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Solute transport solved with the Nernst-Planck equation for concrete pores with ‘free’ water and a double layer

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ABSTRACT

For calculating ion transport in electro-migration experiments in concrete, the pore space is divided between free pore water and a double layer that compensates the surface charge of minerals lining the pore. The concentrations of counter-ions and co-ions in the double layer are averaged in a Donnan layer, which allows to solve the flux equation of the individual ions. A numerical model is developed for transient states, with the harmonic mean of the chemical activity coefficients and the physical parameters to adapt cell sizes in zones with high concentration gradients. Diffusion coefficients of the ions are corrected for temperature and ionic strength with an empirical equation with three parameters optimized on published transport numbers and specific conductances. The current and the Cl^- breakthrough is calculated in an electro-migration experiment with a concrete sample. The surface charge is positive in the experiment, enhancing and reducing the diffusivity of anions and cations.

1. Introduction

The application of an electrical potential gradient of a few hundred V/m on a concrete sample enhances the diffusion of charged species by orders of magnitude and facilitates the determination of the diffusion coefficient of Cl^- and other species in concrete samples. Analytical and numerical models can be used to extract the transport properties from the electrical current or by analyzing the Cl^- throughput [1–3]. However, to model both the Cl^- breakthrough and the current is still a challenge, as can be illustrated with an experiment by Friedmann et al. [4] shown in Fig. 1. In the experiment, a concrete sample was cured and equilibrated with Na, KOH solution, and the same solution was placed in the anode and cathode reservoirs at the column ends. A 3 V gradient was applied over the 1 cm sample, and, after 44 h, NaCl was added to the cathode reservoir. The current falls when NaCl is added, and increases again a few hours later. Fig. 1 shows the measured current density and the Cl^- increase in the anode reservoir over time, and model calculations with the Nernst-Planck equation.

The Cl^- increase in the anode reservoir allows to calculate the effective diffusion coefficient of Cl^-, $D_{e,Cl} = D_{w,Cl} \times \varepsilon / G$, where ε is the porosity, D_w is the diffusion coefficient in water, and G is the geometrical factor that corrects for the tortuosity of the porous medium. Alternatively, the current can be used to find these transport properties [2,4,6,7]. The resulting D_e values (in 10^{-12} m^2/s) for the experiment shown in Fig. 1 are 25.6 ([4], Eq. (15)), 23.5 [5], and 12.7 [2]. Unfortunately, such differences are not uncommon and the incorrect number can permeate through the literature [3].

In Fig. 1, the full and dashed lines are calculated with Krabbenhøft and Krabbenhøft's number for ε / G, and the increase of Cl^- is well modeled. However, the calculations were done with porosity of 1, thus, with the apparent diffusion coefficient. If carried out with a porosity of 0.24 (obtained by Narsilio et al., [2]) and the geometrical factor is adapted to keep $D_{e,Cl} = 23.5 \times 10^{-12}$ m^2/s, the current density is the same in the first 44 h since the system in that period is in steady state with a uniform Na,KOH solution throughout. However, when NaCl is added, the current change and the Cl^- breakthrough arrive four times earlier because the geometrical factor is four times smaller (model lines with ε = 0.24 in Fig. 1). For transient conditions, the water-filled porosity must be used in a numerical model, and the effective diffusion coefficient may be more in line with Narsilio's number.

On the other hand, the modeled current is smaller than measured, which suggests that the factor ε / G is higher. In that case, Cl^- would arrive even earlier, and the breakthrough is then retarded by sorption or ion exchange [8–10], or by mass-exchange with stagnant or unconnected water [11–16] since the capillary porosity, for the $w/c = 0.7$ ratio in this experiment, may be higher than 0.24 [17]. In addition, when comparing current and Cl^- breakthrough, the changes of the diffusion coefficients with solution composition and the accompanying variations of the transport numbers (the fraction of the current carried by the ions) must be accounted for [18,19].

Before discussing the details needed for modeling, it is helpful to consider what happens in the experiment shown in Fig. 1. First, when

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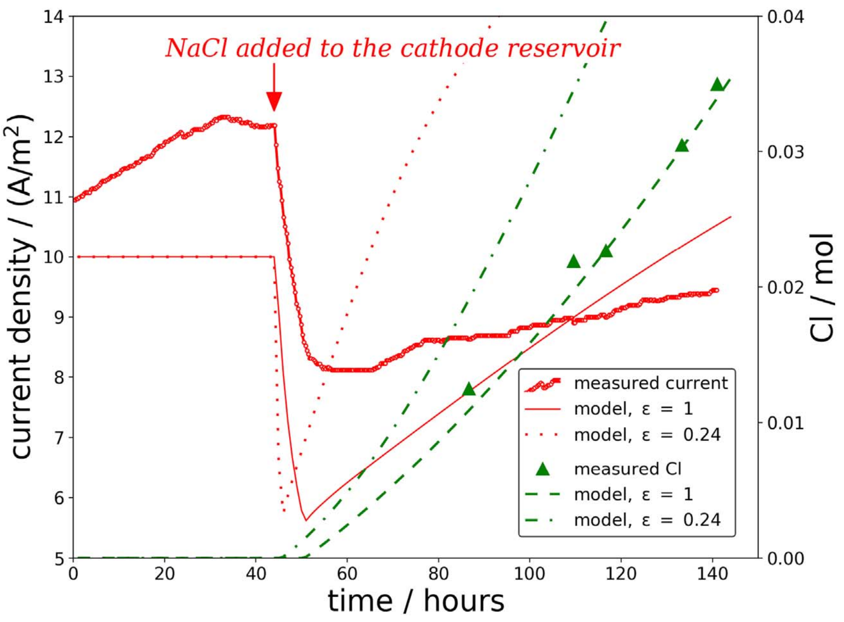

Fig. 1. Current density and Cl increase in the anode reservoir in Friedmann's [4] experiment with $w/c = 0.7$. The model lines are calculated with the parameters from Krabbenhøft and. Krabbenhøft [5] ($\varepsilon/G = 0.0116$, $\varepsilon = 1$) and with porosity $\varepsilon = 0.24$ from Narsilio et al. [2] ($\varepsilon/G = 0.0116$).

the potential is applied on the sample, the modeled current remains constant, whereas the measured current increases with time, probably as result of chemical reactions of cement minerals [20,21]. Dissolution of portlandite is relatively quick [22–24], which increases the concentrations of Ca^{2+} and OH^- in the pore water and thus, the current. But, if the dissolution reaches equilibrium too quickly, the Ca^{2+} and OH^- concentrations are fixed in the column, providing steady state conditions that will not produce the gradual current increase in time that the experiments show.

Second, when NaCl is added to the cathode reservoir, the current falls, and the reason is known [4,5]: Cl^- enters the column by both the concentration- and the electric potential-gradient, while the diffusion of Na^+ is counter to the electric potential-gradient. This implies that, in the beginning, the total anion concentration is limited by the original cation concentrations in the column. The conductivity is reduced when OH^- is partially replaced by Cl^- while the total anion concentration remains the same because Cl^- has a smaller diffusion coefficient than OH^- (see [5] for instructive calculations). When the Cl^- front arrives at the anode-end, the current cannot go down further, but it can increase because a slow diffusion of Na^+ augments the total concentrations in the column. Fig. 1 shows that the model overestimates the increase rate of the current density in that part of the experiment.

One possible explanation for the much slower increase rate of Na^+ is exclusion of cations from part of the pore space [5,25]. Ion exclusion originates from the surface charge of minerals, which creates an electrical double layer in the pores in which counter-ions accumulate and co-ions are excluded relative to 'free' water that is charge-neutral. Of the major cement minerals, AFm is an anion exchanger [26,27] and portlandite sorbs Cl^-, at least when the concentration is below 1 M NaCl [9], and these minerals have a positive surface charge at the pH of the experiment [9]. The surface charge on CSH is primarily a function of the Ca^{2+} activity, with the isoelectric point (where the surface is without charge) attained when the Ca^{2+} activity is about 0.0015 [28], and this mineral probably has a negative surface charge in the experiment. Exclusion of cations means that the pore circumference is positively charged, and that the concentration of OH^- is higher in the electrical double layer than in 'free' pore water. A higher concentration of OH^- in the concrete pores may explain the higher measured than modeled current, and a model for calculating it is the subject of this paper.

The proposed model uses the Nernst-Planck equation for calculating the flux, which accounts for the effects of both chemical-potential and electrical-potential gradients in transport processes. For the steady state, the calculations can be done by hand. For transient states, the equation is solved with finite differences, programmed in PHREEQC [29], with the non-linear distribution of the electrical potential obtained from Ohm's law. Furthermore, parameters are derived for calculating the temperature and ionic strength dependence of the transport numbers of individual ions. The model is applied to calculate the current and Cl^- breakthrough in Friedmann's experiment.

2. Finite difference solution for electro-migration

The Nernst-Planck equation for the flux of a solute species is:

$$J_i = -D_i\left(\frac{\mathrm{d}c_i}{\mathrm{d}x} + c_i\frac{\mathrm{d}\ \ln\gamma_i}{\mathrm{d}x} + z_i c_i\frac{\mathrm{F}}{\mathrm{R}T}\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) \tag{1}$$

where J_i is the flux of solute i (mol/m^2/s), D_i is the diffusion coefficient in the solution (m^2/s), c is the concentration (mol/m^3), x is the distance (m), γ is the activity coefficient (−), z_i is the charge number of i (−), F is the Faraday constant (96 485 C/eq), R is the gas constant (8.3145 V·C/eq/K), T is the absolute temperature (K), and ψ is the electrical potential (V). Chemical models use molality (mol/kg H_2O) as the temperature- and pressure-independent concentration unit, here assumed numerically equal to molarity (mol/dm^3) that is in the flux equation.

In transient states, the concentrations change by:

$$\frac{\partial c_i}{\partial t} = \frac{\partial J_i}{\partial x} - \frac{\partial q_i}{\partial t} \tag{2}$$

where q_i is the concentration in the solid (mol/m^3 H_2O), which changes as a result of mineral reactions, sorption and ion exchange, and exchange with stagnant zones.

2.1. *Concentrations in free and charged pore water*

If the pores are lined with minerals that have a surface charge, the concentrations of the charged ions vary gradually from the surface, and the value for c_i in Eq. (1) varies accordingly. Appelo and Wersin [30] simplified the resulting complications for a transport model by subdividing the pore into a charge-neutral, 'free' water part, and a Donnan layer as shown in Fig. 2.

The concentrations in the Donnan layer are a function of the concentrations in the free pore water and the surface charge that must be