Determination of the chloride diffusion coefficient in blended cement mortars

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ABSTRACT

The rapid chloride migration test (RCM) is a commonly used accelerated test for the determination of the chloride diffusion coefficient in concrete. Nevertheless, the initial development and further experience with the RCM test concern mainly the ordinary Portland cement system. Therefore, the objective of this work is to analyse the application of this test method for other types of binders, by performing and analysing the RCM test results for mortars prepared with additions of supplementary cementitious materials. A comparison is given between the total chloride concentration profiles measured in concrete after the RCM test and the colourimetric test results. The presented results show that the accuracy of the silver nitrate colourimetric technique is sufficient for the determination of the chloride penetration front and that the RCM test is a suitable method also for the determination of chloride diffusion coefficient in mortars with blended cements.

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1. Introduction

The key performance requirements for the design, construction and maintenance of concrete structures are related to safety, serviceability and durability. The highly alkaline environment of concrete forms a passive film on the surface of steel bars, which normally prevents the steel from corrosion. However, under chloride attack, the passive film vanishes and the steel spontaneously corrodes. Chloride-induced corrosion of reinforcing steel occurs in chloride-bearing environments (e.g. sea water, de-icing salts) and is directly related to the shortened service life of concrete structures/elements. In order to quantify the chloride ingress speed in concrete, the chloride diffusion coefficient is used, because the diffusion controls the ingress of chlorides at a certain depth in concrete, while the capillary suction is only significant in the surface layers [1,2].

Several laboratory test methods are being commonly used for determining the chloride diffusion coefficient. The bulk immersion tests, described e.g. in NT Build 443 [3] or ASTM C1556–03 [4], are long term diffusion tests in which concrete samples are exposed to a chloride solution for a relatively long period of time. However, the long term methods are often not preferred in practice because they are time consuming and laborious. The rapid chloride migration (RCM) test developed by Tang [5], described in the guideline NT Build 492 [6], is one of the accelerated test methods in which chlorides penetrate the concrete at high rates due to the applied electric field. The output of the test is the chloride diffusion coefficient D_{RCM} (often called the migration coefficient — to distinguish it from immersion tests). This method is concluded by some researchers to be the most suitable of all the reviewed accelerated chloride tests, on the basis of its simplicity, short duration and often is assumed to have a clear theoretical basis [7]. In the RCM test, after a period of the application of electric field to concrete, the chloride penetration depth in a split concrete sample is measured by an easy and quick $AgNO_3$ colourimetric method (0.1 $mol \cdot dm^{-3}$ $AgNO_3$ solution sprayed onto the fractured concrete surface). The $AgNO_3$ colourimetric method involves two parameters — the indicated chloride penetration depth x_d and the free-chloride concentration c_d at which the colour change occurs in concrete. Both these values are used to calculate the non-steady-state diffusion coefficient of chloride (D_{RCM}). The D_{RCM} is obtained from the following mathematical model [5]:

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

A solution of this model is presented in [5] and yields the following equation for the D_{RCM}:

$$D_{RCM} = \frac{RT}{zFE}\cdot\frac{x_d - \alpha\sqrt{x_d}}{t} \quad (2)$$

where: c — concentration of free-chlorides in pore solution, t — time, J_x — total flux of chlorides in x direction, x — distance, D_0 — intrinsic chloride diffusion coefficient in pore solution of concrete, c_b —

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concentration of bound chlorides, E — electric field, equal to $(U − 2)/L$, where U — applied electrical voltage and L — thickness of sample (0.05 m), R — gas constant (8.314 J·mol^{-1}·K^{-1}), T — temperature (293 K), z — ion valence (-1 for Cl$^-$), F — Faraday constant (96,485 C·mol^{-1}), x_d — chloride penetration depth indicated by the colourimetric indicator AgNO$_3$, α — laboratory constant defined as [5]:

$$\alpha = 2\sqrt{\frac{RT}{zFE} \cdot erf^{-1}\left(1 - \frac{2c_d}{c_0}\right)} \qquad (3)$$

where: c_d — free-chloride concentration at colour change boundary (0.07 mol$_{Cl}$/dm$^3_{solution}$) and c_0 — concentration of chlorides in the external bulk solution (64.95 g$_{Cl}$/dm$^3_{solution}$ = 1.83 mol$_{Cl}$/dm$^3_{solution}$).

As previously stated, the free chloride penetration depth x_d is used for the calculation of the D_{RCM} according to Eq. (2) and it is determined using the AgNO$_3$ solution. Spraying the silver nitrate solution onto a freshly fractured concrete cross-section leads to a chemical reaction which results in a clear colour change boundary between the chloride-contaminated and chloride free-zones. This is due to the fact that in the regions not containing chloride ions, AgNO$_3$ reacts with OH$^-$ to form a mixture of precipitates of silver hydroxide, according to Eq. (5). The precipitates of AgOH formed on the surface are unstable and quickly decompose to a brownish precipitate (Ag$_2$O) [8–10]. The zone containing chlorides is indicated by a white precipitate resulting from formation of silver chloride (AgCl), as Eq. (4) shows. The chemical reactions can be expressed as follows [9]:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow (silvery\ white\ colour = 100\%\ AgCl + 0\%\ Ag_2O) \quad (4)$$

$$Ag^+ + OH^- \rightarrow AgOH \rightarrow Ag_2O\downarrow (brown\ colour = 0\%\ AgCl + 100\%\ Ag_2O) \quad (5)$$

Otsuki et al. [10] found that 0.1 M AgNO$_3$ solution is the most appropriate concentration for giving the visually clearest boundary between the chloride- and chloride-free zones in the case of OPC. From the data reported in the literature [8–13] it is known that the total chloride content at the colour change boundary detected by silver nitrate varies in a wide range, from 0.19% [14] to 1.41% [11] by the mass of ordinary Portland cement, and from 0.02% [11] to 0.5% [10] by mass of concrete, depending on the sample preparation and the measurement technique. Nevertheless, this concentration of AgNO$_3$ may be different for other binders due to the differences in chloride binding, hydration products, or pore solution chemical composition and therefore, may not be suitable for all types of concrete [5,8–13,15,16]. Yuan [14] reported some difficulties with the accuracy of the chloride penetration depth measurement in concrete after using the AgNO$_3$ solution as a chloride indicator. Moreover, the free-chloride concentration at the colour change boundary of 0.07 mol·dm^{-3} was questioned in [14]. Such value was

proposed by Tang [5,17], based on the experiments of Otsuki et al. [10], and applied for the D_{RCM} calculation. Otsuki et al. [10] found a free chloride concentration at the colour change boundary of approximately 0.14 mol·dm^{-3}. Tang [5,17] used value of 0.07 mol·dm^{-3} considering a chloride condensation factor of 2 due to the pore solution extraction technique. However, this concentration may be different for blended cements, which has been experimentally confirmed by Maes et al. [15], who reported the chloride concentration at the colour change boundary of 0.35 mol·dm^{-3} for concretes based on OPC–GGBS blends. This is in line with [18,19], which suggest that mineral additions may influence the chloride concentration at the colour change boundary.

Many researchers have shown that the chloride profiles determined experimentally after performing the RCM test have significantly different shape compared to the theoretical profile shape predicted from Eq. (1) [14,16,20]. The difference between the theory and experimental measurements gives an evidence that the basic chloride transport model for the RCM test unsatisfactorily describes the real process. Tang [5] suggested the possible explanations for the differences between the theoretical and experimental chloride concentration profiles, such as (a) different pore distribution resulting in different penetration front; (b) reaction kinetics which changes the shape of the profile without changing the penetration depth or (c) influence of other ions on the chloride binding [5]. Recently, Šavija et al. [21] attributed the discrepancy between the theoretical and experimental chloride profiles to the tortuosity of the pore structure and heterogenity of concrete, yet without considering chloride binding in the simulations. As explained in [16,20,22] the oversimplification of chloride binding in the transport model can explain the observed discrepancies. Eq. (1) assumes a constant $\partial c_b/\partial c$ term, which implicitly implies that either no binding or an instantaneous linear chloride binding in equilibrium is present in concrete. For the linear chloride binding in instantaneous equilibrium, the free-chloride concentration would be reduced in concrete by binding, but the shape of the free-chloride concentration profile would remain unaffected (i.e. the abrupt chloride profile, instead of the gradual profile, as experimentally determined after the test). Therefore, Spiesz et al. [16, 23] presented an extended chloride transport model which considers chloride binding more properly, assuming a non-linear chloride binding isotherm (represented by Freundlich isotherm $C_b = K_b \cdot c^n$) and non-equilibrium conditions between the free and bound chlorides. This
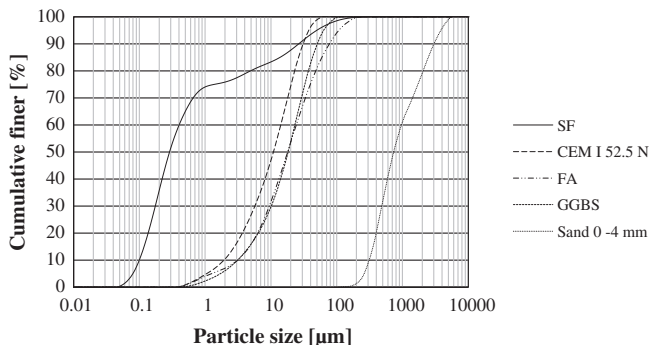
Table 1
Specific densities (ρ_s) of used materials.

Material	ρ_s [g · cm^{-3}]
CEM I 52.5 N	3.19
GGBS	2.91
FA	2.36
SF	2.25
Sand 0–4 mm	2.65
SP	1.10

Fig. 1. Particle size distribution of the used materials.

Table 2
Chemical composition of OPC, GGBS, FA and SF.

Chemical composition [%]	OPC	GGBS	FA	SF
CaO	64.60	38.89	4.46	0.28
SiO$_2$	20.08	34.18	55.32	94.25
Al$_2$O$_3$	4.98	13.63	22.45	0.96
Fe$_2$O$_3$	3.24	0.51	8.52	0.14
K$_2$O	0.53	0.43	2.26	0.95
Na$_2$O	0.27	0.33	1.65	0.18
SO$_3$	3.13	1.41	1.39	–
MgO	1.98	10.62	1.89	0.40
TiO$_2$	0.30	–	1.17	0.01
Mn$_3$O$_4$	0.10	–	0.11	–
P$_2$O$_5$	0.74	–	0.76	0.08