calculated by the Nernst–Planck equation, which describes the diffusion and migration of the species. The Langmuir model is used to simulate the chloride chemical fixation by the material (chloride isotherms). The chemical activity is neglected according to [3]. The considered ions are Cl^- , Na^+ , K^+ , OH^- , H^+ , Ca^{2+} and SO_4^{2-} . The migration cell used is composed of two compartments: (1) upstream containing 25 mM NaOH and 83 KOH and 500 mM NaCl; (2) downstream containing only 25 mM NaOH and 83 KOH (boundary conditions). The composition of the pore solution of the material tested was considered the initial condition. An electrical field of $300 \text{ V}\cdot\text{m}^{-1}$ was applied at the sample boundaries and monitored using two calomel reference electrodes. The latter were placed at each side of the sample tested in order to maintain the electrical field constant modelling outputs are as follows:

- The ion profiles in the material that can be used for the calculation of the ion diffusion coefficients in the non-steady state (from the ion-penetration depth), with and without the electrode processes.
- The electroneutrality in the sample tested with and without integrating the electrode processes in order to highlight the need for the consideration of the electrode processes in the chloride migration modelling proposed.

2. Methodology

2.1. Modelling Principle

The time evolution of the ion concentration (C_i) during the migration test is calculated by using the mass balance equation (Equation (1)), which takes into account the porosity of the material tested (φ), the chloride concentration bonded to the cement matrix ($C_{i,b}$) calculated by the Langmuir's model and the ion flux (J_i) calculated by the NP equation (see Equation (2)). The internal electrical potential between ions is neglected in front of the applied electrical field of $300 \text{ V}\cdot\text{m}^{-1}$. The mass exchange term (q_i), added to the mass balance equation, describes the ion gain/loss in the pore solution due to the dissolution/precipitation of the solid phases considered (C-S-H, portlandite, monosulfoaluminates and trisulfoaluminates). Further details about the calculations of the term (q_i) and the

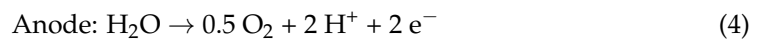
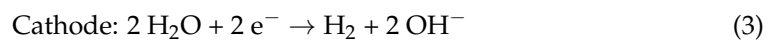
thermodynamic equilibrium constants used are shown in [8]. The ions considered in this study are: Cl^- , Na^+ , K^+ , OH^- , H^+ , Ca^{2+} and SO_4^{2-} . Note that the proposed modelling concerns ion transport in saturated materials that do not require coupling with convection and moisture transfer.

$$\frac{\partial C_i}{\partial t} + \frac{((1 - \varphi)C_{i,b})}{\partial t} = -\text{div}(J_i) - \frac{\partial q_i}{\partial t} \quad (1)$$

$$J_i = -D_{E,i} \left(\nabla C_i + \frac{z_i C_i F E}{RT} + C_i \nabla \ln \gamma_i \right) \quad (2)$$

where $D_{E,i}$ [$\text{m}^2 \cdot \text{s}^{-1}$] is the effective diffusion coefficient of the ion i , z_i is the valence of the ion i , F [$\text{C} \cdot \text{mol}^{-1}$] is the Faraday constant, E [$\text{V} \cdot \text{m}^{-1}$] is applied electric field, R [$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$] is the ideal gas constant and T [K] is the temperature γ_i is the ion activity coefficient.

The electrode processes responsible for the generation of OH^- in the catholyte (upstream) and H^+ in the anolyte (downstream) are given in the following. Note that non-corrodible Platine electrodes were used.



2.2. Case Study

The multispecies approach proposed is used to simulate all the ion movements in the migration cell during the standard migration test on ordinary concrete for 15 days. The composition of the concrete used is given in Table 1. The chemical composition of the pore solution of the concrete used is taken from Refs. [8,34] (see Table 2). The standard migration test simulated is composed of two compartments: the upstream and downstream compartments containing a basic solution of 25 mM NaOH and 83 KOH. In addition, 500 mM of NaCl is added to the upstream. An electrical field of $300 \text{ V} \cdot \text{m}^{-1}$ is applied at the sample boundaries. Concrete samples of 1 cm thickness are used (1D modelling). In this study, the numerical results show the ion profiles in the material tested that are useful for the calculation of the diffusion coefficient at the non-steady state [4,35].

Table 1. The composition of the concrete used.

	Cement [$\text{kg} \cdot \text{m}^{-3}$]	Sand [$\text{kg} \cdot \text{m}^{-3}$]	Coarse Aggregate [$\text{kg} \cdot \text{m}^{-3}$]	Water [$\text{kg} \cdot \text{m}^{-3}$]	W/C
Concrete	300	710	1242	180	0.6

Table 2. Initial and boundary conditions used.

	Boundary Conditions		Initial Conditions
	Upstream ($x = 0, t$) [$\text{mol} \cdot \text{m}^{-3}$]	Downstream ($x = L, t$) [$\text{mol} \cdot \text{m}^{-3}$]	Sample ($t = 0, 0 < x < L$) [$\text{mol} \cdot \text{m}^{-3}$] [8,34]
C_{Cl^-}	500	0	4
C_{Na^+}	525	25	51
C_{K^+}	83	83	117
C_{OH^-}	108	108	158
$C_{\text{Ca}^{2+}}$	0	0	2
$C_{\text{SO}_4^{2-}}$	0	0	2

3. Results and Discussion

Figures 1 and 2 show the simulated profiles of Cl^- , Na^+ , K^+ , OH^- , H^+ , Ca^{2+} and SO_4^{2-} in the sample at the end of the migration test (after 15 days) with and without considering the electrode processes, respectively. The free chloride concentration in the pore solution is maximum along the sample depth ($\sim 459 \text{ mol}\cdot\text{m}^{-3}$) because of their migration from the upstream to the sample. The max concentration is relatively different compared to the literature's data without considering the thermodynamic equilibrium (the participation of chloride with the other ions in the pore solution to form salts). For these models in the literature, the max concentration is equal to the boundary condition on the side of the upstream ($500 \text{ mol}\cdot\text{m}^{-3}$) [2]. Bulleted lists look like this:

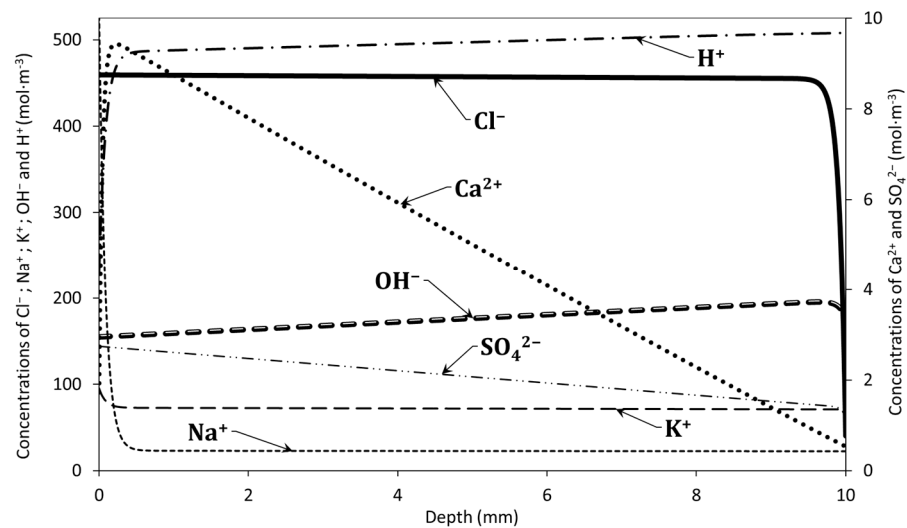


Figure 1. Profiles of Cl^- , Na^+ , K^+ , OH^- , H^+ , Ca^{2+} and SO_4^{2-} in the sample at the end of the migration test (15 days) considering electrode processes.

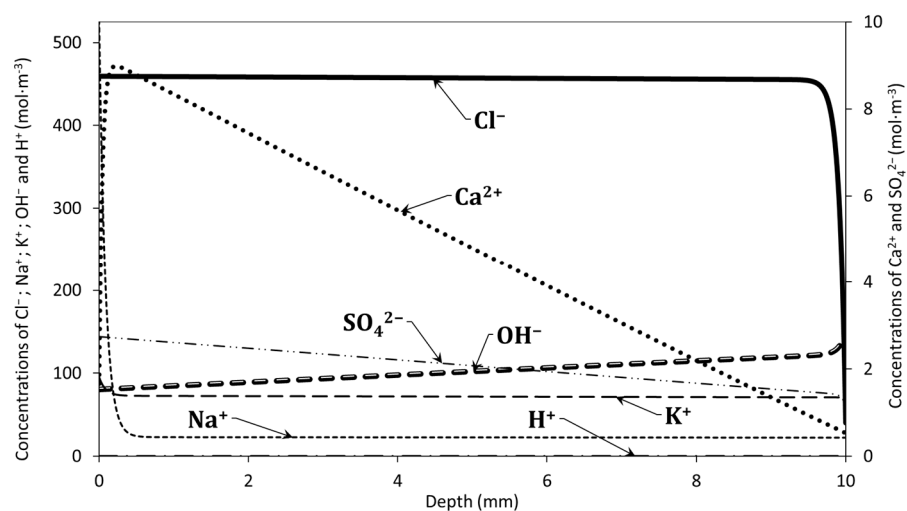


Figure 2. Profiles of Cl^- , Na^+ , K^+ , OH^- , H^+ , Ca^{2+} and SO_4^{2-} in the sample at the end of the migration test (15 days) without considering electrode processes.

Moreover, we noted an increase in the concentrations of Na^+ and K^+ in the pore solution due to their migration from the downstream to the sample tested. The increase in Ca^{2+} and SO_4^{2-} concentrations are due to the dissolution of the portlandite, monosulfoaluminates, and trisulfoaluminates under the electrical field [36,37].

Finally, a difference between the concentration of H^+ and OH^- with and without considering the electrode processes is noticed. This is reflected by the electroneutrality

ensured in the case of the migration modelling with electrode processes and not ensured in the case of the modelling without electrode processes (see Figure 3). This impacts also the concentration of the other ions in the pore solution. The electroneutrality was calculated using Equation (5). The results obtained confirm the need of considering the electrode processes in the chloride migration modelling.

$$\sum C_i z_i = 0 \quad (5)$$

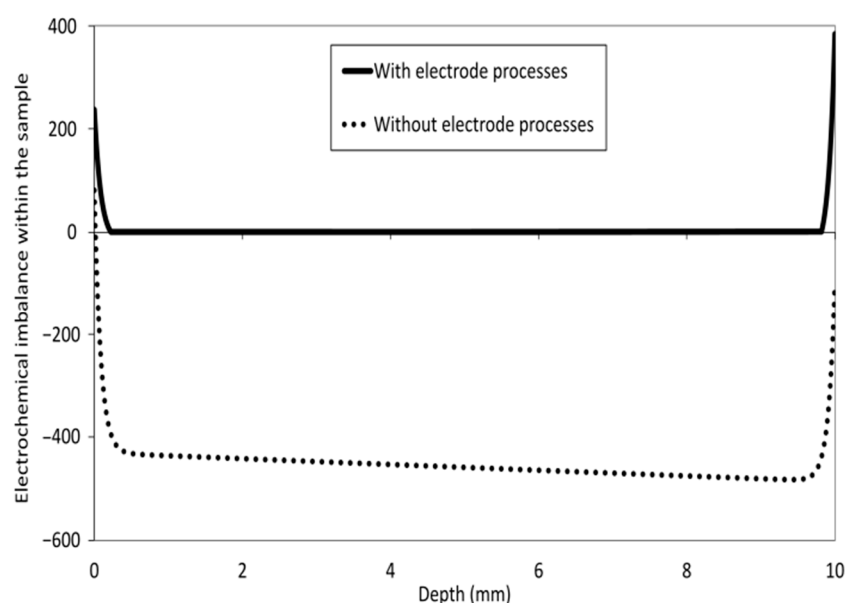


Figure 3. Electrochemical imbalance in the pore solution of the sample, deduced from ion concentrations in the steady state with and without considering electrode processes.

4. Conclusions

From the obtained results, the following main conclusions are made:

- The modelling proposed allowed us to simulate the standard migration test at the steady and non-steady states considering the real pore solution of the material tested and the dissolution/precipitation phenomena during the migration. The modelling was applied to OPC-based materials.
- Outputs of the modelling proposed are the ion profiles in the material tested during the migration test.
- The numerical results show the need of considering the electrode processes in the chloride migration modelling in order to better simulate the standard migration test. The model proposed could be improved by considering more solid phases of the material such as C-S-H, oxychloride, etc.

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