Determination of the chloride diffusion coefficient in mortars with supplementary cementitious materials

DETERMINATION OF CHLORIDE DIFFUSION COEFFICIENT IN MORTARS WITH SUPPLEMENTARY CEMENTITIOUS MATERIALS

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Abstract

The Rapid Chloride Migration (RCM) test, described in the guideline NT Build 492, is one of the most commonly applied accelerated test methods in which chlorides penetrate the concrete at high rates due to the applied electrical field. The output result of the test is the chloride diffusion coefficient D_{RCM}. Literature shows that the RCM test development and experience concerns only ordinary Portland cement. Therefore, a validation of this test method is needed also for other types of binders. This study analyzes the application of the RCM test on mortars prepared with different binder blends: ordinary Portland cement (OPC), ground granulated blast – furnace slag (GGBS), fly ash (FA) and silica fume (SF). The diffusion coefficients are obtained by two approaches: the basic RCM test model and the extended model which considers non-linear chloride binding in non-equilibrium. The analyses presented in this study show that the RCM test can be used for the determination of chloride diffusion coefficient in mortars with supplementary cementitious materials, and the accuracy of $AgNO_3$ colourimetric method is sufficient for the determination of the chloride penetration front in these mortars.

1. INTRODUCTION

Many researchers have shown that the total chloride concentration profiles determined experimentally after performing the Rapid Chloride Migration (RCM) test have significantly different shape than the one predicted from the underlying theory. This difference gives evidence that the basic chloride transport model for the RCM test describes the real process unsatisfactorily. Tang [1] presented a chloride transport model (Eq. 1) that assumes a constant $\partial c_b / \partial c$ term, which implicitly implies that no binding or an instantaneous linear chloride binding is present in concrete. This means that binding of chlorides will influence the values of the total chloride concentration in the measured profile, but will not affect the profile's shape.

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

Chloride binding in concrete is a non-linear process and the equilibrium between free and bound chlorides cannot be achieved within such a short period of time as the duration of the RCM test [2,3]. Hence, Spiesz et al. [3] presented an extended chloride transport model which includes the non-linear binding isotherm (represented by Freundlich isotherm $C_b = K_b \cdot c^n$) and non-equilibrium conditions between free and bound chlorides. This model is based on the simplified Nernst – Planck equation in transient conditions, coupled with the reaction term. Hence, the extended model describes chloride binding in concrete in a more proper way than the traditional RCM model. The study of Spiesz and Brouwers [4] demonstrated that the D_{RCM} as determined following NT Build 492 [2] is not affected by chloride binding, and therefore, is correct for OPC-based concretes [4]. Nevertheless, for binders other than OPC, the D_{RCM} has not been analyzed yet. The $AgNO_3$ solution used as a chloride colourimetric indicator involves two parameters which are needed for the calculation of the D_{RCM} [1] – chloride penetration depth x_d and free chloride concentration c_d at which the colour of the sprayed concrete changes. Although the c_d for OPC-based concrete is very low, it can be different for other binders due to different binding mechanism and capacity, hydrated phases, or concrete pore solution and therefore may be different for other types of binders.

Therefore, the aim of this study is to analyze the possibility of determination of the chloride diffusion coefficient in accelerated chloride migration test for mortars prepared with various blended cements. The diffusion coefficients are obtained with two approaches: the basic RCM test model (D_{RCM}) [1,2] and the extended model (D_{RCM}*) presented by Spiesz et al [3]. Both these chloride diffusion coefficients are then compared. Additionally the $AgNO_3$ colourimetric indicator is verified for concrete with blended cements.

2. USED MATERIALS AND MORTAR COMPOSITION

In this study, four mortars based on different binder blends are prepared and tested. Mortars are chosen instead of concrete as they do not contain coarse aggregates, which are impermeable for chlorides and therefore may disturb the chloride penetration front. The reference mortar consisted of OPC (CEM I 52.5N) as a binder. The other mixtures included OPC replaced at different levels by supplementary cementitious materials – 40% of GGBS (ground granulated blast-furnace slag), 15% of FA (fly ash) and 10% of SF (silica fume). The binders are prepared by blending OPC with GGBS, FA and SF in such a way to achieve the same percentage of additives as specified for CEM III/A, CEM II/A-V and CEM II/A-D. The water/binder ratio is kept constant in all prepared mixes (w/b = 0.4). Sand 0–4 mm is used as aggregate. At the age of 28 days the RCM test was performed following NT Build 492. The test lasted 24 hours for all the samples and the voltage of 25 V, 30 V, 25 V and 50 V was applied for OPC, GGBS, FA and SF-mortars, respectively.

3. RCM TEST

In the traditional RCM model [1,2] the assumptions of linear binding and the equilibrium between free and bound chlorides are introduced, as explained earlier in Eq. 1. Spiesz et al. [3] presented an extended chloride transport model for the non-steady-state migration which accounted for non-linear chloride binding and non-equilibrium between free and bound chloride concentrations, in a system based on the Nernst - Planck equation.

$$\varphi \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = -k \left[c - \left(\frac{C_b}{K_b} \right)^{1/n} \right] \tag{2}$$

$$(1-\varphi)\rho_s \frac{\partial C_b}{\partial t} = k \left[c - \left(\frac{C_b}{K_b} \right)^{1/n} \right] \tag{3}$$

with following boundary and initial conditions:

$$c(x=0;t) = c_0,$$

$$C_b(x;t=0) = C_{bi}, \tag{4}$$

where: φ is the water accessible porosity of concrete, ρ_s the specific density of concrete, C_b is the concentration of bound chlorides, t is time, c the concentration of chlorides in pore solution of concrete, u is the ionic migration velocity, c_0 the concentration of chlorides in the external bulk solution and C_{bi} is initial bound chloride concentration in concrete (assumed $C_{bi} = 0$).

This extended model includes several parameters, among the others the effective chloride diffusion coefficient (D_{eff}) and binding parameters (K_b – chloride binding capacity constant, n – binding intensity parameter, k – mass transfer coefficient). Based on the experimental total chloride concentration profiles measured after performing the RCM test (shown in Figure 1 as an average of 3 measurements), the values of D_{eff}, k, K_b and n are optimized using a similar routine as presented in [3]. In such on optimization process, the difference between the measured chloride concentration profile and the chloride profile computed from Eq. (2) and (3) is minimized by adjusting the values of mentioned parameters. The values of optimized parameters for OPC and blended cement mortars analyzed in this study are presented in Table 1. The simulated and measured total chloride concentration profiles for the investigated mortars are shown in Figure 1.

Table 1: Optimized model parameters

Mortar mixture	D_{eff} [$\cdot 10^{12}$ $m^2 \cdot s^{-1}$]	k [$\cdot 10^6$ $l \cdot s^{-1}$]	K_b [$\cdot 10^4$ dm^{3n}/g^n]	n [-]
OPC-mortar	1.39	1.56	6.30	0.53
GGBS-mortar	0.87	4.02	8.30	0.49
FA-mortar	1.71	1.43	6.50	0.51
SF-mortar	0.47	2.03	6.10	0.52

a) b)

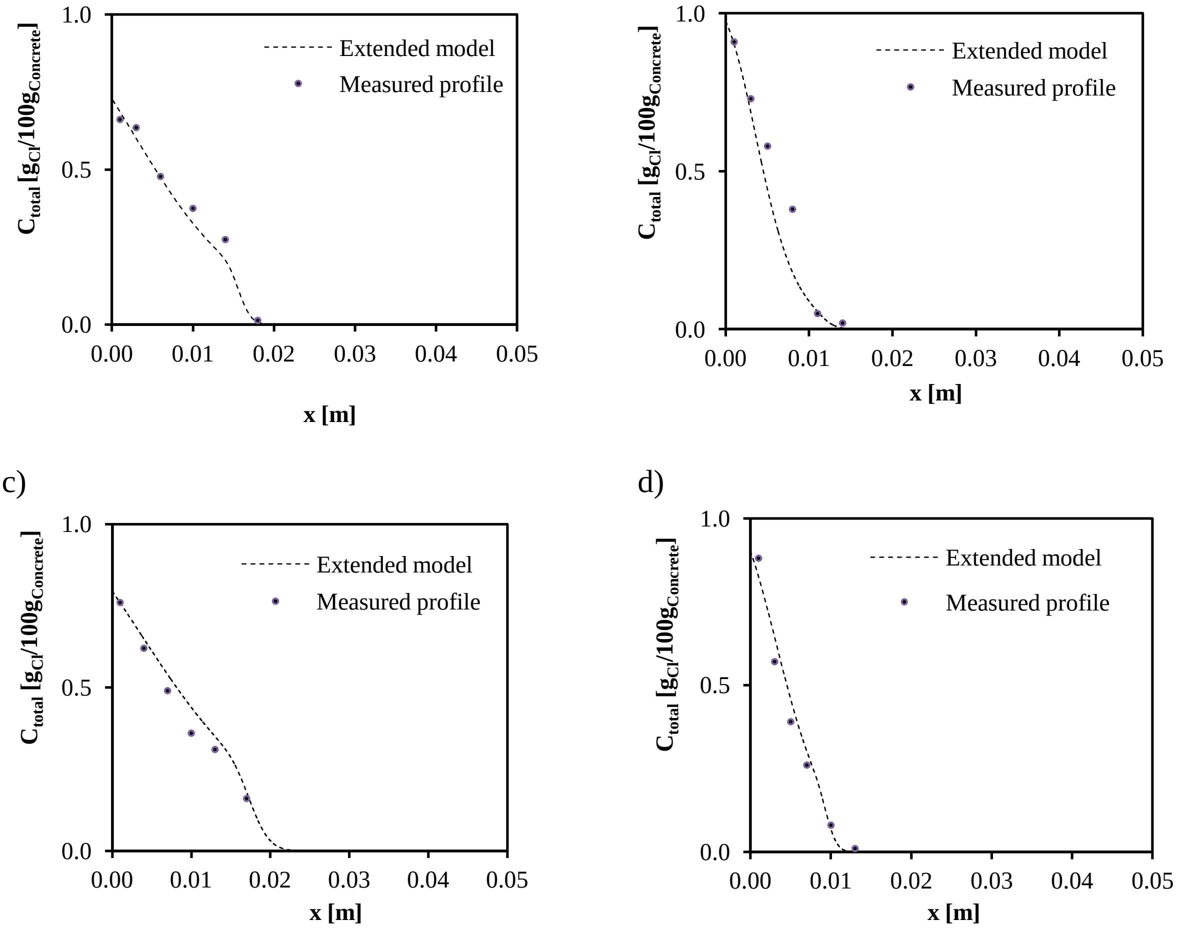

Figure 1: Total chloride concentration profiles obtained from the extended model, mortars with w/c = 0.4, a) OPC-mortar, b) GGBS-mortar, c) FA-mortar, d) SF-mortar

When analyzing the values of the obtained chloride binding capacity K_b and chloride binding intensity *n*, the results for OPC mortar are in line with chloride binding data found in literature for the same type of cement [3,5]. When replacing cement with GGBS, the binding capacity constant K_b is increases, which shows that GGBS-mortar can bind more chlorides compared to the OPC-mortar. On the other hand, when cement is replaced with SF, the binding capacity is slightly reduced, as shown in Table 1. The mass transfer coefficient *k* plays a decisive role on the shape of the profile. When chlorides are bound faster (higher values of *k*), they do not have much freedom to penetrate farther into the mortar which results in a more abrupt chloride profile, as shown in Figure 1 (b and d). The more gradual profile shape can be seen in OPC and FA-mortar (Figure 1 a and c), which is reflected by lower *k* values. The effective chloride diffusion coefficient D_{eff}, shown in Table 1, is obtained indirectly from the extended model presented by Spiesz et al. [3]. This parameter can be used to estimate the chloride diffusion coefficient D_{RCM}* which is computed from the following relationship given in [4] and assuming $\partial c_b / \partial c$ equal 0, as explained in [4]:

$$D_{RCM}{}^{*} = \frac{D_{eff}}{\varphi}, \qquad (5)$$

The total chloride concentrations C_{total} at the penetration depths x_d have been determined from the experimental profiles by linear interpolation, as shown in Figure 2. The depths of chloride penetration indicated by $AgNO_3$ solution are plotted in Figure 2. The values for mortars obtained in this study after the RCM tests are summarized in Table 2. The results in Table 2 show that silver nitrate colourimetric method is an efficient method for detecting the chloride penetration depth for mixtures with supplementary cementitious materials. For these mortars, the total chloride concentration measured at the colour change boundary is even lower compared to the OPC-mortar.

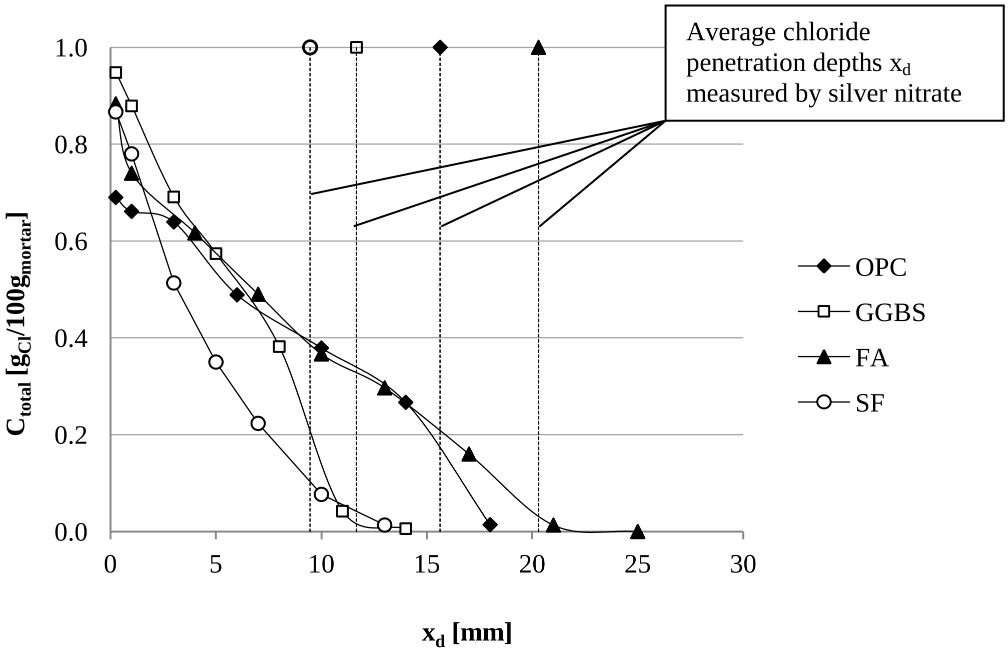

Figure 2: Total chloride concentration profiles in mortars after the RCM test

Table 2: Determined range of the total chloride concentration at the $AgNO_3$ colour change boundary

Mortar mixture	Total chloride concentration by mass of concrete [%]
OPC-mortar	0.17 – 0.18
GGBS-mortar	0.01 – 0.02
FA-mortar	0.03 – 0.04
SF-mortar	0.10 – 0.11

The D_{RCM}, shown in Table 3, is calculated in traditional way following NT Build 492 [2], using the measured chloride penetration depth x_d. The values of x_d were obtained with $AgNO_3$ colourimetric method and average results are reported in Table 3. The relationship between the D_{RCM} obtained from the colourimetric method and the D_{RCM}* from the extended model is presented in Figure 3 and as can be seen, these two coefficients are well correlated. This good correlation demonstrates that the chloride diffusion coefficient can be properly obtained with RCM test and the chloride penetration depth can be obtained by spraying $AgNO_3$ colourimetric method. Therefore, it can be concluded, that these methods are reliable also for blended cement mortars.

Table 3: Measured chloride penetration depths x_d and computed chloride diffusion coefficients D_{RCM} and D_{RCM}*

Mortar mixture	x_d [mm]	D_{RCM} [$\cdot 10^{12}$ $m^2 \cdot s^{-1}$]	D_{RCM}* [$\cdot 10^{12}$ $m^2 \cdot s^{-1}$]
OPC-mortar	15.7	8.56	9.56
GGBS-mortar	11.6	5.13	5.93
FA-mortar	20.3	11.15	9.79
SF-mortar	9.5	2.49	2.69

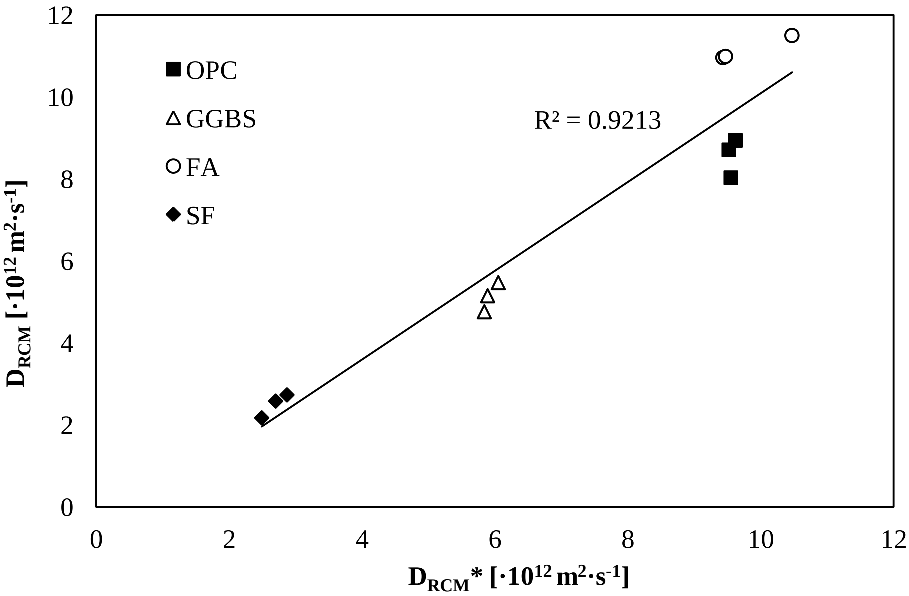

Figure 3: Comparison of diffusion coefficients obtained from basic and extended chloride transport models

4. CONCLUSIONS

The conclusions can be summarized as follows:

– The Rapid Chloride Migration test can be used for the determination of the chloride diffusion coefficient D_{RCM} in mortars based on blended cements.
– The chloride diffusion coefficient D_{RCM} calculated according to NT Build 492 [2] is well correlated with the chloride diffusion coefficient D_{RCM}* obtained from extended chloride transport model.
– The accuracy of $AgNO_3$ colourimetric technique to determine the chloride penetration depth is sufficient for blended cement mortars.

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