

Determination of the chloride diffusion coefficient in blended cement mortars

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DETERMINATION OF CHLORIDE DIFFUSION COEFFICIENT IN BLENDED CEMENT MORTARS

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Abstract

Literature shows that the RCM test development and experience concerns only Ordinary Portland cement. Therefore, a validation of this test method is needed for other types of binders. This study analyzes the application of RCM test for mortars prepared with different binders: Ordinary Portland cement (OPC), ground granulated blast – furnace slag (GGBS), fly ash (FA) and silica fume (SF). The silver nitrate colourimetric method is applied here to assess of the chloride penetration depth, which is subsequently used for the calculation of the chloride diffusion coefficient D_{RCM} according to NT Build 492. A comparison is given between the results of the total chloride concentration profiles measured in mortar after the RCM test and results indirectly obtained from extended chloride transport model. The performed analyses show that the accuracy of $AgNO_3$ colourimetric method is sufficient for the determination of the D_{RCM} for different type of binders.

Key Words: RCM test, chloride diffusion coefficient, colourimetric method

1. INTRODUCTION

There are several test methods used for determining the chloride diffusion coefficient. The bulk immersion tests, described e.g. in NT Build 443 or ASTM C1556-03, are long term diffusion tests in which concrete samples are exposed to a chloride solution for a relatively long period. However, long term methods are often not preferred in practice because they are time consuming and laborious. The Rapid Chloride Migration (RCM) test described in the guideline NT Build 492 [1], is one of the accelerated test methods in which chlorides penetrate the concrete at high rates due to the applied electrical field. The output of the test is the chloride diffusion coefficient D_{RCM} . This method is the most commonly used accelerated chloride test because of its simplicity, duration and theoretical basis. After performing the RCM test, the chloride penetration depth in concrete is measured by easy and quick $AgNO_3$ colourimetric method. The silver nitrate colourimetric method involves two parameters which are used to calculate the non-steady-state chloride diffusion coefficient D_{RCM} – the chloride penetration depth x_d and free chloride concentration c_d at which the colour change of the sprayed concrete changes. Therefore, for a better accuracy of the D_{RCM} , the exact values of x_d and c_d are critical.

From literature it is known that the total chloride content at the colour change boundary detected by silver nitrate varies from 0.02 to 0.5% by weight of OPC concrete. However, this concentration range may be different for other binders due to binding chlorides, hydrated phases, or changes of the pH of the pore solution and therefore may be different for other types of concrete. Therefore, the aim of this study is to analyze the possibility of determination of the chloride

diffusion coefficient in accelerated chloride migration test for various concretes and whether the applied blended cements influence the silver nitrate colourimetric method. The diffusion coefficients are obtained by two approaches: the basic RCM test model [1] and the extended model presented by Spiesz [2].

2. MATERIALS AND TEST METHODS

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 (SCM) – 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. The workability of mortars is adjusted with superplasticizer.

Fresh mortars are cast in cubes and prisms. The specimens are cured in water until the age of 27 days, when the RCM test samples are extracted from the cubes and at the age of 28 days the RCM test (NT Build 492) began, using the set-up shown in Fig. 1. Mortar prisms are used for determination of flexural and compressive strengths according to EN 196-1, after 7, 28 and 91 days of water curing.

3. RESULTS

After the RCM test the colourimetric indicator for chlorides (AgNO_3 solution) is applied and sprayed onto freshly split samples to determine the chloride penetration depth. The boundary between the regions with and without chlorides is clearly visible due to the chemical reaction of Ag^+ and free Cl^- and formation of white precipitate as it is illustrated in Fig. 2a-d. The observed chloride penetration fronts are straight and not distorted, as was expected for mortar. Subsequently, the chloride penetration depth x_d was measured and used for calculation of D_{RCM} , as reported in Table 1.



Fig. 1: RCM test set – up

This work shows that silica fume is the most effective SCM in reducing chloride diffusion coefficient, followed by GGBS. It can be concluded that it is a result of microstructural changes induced by filler effect and pozzolanic reaction. A further reduction of the chloride diffusion coefficient is expected for FA-mortar in the course of the time, as the hydration of FA blended cements is slower than for other pozzolanic additives.

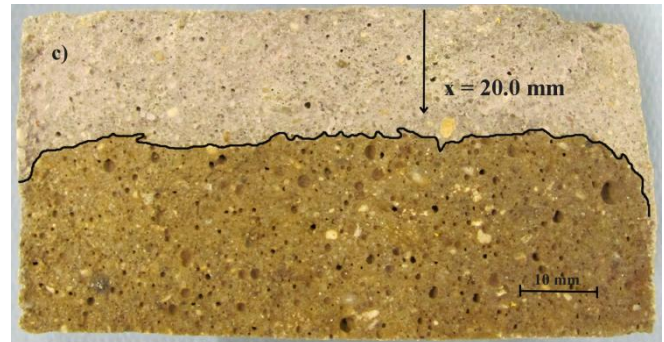
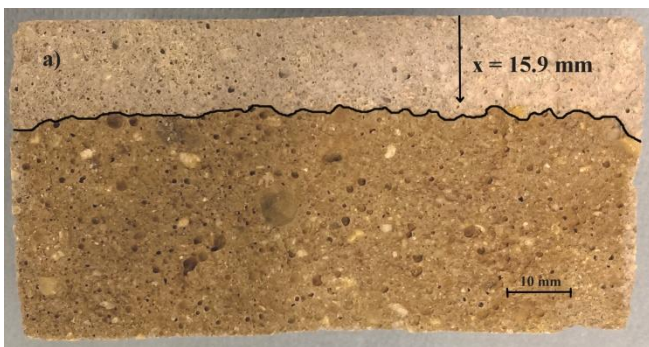


Fig. 2: Examples of chloride penetration depths revealed by AgNO_3 solution applied onto freshly split mortars after RCM test – a) OPC-mortar, b) GGBS-mortar, c) FA-mortar, d) SF-mortar

Table 1: Measured chloride penetration depth and calculated D_{RCM} following NT Build 492

Mortar mixture		x_d [mm]	D_{RCM} [$\cdot 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$]
OPC-mortar	1	15.9	8.71
	2	14.8	8.03
	3	16.3	8.94
GGBS-mortar	1	11.7	5.15
	2	12.4	5.47
	3	10.9	4.76
FA-mortar	1	20.9	11.50
	2	20.0	10.96
	3	20.9	10.99
SF-mortar	1	10.3	2.72
	2	8.3	2.17
	3	9.8	2.58

The total chloride concentrations c_t at the penetration depths x_d have been determined from the experimental profiles by linear interpolation, as shown in Fig. 3. The depths of chloride penetration indicated by $AgNO_3$ solution are plotted in Fig. 3, indicated as vertical lines. The values obtained for mortars developed in this study after the RCM tests are summarized in Table 2. It can be seen that the chloride content for OPC obtained here is very comparable to the data reported by [3-5] and is shown in Table 3.

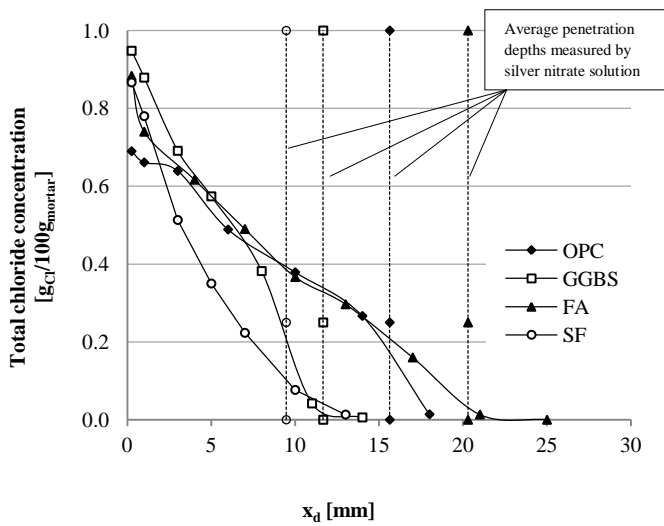


Fig. 3: Total chloride concentration profiles measured after RCM test

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

Table 3: Total chloride concentration at the $AgNO_3$ colour change boundary for OPC concrete reported in the literature

Reference	Total chloride concentration by mass of concrete [%]
This study	0.17 – 0.18
Yuan et al. [4]	0.028 – 0.207
Meck et al. [3]	0.02 – 0.23
Andrade et al. [5]	0.18

The results in Table 2 show that $AgNO_3$ colourimetric method is an efficient method for detecting the chloride penetration front for mixtures incorporating SCM. For the mixture containing SCM additions, the total chloride concentration measured at the colour change boundary is even lower compared to the OPC mortar.

Chloride binding in mortar is a non-linear 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. Therefore, Spiesz [6] presented an extended chloride transport model which includes non-linear chloride binding. The total chloride concentration profiles are obtained as a sum of free and bound chloride profiles, taking into account their proper units, volumes, densities and these profiles can be simulated by adjusting several parameters [6]. These parameters can help to estimate indirectly the chloride diffusion coefficient D_{RCM}^* and chloride penetration depth x_d^* . Table 4 shows the values of the predicted chloride penetration depth x_d^* obtained from the computed free chloride profiles in the extended model and the chloride diffusion coefficient D_{RCM}^* computed from the relationship between the effective chloride diffusion coefficient and porosity of mortar sample [2,6]. The D_{RCM} is computed according to [1], applying the measured chloride penetration depth x_d . The values of x_d were obtained with $AgNO_3$ colourimetric method for chlorides, as it is already explained earlier.

Table 4: Obtained chloride penetration depths x_d , x_d^* and chloride diffusion coefficients D_{RCM} , D_{RCM}^*

Mortar mixture	x_d [mm]	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	1	15.9	17.5	8.71	9.52
	2	14.8	17.4	8.03	9.55
	3	16.3	17.6	8.94	9.62
GGBS-mortar	1	11.7	12.3	5.15	5.89
	2	12.4	12.5	5.47	6.05
	3	10.9	12.0	4.76	5.84
FA-mortar	1	20.9	20.5	11.50	10.47
	2	20.0	18.6	10.96	9.43
	3	20.0	18.4	10.99	9.47
SF-mortar	1	10.3	10.9	2.73	2.87
	2	8.3	9.7	2.17	2.49
	3	9.8	10.3	2.58	2.70

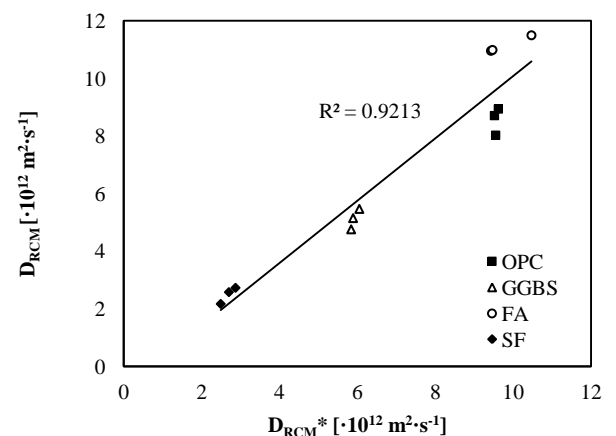


Fig. 4: Comparison of diffusion coefficients obtained from colourimetric method and extended model

The relationship between the chloride diffusion coefficients obtained from the colourimetric method and extended model is presented in Fig. 4 and as can be seen, these two coefficients are well correlated. This good correlation demonstrates that the chloride penetration depth in blended cement mortars can be obtained by spraying AgNO_3 colourimetric method. Therefore, it can be concluded that the AgNO_3 method is reliable also for binders other than OPC.

CONCLUSIONS

The main conclusions that can be drawn are:

- In the present study, the determined 28-days diffusion coefficients follow the order: 15% fly ash mortar > plain OPC mortar > 40% slag mortar > 10% silica fume mortar.
- Accelerated Rapid Chloride Migration (RCM) test can be used for the determination of the chloride diffusion coefficient D_{RCM} in mortars based on blended cements.
- The accuracy of AgNO_3 colourimetric technique to determine the chloride penetration depth is sufficient for different types of binders.
- The chloride diffusion coefficient D_{RCM} calculated based on the colourimetric method according to NT Build 492 [1] is well correlated with the chloride diffusion coefficient D_{RCM}^* obtained by extended chloride transport model.

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BIOGRAPHIES



Veronika Elfmarkova has received her Master's degree from the Brno University of Technology, Czech Republic. She is currently working as a PhD student at the Department of Built Environment, Eindhoven University of Technology. Her research focuses on the durability of reinforced concrete in terms of chloride penetration and carbonation



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