Cement and Concrete Research 48 (2013) 116–127

Contents lists available at SciVerse ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

The apparent and effective chloride migration coefficients obtained in migration tests

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ARTICLE INFO

Article history:
Received 22 August 2012
Accepted 15 February 2013

Keywords:
Diffusion (C)
Chloride (D)
Transport properties (C)
Modeling (E)
Durability (C)

ABSTRACT

The apparent (D_{app}) and effective (D_{eff}) migration coefficients obtained in chloride migration tests are investigated in this study. The presented D_{app} profiles in concrete show that the apparent migration coefficient is strongly concentration-dependent. As demonstrated, the binding of chlorides during the migration tests is very low at low free-chloride concentrations and therefore the chloride penetration front progresses throughout the concrete only slightly retarded by the binding. The diffusion flux during migration tests is shown to be insignificant compared to the migration flux. The D_{RCM} obtained from the Rapid Chloride Migration (RCM) tests are found to be equal to the computed D_{app} at the locations of the chloride penetration fronts, which gives an indication that the D_{RCM} represents only the migration coefficient at the front. A linear correlation is found between the D_{RCM} obtained from the traditional RCM model and the D_{eff} obtained from the chloride transport model which includes non-linear chloride binding and concentrations in non-equilibrium.

1. Introduction

Chloride induced corrosion of steel rebars is the main cause of deterioration of concrete elements and structures being exposed to chloride bearing environments. Therefore, it is of vital importance to design new structures with minimized risk of this type of deterioration. The concrete cover, which is the layer of concrete that separates the steel rebars from the external environment, plays a crucial role in resisting the ingress of chlorides during a certain time (so-called service lifetime), after which the critical chloride concentration is reached at the level of the rebars so that the corrosion of the steel is triggered. Two main properties of the concrete cover determine the service lifetime of concrete: its thickness and permeability to chlorides, and both these properties may be adjusted in order to meet the service lifetime criteria in the design stage. Chloride ingress speed in concrete is diffusion controlled and in order to quantify it various test methods can be used. In the past, mainly the natural diffusion test methods were used, but nowadays the importance and applicability of accelerated migration tests have significantly increased. Chloride migration tests were developed to obtain the chloride diffusion coefficient in a much shorter test period compared to natural diffusion tests, by accelerating the chloride ingress rate with the applied electrical field. The chloride transport process in concrete during electrically forced migration in transient conditions can be described by the Nernst–Planck equation, as follows [1,2]:

$$\frac{\partial c}{\partial t} = D_0 \left(\frac{\partial^2 c}{\partial x^2} - \frac{zFE}{RT} \frac{\partial c}{\partial x} \right) \tag{1}$$

where: c — free-chloride concentration, t — time, D_0 — intrinsic chloride migration coefficient, x — distance, z — ionic valence, F — Faraday constant, E — electric field, R — universal gas constant and T — temperature. The Nernst–Planck equation shown in the present form Eq. (1) can be termed simplified, as it assumes a linear decay of the applied potential in the sample, a constant value of the chloride diffusion/migration coefficient, a negligible effect of ionic activities and no advection. Because the coefficient D_0 in Eq. (1) is obtained from chloride migration tests, it is often called "migration coefficient" to differentiate it from the diffusion coefficient obtained in diffusion tests [3]. Tang [3,4] explains that these two coefficients are not the same because of different counter-electrical potentials (caused by differences in drift velocities of cations and anions in pore solution) and ionic frictions during diffusion and migration processes.

The intrinsic migration coefficient D_0 in Eq. (1) represents the diffusion/migration rate of chlorides in the pore solution of concrete, i.e. it does not refer to the overall volume of concrete but just to its liquid phase, and therefore is related to the diffusivity of chlorides in free liquid constrained by the pore structure of the porous medium (its tortuosity and constrictivity). In order to quantify the chloride diffusion/migration coefficient referring not only to the volume of pores, but to

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0008-8846/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.cemconres.2013.02.005

the total volume of concrete, the effective and apparent diffusion/migration coefficients are used. The effective chloride diffusion/migration coefficient refers to the diffusivity of chlorides in the pore solution by taking into account the volume fraction of the permeable pores in the entire volume of concrete (i.e. porosity) [5]:

$$D_{eff} = \varphi \cdot \frac{\delta}{\tau^2} D_f = \varphi D_0 \tag{2}$$

where: D_{eff} — effective chloride diffusion/migration coefficient, φ — total water-permeable porosity, δ — constrictivity of pore structure, τ — tortuosity of pore structure, D_f — chloride diffusion coefficient in free liquid (infinite dilution) and D_0 — intrinsic chloride diffusion/migration coefficient in pore solution. The effective diffusion/migration coefficients are determined in steady-state diffusion/migration tests, i.e. with a constant chloride flux (c is independent of distance and time). Nevertheless, steady-state tests are often not preferred from the practical point of view as they are time consuming and laborious (the upstream chloride solution must be periodically replaced and the concentration of chlorides in the downstream solution must be regularly measured). To overcome these drawbacks, non-steady-state chloride diffusion and migration tests were developed. The apparent diffusion/migration coefficients obtained in the non-steady-state tests represent the diffusion/migration of chlorides in the pore solution of concrete, taking into account the reaction between the chlorides and the porous medium (so-called chloride binding). Following Atkinson and Nickerson [5], assuming that the effective diffusion coefficient is independent of the free-chloride concentration, the apparent chloride diffusion/migration coefficient can be defined as follows:

$$D_{app} = \frac{\varphi}{\lambda} \cdot \frac{\delta}{\tau^2} D_f = \frac{\varphi}{\lambda} D_0 = \frac{D_{eff}}{\lambda} \tag{3}$$

where: D_{app} — apparent chloride diffusion/migration coefficient and λ — distribution coefficient of chlorides between the solid and liquid. The distribution coefficient can be further defined as [5,6]:

$$\lambda = \varphi\left(1 + \frac{\partial c_b}{\partial c}\right) \tag{4}$$

where: c_b — bound-chloride concentration [$\mathrm{g_{Cl}/dm^3_{liquid}}$] and c — free-chloride concentration [$\mathrm{g_{Cl}/dm^3_{liquid}}$].

Combining Eqs. (3) and (4), the following relationship can be derived [1,5,6]:

$$D_{app} = \frac{D_0}{1 + \frac{\partial c_b}{\partial c}} = \frac{D_{eff}}{\varphi\left(1 + \frac{\partial c_b}{\partial c}\right)} \tag{5}$$

The apparent chloride diffusion/migration coefficient, as shown in Eq. (5), depends on the chloride binding capacity defined as $\partial c_b/\partial c$, i.e. the ability of concrete to bind further chlorides when the free-chloride concentration increases [1,6]. As can be seen in Eq. (5), the D_{app} can be equal to the D_0 or D_{eff}/φ in two cases: *i*) if there is no chloride binding (as e.g. for inert porous media) and *ii*) if chloride binding is completed (as e.g. during steady-state chloride diffusion/migration tests).

Tang [3] shows that the relationship between the D_{app} and D_{eff}, given in Eq. (5), should also include the concentration dependency of the chloride migration coefficient, as follows:

$$D_{app} = \frac{D_{eff} + \left(\frac{RT}{zFE}\frac{\partial c}{\partial x} + c\right)\frac{\partial D_{eff}}{\partial c}}{\varphi\left(1 + \frac{\partial c_b}{\partial c}\right)}. \tag{6}$$

It is known that the effective chloride migration coefficient is a function of the concentration [3,4,7–9]; nevertheless, for the sake of simplicity, in chloride transport models the migration coefficients are assumed to be independent of the free-chloride concentration. In such a case Eq. (6) can be simplified to Eq. (5), as for example adopted in Tang's chloride migration transport model for the Rapid Chloride Migration (RCM) test [1,10].

The non-steady-state chloride migration coefficient, which is obtained in the RCM test, is based on the simplified Nernst–Planck equation (Eq. (1)) and reads [1]:

$$\frac{\partial c}{\partial t} = D_{RCM}\left(\frac{\partial^2 c}{\partial x^2} - \frac{zFE}{RT}\frac{\partial c}{\partial x}\right) \tag{7}$$

and

$$D_{RCM} = D_{app} = \frac{D_0}{1 + \frac{\partial c_b}{\partial c}} = \frac{D_{eff}}{\varphi\left(1 + \frac{\partial c_b}{\partial c}\right)} = constant. \tag{8}$$

The assumption of a constant binding capacity $\partial c_b/\partial c$ in Eq. (8) is very questionable as it only represents the case when chloride binding follows a linear isotherm (i.e. $c_b = A \cdot c$, where A is a binding constant) and is in instantaneous equilibrium. The binding of chlorides is a very complex process because different hydrated cement phases are able to bind different amounts of chloride, in different ways (chemically or physically) and at different rates [11]. In fact, chloride binding obeys the non-linear Freundlich isotherm (i.e. $c_b = K_b \cdot c^n$, where K_b and n are binding constants) very well in a wide concentration range of c, as demonstrated in [1]. Fig. 1a shows the chloride binding curve determined experimentally by Zibara [12] (units of concentrations were recalculated to the units used in this paper) for an OPC paste with w/c ratio of 0.3, fit to both Freundlich and linear isotherms. These measurements represent the equilibrium between the free- and bound-chloride concentrations, reached within about two weeks. Fig. 1b shows the $\partial c_b/\partial c$ term derived for the isotherms given in Fig. 1a. It can be seen that for the linear binding isotherm the binding capacity is constant, which obeys the assumption adopted in Eq. (8). In the case of the Freundlich isotherm, the binding capacity is concentration dependent and is much larger for lower c than for larger c. In the case of short-term chloride migration tests, the duration of which most often amounts to just 24 h [10], the term $\partial c_b/\partial c$ in Eqs. (5) and (8) becomes even more complicated as the concentrations are obviously in non-equilibrium. In the literature, the equilibrium concentration for chloride binding is reported to be reached between seven days up to two months of exposure [1,12,13]. These facts give evidence that the chloride migration coefficient D_{RCM}, as defined in Eq. (8), will not be constant, but instead, will depend on the local free- and bound-chloride concentrations in the concrete sample.

In this article, the apparent chloride migration coefficient obtained in the Rapid Chloride Migration test is estimated along the depth of the tested concrete sample, to investigate if/how its value changes during the test. Both our own test results and empirical data obtained from the literature are used. The chloride transport model presented in Spiesz et al. [14] is firstly extended by adding a non-zero chloride flux due to the diffusion (in the original model that flux was neglected) and then applied to experimental data, to compute the effective chloride migration coefficient as well as the free-, bound- and total-chloride concentration profiles after the migration tests. From the effective chloride diffusion coefficient and the term $\partial c_b/\partial c$ (see Eq. (5)), the D_{app} is computed. Additionally, this computed D_{app} is verified against the D_{RCM} obtained from the traditional RCM test model.