



Calculation of chloride ion concentration in expressed pore solution of cement-based materials exposed to a chloride salt solution



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ABSTRACT

To investigate the relationship between the chloride ion concentration of the expressed pore solution (C_e) and the exposure solution (C_{es}) of cement-based materials exposed to a chloride salt solution, a calculation of the C_e based on an electrical double layer (EDL) model was proposed. The C_e values were calculated using the proposed equations, applying the measured parameters: relative potential (ϕ/ϕ_0), dielectric constant (ϵ), porosity (P), bulk density (D), volume percentage (p_i) of pores with diameter d_i . The calculations explain why C_e does not always equal to C_{es} . The results indicate that the expression method does not test the concentration of free chloride ions in the bulk solution (C_{Cl^-b}) or the average concentration of the transportable chloride ions (C_{tra}) in the pores. However, the ratio (C_r) of C_e to C_{Cl^-b} and the relationship between C_e and C_{tra} can be calculated to more accurately measure chloride ion migration in cement-based materials.

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1. Introduction

There are three types of chloride ion in cement-based materials: free chloride ions, physically-bound and chemically-bound chloride ions [1]. Among these chloride ions, free chloride ions are reported to be responsible for corrosion of steel in concrete. Methods, such as water extraction [5–8] and pore solution expression [2–4], have been widely used for determination of the free chloride ion concentration in cement-based materials exposed to chloride environment. However, the water extraction method detects only the content of water-soluble chloride, which is not equal to free chloride ions [9]. He et al. [9] found that given a high water solid ratio and long extraction time, water-soluble chloride ion concentration is always higher than free chloride ion concentration [9]. On the other hand, when using low water solid ratio or short extraction time, the water-soluble chloride ion concentration is close to the free chloride ion concentration [9]. Accordingly, it is very difficult to use a water extraction method to determine free chloride ions in cement-based materials [9]. The expression method has been widely used for analysis of the ion concentration in a pore solution of cement-based materials [11–14]. Studies using the expression method [3–4,10] have mainly focused on its feasibility, while few studies have focused on the reliability of the results, which is assumed to be very close to the actual ion concentration in the pore solution.

Yuan et al. [15–16] found a homogeneous distribution of chloride ion concentration from one side to the other of the 5 mm thick specimens exposed to NaCl solution for 35 and 56 days. Given these results and considering the concentration gradient as the driving force of the diffusion of the chloride ions, the chloride ion concentration of the expressed solution should be equal to that of the pore solution and the exposure solution when the exposure time is long enough to make the chloride ion diffusion reach a steady state. However, Nagataki et al. [17–19] have suggested that the chloride ion concentration in the expressed pore solution was actually higher than that in the exposure solution. The results given by Nagataki et al. [18] showed that the chloride ion concentration of the pore solution increased with increasing exposure time. After 13 weeks, the chloride ion concentration of the expressed pore solution was nearly twice that of the exposure solution with 0.547 mol/L chloride ion concentration. Similarly, other researchers [15,20–22] have found that the chloride ion concentration of the expressed pore solution was higher than that of the exposure solution. Nagataki et al. [18] proposed a “condensation factor”, defined as the ratio between the chloride ion concentration in the expressed pore solution and that in the exposure solution. And the finding was used by Tang [23] in the calculation of the non-steady-state migration coefficient in the NT Build 492 model (Nordtest Method). However, the proposed concept of “chloride condensation” seems to be not as sophisticated as argued by other researchers, like Glass et al. [20] who attributed the higher chloride ion concentration of the expressed solution to the release of loosely bound chloride ions into solution at very high pressure.

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Associated with the above discussions, one concern is whether or not the expressed pore solution is a representation of the actual pore solution. Based on the concept of an electrical double layer (EDL), Friedmann et al. [24] suggested that the chloride ions within the diffuse layer of the EDL are soluble, which are able to transport in the pores. Considering the chloride ions in the diffuse layer as being able to transport, the expression operation of the expression method may release chloride ions from the diffuse layer into the bulk solution and thus cause the chloride ion concentration in the expressed solution different from that in the bulk solution. Based on this consideration, this study aims to calculate the chloride ion concentration in the expressed pore solution based on an EDL model in order to explain the differences between the chloride ion concentration in the expressed pore solution and that in the exposure solution.

2. Calculation of the chloride ion concentration (C_e) in the expressed pore solution

2.1. Theoretical basis for the calculation

2.1.1. Electrical double layer (EDL)

An overview of the EDL model is presented in previous publications [24–25]. When liquid is in contact with a solid surface, an EDL will form. The EDL model can be described by the Helmholtz model, Gouy–Chapman model, Grahame model and Stern model (a special case of the Grahame model). The Helmholtz model, which describes capacity as a constant, fails to correctly explain some experimental results dealing with the variation of the capacity in the function of the difference of potential between solid phase and liquid phase [25–26]. In the Gouy–Chapman model, ions are regarded as punctual charges that can approach the solid phase until the distance between them and the interface is zero. However, in the Gouy–Chapman model the calculated capacities are not in agreement with experimental results [25–26]. In the Stern model, the charged domain is structured as a diffuse layer and a compact layer. Grahame improved the Stern model by considering the possibility of chemical adsorption (“specific adsorption”) [24]. In this type of interaction, the charges of the adsorbed ions could be the opposite to that of the EDL. The compact layer is divided into two parts: the inner Helmholtz plane, defined as the center of specifically adsorbed ions, and the outer Helmholtz plane, defined as the center of non-specifically adsorbed ions.

In this study, the Stern model has been used to calculate the effects of the EDL on the chloride ion concentration of the bulk solution in the pores and expressed solution. This model, presented in Fig. 1, was previously used by Friedmann et al. [24] for the calculation of chloride ion transport in cement-based materials.

In Fig. 1, Ox is an axis perpendicular to a surface element, which separates the solid phase from the pore solution. The axis origin $x = 0$ corresponds to the closest approach plane, namely OHP plane in Fig. 1. In this plane, the potential is called the OHP potential and denoted as ψ_0 . Therefore, the diffuse layer extends from the OHP plane to the bulk solution. In the present paper, it is also assumed that ψ is an electrical potential of the diffuse layer as in [24], $\delta\psi$ is the relative electrical potential in the diffusion layer, with respect to the electrical potential (ψ_b) in the bulk solution, namely $\delta\psi = \psi - \psi_b$.

2.1.2. Experimental characterization of the electrical double layer (EDL)

The electrical potential of the shear plane (ζ potential) of the EDL (as shown in Fig. 1) is often measured using various methods [27], such as electrophoresis method, electro-osmosis method, streaming potential and ultrasonic method. Among these methods, the electrophoresis method is the most widely used. However, these methods are suitable for measuring the ζ potential of a liquid system with water and inadequate for the evaluation of ζ potential in pores of porous solid materials. Amiri et al. [28–29] used an electro-diffusion cell to examine the migration of chloride ions in cement-based materials and found that the

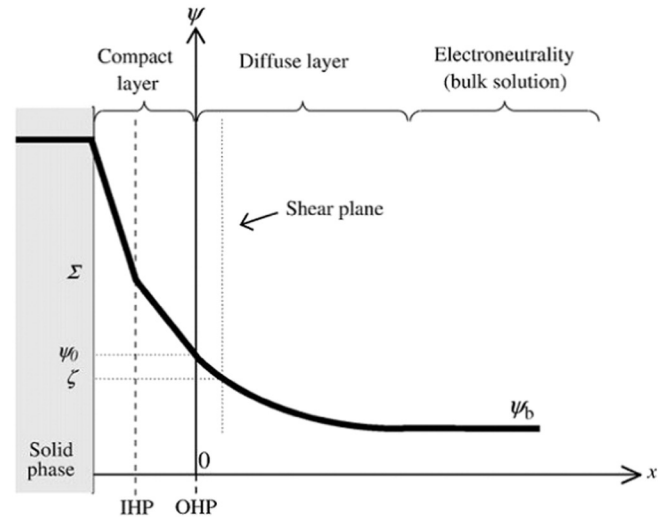


Fig. 1. Schematic view of the electrical double model used for the calculation [24].

electrical migration of chloride ions in pores of cement-based materials is not governed by a simple law of conduction (Ohm's law), but is influenced by the EDL which is quantified by the ratio between thermal and electrical energies (denoted as χ) [29]. The χ value measured by electro-diffusion cell experiment is around 10^{-2} [28]. This indicates that the EDL can be quantified by electro-diffusion cell experiment, which provides a new type of experimental method to investigate EDL for the characterization of chloride ion migration.

2.1.3. Average transportable chloride ion concentration ($C_{tr,a}$) in a single pore

To study the EDL phenomena on a microscopic scale, some basic assumptions were made, which were previously described in detail [24]. The relative potential and ion concentration in the diffuse layer can be expressed as Eqs. (1) and (2) [24,29–30], respectively:

$$\delta\psi_+ = 2 \ln \left(\frac{1 + \tanh\left(\frac{\partial\psi_+}{4}\right) \exp(-x_+)}{1 - \tanh\left(\frac{\partial\psi_+}{4}\right) \exp(-x_+)} \right) \quad (1)$$

In Eq. (1),

$$\delta\psi_+ = \frac{F}{RT} \delta\psi, \quad (1a)$$

$$x_+ = \kappa x, \quad (1b)$$

$$\kappa = \sqrt{\frac{2F^2 C_b}{RT\epsilon}}, \quad (1c)$$

$$C_k = C_{kb} \exp(-z_k \delta\psi_+) \quad (2)$$

where, $\delta\psi_+$ is the dimensionless relative OHP potential; x_+ and $\delta\psi_+$ are the dimensionless length and the dimensionless relative electrical potential, respectively; ϵ is the dielectric constant of the solution, F/m; C_b is the concentration of cations or anions in the bulk solution, mol/L; κ is the Debye constant; R is the gas constant; T is the thermodynamic temperature, K; F is the Faraday constant; C_{kb} is the concentration of species k in the bulk solution, mol/L.

In the case of a pore, ions from the diffuse layer and from the bulk solution are transportable in the solution [24]. In a pore, the two diffuse layers are face to face [24], and when the pore diameter d is small enough, an overlap of two diffuse layers will occur. A schematic diagram

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