Diffusion of Chloride Ions in Unsaturated Concrete: Forecast of Service Life in a Wet-Dry Environment

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Synopsis: In recent years, extensive research on the influence of the saturation degree (SD) on the diffusion of chloride ions has demonstrated the importance of including this factor in models used to forecast the service life of reinforced concrete structures. The current study aims to propose changes to the test method devised by GUIMARÃES (3) in order to allow analyses under unsteady-state flow conditions in the form of Fick's Second Law and then assess the actual influence of the SD of concrete on the diffusion of chloride ions. The results obtained confirm that the SD is a major factor of influence on the diffusion of chloride ions. The curve proposed to account for the influence of the SD on the diffusion of chloride ions showed good accuracy when used as a model of service life applied to a reinforced concrete structure in a maritime pier with 22 years of use.

Keywords: chloride; concrete; diffusion; durability; saturation degree; transport properties

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INTRODUCTION

In recent years, extensive research on the influence of the saturation degree (SD) on the diffusion of chloride ions has demonstrated the importance of including this factor in models used to forecast the service life of reinforced concrete structures (2, 3, 4, 5).

GUIMARÃES (3) produced a model of the influence of the SD on the diffusion of chloride ions and investigated its application in the microenvironment of an existing structure by comparing the results yielded by the model with the chloride profile measured in the structure. It was seen that the model's accuracy is improved when the influence of the SD of the concrete is accounted for. The model comprehends a variation of the SD from approximately 55% to 100%, with test specimens prepared using high initial strength cement and w/c ratio of 0.5;

The study by GUIMARÃES (3) highlights that the influence of the SD was obtained under steady-state flow conditions in the form of Fick's First Law.
The current study aims to propose changes to the original test method devised by GUIMARÃES (3) in order to allow analyses under unsteady-flow conditions in the form of Fick's Second Law.

MODEL OF THE INFLUENCE OF SD ON THE DIFFUSION OF CHLORIDE IONS

GUIMARÃES and HELENE (6) developed a model showing the influence of the SD of the hardened cement paste (w/c = 0.5) on chloride diffusion. In this study, an SD of 100% is meant to represent the amount of water absorbed in relation to the dry mass of the test specimen after immersion and boiling according to ASTM C 642-90.

The results of this model are presented in Fig. 1, where results are represented by an exponential equation showing the zone where a variation of SD values is possible. The ratios between the highest diffusion coefficient (SD = 100%) and the other values is 0.09 for an SD of 57%, 0.28 for an SD of 75% and 0.32 for and SD of 90%. These ratios show very marked differences, and indicate that the SD of concrete is a factor that should be taken into account in analyses of ion diffusion. A steady-state flow of chloride ions was assumed when determining the diffusion coefficients in this study (6).

The following considerations are an attempt at describing a possible mechanism to explain the influence of the SD on the diffusion of chloride ions in the hardened cement paste (6):

- In the saturated hardened cement paste (SD = 100%) (Fig. 2) all pores with sizes above the critical diameter are filled with water, thus facilitating ion diffusion. The cross-section of these pores is the cross-section where the ions undergo diffusion;

- According to MEHTA and MANMOHAN (7) the number of pores above the critical diameter accounts for approximately 15% of the voids in cement pastes with a w/c ratio of 0.5. Thus, a reduction of the SD from 100% to 85% would produce a more dramatic reduction in the water content in the pore network with sizes above the critical diameter (Fig. 2) and the cross-section of ion diffusion falls sharply between the points where the SD = 100% and the SD = 90%, as Fig. 1 shows. The critical diameter for the paste with a w/c ratio of 0.5 is approximately 80nm (8), and condensation in pores of this size happens when RH exceeds 95% (8). Therefore, if RH falls below 95%, these pores tend to be filled with water vapor. A water layer with a thickness of approximately 0.2nm, 0.45nm and 0.9nm for RH values of 10%, 50% and 90%, respectively, becomes adsorbed in the pore walls (9). Thus, when the pore size exceeds the critical diameter, water condensation is reduced and only a thin layer of adsorbed water remains. When the SD falls to approximately 85%, all the interconnected pore network (pore diameter > critical diameter) holds only adsorbed water (Fig. 2). As a result, the cross-section of ion diffusion is greatly reduced. In this case, ions also have to travel greater distances because they have to bypass pores rather than go through them. When the thickness of the water layer is small (≤ 0.9nm) it is to be expected that precipitates such as $Ca(OH)_2$ will act as barriers and block the passage of chloride ions, which measure 0.36nm across;

- For SDs below 85 %, the diffusion coefficient is expected to fall less dramatically. This probably happens because the process of water loss begins in pores whose diameter is smaller than the critical diameter, which do not affect mass transport significantly. It is estimated that this occurs up to the moment when the thickness of the adsorbed water layer on the walls of those pores above the critical diameter starts to decrease, as Fig. 1 shows between SD=90% and SD=75%;

- The diffusion coefficient should again fall sharply (Fig. 1, between SD=75% and SD=57%) when the thickness of the water layer adsorbed on the walls of those pores above the critical diameter begins to decrease (Fig. 2).

When the pore distribution curve in the cement paste (7) is compared with the results of the test of influence of the moisture content in chloride diffusion in the cement paste, it becomes clear that the process above shows high likelihood of occurring. The inflection in the pore distribution curve in the paste with a w/c ratio of 0.6 is observed when the pores are filled with mercury to approximately 15% (pore volume above the critical diameter), which is equivalent to a SD of 85% (Fig. 1, between the points where the SD=75% and the SD=90%).

The method developed in the research by GUIMARÃES and HELENE (6) was validated only for quantitative analyses in the form of Fick's First Law. Therefore, it was necessary to make changes to this method to allow qualitative analyses in the form of Fick's Second Law. In this way, the main process of chloride ion penetration can be addressed, that is, chloride diffusion under unsteady-state flow conditions.

A MODEL FOR UNSTEADY-STATE FLOW

The method developed to allow analyses under unsteady-state flow is described below.

Materials

Thirty cylindrical test specimens measuring 30 mm x 45 mm were cast using a mortar with a w/c ratio of 0.5. The cement/aggregate ratio was 1:3 and the aggregate was quartz sand in four equal fractions: 0.15-0.3, 0.3-0.6, 0.6-1.2 and 1.2-2.4 mm. Pozzolanic cement and distilled water were used.

The test specimens were demolded after 24 hours and kept in wet cure in a saturated solution of calcium hydroxide in distilled water for 30 days.

Experimental program

After 20 days (test specimens 50 days old), 6 test specimens were selected at random for the test of absorption by immersion after boiling and bulk specific gravity, dry according to ASTM C 642-90 [10]. Mean values of 9.60% for absorption and 2122 kg/m^3 for bulk specific gravity, dry were found. The mean mass of the test specimens (69.8g) was also recorded to control the SD.

The remaining test specimens were allowed to dry in the laboratory environment for 11 additional days. After that, they were divided randomly into groups with 6 test specimens each and stabilized with SDs of approximately 55%, 75%, 90% and 100%. To obtain the SDs of 55%, 75% and 90%, test specimens were dried in an oven at 50°C or wetted with distilled water to reach the amount of water needed each SD, as shown by the following equation:

$SD = ((M_{SD} - M_{dry}) / M_{dry}) / A_{max}) . 100$ where (1)

SD – saturation degree (%);
M_{SD} – mass of test specimen for the predicted SD (g);
M_{dry} – mass of dry test specimen (g);
A_{max} - absorption by immersion after boiling (%), according to ASTM C 642-90 (10).

At this period (61 days), the groups of unsaturated test specimens were sealed in two plastic bags (the 6 test specimens were placed inside a sealed bag and this bag was placed inside another sealed bag). Vacuum was applied to remove the air from inside the bags. The group of saturated test specimens was partly submerged in a saturated calcium hydroxide solution to a depth of 30mm in a sealed container to prevent water from evaporating from the section of the test specimens above the level of the solution. This way, the flow of water inside the mortar is interrupted. The test specimens remained in this condition until they reached the contamination age specified for each SD group. This was done in order to ensure a uniform moisture content was maintained during the test and facilitate chloride diffusion.

Previous tests showed that in test specimens with a SD of 100%, the chloride profile allowed the diffusion coefficient to be measured after seven days. If shorter or longer periods were used, these profiles would be poorly defined. Conversely, unsaturated test specimens required longer periods to provide a good chloride profile. Therefore, in order to obtain better-defined profiles the groups of test specimens were contaminated at different times in the test. The test specimens of the four SD groups were contaminated on different dates but sliced on the same date so that different contamination times resulted. The test specimens of the group with an SD of approximately 55% were contaminated after 81 days, those with SDs of approximately 75% and 90% were contaminated after 98 days and the group with an SD of 100% was contaminated after 108 days.

The contamination was made on the bottom surface of the test specimen (using the position of the test specimen in the mold as a reference) with NaCl that was ground until it passed a #100 sieve. This ground sodium chloride dissolves more quickly and quickly reaches a nearly stable concentration of chlorides on the surface of the test specimen. The amount of chloride was so high that at the end of the test chlorides had visibly precipitated on the top surface of the test specimens, proof that this source of contamination had not been exhausted.

During the development of the test method used in the current study, profiles of short-time chloride concentrations compared with the total time of the experiment were made. The chloride concentration on the surface of test specimens (Cs) obtained by regression of these short-time curves shows that values close to the maximum concentration are reached after a very short time. For this reason, the chloride content on the surface of the test specimens was assumed as constant during the contamination stage.

To make sure the contaminant would not be removed from the surface of the test specimen, a protective film was put in place using waterproof tape. An observation window using transparent film was used to observe the contamination behavior during the test (Fig. 3a). The test specimens were then sealed again inside two plastic bags and vacuum was applied. The group of saturated test specimens was contaminated in the same way as the others and the partly submerged (Fig. 3b).

All test specimens were sliced after 115 days. The mean contamination times were 2.9754×10^6 s, 1.5039×10^6s, 1.4931×10^6s and 0.5898×10^6s for the groups with SDs of approximately 55%, 75%, 90% and 100% respectively.

After slicing, acid-soluble chloride content in the test specimens was determined according to ASTM C 1152-90 (1). All test specimens were sliced to a depth of 12 mm. The slices were taken from the section of the test specimens that rose above the level of the calcium hydroxide solution. These slices showed no loss of chloride to the environment.

The mass of the unsaturated test specimens was controlled and a very small loss of mass was recorded in those test specimens whose SD was approximately 75% and 90%. For this reason, the mean SD of each group in the contamination phase was calculated. The mean values calculated for the four groups of SDs were 53.7%, 73.2%, 86.8% and 101.5%, with the latter assumed as saturated, i.e. with an SD of 100%.

From the mean mass of the test specimens (69.8±0.64g) and the absorption after immersion and boiling (9.6±0.19%), the SD confidence interval was calculated for each group of test specimens. To calculate the maximum SD, the mass of the smallest test specimens and the lowest values of absorption after immersion were used. To calculate the minimum SD, the mass of the largest test specimens and the highest values of absorption after immersion were used. In this way, a confidence level of 95% was obtained, with an SD range of ± 11%.

After slicing and testing for acid-soluble concrete according to ASTM C 1152-90 (11) the curve profiles (Depth) x (% chloride) shown in Fig. 4 were obtained.

In order to apply the solution of Fick's Second Law:

$$c_{Cl} = 2.\,(z)\,.\,(D_{const.Cl^-}\,.\,t)^{1/2} \quad \text{where} \qquad (2)$$

c_{Cl} : depth in m;
$D_{const.Cl^-}$: diffusion coefficient for concrete, considered constant, in m^2/s;
t : exposure time, in s;
z : argument of the Gauss function,

$$\mathrm{erf}(z) = 1 - (C_{c_{Cl}} - C_O) / (C_S - C_O); \quad \text{where} \qquad (3)$$

$C_{c_{Cl}}$: chloride concentration at depth c_{Cl} and time t;

C_O : initial chloride concentration inside the concrete of the structural component;
C_S : chloride concentration on the surface of the structural element, considered constant;
erf(z) : Gauss error function

A regression is needed to obtain a theoretical curve that can better represent the measured values for a constant diffusion coefficient.

Co was assumed to be equal to zero. To make regression easier, the values were mathematically processed to yield the values of C_S and $(D.t)^{1/2}$.

A regression is valid when the correlation of the curves is equal to or greater than 95% (12). For this reason, this correlation was also calculated. Using this method of assessment, a quantitative analysis is obtained and the subjective component represented by the choice of the point in the curve to be analyzed is eliminated, since this would present a considerable variation. Table 1 presents the final values of C_S and $(D.t)^{1/2}$. Fig. 4 shows the curves of measured chloride values and theoretical chloride values.

Using the values of $(D.t)^{1/2}$ and t for each SD group, the ratio between the diffusion coefficient and the maximum diffusion coefficient (saturated group) is obtained – D / D_{max}. This ratio is shown in Table 2.

The results of this test show that there is a strong influence of the SD of the mortar on chloride ion diffusion.

Comparisons between the tests

A qualitative assessment of the test performed by GUIMARÃES and HELENE (6) and the current study shows that the SD of both the hardened paste and the mortar has a considerable influence on chloride ion diffusion.

Fig. 5 shows the correlations between D(SD)/D(100%) and the SD and it indicates very similar results from the research by GUIMARÃES and HELENE (6) and the present study. The differences between the test methods used, particularly in relation to contamination and quantitative analysis, must be taken into account, since the former was carried out using Fick's First law while the current study uses Fick's Second Law.

Another point is that the first study used only hardened paste prepared with high initial strength cement and the current study used a mortar prepared with pozzolanic cement. The curves of both tests show a characteristic threshold where the influence of the SD is the lowest.

APPLICABILITY OF THE RESULTS

The factors that affect the penetration of chloride ions are used in Eq. 2. The limitation of this model consists of determining the exact value of $D_{constCl^-}$ for a given set of conditions of a concrete sample taken from the structural element in the natural environment under study.

Wet environment

This model was applied to the vertical surface of a concrete beam at the TECON pier, which is located in a wet environment (3). The pier is located in a maritime harbor in the city of Rio Grande - RS – Brazil.

Concrete characteristics

Drilled cores of concrete were extracted according to ASTM C 42-94 (13) for characterization tests. Data from construction site reports were also used. The chloride content profile was obtained from 5-mm deep drilled out samples (20 holes were made in each of the six points selected in a 50-m section of the 300-m pier). The concrete in this structure was made using coarse crushed granite aggregate (maximum diameter - Dmax - 38 mm) and quartz sand. Pozzolanic cement with 34% pozzolan was used and the cement content was 403 kg/m^3.

The w/c ratio was 0.44 with $f_{ck,\,real} = 23.4$ MPa (strength at 28 days). The concrete had a specific mass of 2,275 kg/m^3 and its absorption after immersion and boiling (10) was 5.28% by mass with $f_{ck,\,real} = 41.0$ MPa (strength at 22 years). The chloride penetration profile displayed a penetration coefficient (K) for these ions in the range of 5.44 mm $\cdot$ yr$^{-1/2}$ in the model $c_{Cl^-} = K \cdot t^{1/2}$ for a chloride concentration of 0.4 % in relation to the cement content in the boundaries of the attack front.

Effective diffusion coefficient in laboratory

The effective diffusion coefficient is obtained by comparing the value of the compressive strength in the concrete samples with values found in the literature, as outlined below.

Because of the large increase in compressive strength of concrete mixes prepared with fly ash additions in the first two years of service life, two compressive strength values were selected: a mean value for the two first years and a value that remains practically constant in the remaining 20 years. This adds up to the 22 years of age of the structure in this study.

For the first two years, an f_{ck} of 23.4 MPa was used. An increase of 67% after two years was found [14], and this is equivalent to an average compressive strength of 31.2MPa. For the 20 remaining years the compressive strength was 39.1MPa. According to a model proposed by HELENE (15), the diffusion coefficient assumed constant ($D_{const.Cl^-}$) for a concrete with an f_{ck} of 30MPa and 40MPa is 316.10^{-10} $cm^2 \cdot s^{-1}$ and 600.10^{-10} $cm^2 \cdot s^{-1}$ respectively, for C_S values of 1.2%, C_O values of 0.02% and Ce_{Cl} values of 0.3%. A mean of 342.10^{-10} $cm^2 \cdot s^{-1}$ is thus obtained. This value approximates the value found by PAGE et al. (16) for a w/c ratio of 0.4 using ordinary portland cement (equivalent f_{ck} = 30MPa) and a temperature of 22.5°C, considering $D_{const.Cl^-} = D_{ef}/p$, with porosity p between 0.3 and 0.4 (17) and $D_{ef} = 227 \cdot 10^{-10}$ $cm^2 \cdot s^{-1}$. HELENE's figures (15) are very close to those reported in another paper by the same author (18). The values for the effective diffusion coefficient in high-strength concrete are quite similar to those reported by GJØRV et al. (19) in laboratory tests with cylindrical specimens immersed in seawater at an average temperature of 20°C. For the equations above, HELENE's values (15), a temperature of 22.5°C and ordinary portland cement concrete are considered.

According to ISAIA and HELENE (20) and HELENE's model (15), the concrete cover should be reduced by 20% for concrete mixes prepared with an addition of at least 8% microsilica or 50% fly ash. As $c_{cl^-} = K\,D^{1/2}$, this is equivalent to a 36% reduction in the diffusion coefficient, or a reduction coefficient of the diffusion coefficient (R_C) of 0.64.

Reduction coefficient of the diffusion coefficient due the temperature variation (R_T)

The influence of temperature is given by the Arrhenius equation:

$$D_T = D_{To}\; e^{-k\left(\frac{1}{T}-\frac{1}{To}\right)} \tag{4}$$

where D_T is the effective diffusion coefficient at temperature T, D_{To} is the effective diffusion coefficient at temperature To, k is the reaction constant, and T and To are the temperature (°K).

PAGE et al. (16) performed tests of the effect of temperature changes in chloride diffusion. Using these data, values of k equal to 5,511 and 4,766 were found for w/c ratios of 0.5 and 0.4. A mean value of k was used, and a k_{mean} of 5139 was obtained. For a temperature To of 22.5°C and the average temperature in each season, an annual average *reduction coefficient of the diffusion coefficient* was obtained (R_T), as shown in Table 3. Average temperatures were calculated using daily temperature values from

1988 to 1998, supplied by the Fundação Universidade do Rio Grande - National Weather Forecast Institute –8th District, RS, Brazil.

Reduction coefficient of the diffusion coefficient due the variation of the SD (R_{SD})

The *reduction coefficient of the diffusion coefficient* due to the variation of the SD (R_{SD}) was calculated for mortar line in Fig. 5 for mean SDs measured during the winter and summer. In order to determine the SD of the structure investigated, GUIMARÃES (3) developed the method described below.

Drilled cores were extracted from the vertical surface of the TECON pier, and care was taken to remove and discard the outermost layer. All drilled cores thus obtained measured 9.4cm across and 8 cm long. were obtained. The outer surface of the test specimens was coated with silicone, with the exception of their top surface (Fig. 6a).

In order to compare the variation of moisture contents in the mist zone, the cylindrical specimens were placed in an existing structure hanging approximately 10m above the pier surface and 120m from the vertical wall of the pier. The cylindrical specimens coated with silicone were placed so that the uncoated surface was resting vertically, in the same position as the pier. The cylindrical specimens faced a concrete beam, and were exposed to the same degree of solar irradiation of the vertical surface of the pier (Fig. 6b). To prevent flooding by rainwater, the cylindrical specimens were placed on wedges in a place with good drainage conditions. These precautions were taken to simulate the environmental conditions faced by the vertical surfaces of the pier in this wet environment, and to facilitate access to the cylindrical specimens, which had to be weighed daily at certain periods.

To find out when the cylindrical specimens had reached equilibrium with the environment, high moisture and low moisture content cylindrical specimens were placed on the exposure site. When two cylindrical specimens of the same size and different moisture contents showed a similar behavior, i.e. displayed similar moisture contents and variations, these were deemed to be in equilibrium with the environment. The daily mass of the cylindrical specimens was always taken at the same time, at 9:00 am.

The cylindrical specimens behaved in a similar way after approximately two months of exposure between the spring and summer of 1999. In new exposure to the environment, a similar behavior among cylindrical specimens was observed after approximately one month of exposure in July of 1999. It was observed that in the rainy season a similar behavior is observed in a much shorter period of time.

Summer measurements show that the SD remains constant, with a mean measured value of approximately 70% and a standard deviation of 1.49%. This corresponds to a variation coefficient of 2.2%. Therefore, the SD variation in this season is low.

Winter measurements show an average SD of 85%, with a standard deviation of 4.5% and a variation coefficient of 5.3%. The standard deviation is larger in winter than in summer, but it is still low. This is due to the more frequent rainfall in winter, which is interspersed with dry periods when concrete samples with higher SDs show dry faster. SDs in spring and autumn were considered as the mean of the winter and summer SD values. These results are presented in Table 4.

Reduction coefficient due the difference in the position of the exposed surface in relation to the surface of concrete molding (R_{SC})

GUIMARÃES et al. (21) studied the effect of the position of the attack surface in relation to the position of concrete pouring on the severity of the chloride ion attack. It shows the results for cylindrical specimens whose attack surface corresponds to the lateral surface in relation to the concrete molding orientation (HL) and for those whose attack surface corresponds to the core of the cylindrical specimens (HC) (Fig. 7), obtained in tests of measurement of charge passed according to ASTM 1202-94 (22) for cylindrical specimens prepared with concrete mixes with a slump test value of 10 cm.

The concrete researched is placed on its lateral surface in relation to the surface of concrete molding. This concrete has a slump test value of 8±1 cm. The reduction coefficient due to the difference in the position of the extracted of the lateral surfaces "HL" and within central position with two inner surfaces "HC" (Fig. 7) (R_{SC}) was calculated with the mean of 4 values of charge passed and a resulting R_{SC} of 0.74 was obtained.

Calculated effective diffusion coefficient

The effective diffusion coefficient was calculated with reference to the conditions of the concrete of the structural element studied in this environment and the type of cement used as a function of the diffusion coefficient found in laboratory tests for concrete mixes prepared with portland cement:

$$D_{const.Cl^-\,(ef)} = D_{constCl\,(lab.)} \cdot R_C \cdot R_T \cdot R_{SD} \cdot R_{SC} \quad (5)$$

Thus, $D_{const.Cl^-\,(ef)} = 342 \cdot 10^{-10}\ cm^2 \cdot s^{-1} \cdot 0.64 \cdot 0.81 \cdot 0.346 \cdot 0.74 = 45{,}4 \cdot 10^{-10}\ cm^2 \cdot s^{-1}$

The value of z must be found (value of the Gauss error function) before the value of the depth of the chloride attack front can be determined from Eq. 3.

The chloride content in relation to the mass of cement was considered to be Ce_{Cl}=0.4 % and C_O=0.02%.

The value of C_S was calculated from measurements of chloride content in the first 5 mm of depth. This value corresponds to 0.53 % of the mass of dry concrete.

In the outermost concrete layer, a reduction of the coarse aggregate content must be taken into account because of the wall effect on the contact surface of the mold (23).

It was assumed that the increase in the concentration of coarse aggregate ranged from 0% on the surface of the concrete element to a peak in the section that is located at a depth corresponding to half the diameter of the smallest piece of coarse aggregate with a significant percentage in the particle size distribution of coarse aggregates.

For the concrete used in the samples studied, the diameter of the smallest piece of coarse aggregate with a significant percentage in the particle size distribution of coarse aggregates was 9.5 mm. Therefore, the highest coarse aggregate content was found at a depth of approximately 5 mm and the lowest cement content (403 kg/m^3) was found below this depth.

Since the outer surface of the concrete consists of mortar only, a specific mass of 2,177 kg/m^3 for fresh concrete and 2,068 kg/m^3 for dry concrete was found, with a cement content of 707 kg/m^3. Considering a linear reduction of cement content from the external surface to the depth of 5mm, the average cement content in the first extraction layer (5-mm deep) was found to be 555 kg/m^3. The mean bulk specific gravity, dry in this layer was 2,171 kg/m^3, and the value of C_S in the beam of the vertical surface of pier (wet zone) was:

$C_S = 0.53 \cdot (2171/555)\% = 2.17\%$ (in relation to the mass of cement)

From these values, $erf(z) = 0.8146$ is calculated, which corresponds to $z = 0.94$. Thus, a model for the wet zone in the environment of this study is obtained:

$$e_{Cl} = 2 \cdot (0.94) \cdot (45.4 \cdot 10^{-10}\ cm^2 \cdot s^{-1} \cdot t)^{1/2}$$
$$e_{Cl} = (7.12\ mm \cdot yr^{-1/2}) \cdot (t)^{1/2}$$

It can be observed that the value of 7.12 $mm.yr^{-1/2}$ corresponds to the coefficient of penetration of chloride ions, and that for the same point the coefficient of penetration of chloride ions calculated from the profile of chloride ions is 5.44 $mm \cdot yr^{-1/2}$. The value obtained from the model considering the influence of the variation of the SD and the position of the exposed surface in relation to the concrete molding surface is 31% higher than the coefficient of penetration obtained from the chloride profile measured in the structure. If the SD variation (R_{SD}) and the position of the surface exposed in relation to the surface of concrete molding (R_{SC}) are not considered, this difference increases to 158%, and the chloride penetration coefficient is 14.05 $mm.yr^{-1/2}$ (Fig. 8), with the SD variation (R_{SD}) being the most significant factor. If only the SD variation is not considered, the difference increases from 31% to 122%.

CONCLUSIONS

The results obtained confirm that the SD is a factor of great influence on chloride ion diffusion. Therefore, this factor must be included in models of service life of reinforced concrete structures.

Although results obtained may be similar, the test method developed in the current research is more appropriate for use than the one developed in the research by GUIMARÃES and HELENE [6], because it is based on unsteady-state diffusion and it was developed in a mortar, whose structure resembles that of concrete more than cement paste does.

The curve proposed to account for the influence of the SD on the diffusion of chloride ions provided good accuracy when considered in a service life model applied to a reinforced concrete structure of a 22-year-old maritime pier.

The current study requires further research to account for the variation of the diffusion coefficient in relation to the SD in different environments, concentrations and types of materials used in concrete.

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REFERENCES

1. G. Hedenbland, "Influence of moisture and carbonation on the transport of chlorides in concrete - some ideas. In: Corrosion of Reinforcement - Fiel and Laboratory Studies for Modelling and Service Life", Lund, feb/1995. Proceedings. Lund, Kyösti Tuutti, 1995. pp. 227-37.
2. N. S. Martys, "Diffusion in partially-saturated porous materials". Materials and Structures 32, pp. 555-62, 1999.
3. André T. C. Guimarães, "Vida útil de estruturas de concreto armado em ambientes marítimos [Service life of reinforced concrete structures in marine environments]". São Paulo, 2000. Doctorate Thesis, Universidade de São Paulo - PCC/USP, Engenharia Civil.

4. M. A. Climent, G. Vera, J. F. López, E. Viqueira, C. Andrade, "A test method for measuring chloride diffusion coefficients through unsaturated concrete – Part I: The instantaneous plane source diffusion case". Cement and concrete Research, v 32, pp. 1113-1123, 2002.

5. P Nielsen, M. R. Geiker, "Chloride diffusion in partially cementitious material". Cement and Concrete Research, v33, pp. 133-138, 2003.

6. André T. C. Guimarães, P. R. L. Helene, "The moisture effect on the diffusion of chloride ion in hydrated cement paste". In.: SYMPOSIUM ON MARINE CORROSION IN TROPICAL ENVIRONMENTS, 2000, Orlando. Proceedings. Marine Corrosion in Tropical Environments – ASTM STP 1399, Chelsea S. W. Dean, G. H. Degadillo, J. B. Bushman, Eds., 2000, pp. 135 – 149.

7. P. K. Mehta, D. Manmohan, "Pore size distribution and permeability of hardened cement paste". In: 7th INTERNATIONAL CONGRESS ON THE CHEMISTRY OF CEMENT. Paris, 1980. Proceedings. Vol. III. Paris. 1980. pp.VII-1 - VII-5.

8. D. Quénard, H. Sallée, "Le transfert isotherme de la vapeur d'eau condensable dans les matériaux microporeux du bâtiment". Cahiers du CSTB. Livraison 323, Cahier 2525, oct./1991.

9. D. Quénard, H. Sallée, "Water vapour adsorption and transfer in cement-base materials: a network simulation". Materials and Structure, v.25, pp. 515-522, 1992.

10. American Society for Testing of Materials. "Standard test method for specific gravity, absorption, and voids in hardened concrete (ASTM C 642-90)". In: Annual Book of ASTM Standard. Philadelphia, 1990.

11. American Society for Testing of Materials. "Standard test method for acid-soluble chloride in mortar and concrete (ASTM C 1152-90)". In: Annual Book of ASTM Standards. Philadelphia, 1990.

12. L. Nilsson, A. Andersen, T. Luping, P. Utgenannt, "Chloride ingress data from field exposure in a Swedish road environment". In: Second International Rilem Workshop on Testing and Modelling the Chloride Ingress into Concrete, Paris, 2000. CD

13. American Society for Testing of Materials. "Standard test method for obtaining and testing drilled cores and sawed beams of concrete (ASTM C 42-94)". In: Annual Book of ASTM Standards. Philadelphia, 1994.

14. Associação Brasileira de Normas Técnicas. "Extração, preparo, ensaio e análise de testemunhos de estruturas de concreto (NBR-7680) [Extraction, preparation, test and analysis drilled cores of structures concrete]". 1983.

15. P. R. L. Helene,"Contribuição à normalização: A resistência sob carga mantida e a idade de estimativa da resistência característica; Durabilidade e vida útil das estruturas de concreto armado [A Contribution to Standardization: Resistance to Sustained Load and Estimated Age of Typical Strength; Durability and Service Life of Reinforced Concrete Structures]". São Paulo, 1994. (Monografias. EPUSP).

16. C. L. Page, N. R Short, A. El Tarras, "Diffusion of chloride ions in hardened cement pastes", Cement and Concrete Research, v. 11, pp. 395-406, 1981.

17. P. K. Mehta, P. J. M. Monteiro, "Concreto: estrutura, propriedades e materiais [Concrete: Structures, Properties and Materials]", Pini, São Paulo, 1994.

18. P. R. L. Helene, "Contribuição ao estudo da corrosão em armaduras de concreto armado [A Contribution to the Study of Corrosion Processes in Reinforced Concrete Armors]". São Paulo, 1993. Tese (Livre Docente), Escola Politécnica da Universidade de São Paulo, Departamento de Engenharia Civil.

19. O. E. Gjørv, K. Tan, M. Zhang, M. "Diffusivity of chlorides from seawater into high-strength lightweight concrete". ACI Materials Journal, v.91, pp. 447-52, 1994.

20. G. C. Isaia, P. R. L. Helene, "Durabilidade de concreto de alto desempenho com pozolanas [Durability of High Performance Pozzolanic Concrete]". In: Seminário Norie-UFRGS : Qualidade e Durabilidade das Estruturas de Concreto, Porto Alegre, 1993. Proceedings. Porto Alegre, s.ed., dez. 1993. pp. 13-33.

21. A. T. C. Guimarães, L. Tula, P. R. L. Helene, "Performance of surface concrete elements". In: II Internatinal Conference on High-Performance Concrete, and Performance and Quality of Concrete Structures, Gramado, 1999. Proceedings. Gramado, s.ed., 1999. CD

22. American Society for Testing of Materials. Standard test method for electrical indication of concrete's ability to resist chloride ion penetration – ASTM C 1202 94. In: Annual Book of ASTM Standard. Philadelphia, 1994.

23. A. S. Coutinho, "Fabrico e propriedades do betão [Concrete Manufacturing and Properties]". Lisboa, Laboratório Nacional de Engenharia Civil,1973.

Table 1 – Values of C_S and $(D.t)^{1/2}$ obtained by regression and the values of mean error and correlation.

GS - %	C_S - %/ mortar	$(D.t)^{1/2}$ - mm	R^2 - %
53.7	1.23	1.65	98.68
73.2	1.05	2.59	98.24
86.8	1.10	2.82	98.67
100	0.95	2.81	94.9%

Table 2 – Ratio between the diffusion coefficients and the maximum diffusion coefficient – D/D_{max}

SD - %	$(D.t)^{1/2}$ - mm	$t - 10^6$ s	D / D_{max}
53.7	1.65	2.9754	0.068
73.2	2.59	1.5039	0.333
86.8	2.82	1.4931	0.398
100	2.81	0.5898	1.000

Table 3 - Mean values of reduction coefficient of the diffusion coefficients due to the variation of the temperature (R_T)

To = 22,5 °C = 295,5 K				
k =5139,05				R_T mean
Season	Ti (°C)	Ti(K)	R_T *	
Summer	23,4	296,4	1,05	0,81
Autumn	16,46	289,46	0,70	
Winter	14,37	287,37	0,61	
Spring	20,33	293,33	0,88	

$$* R_T = e^{-k\left(\frac{1}{T} - \frac{1}{To}\right)}$$

Table 4 – Mean values of reduction coefficient of the diffusion coefficients due to the variation of the SD - R_{SD}

Season	GS mean- %	R_{GS}	$R_{GS\ mean}$
Summer	70.0	0.289	0.346
Autumn	77.5	0.353	
Winter	85.0	0.389	
Spring	77.5	0.353	

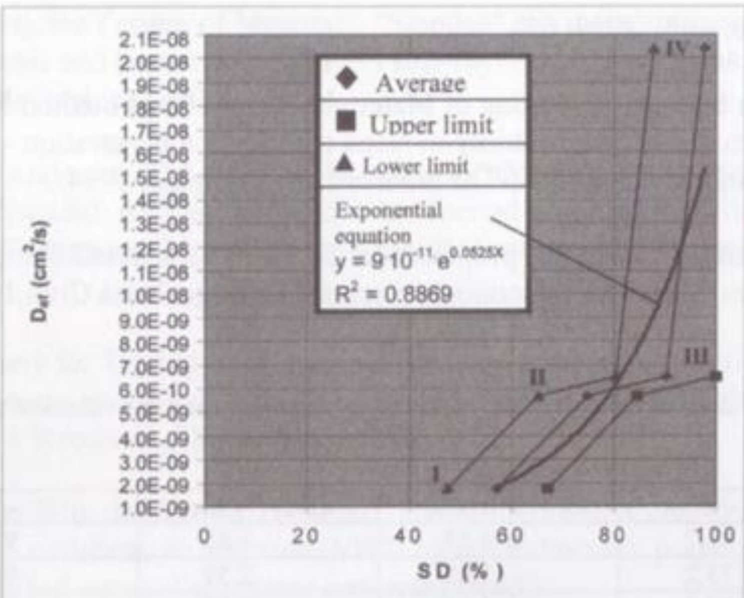

Figure 1—Mean values of the effective diffusion coefficient as a function of SD and the confidence interval of SD mean (95% confidence level) (6)

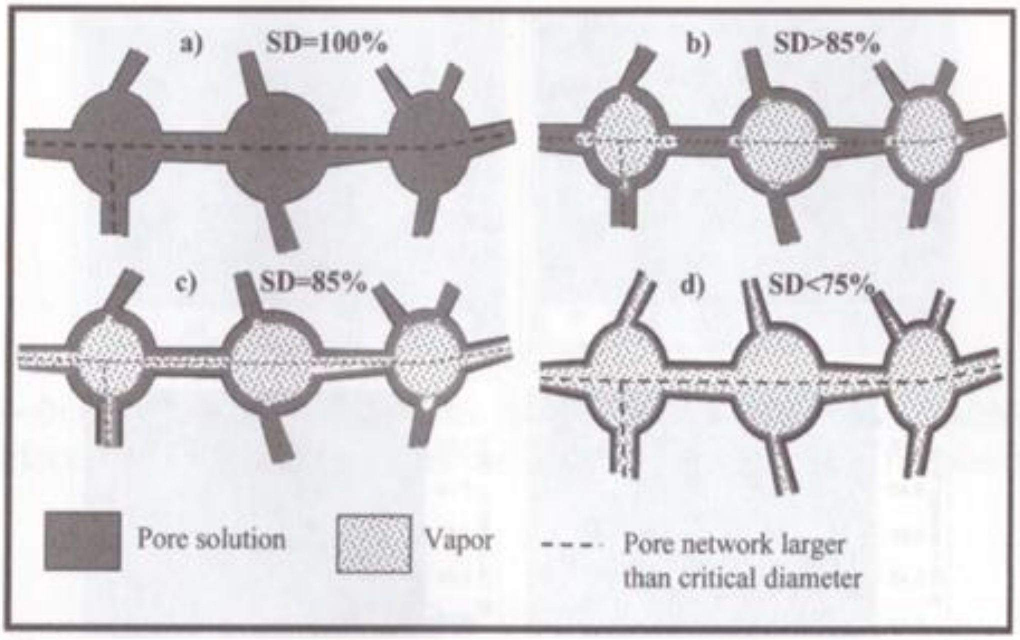

Figure 2—Pore network in hardened cement paste with different moisture content (6)

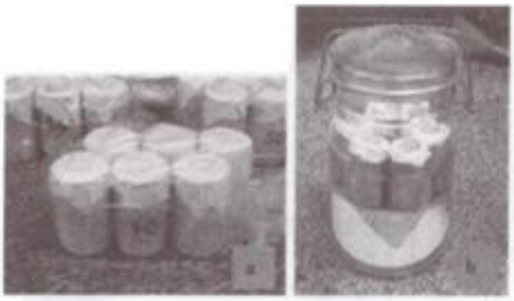

Figure 3—Test specimens contaminated with ground NaC1: a) groups of unsaturated specimens; b) group of saturated test specimens

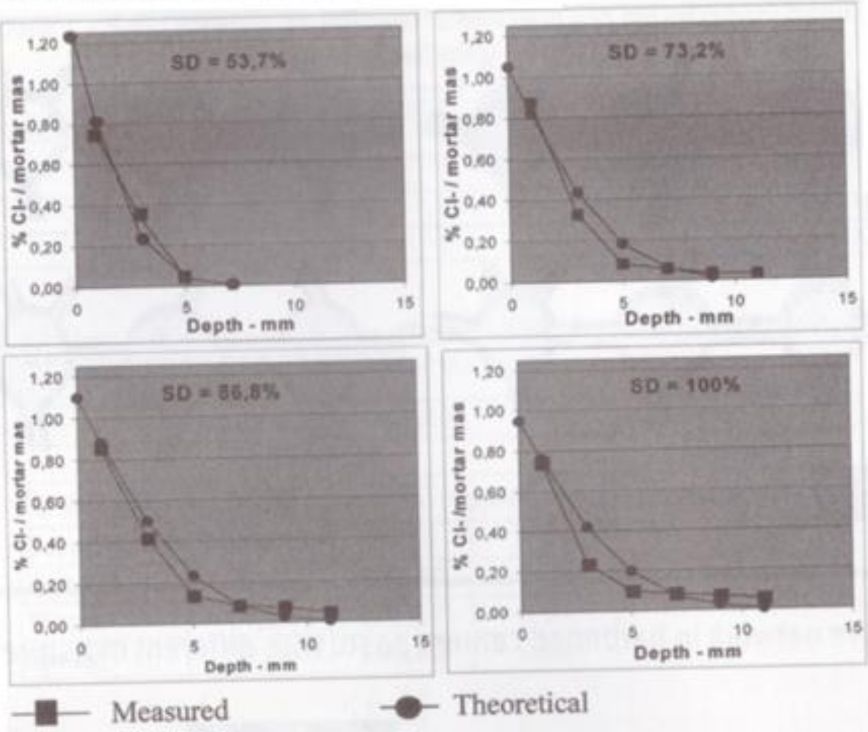

Figure 4—Profiles with chloride concentrations in relation to the weight of mortar for SD of: a) 53.7%; b) 73.2%; c) 86.8%; d) 100%

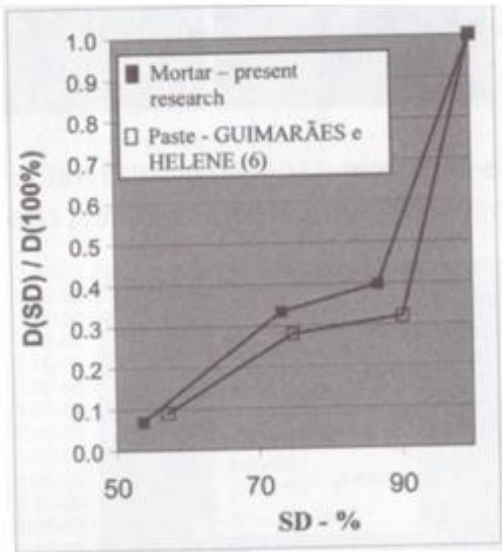

Figure 5—Influence of the SD in mortar (current study) and results obtained in paste by GUIMARÃES and HELENE (6)

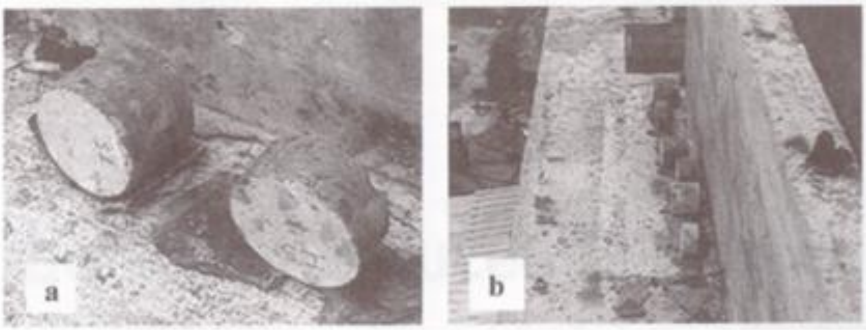

Figure 6—Drilled test specimens - a) uncoated; b) coated with silicone; c) with vertical surface exposed in the same position as the vertical surface of the pier (3)

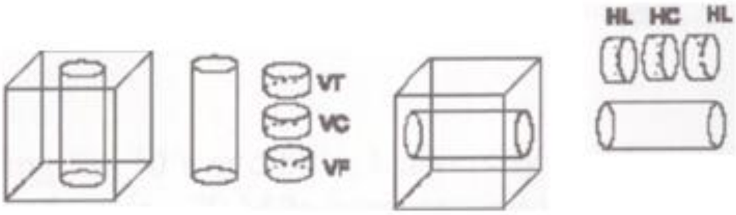

Figure 7—Position of the sample extraction (21)

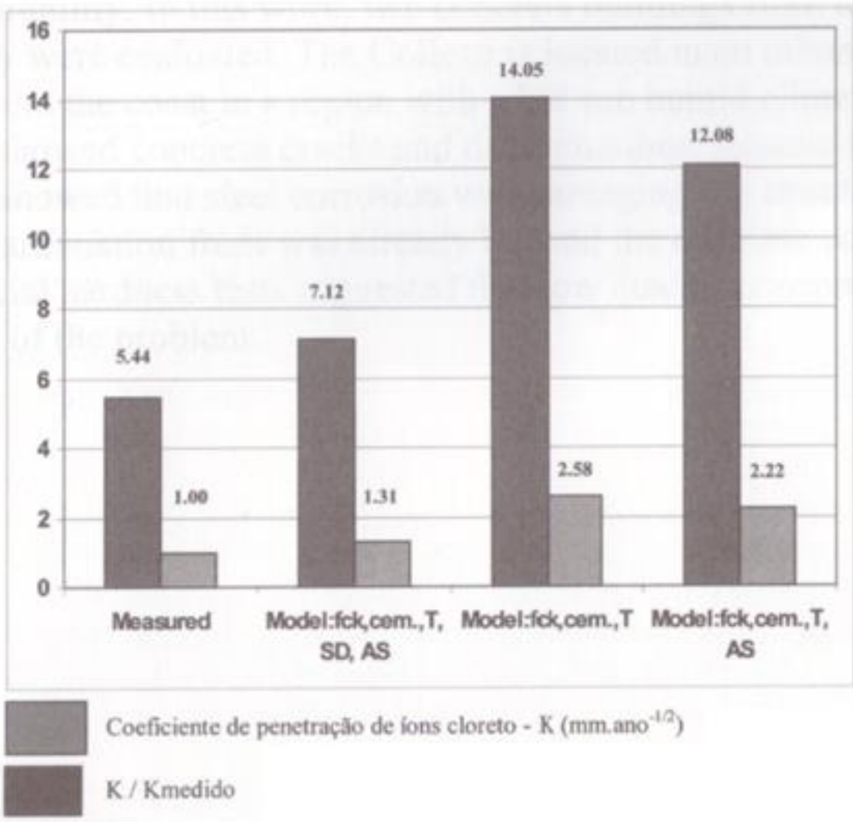

Figure 8—Chloride penetration coefficient - K (mm.yr$^{1/2}$) - wet zone using measured profiles; predicted values considering attack surface (AS) and SD; predicted values not considering attack surface and SD; and predicted values not considering SD