

Analysis of the theoretical model of the Rapid Chloride Migration test

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Abstract

Chloride ion diffusion coefficient in concrete is estimated very often by using electromigration tests, among which the Rapid Chloride Migration (RCM) test is becoming more and more popular. Nevertheless, this test receives much criticism due to lacks in its scientific background. In this paper the theoretical background of the RCM test is critically evaluated in order to show the weak points. Chloride concentration profiles measured after the migration tests give serious evidence of oversimplification of the chloride transport model adopted in the RCM test as they are substantially different from the theoretical ones. Besides this, foregoing research unveils that the chloride ion diffusion coefficients obtained from the traditional non-steady-state diffusion test and from the RCM test are correlated but not identical. As concluded in this paper, the chloride transport model currently adopted for the RCM test should be modified with the non-linear chloride binding isotherm and non-equilibrium between the concentrations of free and bound chlorides. With these phenomenon included, the diffusivity of chlorides obtained from the RCM test should have a new and correct meaning.

1. Introduction

In view of problems with chloride-induced corrosion of reinforcing steel, there is a need for quantified information on chloride transport properties in concrete. Thus, a reliable prediction model of chloride ingress into the concrete cover is considered as the key point for an assessment of the long-term behaviour of concrete exposed to sea water or de-icing salts.

Several laboratory testing methods (long- and short-term) have been developed in order to quantify the chloride transport in concrete. Nevertheless, the long-term methods are usually not preferred from the practical point of view because they are laborious, time consuming and costly. To overcome these disadvantages, an accelerated test - the Rapid Chloride Migration test (RCM) with the associated resulting D_{RCM} (chloride-ion migration coefficient) has been developed by Tang [1]. NT Build 492 [2] and BAW-Merkblatt [3] describe in detail the execution of the test.

Within the European DuraCrete project [4] the D_{RCM} has been introduced into service life model for concrete, which has lately resulted in even higher popularization of the test method. However, 11 years after the standardization of the RCM test, there are still some major concerns regarding its theoretical principles.

This paper points out the biggest controversy of the theoretical RCM model: the sharp free chlorides concentration profile, representing the chloride transport model in concrete during the electromigration, being in contradiction with the experimentally determined chloride concentration profiles presented among the others in Stanish [5], Castellote et al. [6, 7] or Yuan [8]. The latter are not that sharp in shape, but very similar to diffusion profiles. This indicates that the currently adopted chloride transport model for the RCM test is

oversimplified. Hence the equations developed for the RCM test for the diffusivity of chlorides should be treated carefully, as they lead to an incorrect estimation of the migration coefficient. This also might be a reason for the discrepancies between D_{RCM} obtained from the RCM test and D_{app} obtained from the non-steady-state diffusion test methods, which are reported in literature.

2. Theoretical model of the Rapid Chloride Migration test

The Rapid Chloride Migration test (RCM), also known as CTH or RMT, proposed initially by Tang [1] and standardized in [2, 3], is currently often used to investigate the durability of concrete. The RCM is an electrically-accelerated test method which yields the rapid chloride migration coefficient. A schematic and actual RCM test set-ups are presented in Fig. 1.

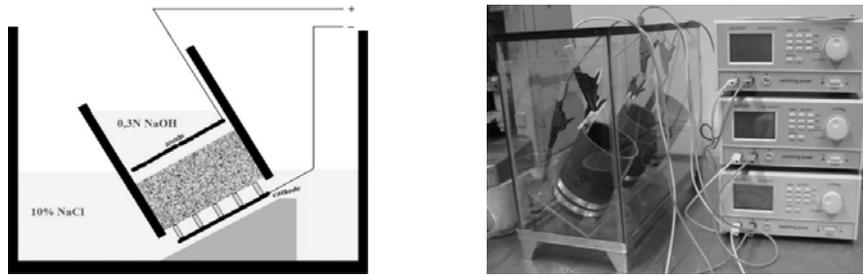


Figure 1: Schematic and actual Rapid Chloride Migration test set-up.

As mentioned before, the RCM test is based on the forced ionic migration induced by the external electrical voltage applied across the $\text{Ca}(\text{OH})_2$ -saturated concrete specimen. Due to the potential difference between the electrodes, chloride ions migrate from the upstream solution (10% NaCl), through the concrete specimen, towards the downstream solution (0.3N NaOH), for a certain time. Afterwards, the specimen is split open and sprayed with AgNO_3 – an indicator for chlorides (Fig. 2). Finally, the chloride penetration depth is measured and based on this value the D_{RCM} is calculated.

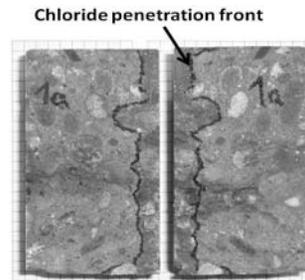


Figure 2: Split open concrete specimen sprayed with a colorimetric indicator for chlorides.

The governing equations for the transport of chlorides during the RCM test are based on the Nernst-Planck equation, describing the flux of chloride ions under the action of chemical and electrical potential [1]:

$$J = J_M + J_D = -D \left(\frac{\partial c}{\partial x} - \frac{zFE}{RT} c \right) \quad (1)$$

where: J – total flux of chlorides [$\text{gs}^{-1}\text{m}^{-2}$], J_M – flux of chloride due to electrically forced migration [$\text{gs}^{-1}\text{m}^{-2}$], J_D – flux of chlorides due to diffusion [$\text{gs}^{-1}\text{m}^{-2}$], D – chloride ion migration coefficient [m^2/s], c – concentration of chlorides in pore solution in concrete [g/dm^3], x – depth in concrete [m], z – ion valence, F – Faraday constant [$9.65 \cdot 10^4 \text{ C/mol}$], R – gas constant [$8.314 \text{ Jmol}^{-1}\text{K}^{-1}$], T – temperature [K] and E – electrical field [V/m].

For a non-steady state process Eq. (2) is used as follows [1]:

$$\frac{\partial c}{\partial t} = -\frac{\partial J_0}{\partial x} = \frac{D_0}{1 + \frac{\partial c_b}{\partial c}} \left(\frac{\partial^2 c}{\partial x^2} - \frac{zFE}{RT} \frac{\partial c}{\partial x} \right) = D_{RCM} \left(\frac{\partial^2 c}{\partial x^2} - \frac{zFE}{RT} \frac{\partial c}{\partial x} \right) \quad (2)$$

where: c_b – bound chloride concentration [g/dm^3], J_0 – flux of chlorides through a unit area of solution [$\text{gs}^{-1}\text{m}^{-2}$] and D_0 – chlorides migration rate through pore solution in concrete [m^2/s].

It is worth to emphasize that the chloride binding, included in the chloride transport model in term $(1 + \partial c_b / \partial c)$, is assumed to be constant, which represents either no binding or linear binding with an instantaneous equilibrium between free and bound chloride concentrations.

Solving Eq. (2) with the following initial and boundary conditions for a semi-infinite medium:

$$\begin{aligned} c &= 0, x > 0, t = 0 \\ c &= c_0, x = 0, t > 0 \\ c &= 0, x \rightarrow \infty, t = t_M \end{aligned} \quad (3)$$

where: c_0 – concentration of chlorides in bulk solution [g/dm^3], t – time [s] and t_M – large finite number, gives the following analytical solution [1]:

$$c(x,t) = \frac{c_0}{2} \left[e^{ax} \operatorname{erfc} \left(\frac{x + aD_{RCM}t}{2\sqrt{D_{RCM}t}} \right) + \operatorname{erfc} \left(\frac{x - aD_{RCM}t}{2\sqrt{D_{RCM}t}} \right) \right] \quad (4)$$

where: $a = zFE/RT$ and erfc – complement to the error function: $\operatorname{erfc} = (1 - \operatorname{erf})$.

Assuming that the electrical field (E) and the penetration depth (x) are large enough, the $e^{ax} \operatorname{erfc}$ term tends to zero, thus Eq. (4) can be simplified to:

$$c(x,t) = \frac{c_0}{2} \operatorname{erfc} \left(\frac{x - aD_{RCM}t}{2\sqrt{D_{RCM}t}} \right) \quad (5)$$

In Fig. 3 a graphical solution of Eq. (5) is plotted, in which the free chlorides concentration in concrete after the migration test changes rapidly from the bulk concentration (c_0) to 0 within a small distance.

From Eq. (5) the inflection point x_f (see in Fig.3) can be find as:

$$x_f = aD_{RCM}t \quad (6)$$

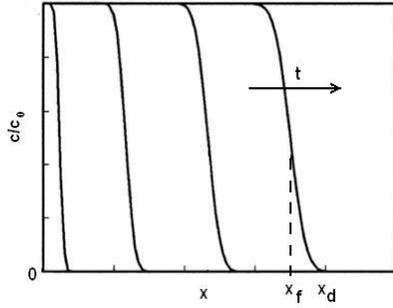


Figure 3: Theoretical chloride concentration profile after the RCM test [1].

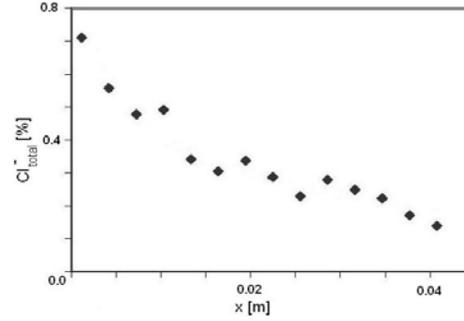


Figure 4: Experimental chloride concentration profile after the RCM test [5].

In practice it is difficult to measure the inflection point, thus x_d representing the chloride penetration depth indicated by AgNO_3 (a colorimetric indicator for chlorides) is introduced. The relationship between x_f and x_d reads:

$$x_f = x_d - \alpha \sqrt{x_d} \quad (7)$$

where:

$$\alpha = 2\sqrt{\frac{RT}{zFE}} \times \text{erf}^{-1}\left(1 - \frac{2c_d}{c_0}\right) \quad (8)$$

and: α – laboratory constant and c_d – chloride concentration at which the colorimetric indicator changes the color [0.07 mol/dm^3].

Introducing Eqs. (7) and (8) into Eq. (6) and solving for D_{RCM} gives [1]:

$$D_{RCM} = \frac{RT}{zFE} \times \frac{x_d - \alpha \sqrt{x_d}}{t} \quad (9)$$

The output of the test – D_{RCM} – is a chloride ion transport parameter expressed in m^2/s . This parameter has been introduced in the European DuraCrete project [4] for service life design for concrete structures. Such an application puts strict requirements on the test method.

3. Verification of the theoretical model of the RCM test

As mentioned above, the chloride concentration profile presented in Fig. 3 is representing the chloride transport model in concrete for the RCM test. However, several authors have measured these profiles and reported that they are characterized by a different shape. In Fig. 4 an experimental RCM chloride concentration profile presented by Stanish [5] is shown.

Similar experimental chloride concentration profiles in concrete after chloride migration tests were presented among the others in Castellote et al. [6, 7] or Yuan [8]. It is clear that the profile in Fig. 4 is not sharp in comparison to the theoretical profile in Fig. 3. This difference between the theoretical and the experimental results gives an evidence of inaccuracy of the currently adopted chloride transport model for the migration test. Thus, the developed system

of equations should be treated carefully, as it leads to an inaccurate estimation of the migration coefficient.

It was also reported in the literature that the apparent chloride diffusion coefficients obtained from the migration test (D_{RCM}) and from diffusion test performed e.g. according to [9] (D_{app}) are not identical. Although some linear correlations were found between these e.g. in Yuan [8] (Fig. 5) or in Tang [10], these relationships are not clear and purely empirical. The discrepancies between the results obtained from migration and diffusion test can be explained by the inaccuracy of the theoretical background of the migration tests.

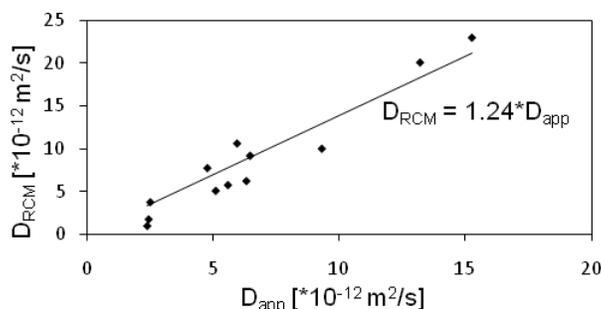


Figure 5: Comparison between the non-steady-state chloride diffusion coefficients [8].

4. Non-linear binding of chlorides in non-equilibrium conditions

As mentioned earlier in this paper, the chloride binding term $(1 + \partial c_b / \partial c)$ is assumed constant in the RCM's mathematical model. This represents either no binding or linear binding with an instantaneous equilibrium between free and bound chloride concentrations. This is though in a contradiction with the nature of the chloride binding phenomenon in concrete, which is non-linear and needs a certain time in order to reach the equilibrium between free and bound chloride concentrations.

The amount of bound chlorides increases non-linearly with an increase of the free chlorides concentration and this relationship is most often described using chloride binding isotherms. Among the binding isotherms the most commonly used are the isotherms of Langmuir, Freundlich and BET. The linear chloride binding isotherm does not predict in a proper way the relation between bound and free chlorides: it can be applicable only within a limited range of free chlorides concentration [1]. Tang in [1] shows that the experimental data for the chloride binding in concrete obeys the Freundlich isotherm in free chlorides concentrations in the range of 0.01 - 1 [mol/dm^3]. The chloride binding data presented by Zibara [12] shows that even for a higher chloride concentration (up to 3 [mol/dm^3]) the Freundlich isotherm is obeyed. During the RCM test the concentration of chlorides in the bulk solution yields 2 [mol/dm^3] [1, 2], thus the Freundlich isotherm can adequately represent the chloride binding for the migration process.

From literature it is known that the equilibrium for chloride sorption in concrete can be achieved after 7 days [1] or 10 - 14 days [11] of exposure. For the diffusion tests [9] the assumption of equilibrium is acceptable since the chloride exposure period is sufficiently long. However, the duration of the RCM test usually amounts to 24 hours [2], and only sometimes varies from 6 hours (for poor quality concrete) up to 4 days (for very good quality concrete). Thus, during the migration process, equilibrium between free and bound chlorides cannot be achieved and this phenomenon should also be included in the mathematical model.

It is worth to mention that the D_{app} obtained from diffusion tests and the D_{RCM} obtained from RCM tests cannot be equal to each other because the assumption of equilibrium in their theoretical models is fulfilled for diffusion tests, but not valid for migration test.

5. Conclusions

Although the RCM test is becoming a very popular test quantifying the resistance of concrete against the intrusion of chlorides, it is still necessary to improve its theoretical background. The analysis of the RCM test presented in this paper points out that the theoretical model for the chloride transport during the migration process is oversimplified thus should be treated carefully. This model leads to an incorrect D_{RCM} estimation and can explain the origin of the differences between D_{RCM} and D_{app} obtained from diffusion tests. A new chloride transport model should be developed taking into account the non-linear nature of chloride binding in concrete and non-equilibrium conditions between the concentrations so the D_{RCM} could be calculated in an improved way.

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