



Chloride diffusion in partially saturated cementitious material

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Abstract

The paper proposes a combined application of composite theory and Powers' model for microstructural development for the estimation of the diffusion coefficient as a function of the moisture content of a defect-free cementitious material. Measurements of chloride diffusion in mortar samples (440 kg/m³ rapid-hardening Portland cement, w/c = 0.5, maturity minimum 6 months) stored at 65% and 85% RH, as well as in vacuum-saturated mortar samples, illustrate the applicability of the method.

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1. Introduction

Durability aspects are increasingly determined for the design of reinforced concrete structures in aggressive environment (e.g., structures exposed to seawater or deicing salts). Except in submerged parts of marine structures, concrete is rarely saturated when exposed to chlorides. Therefore, models for the ingress of chloride into partly saturated concrete are relevant for the service life design and reassessment of reinforced concrete structures.

Both capillary suction of chloride-contaminated water and diffusion of chloride ions are likely transport mechanisms for chlorides in partly saturated concrete. Capillary suction will be dealt with in a separate paper.

An equation for the effect of relative humidity on the rate of diffusion of ions in cementitious materials has been proposed by Saetta et al. [1]. However, as the diffusion coefficient is expected to be dependent on the amount of moisture available for the diffusing substance, a model taking this parameter into account is expected to provide more accurate estimations. Such an approach is proposed in the present paper, where the diffusion coefficient is calculated by combining the composite theory with Powers' model for the development of the microstructure in cement

paste. Jensen [2] has applied a similar approach for simulating the ingress in saturated cement paste and mortar. A similar approach has recently been applied to partly saturated cementitious materials, but without distinguishing between the rate of diffusion in the capillary and gel pores [3,4], which causes an overestimation of the diffusion coefficient at low degrees of moisture saturation.

In contrast to the proposed approach, existing models are semiempirical and require extensive calibration.

The present paper is, with some modifications, based on recent studies of diffusion in partly and fully saturated cementitious material given in Ref. [5].

2. Theory

2.1. Diffusion

Diffusion is the transport of ions caused by differences in concentration. Descriptions of the mechanism can be found elsewhere (e.g., Refs. [6,7]). For the calculations presented in the present paper, two solutions to Fick's second law of nonsteady state diffusion are applied: (1) the 'instant plane source' solution for an instantaneous limited supply of ions [8]:

$$c(x, t) = \frac{m_{Cl}}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (1)$$

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and (2) the commonly used error function solution for constant supply of diffusing substance [7]:

$$c(x, t) = C_s - (C_s - C_i) \operatorname{erf} \frac{x}{\sqrt{4tD}} \quad (2)$$

where $c(x, t)$ is the total content of chlorides at a depth x and exposure time t ; m_{Cl} is the total mass of diffusing ions; C_s is the chloride content at the surface; and C_i is the total background chloride content. D is the chloride ion diffusion coefficient of the porous material assuming no interaction between the ions and the material.

For service life design and redesign, D in Eqs. (1) and (2) is generally substituted by D_{app} , which is the ‘apparent’ diffusion coefficient fitted by the least sum of squares method and including the interaction of the ions with the solids.

Saetta et al. [1] have proposed that the diffusion coefficient of chloride ions at a given relative humidity, RH, relative to the diffusion coefficient at 100% RH can be given as:

$$\left(1 + \frac{(1 - RH)^4}{(1 - RH_c)^4} \right)^{-1} \quad (3)$$

where RH_c is the RH at which $D(RH_c) = 1/2D(100\%)$.

2.2. Numerical modeling of chloride diffusion

The following numerical solution to Fick’s second law of diffusion (see, e.g., Ref. [2]) is adopted in the present paper:

$$c_f(x, t) = c_f(x, t - \Delta t) + D \frac{\Delta t}{(\Delta x)^2} [c_f(x - \Delta x, t - \Delta t) + c_f(x + \Delta x, t - \Delta t) - 2(c_f(x, t - \Delta t))] \quad (4)$$

where $c_f(x, t)$ denotes the concentration of chlorides at the depth x from the surface at the exposure time t , and D is the chloride ion diffusion coefficient of the porous material assuming no interaction between the ions and the material.

The boundary conditions for the simulation can be adjusted for each time step, when the concentration of chloride ions in the environment as a function of time is known and when the depth considered is high enough to ensure that the chloride concentration in the innermost part of the sample remains unchanged during the exposure time.

To ensure stability of the numerical procedure, the Fourier steps should be maximum 0.5 (see, e.g., Ref. [2]), thereby obeying the relation:

$$0.5 < \frac{\Delta t D}{\Delta x^2}. \quad (5)$$

A considerable amount of the chloride ions may become fixed in the hydrate phases through processes collectively referred to as binding. The mechanisms are still not fully

described [9], but it is assumed that it is mainly the aluminum-bearing hydration products that react chemically with the chloride ions and form Friedel’s salt or solid solutions, which include Friedel’s salt [10].

The binding process is normally quantified by measuring the amount of bound chlorides in equilibrium with a chloride-containing exposure solution, for increasing concentrations of chlorides. The results are commonly expressed by means of the so-called Freundlich or Langmuir isotherms [2,9], depending on which provides the best correlation to the data. Considering the Freundlich isotherm, the equilibrium between bound, c_b [mg Cl/g gel], and free chloride ions, c_f [mol Cl/l pore solution], is expressed by:

$$c_b = \alpha c_f^\beta \quad (6)$$

where α and β are constants (regression parameters) with no physical meaning. When the binding capacity becomes exhausted, any further addition of chlorides will result in an increase in the concentration of free chlorides in the pore solution.

There is no clear information available on whether binding is an instantaneous process or if a binding rate should be introduced. Instantaneous binding is easy to compute as quasi-instantaneous by recalculating the binding equilibrium for each time increment at each depth. Following this procedure, Jensen [2] found satisfying correlation between measured and calculated chloride profiles in cement pastes. Therefore, instantaneous binding is assumed for the later calculations.

2.3. Chloride diffusivity in cementitious materials

Powers and Brownyard [11] carried out a thorough investigation on, among others, the porosity of Portland cement systems. The so-called Powers model (due to this author’s later work) provides an approximation of the volume fraction of the different phases [characterised as cement, capillary (free) water, gel solid, gel water, and capillary water from chemical shrinkage, i.e., empty or refilled capillary pores] that constitute the cement paste throughout the hydration process.

Before presenting the model, two constants, which are characteristic of the cement paste examined, are calculated: $k = 0.23(C_3S) + 0.32(C_2S) + 0.32(C_3A) + 0.37(C_4AF)$ and the initial porosity, $p = (w/c) / (w/c + \rho_w / \rho_c)$, where w/c is the water-to-cement ratio, and ρ_w and ρ_c are the density of water and cement. For a cement paste composed of the investigated rapid-hardening Portland cement (Bogue composition $C_3S = 50\%$, $C_2S = 24\%$, $C_3A = 7\%$, and $C_4AF = 11\%$) with $w/c = 0.50$, k and p become 0.26 and 0.61, respectively.

According to Ref. [11], the total volume of gel water in a cement paste can be calculated from $0.9n_1kw_n$, where n_1 is the number of monolayers of water that are physically adsorbed to the gel solid, and w_n is the loss of ignition for the given paste at the actual degree of hydration. According

to Ref. [12], the fourth monolayer can be regarded as free water, i.e., capillary water, i.e., $n_1=3$. Hence, the volume fraction of gel water, V_{gw} , as a function of the degree of hydration (loss of ignition of approximately 22% at 100% hydration, estimated from Refs. [13,14]) in a Portland cement paste with the clinker composition mentioned above, can be written as:

$$V_{gw} = 0.48(1 - p)\alpha \quad (7)$$

where α is the degree of hydration, ranging from 0 to 1.

The volume fraction of empty or refilled capillary pores generated by the chemical shrinkage, V_{cs} , is according to Ref. [12] given by the following equation:

$$V_{cs} = 0.2(1 - p)\alpha. \quad (8)$$

Powers and Brownyard [11] and Powers [15] found that the volume of capillary water unconsumed during hydration was $w_0 - 0.75(1 + 3k)w_n$, where w_0 is the initial amount of water in the system. The volume fraction of capillary water, V_{cw} , in a paste of the actual cement can be expressed:

$$V_{cw} = p - 1.14(1 - p)\alpha. \quad (9)$$

The volume fraction of the unreacted cement, V_{ce} , at a certain degree of hydration can be calculated as:

$$V_{ce} = (1 - p)(1 - \alpha). \quad (10)$$

The volume fraction of solid products of reaction, V_{gs} , can be calculated by subtracting Eqs. (7)–(10) from 1.0, i.e.,

$$V_{gs} = 1.46(1 - p)\alpha. \quad (11)$$

In cement paste, diffusion through both the solid gel products and the unhydrated cement is essentially nonexistent. Transport can, therefore, only take place through the pore system of the paste. The volume fraction of the pore system in a paste (the capillary porosity, $V_{cw} + V_{cs}$, and gel porosity, V_{gw}) at a given degree of hydration can be described according to the equations listed above.

Powers and Brownyard [11] concluded that ‘capillary water does not exist at pressures below about $0.45p_s$ ’, where p_s is the saturated vapor pressure, as well as that ‘at vapour pressures greater than $0.45p_s$ and less than p_s , the capillary water is present.’ Based on that, it will be assumed in the present paper that there exists a threshold vapour pressure (i.e., $0.45p_s$) where all gel pores are water-filled and all capillary pores are empty. This assumption has been validated by comparing values calculated by Eqs. (7)–(9) with a measured desorption isotherm of a 5-year-old w/c=0.45 rapid-hardening Portland cement paste [16] (similar clinker composition as that used for the present experiments). The moisture content of that paste in equilibrium with $0.45p_s$ was 15 wt.%, while the gel water content calculated according to Eq. (7) was 17 wt.% of the sample.

Jensen [2] has, based on an equation proposed by Maxwell for the diffusion coefficient of a composite,

applied the following equation for the diffusion coefficient of the gel matrix (i.e., $V_{gs} + V_{gw} + V_{ce}$), D_{gm} . It is assumed that the cement and calcium hydroxide exist as inclusions in the so-called gel proper, V_{gp} (i.e., $V_{gs} + V_{gw} - V_{CH}$):

$$D_{gm} = D_{gp} \frac{V_{gp}}{V_{gp} + \frac{3}{2}(V_{ce} + V_{CH})} \quad (12)$$

where D_{gp} is the diffusion coefficient of the gel proper. V_{CH} can be estimated from the reactions taking place and the degree of hydration. Garboczi and Bentz (Ref. [20]) have proposed the following value for the diffusion coefficient of chloride ions, $D_{gp} = 4.6 \times 10^{-12} \text{ m}^2/\text{s}$, corresponding to 1/400 of the diffusion coefficient through water-filled capillaries, $D_{cw} = 1.81 \times 10^{-9} \text{ m}^2/\text{s}$.

Assuming phase symmetric crumbled foil composites, Nielsen [17] proposed the following equation for the diffusion coefficient through the cement paste, D_p :

$$D_p = D_{gm} \frac{n + 2\sqrt{n}(1 + c(n - 1))}{n + 2\sqrt{n} - c(n - 1)} \quad (13)$$

where $n = D_{cw}/D_{gm}$ and $c = V_{cw} + V_{cs}$.

Finally, if the aggregates are impermeable, the diffusion coefficient, D , through a mortar or concrete can be estimated by the following equation proposed by Maxwell (e.g., in Ref. [2]):

$$D = D_p \frac{1}{1 + (\phi/2)} (1 - \phi) \quad (14)$$

where ϕ is the volume fraction of aggregates and air.

3. Materials and experiments

A mortar with w/c ratio of 0.5 was selected for the experiments. The mix composition is given in Table 1. The cement used was rapid-hardening Portland cement with the clinker composition mentioned in Section 2.3.

Beams ($300 \times 100 \times 100 \text{ mm}^3$) were cast and stored for 1 day at 20 °C in moulds. After demoulding, the beams were cured in saturated lime curing tanks at 20 °C for 4 days and subsequently at 50 ± 4 °C until a maturity of 4.6 months was achieved. The maturity is the equivalent age at 20 °C, based on the maturity function given in Ref. [18] and activation energy at 33,500 J/mol.

Table 1
Mix composition of the mortar (dry density 2075 kg/m³)

Component	Unit	Amount
Rapid-hardening Portland cement	kg/m ³	440
Water	kg/m ³	220
Sand (0–4 mm)	kg/m ³	1575
Air content	vol.%	4

Table 2
Moisture content

Conditioning	Moisture content (mass%)	Degree of saturation (%)	
		Capillary	Vacuum
65% RH	4.9	66.2	53.8
85% RH	5.4	73.0	59.4
Capillary saturation	7.4	100	81.3
Vacuum saturation	9.1		100

At 4.6 maturity months, the beams were conditioned at $65 \pm 2\%$ RH (22.5 ± 1 °C) for 20 days, when approximately 85% RH was measured in the centre of the samples. Some beams were then transferred to $85 \pm 1\%$ RH (20 °C), while others were left at 65% RH.

At a maturity of approximately 6 months, the beams were cut or split (see dimensions below) and conditioned to 65% and 85% RH until constant weight.

The moisture content was determined for the different conditionings applied (see Table 2). Due to the applied conditioning procedures, the equilibrium of the samples conditioned at 65% RH was achieved by desorption, whilst the equilibrium of the samples conditioned at 85% RH was reached by desorption at the centre, but absorption at the surface. Absorption and desorption curves in the range from 65% to 95% RH indicated negligible hysteresis for the examined material as to why any effect of such phenomenon has been disregarded in the present paper.

All experiments were carried out on samples more than 6 maturity months old. At this age, the influence of changes in the maturity of the paste on the diffusion properties is assumed to be negligible [7]. The degree of hydration is estimated to be 80–85% based on data presented in Ref. [19] from the development of nonevaporable water in RPC pastes and a maximum nonevaporable water content at 22% for the actual cement estimated according to Refs. [13,14].

Chloride diffusion in partly saturated mortar was measured on four samples. The near-surface region of two times two samples ($70 \times 100 \times 100$ mm³) conditioned at 65% and 85% RH, respectively, was contaminated by chlorides and subsequently returned to the conditioning rooms for 60 days. The chloride contamination was obtained by immersion of the samples in a 26 mass% NaCl solution for 2 h followed by drying the surface with a hair drier (avoiding excessive heating) until the samples reached the weight prior to chloride exposure. Chloride profiles were determined 4 days after immersion and revealed background concentration at 5 mm or less.

The chloride diffusion in saturated mortar was measured on two samples ($60 \times 100 \times 100$ mm³), which originally were conditioned at 85% RH and subsequently vacuum-saturated and left for 3 days in tap water before being submerged in a 3 mass% NaCl solution for 30 days.

The chloride profiles were determined by profile grinding in 2-mm steps and potentiometric titration of the powder samples. Prior to titration, the samples were prepared

according to the NT Build 208 method [7], except that the powder was not sieved, and the amount of HNO₃ was reduced to 5 ml (enough to reduce the pH to 1).

4. Results and discussion

Chloride profiles in samples preconditioned and stored for 60 days at 65% and 85% RH after a limited exposure to chlorides are given in Figs. 1 and 2 (circles). Fig. 3 illustrates the chloride profile obtained in a vacuum-saturated mortar after 30 days of exposure to a 3 wt.% NaCl solution (circles). By fitting Eq. (1) to the two first mentioned profiles, and Eq. (2) to the last (dotted curves), the apparent diffusion coefficients, D_{app} , given in Table 3 are obtained. The best fit was obtained by the least sum of squares method.

The applicability of Eq. (3) is illustrated in Fig. 4. The calculations are carried out by applying Eq. (3) to the apparent diffusion coefficients (D_{app} in Table 2) and fitting by the least sum of squares method in order to find the best value for RH_c. Eq. (3) appears to underestimate the transport by factor of approximately 5–10 on the diffusion coefficients at 65% RH. The fit would become slightly poorer if the diffusion coefficient at 100% RH was lower, as expected if the diffusion coefficient for 100% capillary saturation (81% vacuum saturation, according to Table 2) was applied.

The composite theory has been applied on volume fractions estimated by Powers' model (see Section 2.3) to derive the dependency of the diffusion coefficients on the degree of vacuum saturation of the material. It is assumed that 100% vacuum saturation is the degree of saturation at

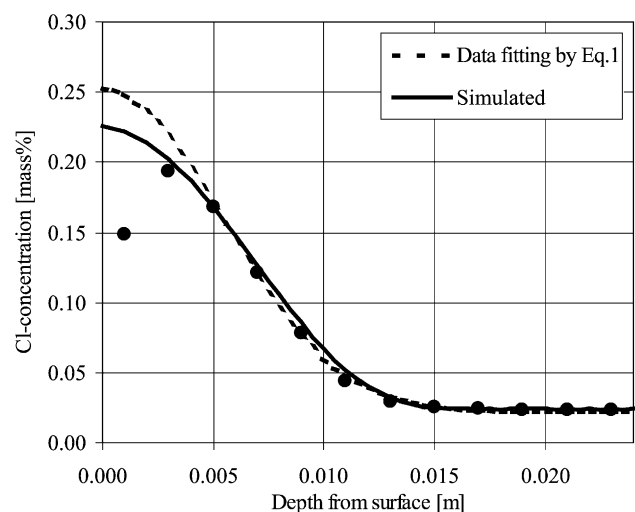


Fig. 1. Chloride profile (circles) after 60 days of exposure for a limited supply of ions. Degree of vacuum saturation 0.53. Dotted curve: Best fit by Eq. (1) with $D_{app} = 2.7 \times 10^{-12}$ m²/s and $m_{Cl} = 1.53$ g. Straight curve: Simulated ingress by the numerical procedure with $D = 5.5 \times 10^{-12}$ m²/s, calculated by means of the suggested approach (Eqs. (7)–(14)).

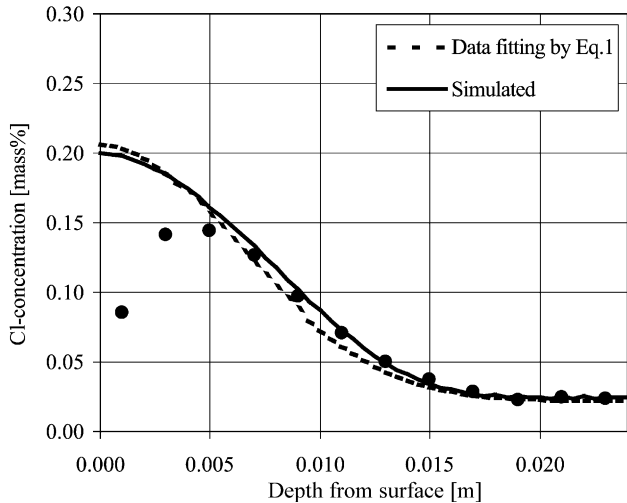


Fig. 2. Chloride profile (circles) after 60 days of exposure for a limited supply of ions. Degree of vacuum saturation 0.60. Dotted curve: Best fit by Eq. (1) with $D_{app}=3.8 \times 10^{-12} \text{ m}^2/\text{s}$ and $m_{Cl}=1.45 \text{ g}$. Straight curve: Simulated ingress by the numerical procedure with $D=7.9 \times 10^{-12} \text{ m}^2/\text{s}$, calculated with the suggested approach (Eqs. (7)–(14)).

which all of the capillary pores are water-filled. Furthermore, it is assumed that air voids remain empty.

The degree of saturation where only gel water exists is assumed to be 45% vacuum saturation (see Section 2.3), i.e., $V_{gw}=0.45(V_{cw}+V_{cs}+V_{gw})$. The assumption is supported by extrapolation of desorption isotherms for the investigated mortar measured in the range from 100% to 65% RH.

Based on the above, the estimated amount of water in the capillary pores of the actual material varies linearly from 0 to $0.30 \text{ cm}^3/\text{cm}^3 [(V_{cs}+V_{cw})]$, calculated from Eqs. (7) and (8) in the range from 45% to 100% vacuum saturation.

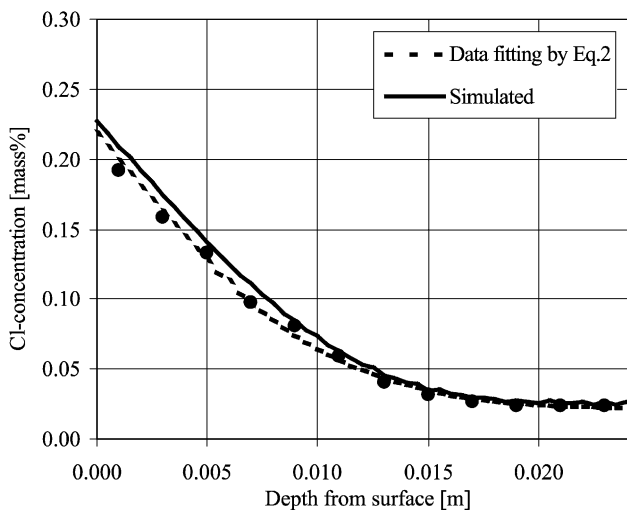


Fig. 3. Chloride profile (circles) after 30 days of exposure to a 3% NaCl solution. Degree of vacuum saturation 1.0. Dotted curve: Best fit by Eq. (2) with $D_{app}=12.9 \times 10^{-12} \text{ m}^2/\text{s}$ and $C_s=0.218 \text{ wt.}\%$. Straight curve: Simulated ingress by the numerical procedure with $D=20.2 \times 10^{-12} \text{ m}^2/\text{s}$, calculated with the suggested approach (Eqs. (7)–(14)).

Table 3

Exposure conditions, apparent diffusion coefficients (D_{app}) determined from experiments, and simulated diffusion coefficients ($D_{simulated}$) using the proposed approach

Conditioning	Exposure	D_{app} (m^2/s) $\times 10^{12}$	$D_{simulated}$ (m^2/s) $\times 10^{12}$
65% RH	26.4% NaCl for 2 h followed by drying and 65% RH	2.7	5.5
85% RH	26.4% NaCl for 2 h followed by drying and 85% RH	3.8	7.9
Vacuum saturation	Immersed in 3% NaCl	12.9	20.2

Following the procedure described in Section 2.3, the effective diffusion coefficient of the examined mortar is calculated to 5.5×10^{-12} , 7.9×10^{-12} , and $20.2 \times 10^{-12} \text{ m}^2/\text{s}$ (see Table 2) for degrees of vacuum saturation at 0.54, 0.60, and 1.0.

The chloride adsorption isotherm for a rapid-hardening Portland cement paste is given in Ref. [9]. α and β in Eq. (6) are determined to 7.04 and 0.50 by fitting by the least sum of squares method. The maximum binding capacity of the cement paste is 6.8 mg Cl/g gel (deduced from Ref. [9]).

The ingress curves in Figs. 1–3 are obtained (i.e., straight curves) when using the numerical routine in Section 2.2 and the approach defined previously for estimating the diffusion coefficients at different degrees of saturation. For the simulations in Figs. 1 and 2, it is assumed that the total chloride in the sample is distributed within the outermost 2 mm at time 0.

The correlation between the simulated ingress in partly saturated material, according to the suggested approach and

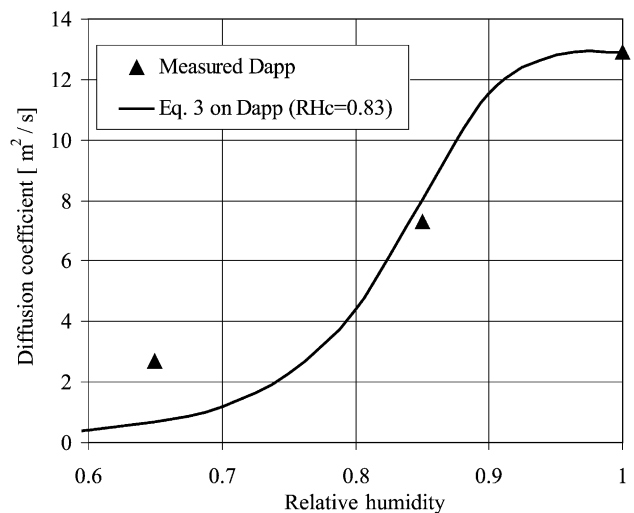


Fig. 4. Application of Eq. (3) on apparent diffusion coefficients, with RH_c selected in order to offer the best fit by the method of least sum of squares. The y-axis denotes the diffusion coefficient independent of type, and the x-axis denotes the relative humidity of the sample.

the measured profiles, supports the application of the approach.

By the proposed approach, the dependency of the diffusion coefficient on the degree of saturation can be estimated for any cementitious material if Powers' model for the phase composition in the paste is applicable for the cementitious materials used, and the degree of hydration can be determined.

5. Conclusion

An application of the composite theory on volume fractions of the microstructural phases estimated by Powers' model for deriving the dependency of the diffusion coefficients on the degree of saturation has been proposed. The approach is based on the assumption that diffusion in porous material is dependent on the moisture content. Initial experimental verification shows agreement between measured and simulated chloride profiles in mortar samples (rapid-hardening Portland cement, $w/c=0.5$) conditioned at 65% and 85% RH, and vacuum-saturated. The model takes into account the composition and degree of hydration of the actual cementitious material.

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