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Determination of chloride diffusivity through partially saturated Portland cement concrete by a simplified procedure

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ABSTRACT

A recently proposed methodology for measuring the diffusion coefficient of chloride ions through concrete partially saturated with water, has been applied to five high-early-strength Portland cement mortars. The method is based on putting solid NaCl in contact with the concrete surface during the diffusion test. The results obtained indicate a strong dependence of the diffusion coefficient on the water saturation degree. The ionic diffusivities through these mortars are higher than those obtained with the same approach for five pozzolanic cement mortars of similar compositions. It has been also shown that the proposed test methodology and a different one based on the interaction of HCl(g) with the tested concrete surface, can yield comparable results. The *D* values obtained are of similar magnitude, and the same type of dependence on the water saturation degree is found through both methods, when applied to similar Portland cement concrete mixes with cement content of about 350 kg/m^3 and water/cement ratios between 0.5 and 0.6.

1. Introduction

It is known that chloride content and penetration depth into concrete are highly dependent on microclimatic conditions, including the relative humidity at the material surface [1]. The amount of pore water in concrete can greatly affect field performance and the transport properties of test specimens [2,3]. Ions can only diffuse through the liquid phase contained in the pore network of concrete. This means that ionic diffusion is more efficient through saturated pores, while it is more restricted through those only partially filled with water [4,5]. When the water content of concrete decreases, the diffusion process is hindered by the decrease of the number of porous channels, which have a continuity of pore solution [6], this implies a lengthening of the ionic diffusion pathways. Another contribution to the decrease of the ionic diffusion coefficients can be the rise of the interaction forces between cement paste and ions due to the decrease of the thickness of the adsorbed water layers [6,7].

Some studies have been dedicated to the theoretical and numerical analysis of ionic diffusion through partially saturated concrete [8,9], and several works have been done on modelling the chloride ingress into these partially saturated concretes [6,10–15]. These latter works need to include into the mathematical models the dependence of the chloride (Cl$^-$) diffusion coefficient with the moisture content of concrete, or with the relative humidity of the atmosphere in equilibrium with concrete. Nevertheless, only recently some test procedures have been proposed for experimentally determining the diffusivity of Cl$^-$ ions through unsaturated concrete, due to the difficulty of maintaining the water saturation degree of concrete during the test. Climent et al. [16–19] proposed a test method based on an instantaneous deposition of Cl$^-$ due to interaction of the concrete surface with gaseous HCl produced in PVC combustion. The boundary conditions inherent to this methodology imply that the Cl$^-$ content profiles derived from the tests must be adjusted to a particular solution of Fick's second law of diffusion [16,17]. Guimarães and Helene [20–24] developed a simplified testing procedure in which solid NaCl is put in contact with the concrete surface during the diffusion test. The Cl$^-$ content profiles derived from these tests must be adjusted to the habitual error-function solution of Fick's second law of diffusion [23]. Nielsen and Geiker [25] obtained an initial Cl$^-$ supply to the concrete surface by a temporal immersion in a concentrated NaCl solution, followed by a drying until recovering the initial mass of the specimens.

The objective of the present work is to obtain more data with the simplified procedure based on the interaction of the concrete surface with solid NaCl [20–24], and to compare these results with those obtained from experiments based on an instantaneous HCl deposition on the tested concrete surface [16–19]. This comparison

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would allow to check if both methodologies are able to yield similar results, in order to advance towards a proposal of an optimised test method for measuring ionic diffusion coefficients through partially saturated cementitious materials.

2. Experimental

2.1. Materials

The concretes tested were prepared using a high-early-strength and sulphate resistant cement, type CP V RS, according to Brazilian standards [26,27]. This cement had a content of fly ash of 12% by mass. Table 1 shows the composition and characteristics of the cement. The fine and coarse aggregates used were a quartzite sand with a 4.8 mm maximum size, and a granite gravel with a 19 mm maximum size, respectively. Tap water was used for all these mixes, without adding any plasticizer.

Five concrete mixes (H1–H5) were selected for this work. These mixes were designed to obtain medium compressive strengths at 28 days, (30–45 MPa), and using water/cement (w/c) ratios between 0.48 and 0.66, cement contents between approximately 300 kg/m^3 and 420 kg/m^3, and aggregate/cement mass ratios in the range 4–6. Table 2 shows the compositions of the mixes, and Table 3 shows some measured properties of the concretes in the fresh state (slump), and hardened state (bulk densities and mean compressive strengths both at 28 and 60 days). It can be appreciated from Tables 2 and 3 that the series H2, H1, H3 increases consistently both the w/c ratio from 0.48 to 0.66 and the aggregate/cement ratio from 4 to 6, while the cement content is decreased from 419 kg/m^3 to 297 kg/m^3. These latter three mixes had all equal slump values of about 10 cm. On the other hand, for series H4, H1, H5 the aggregate/cement ratio increases consistently from 4 to 6 and the cement content is decreased from 416 kg/m^3 to 304 kg/m^3, while keeping the w/c ratio constant at an approximate value of 0.55. These latter compositional conditions raised very different slump values in this series, ranging from 22.5 cm for H4 to 1.8 cm for H5, due to the absence of plasticizer. Mix H1 was common to both series. All five mixes had the same value (52%) for the mortar content, i.e., the ratio (cement + fine aggregate)/(total solids).

Due to experimental restrictions related with the size of the diffusion test specimens, (see next section), after casting the compressive strength specimens, the fresh mixes were sieved through a 9.5 mm sieve, in order to remove the large coarse aggregates. The sieved mortars were used for casting the specimens for diffusion and mercury intrusion porosimetry (MIP) tests.

Table 1
Composition (mass percentages) and characteristics of the cement (mean values).

CaO	52.4
SiO_2	23.3
Al_2O_3	7.2
Fe_2O_3	3.3
MgO	5.9
K_2O	1.06
Na_2O	0.07
SO_3	3.3
CO_2	2.2
Ignition loss	3.3
Insoluble residue	12.8
Specific mass (g/cm^3)	2.99
Fineness Blaine (cm^2/g)	5026
Setting start (h)	3:56
Setting final (h)	5:07
Mortar compressive strength @ 28 days (MPa)	48.0

Table 2
Composition of concrete mixes.

Concrete	Dosage (cement:fine agg.:coarse agg.)	Cement content (kg/m^3)	Water/cement ratio	Aggregate/cement ratio
H1	1:2.12:2.88	355	0.55	5
H2	1:1.60:2.40	419	0.48	4
H3	1:2.64:3.36	297	0.66	6
H4	1:1.60:2.40	416	0.55	4
H5	1:2.64:3.36	304	0.57	6
H-25[a]	1:1.80:3.27	350	0.60	5.1
H-35[a]	1:1.89:3.44	350	0.50	5.3

[a] Data corresponding to concretes tested in Ref. [17].

Table 3
Properties of concretes.

Concrete	Slump (cm)	Bulk density (kg/m^3)	Compressive strength (MPa)	
			@ 28 days	@ 60 days
H1	9.5	2220	39.2	46.3
H2	10.0	2205	42.5	50.1
H3	9.5	2170	29.4	37.2
H4	22.5	2160	35.7	47.9
H5	1.8	2250	36.3	45.6

2.2. Preparation and conditioning of diffusion specimens

The procedures used for the conditioning and the diffusion tests are based on previous publications [20–24]. For each concrete mix 50 cylindrical specimens, 50 mm in height and 30 mm in diameter, were cast using the corresponding sieved mortar. These specimens were demoulded after 24 h, and cured for 28 days in a wet chamber. After curing, the specimens were kept under laboratory environment until reaching 150 days age from casting. At this age six mortar specimens corresponding to each mix were tested for obtaining their bulk densities, water absorptions in immersion after boiling and dry masses [28]. All these data are necessary for calculating and controlling the water saturation degrees of the diffusion test specimens.

At 165 days age, and for each mix, four groups of six mortar specimens were formed choosing specimens randomly. Each group corresponds to one of the following water saturation degrees: 50%, 75%, 90% and 100%. The specimens were stabilised at their corresponding saturation state either by drying in an oven at 50 °C [2,17], or by wetting with distilled water until getting the adequate mass. The water saturation degree of the concrete specimens is defined in this work according to the following equation:

$$SD = 100\frac{m_{SD} - m_{dry}}{m_{dry}} \cdot \frac{100}{A} \tag{1}$$

where SD is the water saturation degree in %, m_{SD} is the mass in grams of the specimen for the target SD, m_{dry} is the mass in grams of the dry specimen, and A is the water absorption, in %, after immersion and boiling [28].

After getting the target SD, the specimens were allowed to equilibrate and homogenize their moisture content during a minimum of a month in the following conditions: the non-saturated specimens were isolated with three plastic layers perfectly closed by heating, and extracting as much air as possible; the saturated specimens were stored in a desiccator partially immersed in a saturated $Ca(OH)_2$ solution. The part of the specimens penetrated by chlorides during the diffusion tests remained above the liquid level.

2.3. Chloride diffusion tests

The chloride source in this methodology is ground solid NaCl (passing number 100 sieve) deposited at 199 days age (from casting) onto the surface test, which was always the lower (mould) surface of the cylindrical mortar specimens. For the non-saturated specimens the deposited NaCl was protected with water-proof tape, and the specimens were again closed with three plastic layers. For the saturated specimens a pool of plastic tube was attached to the top, and the solid NaCl was deposited within the pool, in order to avoid the falling of a chloride solution over the lateral surface of the mortar cylinders, due to water condensation at the top during the diffusion experiment, Fig. 1.

The diffusion times for these tests were chosen according to previous experiences [20–24], and were set at: 7 days, 16 days, 21 days and 130 days, for the 100%, 90%, 75% and 50% SD, respectively. After completion of these periods the remaining NaCl at the top of the specimens was removed, and the surface cleaned with compressed air. Immediately, the specimens were submitted to a grinding process with a lathe, in order to obtain powdered concrete samples corresponding to thin successive parallel layers to the exposed surface of 2 mm thickness, up to a depth of 12 mm. This latter maximum depth was chosen according to previous experience [20–24], showing that an adequately developed Cl^- content profile can be obtained in these conditions for the diffusion times used in this work.

The powdered samples corresponding to a single depth step for the six specimens in each group, (same mortar and SD), were mixed in order to obtain an adequate concrete sample for the Cl^- analysis, which was carried out by potentiometric titration [29]. All chloride concentrations in this work are expressed as% Cl^- relative to total mass. The results allowed to obtain representative Cl^- content profiles of each mortar and SD value. Two samples of each mortar, were subjected to mercury intrusion porosimetry (MIP) tests at 240 days age, with a Micromeritics Autopore IV 9500 equipment.

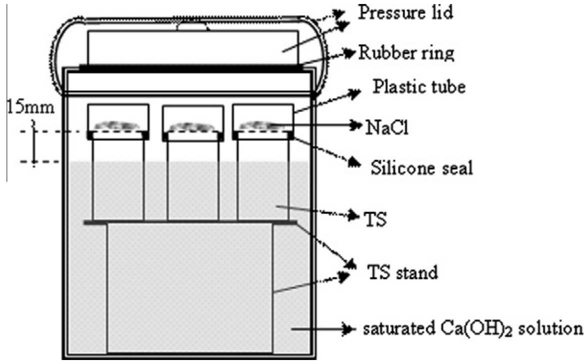

Fig. 1. Test specimens (TS) during diffusion experiments in saturated conditions.

3. Results and discussion

3.1. Analysis of the chloride content profiles and derivation of the diffusion parameters

The measured chloride content profiles obtained for H1 mortar are shown in Fig. 2. The Cl^- profiles for the rest of the mortars, and their variations with *SD* are qualitatively similar to those shown in Fig. 2, but they are not shown here for the sake of conciseness. It is apparent from these profiles that chloride ions have penetrated considerably for *SD* values equal or higher than 75%, while for 50% *SD* the ingress of Cl^- is practically negligible. This indicates that most probably for a moisture content of 50%, and for the materials tested in this work, there is no continuous water way through the pore network of the mortars, thus preventing significantly ionic diffusion. The maximum Cl^- penetrations are obtained for the *SD* value of 90%, while for saturated specimens the chloride concentrations at each depth are lower than those corresponding to 75% and 90% *SD*, see Fig. 2. This is due to the short duration of the diffusion tests for the saturated specimens (7 days), as compared with the 16 days and 21 days duration of the tests for *SD* values of 90% and 75%, respectively.

All the experimental Cl^- profiles have been fitted to the habitual error-function solution of Fick's second law of diffusion [30]:

$$C(x,t) = C_S\, erfc\left(\frac{x}{2\sqrt{Dt}}\right) \tag{2}$$

where *C* is the chloride concentration (% Cl^- relative to total mass), *x* is depth, *t* is time, and the fitted parameters are *D* (diffusion coefficient) and C_S (surface concentration). In applying Eq. (2) it is assumed that the diffusion coefficient and the surface concentration have constant values. The results of the fittings are shown in Table 4. Good correlation coefficients, higher than 0.95, are obtained for all the cases.

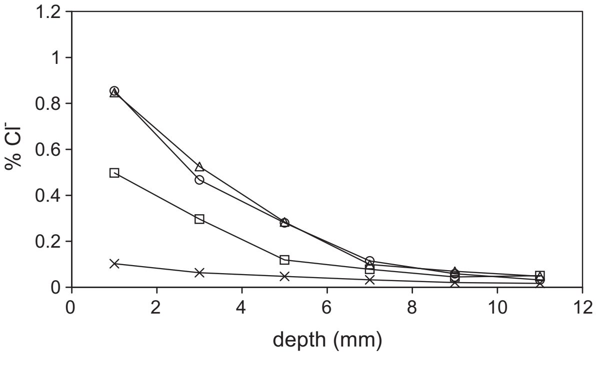

Fig. 2. Experimental chloride profiles for mortar H1 and water saturation degrees of approximately: 50% (cross), 75% (circle), 90% (triangle), and saturated (square).

It is appreciable from Table 4 that *D* values increase steadily with the water saturation degree, reaching their maximum values at saturation. On the other hand, the calculated C_S values are maximum for the 90% *SD* and are a little bit lower for the saturated states. This latter fact can also be attributed to the short duration of the diffusion tests for the saturated specimens.

3.2. Dependence of the diffusion coefficients on the water saturation degree

Data of diffusion coefficients against saturation degree for H mortars in Table 4 have been fitted, as suggested previously [8,17], to polynomial equations of the form:

$$D = a \cdot SD^2 + b \cdot SD + c \tag{3}$$

where *SD* is the saturation degree in percentage and *D* is the diffusion coefficient in m^2/s. Fitted parameters *a*, *b*, and *c*, and correlation coefficient for each mortar are shown in Table 5. Good correlation coefficients, higher than 0.96, are obtained for all cases. The fitting parameters of Table 5 are valid only for the materials studied in this work and in the range $44\% \leqslant SD \leqslant 100\%$.

Fig. 3 shows the dependences of the Cl^- diffusion coefficients with the water saturation degree for the five mixes tested in this work (H1–H5) and for five similar families of mortars (P1–P5) prepared with a pozzolanic cement [31] and tested in a previous work [24]. It is apparent from Fig. 3 that H mortars show higher *D* values than the corresponding P mortars for the whole range of *SD* tested. Data in Fig. 3 indicate, in agreement with previous results [17,22,25], strong dependences of *D* with *SD*: for the high-early-strength Portland cement mortars (H) *D* values are reduced approximately one order of magnitude when the *SD* is decreased

Table 4
Results of data fitting to Eq. (2).

Mortar	*SD* (%)	*D* (10^{-12} m^2/s)	C_S (%)	*r*
H1	100.0	13.39	0.603	0.9923
	91.6	7.52	1.026	0.9981
	75.0	5.36	1.021	0.9975
	47.1	2.00	0.110	0.9870
H2	100.0	9.13	0.637	0.9880
	90.8	6.69	1.248	0.9836
	76.2	3.35	1.025	0.9951
	47.0	1.55	0.045	0.9899
H3	100.0	14.50	0.658	0.9991
	88.7	14.31	1.016	0.9849
	75.5	14.16	0.876	0.9949
	44.1	2.58	0.035	0.9585
H4	100.0	12.26	0.758	0.9993
	91.1	11.37	1.293	0.9954
	78.1	11.19	0.963	0.9978
	47.0	2.49	0.046	0.9747
H5	100.0	13.84	0.643	0.9991
	92.3	11.86	0.878	0.9968
	76.1	8.48	0.768	0.9974
	47.1	5.18	0.031	0.9552

Table 5
Results of data fitting to Eq. (3).

Mortar	*a*	*b*	*c*	*r*
H1	4.4669×10^{-15}	-4.624×10^{-13}	1.402×10^{-11}	0.968
H2	3.342×10^{-15}	-3.464×10^{-13}	1.044×10^{-11}	0.999
H3	-5.995×10^{-15}	1.072×10^{-12}	-3.296×10^{-11}	0.997
H4	-4.075×10^{-15}	7.770×10^{-13}	-2.498×10^{-11}	0.995
H5	2.087×10^{-15}	-1.432×10^{-13}	7.296×10^{-12}	1.000

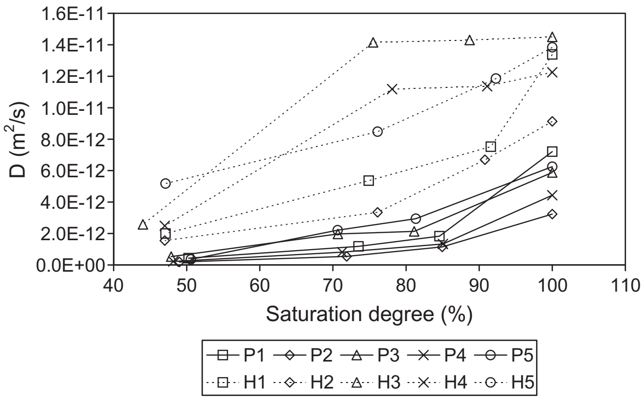

Fig. 3. Dependences of the measured chloride diffusion coefficients with the water saturation degree, for the mixes tested in this work (H1–H5), and for a similar family of mixes prepared with a pozzolanic cement (P1–P5) [24].

from 100% to 50%, while the reduction is not as high for the pozzolanic cement mortars (P). It is also worth pointing out that for some of the H mixes, especially H3 and H4, *D* values decrease only slightly in the range of *SD* between 100% and 75%, while for the rest of H mortars and all P mixes the diffusion coefficient is strongly reduced in the same *SD* range. All these facts can be attributed to the different porous microstructures of mortars H and P, as it will be discussed later.

3.3. Dependence of the diffusion coefficients on concrete microstructure and characteristics

MIP measurements were performed on duplicate samples of each one of the mortars tested. Fig. 4 presents plots of the logarithmic differential intrusion volume vs. pore size, for only some of the samples, since all H mortar samples show qualitatively similar porosity distributions: a main peak at mean pore diameters between 57 nm and 84 nm, while the porosity contributions for pore diameters higher than 200 nm are variable for the different H mortars. Total porosities derived from MIP measurements are reported in Table 6, while Fig. 5 shows the quantitative distributions, expressed as percentages relative to the total pore volume, for three pore diameter ranges: diameters lower than 50 nm (this range includes the gel pores and the finest capillary pores); diameters between 50 and 200 nm (corresponds to the mid-range capillary porosity); and diameters higher than 200 nm (larger capillary and coarse pores) [32]. Fig. 5 also includes, for the sake of comparison, the percentage porosity distributions corresponding to the pozzolanic cement mortars (P).

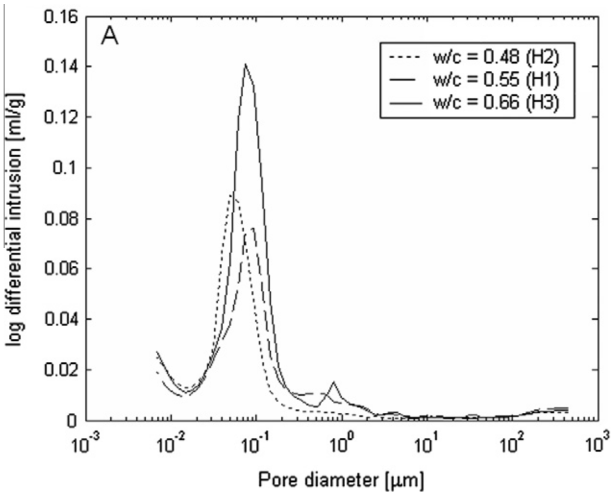

Fig. 4. Log differential intrusion curves of H1, H2 and H3 mortars.

Table 6
Total porosities of mortars, measured by MIP.

Mix	H1	H2	H3	H4	H5
Porosity (%)	12.35	12.20	17.36	13.22	14.81

It has been analyzed if the proposed methodology is able to discriminate the ionic diffusion properties of concretes of different quality or composition. If it is considered only the mortar series H2, H1, H3, the obtained *D* values increase consistently with the increasing values of w/c ratio for the whole range of *SD* tested, as shown in Table 4 and Fig. 3. This is as expected, since many previous results have indicated that a reduction in w/c ratio leads to a significant reduction in diffusivity [33–35]. On the other hand, the mortar series H4, H1, H5, which increases the aggregate/cement ratio and decreases the cement content, while keeping the same w/c ratio, does not show a systematic ranking of the *D* values of these three mortars. H4 and H5 mortars are those introducing more variability in the ranking of *D* values for this series, as it may be appreciated in Table 4 and Fig. 3. It is worth noting also that the ranking of H concretes according to their compressive strengths is different at 28 days and 60 days, (see Table 3), and this variability is due to H4 concrete. It seems that H4 concrete and mortar show some intrinsic variability in properties, which can be attributed, in principle, to the high slump of H4 concrete (22.5 cm), which could eventually lead to some segregation, for instance in case of using compaction energies higher than necessary. Conversely, H5 mix may have suffered some difficulty in compaction, so introducing some heterogeneity, due to its low workability (1.8 cm slump in Table 3).

A more clear explanation of the rankings of diffusivities for H mortars can be obtained by analyzing their microstructural properties. Figs. 4 and 5 show that H2 mortar has a more refined porous network, with higher proportion of pores of low diameter and lower total porosity (Table 6), than the rest of H mortars, as a consequence of having the lowest w/c ratio (0.48). Fig. 5 indicates that the rest of H mortars show more similar pore diameter distributions. For the pore range diameters between 50 nm and 200 nm (mid-range capillary porosity) the percentage porosities (referred to total pore volume) are 45.9%, 50.4%, 58.3%, 60.1% and 63.0%, for the H2, H1, H4, H5 and H3 mortars, respectively. These values show the same ranking as that of total porosities in Table 6, and that corresponding to *D* values at 90% *SD* (Fig. 3). It may be concluded that Cl^- diffusion coefficients at partial water saturation states are related to the microstructural properties of H mortars, especially the total porosity and the percentage of porosity corresponding to mid-range capillary pores.

The comparison of pore size distributions of H and P mortars in Fig. 5 allows to understand the different ionic diffusion properties, at the whole *SD* range tested, of both mortar series. P mortars show always higher percentages of porosity falling in the pore diameter range below 50 nm (gel and smallest capillary pores) than H mortars. Conversely, H mortars show always higher percentages of porosity falling in the pore diameter ranges between 50 nm and 200 nm (mid-range capillaries), and higher than 200 nm (large capillaries and coarse pores), than P mortars. The more refined porous network of P mortars accounts for the systematically lower *D* values of these mixes, as compared with H mortars in Fig. 3. Only H2 mortar, whose porosity distribution is more close to those of P mortars, shows diffusion coefficients slightly higher than the corresponding values for P mortars.

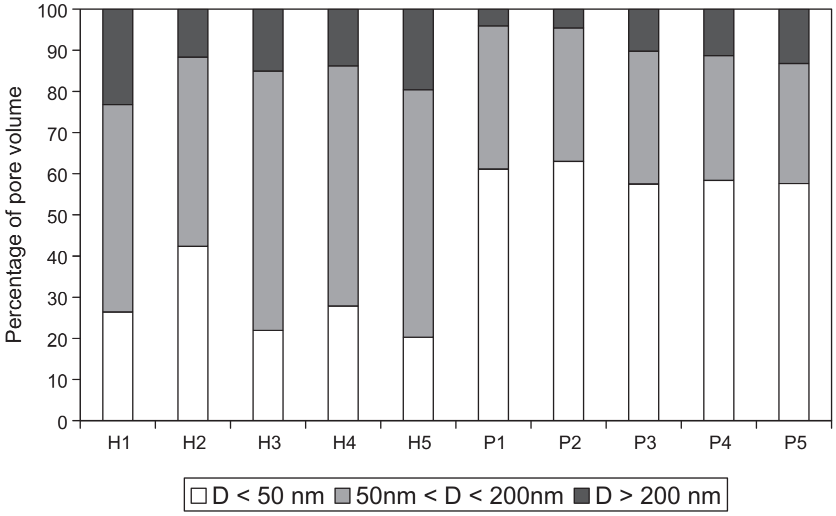

Fig. 5. Pore size distributions, expressed as percentages relative to the total pore volume, corresponding to three pore diameter ranges, see text for details. The data correspond to the mortars tested in this work (H1–H5), and to a similar family of mortars prepared with a pozzolanic cement (P1–P5) [24].

3.4. Comparison of D values with those obtained through an alternative method

The results reported in this work can be compared with those obtained for the Cl^- diffusion coefficient, at partial water saturation states, through an instantaneous HCl(g) deposition on the tested concrete surface [16,17]. The boundary conditions in these latter diffusion tests are different from those of this work, due to the different experimental procedures, and hence the solution of Fick's second law is given by Eq. (4) instead of Eq. (2). The Cl^- profiles in Refs. [16,17] were fitted to the following expression:

$$C(x,t) = \frac{m}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right) \tag{4}$$

The fitted parameters are diffusion coefficient D (m²/s) and total chloride deposited m (kg/m²) which remain constant during the test [16,17]. In these latter works two concretes (H-25 and H-35) were tested, whose mean compressive strengths at 28 days were 27.9 MPa and 40.8 MPa, respectively [17]. The details of composition of these mixes, also included in Table 2, indicate that their characteristics are rather similar to those of mix H1 in this work. Fig. 6, plotting together the obtained D values vs. saturation degrees, indicates that the three data sets (H1, H-25 and H-35) show a similar dependence with the water saturation degree, which can be fitted to the following polynomial function (solid line in Fig. 6):

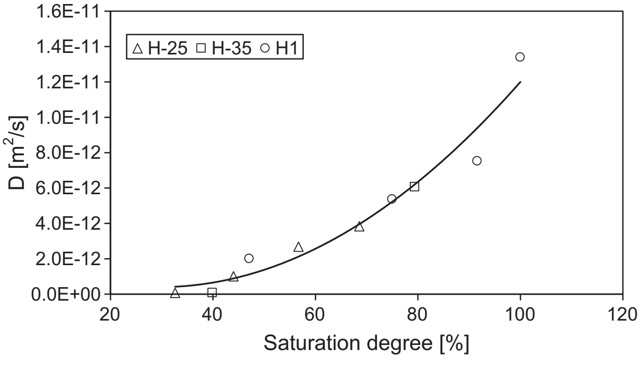

Fig. 6. Comparison of chloride diffusion coefficients at different water saturation degrees. The data correspond to different types of samples, see text for details, and were obtained using two different methodologies: H-25, and H-35 data come from Ref. [17], while H1 data correspond to this work.

$$D = 2.336 \times 10^{-15}\ SD^2 - 1.380 \times 10^{-13}\ SD + 2.437 \times 10^{-12}\quad r = 0.976 \tag{5}$$

where D is expressed in m²/s and SD in %. It is worth to recall that the experimental methodology of Refs. [16,17] is different to that used in this work. Furthermore, the specimens tested in these latter references were concrete samples, while those of this work are mortar samples sieved from concretes. Nevertheless, the good agreement found in Fig. 6 seems to indicate that both approaches yield comparable results.

The methodology used in this work has some appealing characteristics: the experimental setup and procedure are simpler than those corresponding to the gaseous HCl deposition on the concrete surface [16–19]; and the source of chloride ions is NaCl, which is the chemical species mainly acting in marine or de-icing salt environments to which concrete may be exposed. On the other hand, some drawbacks of this approach must be also considered: the boundary condition of constant surface Cl^- concentration seems to be not rigorously fulfilled during the tests, if one consider the variation of C_S values (Table 4) and the different development of the Cl^- content profiles for different durations of the diffusion tests (Fig. 2). Another fact to be taken into account is the almost negligible amount of ingressed Cl^- for low SD of about 50% (Fig. 2). The scarce development of the Cl^- profiles at low saturation degrees, with very low concentrations at all depths, is likely to lower the reliability of the D values derived from such profiles. Further research is in progress to compare chloride diffusion coefficients obtained through both abovementioned approaches, using the same concrete samples and the same conditioning procedures previous to diffusion tests, in order to confirm the concordance of results.

4. Conclusions

It is possible to obtain experimental values for the Cl^- diffusion coefficients through concrete, at water saturation degrees between 50% and 100%, using a simplified methodology based on putting solid NaCl in contact with the concrete surface during the diffusion test.

The results obtained for five high-early-strength Portland cement mortars indicate a strong dependence of D with SD. The ionic diffusivities through these mortars are higher than those obtained with the same approach for five pozzolanic cement mortars of similar compositions. This latter difference of properties and the rankings of *D* values of the mortars tested in this work, can be related to differences in the microstructural properties of the mortars, mainly their total porosity and pore size distributions.

It has been shown that the proposed test methodology and a different one based on the interaction of HCl(g) with the tested concrete surface, can yield comparable results, i.e., *D* values of similar magnitude and the same type of dependence on the water saturation degree, when applied to similar Portland cement concrete mixes with cement content of about 350 kg/m^3 and water/cement ratios between 0.5 and 0.6.

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