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A test method for measuring chloride diffusion coefficients through partially saturated concrete. Part II: The instantaneous plane source diffusion case with chloride binding consideration

Guillem de Vera [a], Miguel A. Climent [a,*], Estanislao Viqueira [a],
Carlos Antón [a], Carmen Andrade [b]

[a] Dept. d'Enginyeria de la Construcció, Obres Públiques i Infrastructura Urbana, Universitat d'Alacant, Ap. 99, 03080 Alacant/Alicante, Spain
[b] Instituto de Ciencias de la Construcción Eduardo Torroja, CSIC, C/ Serrano Galvache s/n, 28033 Madrid, Spain

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Abstract

A test method is proposed for measuring chloride diffusion coefficients through partially saturated concrete specimens with well characterized water contents. It includes an experimental procedure for supplying a limited amount of Cl^- to the tested concrete surface, and two mathematical models for processing the experimental Cl^- content profiles obtained at selected diffusion times. The use of the more refined model, taking into account the chloride binding by concrete, allows to increase the reliability of the determined diffusion coefficients. For the two tested Portland cement concretes, (water/cement ratios 0.6 and 0.5), the Cl^- diffusion coefficient decreases about two orders of magnitude, from $6 \cdot 10^{-12}$ to $2 \cdot 10^{-14}$ m^2/s, when the relative humidity of the atmosphere in equilibrium with concrete is lowered from 95% to 54% approximately.

Keywords: Chloride; Diffusion; Concrete; Humidity; Modeling

1. Introduction

One of the most important obstacles to the description of chloride ingress into concrete structures through diffusion equations is the habitual partial water saturation state of concrete in structures, as compared with concrete specimens tested in laboratory conditions [1]. Furthermore it has been expressed the interest in developing a permeability test which could be performed on unsaturated specimens [1]. Recently a new methodology has been described [2,3], which allows studying the influence of the degree of water saturation of concrete upon chloride diffusion, avoiding contributions of other mechanisms of Cl^- transport, such as capillary suction and permeation. In order to perform this study samples with controlled water contents were used, and an experimental setup was developed to allow one to supply an initial limited amount of Cl^- to the tested concrete surface, without disturbing the water content of the concrete. The procedure consists of subjecting the surface of the concrete specimens to the interaction with the products of combustion of PVC [4], which contain mainly gaseous hydrogen chloride. After returning the specimens to their controlled humidity exposure conditions, the kinetics of Cl^- diffusion from the surface inwards may be studied. Nielsen and Geiker [5] used an alternative experimental procedure for obtaining the initial Cl^- supply to the test surface, based on immersion during 2 h in a 26% mass NaCl solution followed by drying the surface with a hair drier (avoiding excessive heating) until the samples reached the weight prior to chloride exposure [5]. These authors applied this procedure to the study of the dependence of the Cl^- diffusion coefficient on the degree of saturation of a Portland cement mortar with a water/cement ratio of 0.5. Guimarães and Helene have also made research on diffusion of chloride ions through unsaturated cement paste [6] and mortar [7] specimens.

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[*] Corresponding author. Tel.: +34 96 5903707; fax: +34 96 5903678.
E-mail address: ma.climent@ua.es (M.A. Climent).

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The mathematical model used for the study of chloride diffusion on partially saturated concrete [2,3] was based on the particular solution of Fick's second law of diffusion corresponding to the case of an "instantaneous plane source" [8]. The fitting of the experimental Cl^- concentration profiles, obtained at selected diffusion times, to the abovementioned solution allowed the determination of an apparent diffusion coefficient since the Cl^- binding by solid phases of concrete was not considered. The objective of this work is to apply a more refined model, taking into account the effect of chloride binding by concrete, to the experimental data obtained in tests of Cl^- diffusion through non-saturated concrete, with diffusion times up to three years. The model is similar to that used previously by Sagüés and Kranc [9] to describe Cl^- transport through concrete in marine service, i.e. under a continuous Cl^- supply regime. In this work the model has been applied to experimental results obtained under different boundary conditions: the ionic diffusion takes place after an instantaneous limited Cl^- supply [2,3]. The chloride binding was considered in terms of a Langmuir's isotherm, as in Ref. [9]. The parameters of the isotherm were obtained experimentally on the base of data corresponding to acid-soluble and water-soluble chloride contents for a large number of samples obtained from the specimens under test. The experimental bound and free Cl^- concentrations of these samples were found to fit adequately to the mathematical expression of the Langmuir's isotherm. The mathematical model, which is detailed in the Appendix, incorporates the chloride binding isotherm within the diffusion differential equations, which are solved through an explicit finite difference method [10]. It must be taken into account that Fick's second law is a simplified approach for describing the diffusion of ionic species through electrolytes of high ionic strength. Several researchers [11–13] have used more refined models, considering ionic interactions, for the transport of ions through porous media.

Saetta et al. [14] modeled the chloride diffusion through partially saturated concrete. By considering the analogy that exists between chloride and water diffusion in unsaturated concrete, they proposed the following equation to describe the dependence of the diffusion coefficient D on the relative humidity of concrete:

$$D_{\mathrm{RH}} = \frac{D_{100\%}}{1 + \left(\frac{1-\mathrm{RH}}{1-\mathrm{RH_c}}\right)^4} \qquad (1)$$

This equation is similar to that used by Bazant for reproducing the phenomenon of water diffusion through unsaturated concrete [15]. Eq. (1) corresponds to an S-shaped curve function describing the non-linear increase of D with RH. It contains two parameters: $D_{100\%}$ is the chloride diffusion coefficient at 100% RH, and $\mathrm{RH_c}$ is the critical relative humidity at which the value of D is half of its corresponding value at 100% RH. When RH drops below $\mathrm{RH_c}$ the ion diffusivity shows a rough drop due to the loss of liquid connectivity inside the porous network. A value of $\mathrm{RH_c} = 75\%$ was proposed [14].

Martys [16] analysed numerically the dependence of diffusivity on the degree of saturation for porous media filled with binary mixtures of fluids of different wetting characteristics. The case of a mixture of a wetting fluid (i.e. water) and a non-wetting fluid (i.e. air) is of particular interest for the subject of this work. The phase separation of fluids was modelled by a lattice Boltzmann method, and the bulk electrical conductivity of each phase was calculated [16]. Finally the diffusivity was obtained by using the Einstein equation which establishes a direct relation between the diffusion coefficient and conductivity [17]. The calculated relative diffusivities, related to the full saturation state, can be described by a third order polynomial function for a significant range of wetting saturation degrees higher than a critical saturation S_c, which is interpreted as the minimum wetting fluid content necessary for the existence of a conducting connected path allowing the diffusion of ionic species. For an ideal model of a three dimensional bead pack of uniform size spheres S_c would be 1/3 [16].

2. Experimental

Cylindrical concrete specimens, 20 cm in height and 10 cm in diameter, were fabricated and cured during 28 days in a fog room. Two mixes, designated as H-25 and H-35 following Ref. [18], were studied. Their composition and characteristics, including water/cement ratios, are shown in Table 1. The porosities and bulk specific gravities (dry) were measured through the hydrostatic balance method [19]. The nature of the components of these concretes (cements, aggregates, water and additives) was as described previously [3].

The concrete water contents selected for this work have been those in equilibrium with atmospheres of relative humidity (RH) 54%, 75%, 86% and >95%. The specimens were preconditioned after curing and before exposure to the PVC combustion gases in the following ways: the specimens in equilibrium with an atmosphere of RH > 95% were kept in the curing chamber, while the specimens in equilibrium with atmospheres of 54%, 75% and 86% RH were subjected to a preconditioning procedure previously described [2,3]. In this procedure the specimens are partially dried in an oven at 50 °C and then kept, for at least 21 days before testing, in closed chambers at 20 °C containing a saturated solution that imposes the selected RH. The salts used were $Mg(NO_3)_2 \cdot 6H_2O$, NaCl, and KCl for 54%, 75% and 86% RH, respectively. The mass of

Table 1
Dosages and characteristics of the concretes tested

	Concrete	
	H-25	H-35
Dosage		
Cement (kg/m^3)	350.0	350.0
Sand (kg/m^3)	630.3	662.8
Gravel 4–6 mm (kg/m^3)	465.5	489.5
Gravel 6–12 mm (kg/m^3)	679.0	714.0
Plasticizer (kg/m^3)	–	1.4
Water/cement ratio	0.6	0.5
Mean compressive strength (MPa)	27.9	40.8
Porosity (%)	16.3	12.7
Bulk specific gravity, dry (g/cm^3)	2.23	2.31

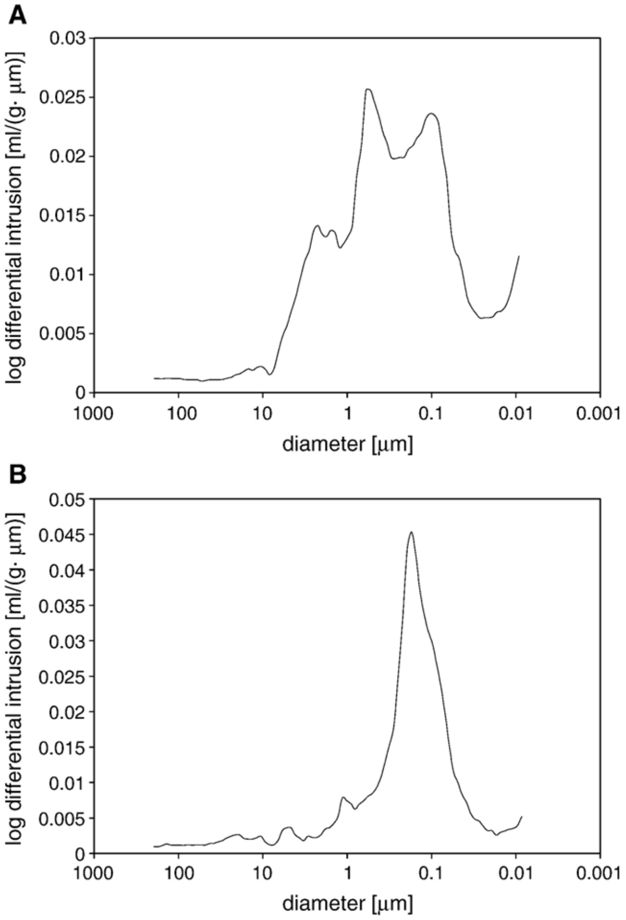

Fig. 1. Mercury porosimetry. A: H-25 concrete; B: H-35 concrete.

the specimens was measured periodically until mass constancy, which indicated the attainment of equilibrium between the concrete specimen and the selected RH atmosphere. The degree of water saturation of the specimens, S, was measured by weighing representative samples with their natural water contents, just after removing them from their controlled humidity enclosures, m_{h}, after saturating them with water, m_{s}, and after oven drying at 105 °C, m_{d}.

$$S=\frac{m_{\mathrm{h}}-m_{\mathrm{d}}}{m_{\mathrm{s}}-m_{\mathrm{d}}} \tag{2}$$

The mass change of the specimens after exposure to PVC combustion gases was always less than 0.1%. Thus, the exposure did not affect the water content of the specimens. After the exposure and during the diffusion period, the specimens were kept in their corresponding constant RH chambers. The electrical resistivity, ρ, was measured on representative specimens of the different concretes and atmospheres tested, as described previously [3].

The concrete specimens were subjected to interaction with PVC combustion gases after the preconditioning step, following a procedure previously described [4]. An airtight plastic chamber with a vitrified ceramic hot plate was used for the thermal decomposition of portions of pure PVC resin. In these experiments, only the mould bases of the cylindrical specimens were exposed, the remaining faces were protected with adhesive insulating tape. The quantity of PVC resin decomposed was adjusted to give a ratio between the mass of burnt PVC and the area of concrete surface exposed (PVC/S) of 40 and 10 mg PVC/cm^2 [4]. The duration of the exposure to PVC combustion gases was always 1 h, after which the specimens were removed, weighed, and returned to their controlled humidity exposure conditions.

A diffusion test program was run after exposure to PVC combustion gases. Specimens were stored in their corresponding RH chambers during 1, 3, 10, 20, 60 and 180 days and 1 and 3 years. After completion of these storage periods, the specimens were removed and immediately submitted to a grinding process, [20], to obtain powdered samples corresponding to thin successive parallel layers to the exposed surface of 1 or 2 mm thickness. The samples were analysed for obtaining their acid-soluble chloride contents by a potentiometric titration procedure [21,22]. The overall amount of Cl$^-$ laden in each concrete specimen was integrated from the measured concentration profile. A number of samples corresponding to some of the concrete specimens were analysed for obtaining their water-soluble chloride contents [23]. An experimental isotherm was obtained by calculating free and bound chloride concentrations from these data.

Pore size distributions of H-25 and H-35 concretes were determined by means of a mercury intrusion porosimeter (porosizer 9320 v2.05), assuming a contact angle of 141.3°, and a maximum pressure of $3\cdot10^4$ psia.

3. Results

The concretes under study were analysed by mercury intrusion porosimetry. Pore size distributions for concretes H-25 and H-35 are shown in Fig. 1A and B, respectively. H-35 pore size distribution shows a single and narrow peak at approximately 0.2 µm. H-25 has a broader distribution with three overlapping peaks at approximately 0.1, 0.5, and 2 µm. Thus, H-25 concrete has a higher proportion of large pores than H-35 concrete.

Fig. 2 shows the experimentally derived isotherm. Data from three concrete specimens, corresponding to tests with RH of >95%, 86%, and 75%, were plotted and fitted to the Langmuir isotherm:

$$C_{\mathrm{B}}=\frac{kC_{\mathrm{C}}C_{\mathrm{F}}}{1+kC_{\mathrm{F}}} \tag{3}$$

where C_{B} and C_{F} are bound and free chloride concentrations, respectively, and k and C_{C} are constants. Data fitting to this equation yielded the constants $C_{\mathrm{C}}=2.498$ kg/m^3 and $k=0.569$ m^3/kg, with a good correlation ($r=0.976$). This isotherm was used for the model through all calculations. Langmuir isotherms have been also found to apply for OPC pastes [24]. Tang and Nilsson [25] reported different kinds of isotherms for OPC pastes and mortars depending on free chloride concentration: Langmuir isotherm was found at low

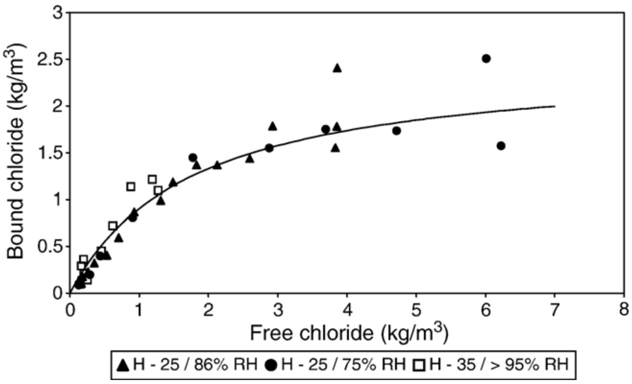

Fig. 2. Isotherm derived from experimental data. The three specimens were analysed after 180 days of diffusion time. Line shows the fitted Langmuir isotherm, see Eq. (3).

free chloride concentrations and Freundlich isotherm was applicable at higher free chloride concentrations. Tuutti [26] found a linear relationship between free and bound chloride at low concentrations. Sandberg [27] also observed a linear chloride binding isotherm in a study on field concrete. This linear relationship may be considered as a limiting case of a Langmuir isotherm, see Eq. (3). Sagüés and Kranc [9] studied theoretically the effect of binding and structural shape on chloride transport through saturated concrete, assuming constant surface chloride concentration. They assumed different Langmuir isotherms depending on exposure conditions. Isotherm constants values found in present work are in agreement with the "soft binding" case ($C_C = 5$ kg/m^3 and $k = 0.6$ m^3/kg) considered by Sagüés and Kranc. It is interesting to note that the same behaviour is observed for all data. Binding capacity seems to be independent of the water saturation degree, at least for these two concretes, and for the RH range tested.

Chloride transport through non-saturated concrete was studied previously without binding consideration [3]. Table 2 shows the results of the application of the non-binding diffusional model incorporating also data corresponding to 3 years diffusion time. The ratio m/m_{ex} in Table 2 (fifth column) is the quotient between the chloride absorption (mg/cm^2) calculated from curve fitting (m) and the experimental chloride absorption (m_{ex}) derived from experimental profile integration. This parameter is used as a guidance to assess the validity of the application of the diffusional model to each case [3]. Data corresponding to cases where the quotient m/m_{ex} is in the range 0.90–1.10 are used to calculate the estimated (mean) apparent diffusion coefficient (seventh column in Table 2).

Fig. 3 shows total, free and bound chloride profiles of some selected specimens. The experimental isotherm has been used to calculate free and bound chloride profiles from the experimental

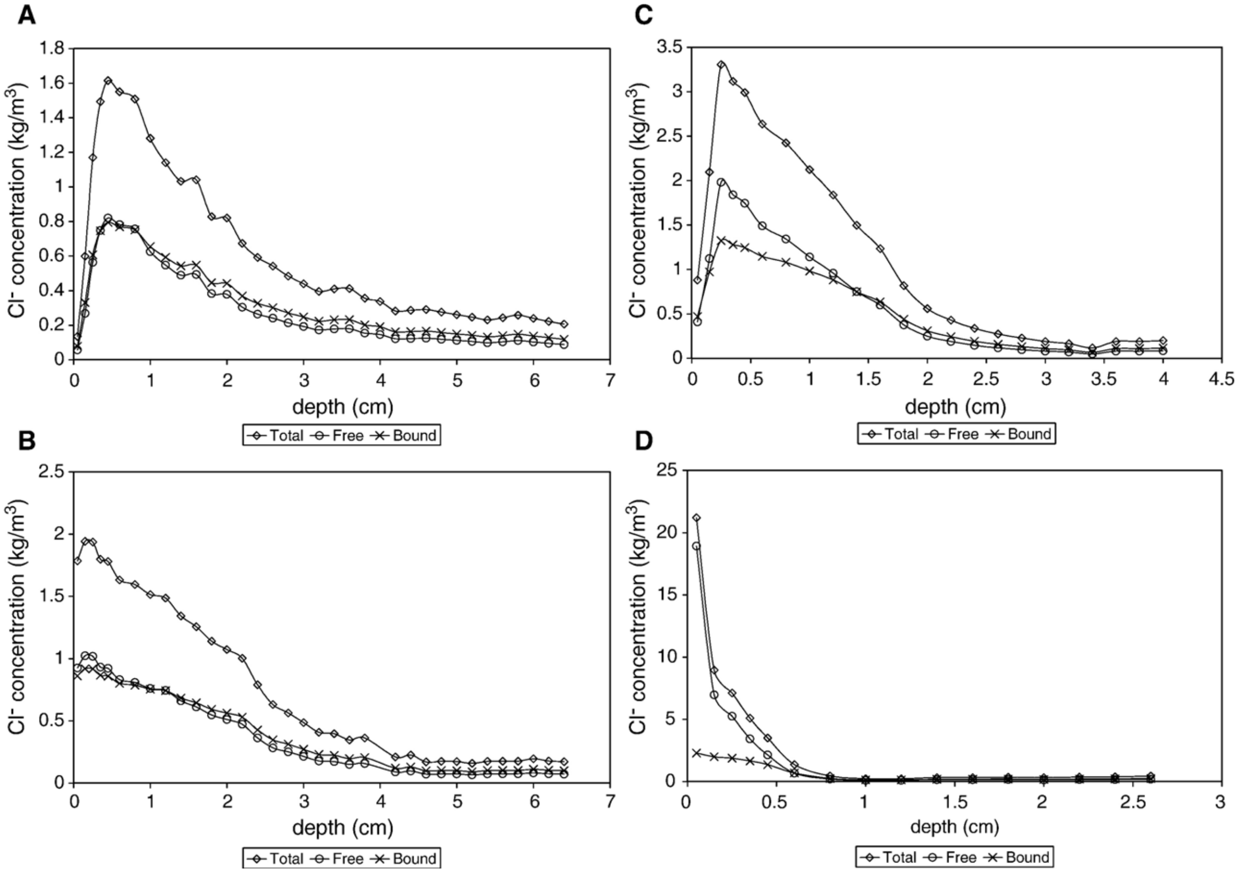

Fig. 3. Experimental total chloride profiles of some samples. Free and bound chloride profiles are also shown according to experimentally derived Langmuir isotherm (see text for details). Concrete, RH and diffusion time are as follows: A: H-35, >95%, and 1 year; B: H-25, 86%, and 3 years; C: H-25, 75%, and 3 years; D: H-25, 54%, and 3 years.

Table 2
Diffusion coefficients obtained without binding consideration

Concrete/ (PVC/S) ratio (mg/cm^2)	Atmosphere RH (%)	Diffusion time (days)	Diffusion coefficient D_{ap} (m^2/s) · 10^{-12}	m/m_{ex}	Linear regression correlation coefficient r	Estimated diffusion coefficient (m^2/s) · 10^{-12}
H-25/40	>95	60	2.89	1.07	0.960	
H-25/40	>95	180	3.73	1.03	0.973	3.85
H-25/40	>95	365	4.93	1.08	0.998	
H-25/40	86	60	3.08	0.99	0.997	
H-25/40	86	180	2.07	1.08	0.974	2.21
H-25/40	86	381	2.25	1.00	0.997	
H-25/40	86	1095	1.44	1.02	0.990	
H-25/40	75	20	1.53	0.90	0.996	
H-25/40	75	60	1.17	0.92	0.987	
H-25/40	75	180	0.67	0.99	0.999	1.01
H-25/40	75	365	0.65	1.08	0.986	
H-25/40	75	1095	0.51	1.12	0.998	
H-25/40	54	180	0.077	0.90	0.989	0.057
H-25/40	54	1095	0.037	0.92	0.988	
H-35/40	>95	10	7.99	0.97	0.991	
H-35/40	>95	20	8.61	1.06	0.998	
H-35/40	>95	60	4.44	1.00	0.947	6.05
H-35/40	>95	180	3.17	1.06	0.999	
H-35/40	54	365	0.071	0.90	0.988	0.054
H-35/40	54	1095	0.037	0.98	0.999	
H-25/10	>95	180	4.00	1.05	0.961	4.00

total chloride profiles. Profiles corresponding to the four RH and two concretes tested are shown in Fig. 3. It can be seen that when total chloride concentration is low, i.e. lower than 2 kg/m^3 approximately, free and bound chloride concentrations are very similar, being free chloride concentration slightly lower than bound chloride concentration (see Fig. 3A and B). At higher total chloride concentration, free chloride concentration is higher than bound chloride concentration (Fig. 3C, depth lower than 1.5 cm). At chloride concentrations higher than 5 kg/m^3 bound chloride concentration attains its saturation value C_C, see Eq. (3) and Fig. 3D at depth lower than 0.5 cm. In Fig. 3D it can be seen that chloride penetration depth is very low at the lowest RH of 54%, even at 3 years diffusion time. Some profiles (Fig. 3A and C) show a maximum at approximately 0.5 cm depth. In such cases surface chloride concentration is low, reaching values lower than 0.2 kg/m^3 in Fig. 3A. The presence of maxima in the profiles was previously described and possible explanations were suggested, see Ref. [3]. It is worth noting that Nielsen and Geiker [5] also observed maxima in their experimental Cl$^-$ profiles corresponding to partially saturated mortar cement.

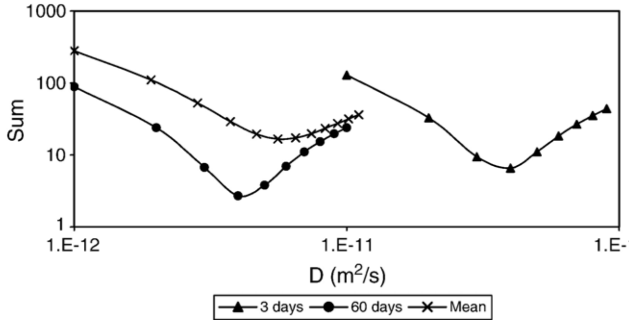

Fig. 4. Sum of the square of the differences between calculated and experimental chloride profiles for some specimens. Legend shows diffusion times. All cases are concrete H-25 with >95% RH. Mean value has been calculated regarding experimental profiles corresponding to 60, 180 and 365 diffusion time days. See text for details.

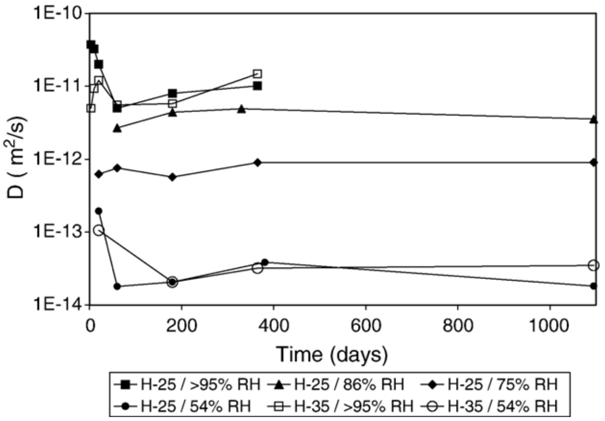

Fig. 5. Diffusion coefficients obtained for each specimen with the model considering chloride binding.

Fig. 4 illustrates the application of the least squares method used for obtaining the value of D for each set of experimental conditions, see Appendix. For each diffusion time and each set of experimental conditions, (RH, type of concrete), a series of chloride content profiles were calculated through the finite difference method, starting with the known initial profile (that corresponding to one day of diffusion). In these series the value of D was systematically varied in order to find the value which gives the best matching between the calculated profile and the experimental profile corresponding to that diffusion time. The sums of the squares of the differences between calculated and experimental profiles have been plotted as a function of the value taken for the diffusion coefficient (Fig. 4). The best values for D are obtained by locating the minima in the curves of Fig. 4. The estimated values of D obtained in this way for each specimen are plotted in Fig. 5, against the diffusion time. Some preliminary results, corresponding to diffusion times up to 1 year, have been presented before [28].

Table 3
Estimated diffusion coefficients obtained by fitting experimental chloride profiles to the proposed diffusional models with and without chloride binding consideration (see text for details)

Concrete	RH (%)	D (m^2/s) · 10^{-12}	
		With binding (D)	Without binding (D_{ap})
H-25	>95	5.86	3.85
	86	3.45	2.21
	75	0.74	1.01
	54	0.03	0.06
H-35	>95	6.55	6.05
	54	0.03	0.05

The fitting method illustrated in Fig. 4 can be used also to obtain a mean value of D for a series of specimens with the same experimental conditions but different diffusion times; 60, 180, 365 and 1095 days were regarded in this case. The sum of the differences between the four experimental profiles and the four calculated ones is minimised to obtain the mean value of D. These values are shown in third column of Table 3. Diffusion coefficients calculated for the same experimental conditions but without binding consideration (see Table 2) are also shown in Table 3 (fourth column) for comparison.

4. Discussion

4.1. Effect of binding consideration on the values of the derived diffusion coefficients

Table 2 shows chloride apparent diffusion coefficients obtained by using the non-binding model [2,3]. Some extra experimental data points have been added to the previously treated profiles corresponding to one year diffusion time. This was done because during the first part of the research [3], not all the obtained concrete dust samples could be analysed due to budget limitations. No significant difference in the diffusion coefficients is observed when these extended chloride profiles are considered. Data fittings show good correlations, yielding high correlation coefficients and m/m_{ex} ratios close to unity. Apparent diffusion coefficients obtained for 3 years diffusion time and RH ≥ 75% are in accordance with earlier data [3], i.e. D_{ap} initially decreases with time and then it attains an approximately constant value for diffusion times longer than 60 days. This D_{ap} evolution with time was previously reported to be slower in an atmosphere of 54% RH [3]. Apparent diffusion coefficients obtained at 3 years diffusion time and 54% RH are lower than those obtained at shorter times and same RH. D_{ap} evolution with time seems to be still important at 3 years diffusion time in a 54% RH atmosphere.

The values of diffusion coefficients obtained with binding consideration also show a variation with time, as can be appreciated in Fig. 5. Diffusion coefficients vary during the first 60 days of diffusion time and then D attains an approximately constant value. However, variations are lower when chloride binding is taken into account, showing a better agreement between theoretical model and experimental results in this case. An explanation of the initial time dependence of D has been previously proposed [2,3], though not proved, assuming the coexistence of two chloride transport mechanisms. The presence of a quick transport mechanism acting only during short periods after sample exposure to PVC combustion gases would lead to an unexpectedly high chloride concentration at relatively high depths into concrete. Fitting experimental data to the model in such conditions would yield an unexpectedly high diffusion coefficient. Diffusion of gaseous hydrogen chloride through non-saturated concrete after PVC combustion gases exposure could be responsible of such quick initial transport mechanism. Nevertheless other explanations for the observed evolution of D with time cannot be ruled out. For instance this evolution can be due to modifications of the microstructures of the tested concretes during the long diffusion periods used in this work, as a consequence of the progress of cement hydration.

Because D variation with time is only transient and probably due to side effects, see Fig. 5, it is more representative for chloride transport characterization to consider only the final constant diffusion coefficient value. Mean values of D for $t \geq 60$ days, calculated as explained in previous section, are shown in Table 3. D_{ap} values without binding consideration are also shown for comparison. D values for RH > 75% are slightly higher than D_{ap} values. The delaying effect of binding on transport is seen as a higher D value when chloride binding is taken into account. Nevertheless, the differences between the results obtained with both models are very small. This can be explained by the "soft binding" character of the isotherm. A different behaviour is observed for RH = 54%: the diffusion coefficient values are about two times lower when chloride binding is taken into account. For RH = 75% D is slightly lower than D_{ap}. These unexpected latter facts may be explained by considering the different mathematical approaches of both models used in this work, and assuming again the hypothesis of a quick initial transport, acting only during short time after the exposure to PVC combustion gases. The mathematical treatment inherent to the model that considers binding, takes the Cl^- profile at one day of diffusion as the initial condition for starting the finite difference calculations. This situation obviates, at least partially, the interference of such quick initial transport on the calculation of the diffusion coefficient. On the other hand the calculations performed with the former model [2,3], without binding consideration, are fully affected by the abovementioned interference, since only the final Cl^- profile is treated in these calculations. These mathematical conditions can lead to lower values for the diffusion coefficients calculated through the binding model, as compared with those obtained for D_{ap} with the non-binding model, mainly at the lowest RH of 54%. For concrete in equilibrium with this latter low RH, chloride transport is very slow [2,3], because the connectivity of

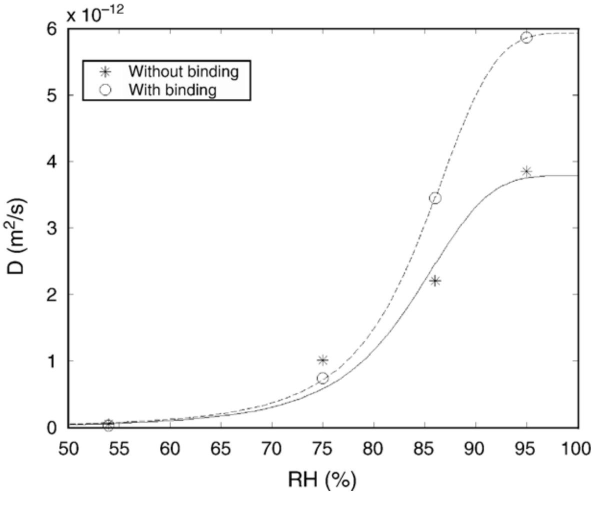

Fig. 6. Relationship between the obtained Cl^- diffusion coefficients for H-25 concrete with and without binding consideration and the relative humidity of the atmosphere. Lines show non-linear curve fittings to Eq. (1).

Table 4
Fitting parameters of H-25 chloride diffusion coefficients to Eq. (1), with and without binding consideration

	Without binding (D_{ap})	With binding (D)
$D_{100\%}$ (10^{-12} m^2/s)	3.79	5.88
RH$_c$ (%)	83.1	84.8
σ (10^{-12} m^2/s)	0.23	0.04

See text for details.

the liquid phase inside the concrete pore network drops sharply for environmental RH lower than 70% [29–31]. This would explain, in principle, why the interference of the hypothetical quick initial transport is more important at the lowest RH, leading to lower calculated values for D than those obtained for D_{ap}.

4.2. Dependence of the chloride diffusion coefficient on the hygric parameters

Data corresponding to H-25 concrete, (Table 3) have been fitted to Eq. (1). The best fit curves are shown in Fig. 6, while the fitting parameters are collected in Table 4. The fitting has been performed without binding consideration (second column in Table 4, and solid line in Fig. 6), and with binding consideration (third column in Table 4, and dashed line in Fig. 6). Both cases show good correlation, yielding low values of the mean quadratic deviation σ (Table 4) defined as:

$$\sigma = \sqrt{\frac{\sum(D_{exp}-D_{calc})^2}{\text{degrees of freedom}}} \tag{4}$$

The results of this work point to a sharp decrease of chloride diffusion rate below approximately 85% RH, for H-25 concrete. It is interesting to note that the calculated critical values of relative humidity, RH$_c$, (Table 4), fall in with the value found by Nielsen and Geiker [5] for partially saturated cement mortars (83%); and are in fairly good agreement with the value proposed by Saetta et al. [14]. The experimental dependence of D on RH, shown in Fig. 6, is also in accordance with that predicted by Nilsson [31].

It is also interesting to study the variation of the ionic diffusivity with the water saturation state of concrete. Fig. 7 shows the strong dependences of the Cl$^-$ diffusion coefficient and the electrical resistivity of concrete on the degree of water saturation. Electrical resistivity data for H-25 concrete specimens have been fitted to a potential function of the saturation degree, S, see Fig. 7 dashed line. The best fit (r=0.992), has been obtained with Eq. (5):

$$\rho = 10.744\ S^{-5.6603} \tag{5}$$

This demonstrates the validity of the semi-empirical Archie's second law [16,32] for H-25 concrete, at least within the range of water saturation degrees tested.

The variation of D within the degree of water saturation range tested for H-25 concrete, is of two orders of magnitude approximately, see Fig. 7. This variation is not high in the range of saturations between 0.7 and 0.45, having obtained values between $6\cdot10^{-12}$ and $1\cdot10^{-12}$ m^2/s approximately, see also Table 3. For lower degrees of water saturation the decrease of D becomes very important, and values as low as $2\cdot10^{-14}$ m^2/s may be reached for a saturation of 0.33. The latter value of D may be considered as a practically negligible value of the Cl$^-$ diffusion coefficient, and indicative of a very slow diffusion rate. For the sake of comparison, reference values of D for a typical bridge deck concrete [33] and for a high performance concrete [33] may be $2.5\cdot10^{-12}$ m^2/s and $3.3\cdot10^{-13}$ m^2/s, respectively. If we consider the habitual error function solution of Fick's second law for unidirectional diffusion, with constant D, the time for reaching a certain threshold Cl$^-$ concentration at a given depth is inversely proportional to the value of D. This means that the time for corrosion initiation with a $D=2\cdot10^{-14}$ m^2/s, would be two orders of magnitude higher than that corresponding to diffusion through a typical good bridge deck concrete.

Martys considered the existence of a critical saturation S_c, corresponding to the minimum liquid content necessary for the existence of a connected path allowing the diffusion of ionic species through a porous material [16]. The results of this work do not allow for an accurate determination of such S_c. Nevertheless the considerations of the precedent paragraph allow us to suggest that a saturation of 0.33 may be considered as a lower bound value of S_c for H-25 concrete. It is worth noting that this value of the critical saturation falls in with that suggested for an ideal model of a three dimensional bead pack of uniform size spheres [16]. Diffusion coefficient data of Fig. 7, corresponding to H-25 specimens, have been fitted to several simple mathematical functions, (potential, polynomial), of the water saturation degree, S, as defined in Eq. (2). The best fit, (r=0.995), shown as a solid line in Fig. 7, has been obtained with the polynomial function:

$$D = 7.791\cdot10^{-13} - 1.189\cdot10^{-11}S + 2.837\ 10^{-11}S^2 \tag{6}$$

Where D is expressed in m^2/s. This equation is empiric and is intended to describe only the variation of chloride diffusion

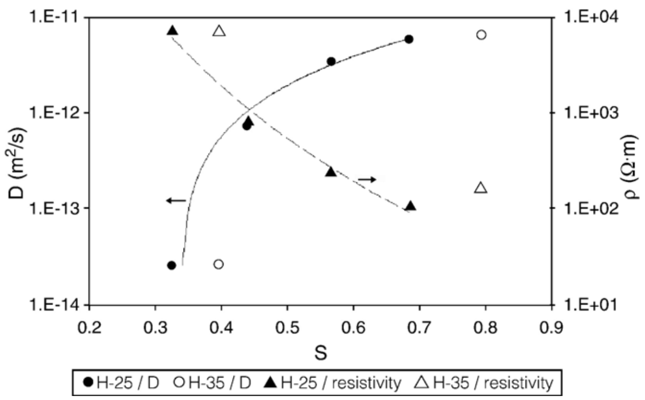

Fig. 7. Variations of the obtained Cl$^-$ diffusion coefficient (with binding consideration) and concrete resistivity with the degree of water saturation of H-25 and H-35 specimens. Lines show fittings of H-25 data, see Eqs. (5) and (6).

coefficient for concrete H-25 within the range of degree of water saturation between 0.33 and 0.69. Nevertheless, it may be considered in agreement with the type of relation proposed by Martys between D and the water saturation degree [16].

Approximately similar D values are obtained when H-25 and H-35 concretes are considered, under the same RH, see Table 3. Since H-35 concrete has a higher degree of water saturation than H-25 at the same RH, D values for H-35 seem to be lower than those of H-25, for the same degree of water saturation, see Fig. 7. This can be adequately explained by the lower porosity and more refined pore network of H-35 concrete as compared with H-25 concrete, see Table 1 and Fig. 1. Following the considerations of the precedent paragraphs a value of 0.40 may be suggested as a lower bound value of S_c for H-35 concrete. It must be taken into account that the number of data corresponding to H-35 in Fig. 7 do not allow for an adequate description of the dependence of D on the degree of saturation of this concrete.

Several authors have proposed the use of the Nernst–Einstein equation for estimating the ionic diffusivity through saturated concrete, by measurements of electrical conductivity or resistivity of concrete [34–38]. Another application of this equation leads to the direct relationship between the diffusion coefficient and electrical conductivity used for calculating relative diffusivities, related to the full saturation state, for partially saturated porous media [16,17]. Fig. 8 shows the experimental relationship found between the measured chloride diffusion coefficient, D, and the electrical concrete resistivity for partially saturated H-25 specimens. These data have been fitted to a potential function. The best fit, ($r=0.992$), shown as a solid line in Fig. 8, has been obtained with the following equation:

$$D = 3.978 \cdot 10^{-9} \cdot \rho^{-1.320} \tag{7}$$

Where D is expressed in m^2/s and ρ in Ω m. The fitting parameters of Eq. (7) are only slightly different to those obtained by fitting data obtained with diffusion times up to 1 year [28]. A similar relationship between D_{ap} and ρ was found for non-saturated concrete, when the previous model, without binding consideration, was used [3]; although the exponent found for resistivity in this work (−1.320) is lower to that found without binding consideration (−0.9997). A careful observation of Fig. 7 shows that the separation from the pure inverse relationship between D and ρ, evidenced by the value of the exponent in Eq. (7), is due to the data corresponding to low S (0.33). A fitting of only the three leftmost data pairs of Fig. 8 (dashed line), i.e. those corresponding to $S>0.4$, yields the following expression: $D=8.467\rho^{-1.035}$. These facts may be considered a demonstration of the applicability of the Einstein relation [16,17], for estimating relative ionic diffusivities of partially saturated H-25 concrete specimens at water saturation degrees higher than 0.4. At lower saturations it seems that Einstein's relation breaks down as percolation effects become important [16]. This last preliminary interpretation needs more data to be adequately confirmed.

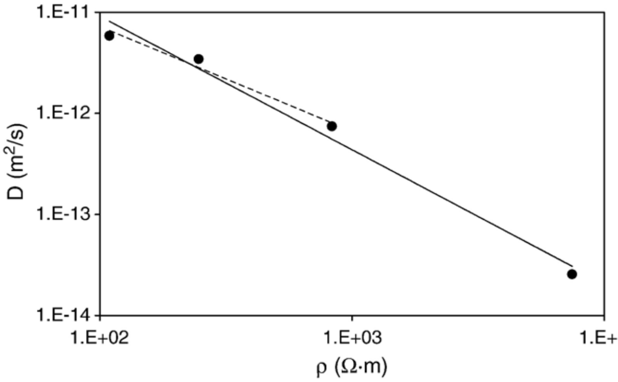

Fig. 8. Relationship between the obtained Cl^- diffusion coefficients (with binding consideration) and the resistivity of the H-25 specimens tested. Solid line shows fitted curve with all data, see Eq. (7). Dashed line shows fitted curve with only the three leftmost data pairs, see text for details.

The use of a more refined mathematical model taking into account the chloride binding, allows one to obtain more reliable values for the Cl^- diffusion coefficients through partially saturated concrete, as compared with those obtained with a previous model not considering the binding [2,3]. A clear improvement due to the use of the refined model is a decrease of the dependence of D values on diffusion time, mainly for specimens in equilibrium with low humidity atmospheres. A feature of the binding model is the higher complexity of the differential equations describing simultaneously the diffusion and the binding of Cl^- ions, which leads to the need of using numerical methods for the calculations. A more simple analytical solution is available for the non-binding model [2,3]. The experimental dependence found for the determined D values on the hygric parameters may be considered in agreement with the predictions of the authors that have studied theoretically and numerically the phenomenon of ionic diffusion through partially saturated concrete [14,16,31]. This fact gives some degree of support to the suitability of the experimental procedure and mathematical model used in this work for obtaining D under partial water saturation conditions. Nevertheless, more research is needed to confirm these results and to obtain new data corresponding to different concrete compositions.

5. Conclusions

The influence of the degree of water saturation of concrete upon chloride diffusivity may be studied by using an experimental procedure allowing to supply a limited amount of Cl^- to the surface of concrete specimens with well characterized water contents. The use of a refined diffusional model, taking into account the chloride binding by concrete, allows to increase the reliability of the determined diffusion coefficients.

For the two tested Portland cement concretes, (water/cement ratios 0.6 and 0.5), D values decrease about two orders of magnitude, from $6 \cdot 10^{-12}$ m^2/s to $2 \cdot 10^{-14}$ m^2/s approximately, when the degree of water saturation is lowered from values of 0.7–0.8 to values of 0.3–0.4. These latter values of water saturation, corresponding to an equilibrium atmosphere of 54%

RH, may be considered as lower bound values for the minimum water content necessary for the existence of a connected path allowing ionic diffusion.

Einstein's relation may be used for assessing adequately the diffusion properties of ions through partially saturated concretes, by measuring the conductivity or resistivity of concrete. Nevertheless, this relation may break down at low saturation degrees, as percolation effects become important.

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Appendix A. Mathematical modelization

The model is based on the following assumptions:

1. A planar semi-infinite diffusion takes place through a concrete with uniform porosity and uniform water saturation degree.
2. Unity activity coefficients are assumed for all species in pore solution.
3. Chlorides can be found in two states: free chloride, which is solved in pore solution, and bound chloride, which is bound to concrete solid phases.
4. Only free chloride can diffuse through the concrete pore solution. The flux is proportional to the concentration gradient, being the diffusion coefficient D the proportionality constant.
5. Binding processes of chlorides to solid phases are fast compared with chloride diffusion, so they can be described by an isotherm. The isotherm expresses the bound chloride concentration C_B as a function of free chloride concentration C_F. Both concentrations are given as kg of chloride per m^3 of sample.
6. No other transport mechanism was taken into account.

From a differential mass balance, the following equation is obtained:

$$\frac{\partial C_T}{\partial t} = \nabla \cdot (D \nabla C_F) \tag{8}$$

In this equation C_T is the total chloride concentration ($C_T = C_B + C_F$), D is the chloride diffusion coefficient, $\nabla\cdot$ is the differential operator divergence, and ∇ is the differential operator gradient. In order to solve Eq. (8) a relationship between C_T and C_F is needed. This relationship can be written as [9]:

$$\nabla C_F = \frac{\nabla C_T}{1 + \partial C_B / \partial C_F} \tag{9}$$

Thus, Eq. (8) becomes:

$$\frac{\partial C_T}{\partial t} = \nabla \cdot [D_{ap}(C_T) \nabla C_T] \tag{10}$$

Here $D_{ap}(C_T)$ is defined as:

$$D_{ap}(C_T) = \frac{D}{1 + \partial C_B / \partial C_F} \tag{11}$$

It is worth noting that $D_{ap}(C_T)$ in Eq. (10) can be regarded as an apparent diffusion coefficient. Eq. (10) is similar to Fick's second law, but in Eq. (10) the diffusion coefficient D_{ap} is a function of total chloride concentration C_T instead of being a constant. This difference arises from the binding processes between chlorides and concrete solid phases, as shown in Eq. (11).

Regarding a one-dimensional diffusion, one obtains from Eq. (10):

$$\frac{\partial C_T}{\partial t} = D'_{ap}(C_T) \left(\frac{\partial C_T}{\partial x} \right)^2 + D_{ap}(C_T) \frac{\partial^2 C_T}{\partial x^2} \tag{12}$$

$D'_{ap}(C_T)$ has been defined as:

$$D'_{ap}(C_T) = \frac{\partial D_{ap}(C_T)}{\partial C_T} \tag{13}$$

The variable x is depth from the exposed concrete surface. Eq. (12) must be solved with the appropriate initial and boundary conditions in order to describe chloride transport through a concrete that can bind chloride according to isotherm $C_B = C_B(C_F)$.

Depending on the isotherm considered different expressions for D_{ap} and D'_{ap} are obtained. Langmuir's isotherm has been considered in this work. It is given by Eq. (3). Here k and C_C are constants. C_C is the saturation value, i.e. the maximum bound chloride concentration available. It is achieved only at high free chloride concentration ($kC_F >> 1$). Substituting Langmuir's isotherm (3) into Eqs. (11) and (13), appropriate expressions are obtained for D_{ap} and D'_{ap}:

$$D_{ap}(C_T) = \frac{D \cdot A^2}{A^2 + 4kC_C} \tag{14}$$

$$D'_{ap}(C_T) = \frac{8Dk^2 C_C A^3 [1 + B + k(C_T - C_C)]}{B(A^3 + 4kC_C)^2} \tag{15}$$

$$A = 1 + k(C_T - C_C) + B \quad ; \quad B = \sqrt{[1 - k(C_T - C_C)]^2 + 4kC_T} \tag{16}$$

A and B have been introduced only to simplify writing in Eqs. (14) and (15).

The following three boundary conditions were applied to solve differential Eq. (12):

1. The initial total chloride concentration profile is known. The experimental total chloride concentration profile at one day of diffusion after the initial chloride supply was taken as the

initial chloride profile for the model. This condition can be written for $t=0$ as:

$$C_{\mathrm{T}}(x,t)=f(x) \tag{17}$$

Where $f(x)$ is a known function. In our case $f(x)$ is given by the experimental profile after one day diffusion time, i. e. $f(x)= C_{\mathrm{exp}}(x,\ t=1$ day).

2. Total chloride concentration far away from the exposed surface remains constant. This is equivalent to assume that specimen length is larger than chloride penetration depth during the experiment. This constant chloride concentration (C_∞) is due to concrete raw materials which have a low but detectable chloride content. This condition can be written as:

$$\lim_{x\to\infty} C_{\mathrm{T}}(x,t)=C_\infty \tag{18}$$

3. Total chloride content in the specimen remains constant during the experiment. An initial amount of chloride is supplied to the specimen during PVC combustion gases exposure. After the exposure this amount is not modified. This condition can be written as:

$$\int_0^\infty C_{\mathrm{T}}(x,t)\mathrm{d}x=\mathrm{const} \tag{19}$$

The solution of differential Eq. (12) with boundary conditions (17), (18) and (19) allows one to describe the diffusion process coupled with binding, if the diffusion coefficient D and the parameters of the isotherm (k and C_{C}) are known. In this work we have used Eq. (12) in a different way to obtain the best estimated values of D. For each set of experimental conditions (RH, type of concrete, diffusion time), a series of chloride profiles were calculated through the finite difference method, starting the calculations with the known initial profile (that corresponding to one day of diffusion). In these series the value of D was systematically varied within a selected range of values. For each D value a calculated profile was obtained and compared with the experimental profile corresponding to the relevant conditions. The best estimated value of D is obtained through a least squares method, as that giving the minimum sum of the squares of the differences between the calculated and the experimental profiles, see Section 3 (Results). Thus, the input data needed for the calculations are: the binding isotherm parameters, the initial Cl^- profile (at 1 day) and the profile corresponding to the relevant diffusion time and experimental conditions. All these inputs are derived from experimental results. The outputs of the calculations are the diffusion coefficients corresponding to partial saturation states of the concretes under study.

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