CONCEPTS ON THE CHLORIDE DIFFUSION COEFFICIENT

C. Andrade
Institute of Construction Science "Eduardo Torroja", CSIC, Madrid, Spain

Abstract

Diffusion coefficient D, is considered the rate determining parameter of chloride ingress in concrete. In the paper D is defined following Crank and emphasis is made in that different D values are obtained from different testing conditions and from the units in which chloride concentration is expressed. Rigour and unit coherence is needed to be stressed. Regarding the comparison between D_{ns} values, it is illustrated how different chloride concentrations at a certain concrete cover depth, are obtained when using the standard error function equation, if the surface concentration C_s is not the same. This evidence together with the influence of the degree of chloride binding and the testing time, may make impossible any comparison among D_{ns} values and, therefore make misleading their use for predictive purposes. The papers ends with some considerations on the test types used for obtaining D_s and D_{ns} values and proposes a multiregime method whose full description was made elsewhere. It proposes as well, a nomenclature to distinguish between the different D values and appraise them, therefore, univocally.

1. Introduction

During the last years chloride ingress into concrete has increasingly been characterized by measuring a Diffusion coefficient considered the rate determining parameter of the whole process (1-3). Assuming a constant external concentration, C_s the chloride ingress is assumed to be a non evolutive process with constant diffusion coefficient. However, chloride profiles analyzed from real structures (4,5) show that chloride ingress seems to be a very complex phenomenon, not well characterized yet.

The present paper shows that not only the whole phenomenon is more complex that expected, but the Diffusion Coefficient is not a unique concept which results in the possibility of defining several D values. The different circumstances are described and a proposal for the naming of the different D values is presented.

2.   Definition of the diffusion coefficient

Following Crank (6) the Diffusion coefficient is defined (figure 1) as the rate of transfer of the diffusing substance across a unit area of a section divided by the space gradient of concentration at the section.

$$D(cm^2/s) = \frac{F}{\partial c/\partial t} \qquad [1]$$

F being the flow in mol/cm²·s and $\partial c/\partial t$ the gradient of concentration.
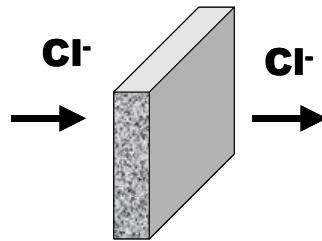

Figure 1. Unit section for defining chloride flow

For this definition to be applied, the total volume should remain constant on either side of the section unit as diffusion proceeds and the same unit of length has to be used in measuring the volume which appears in the definition of concentration.

This definition draws attention on the importance of the units of D and the coherence of them in the whole expression. Thus, figure 2 shows that in concrete the units used for expressing chloride concentration (7):

-    refer to the concrete: in % or in kg/m³ of concrete.
-    refer to the cement content: in % or in kg/kg cement
-    refer to the pore solution: in g or mol Cl/l of solution

Usually, the so-called steady-state Diffusion Coefficient, D_s, refers to the pore solution concentration and therefore expresses the movement of water soluble chlorides. However the non-steady-state, D_{ns}, is expressed by volume of concrete or mass of cement and therefore refers to the total amount of chlorides in the sample.
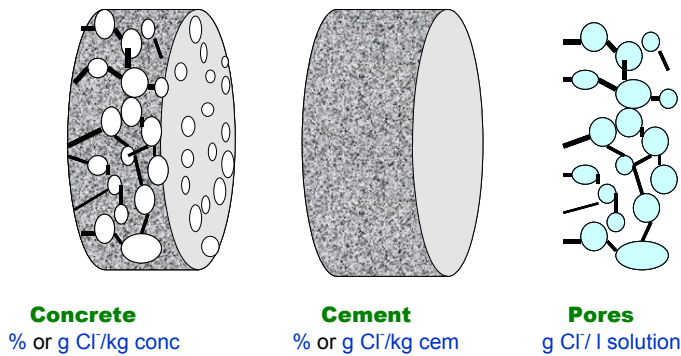
| **Concrete** | **Cement** | **Pores** |
| % or g Cl⁻/kg conc | % or g Cl⁻/kg cem | g Cl⁻/ l solution |

Figure 2. Units of chloride concentration referring to the concrete weight, the cement weight or the amount of evaporable water in the pores.

3.   Types of diffusion coefficient

3.1   Attending the units of chloride concentration

As said, the chloride ions can refer to the total amount of the sample (concrete or cement) or to the pore solution content. Both possibilities aim at different D values that when compared should be transformed in coherent units.

This is due to the fact that in concrete, part of the chlorides which penetrate are combined with the cement phases which makes the process not dependent of the transport only (figure 3), but as well of the proportion of bound chlorides. The binding or reaction of chlorides depends on many factors: type of cement, composition of pore solution, temperature, etc.

Atkinson and Nikerson (7) in 1984 gave expressions for calculating the proportion of total, bound and free chloride concentration assuming a linear binding:

$$C_T = P \cdot C_f t \, (1 - P) \, C_b \qquad\qquad [2]$$

where C_T = total chloride content, C_f = free chlorides, C_b = bound chlorides and P = concrete porosity.

The relation between the Diffusion Coef. referring to the pore solution and that referring to the total volume of concrete is:

$$\frac{D_e}{D_a} = P + (1 - P) \frac{C_b}{C_f} \qquad\qquad [3]$$

where D_e is the effective D referring to the pore solution and D_a= apparent D, referring to the volume of the sample.
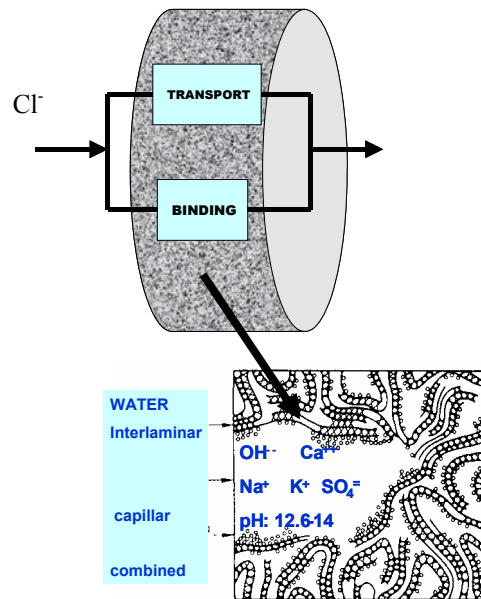

Figure 3. Chloride ingress induces two simultaneous processes: transport and binding with cement phases.

Sergi, Page and Lambert in 1992 (8) gave the expression when the binding is non-linear assuming a Langmuir isotherm

$$C_b = \frac{\alpha\, C_f}{1 + \beta C_f} \qquad\qquad [4]$$

With regard to the effect of the application of an electrical field (migration experiments) to the ability of chloride binding from cement phases, figure 4 depicts the isotherm of Sergi et al (8) calculated from a diffusion experiment and that of Castellote et al (9) made from a migration one. It is worth noting the trend that, when the chloride concentration is low, there is opposite behaviour between diffusion and migration.

Thus, while in diffusion, there is binding from when small quantities of chlorides are present, however in migration, only for chloride amounts higher than 20-30 gr/l reaction with cement phases starts to be significant, and only the isotherms equal when the external testing solution is 1M in NaCl (0.5% by concrete weight in the sample).
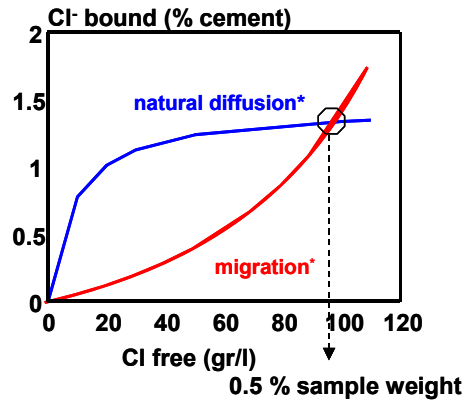
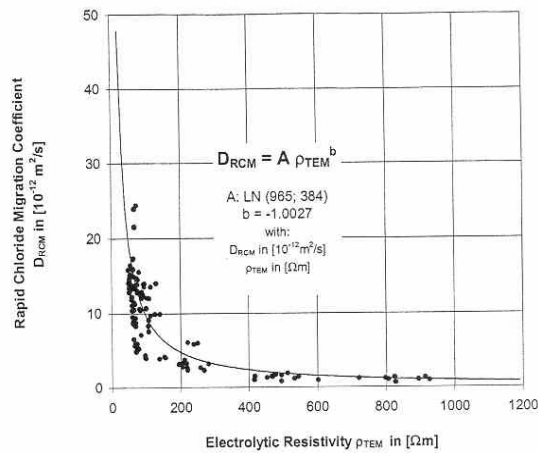Figure 4. Chloride "isotherms" obtained in a diffusion test (8) and that obtained in a migration one (9).

Figure 5. Relation between a D_{ns} and resistivity (11) which denotes that the D_{ns} so obtained is not taking into account binding.

This observation is very important, as migration tests using external solutions with chloride concentrations < 1M NaCl will not aim into full binding and therefore cannot be used for obtaining a D_{ns}. That is the case of the Rapid Chloride Permeability test (10) now modified by Tang and Nilsson to obtain a D_{ns} (11) the results of this last test has been reported (12)

to agree fairly well with resistivity values taken from the current measured and potential applied (figure 5). This agreement between resistivity and the D_{ns} calculated from T&N test confirms that, this migration test does not accounts for chloride binding, as resistivity only can figure the porosity and the connectivity of pores (13).

3.2. Attending the diffusion regime

If the sample thickness is finite the chlorides can permeate through it in a reasonably time, and the Diffusion coefficient can be calculated from a steady-state-regime when the chlorides emerge in the downstream chamber of a diffusion cell. Thus, in figure 6a is shown the typical diffusion cell in which one chamber contain a chloride solution and the other is free from them. After a certain time during which the chlorides penetrate the sample and react with the cement phases, they appear in the chloride-free chamber. The increase in chloride concentration results constant with time if the reaction in the sample has been completed. From the slope of the graph chloride concentration – time, a D_s value is calculated (1) (2). Notice that the chlorides refer to the volume of solution in the chambers and therefore they represent the movement of free chlorides. J denotes the chloride flow.

$$J = - D \frac{dc}{dx} \qquad [5]$$

However, the time taken to appear in the downstream chamber is related to both free and combined chlorides. This time is known as "time lag" and enables the calculation of a non-steady-state D, D_{ns} from the expression [6].

$$t = \frac{l^2}{6 D_{ns}} \qquad [6]$$

where t= time lag and l= sample thickness.

When the test is made in a cylindrical specimen with a pond (figure 6b), the D_{ns} is calculated by fitting the solution of Fick's second law assuming semi-infinite media and constant surface concentration (3):

$$C_x = C_s \left(1 - \mathrm{erf} \frac{x}{2\sqrt{D_{ns} t}} \right) \qquad [7]$$

C_x= chloride concentration at depth x and time t and C_s= surface concentration.
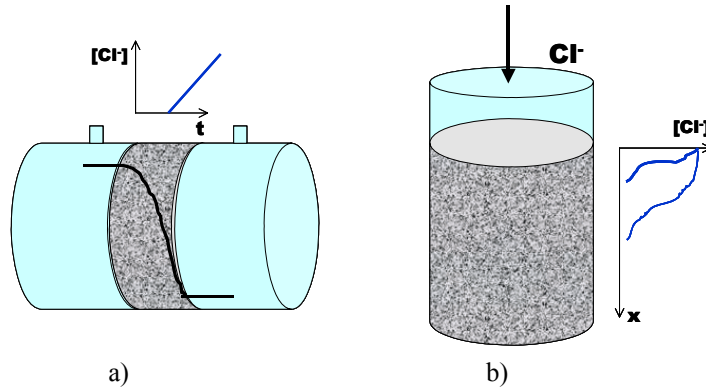

Figure 6. a) Typical diffusion cell in which D_s is calculated from the slope of the graph [Cl⁻] – time and b) typical ponding test where D_{ns} value is obtained from the chloride – cover depth profile.

The values of D_{ns} seem more representative of real conditions as they do take into account the binding, however on the other hand, the real driven forces for chloride ingress are not the chlorides immobilized but the free chlorides. Free chlorides as well are those able to depassivate the steel.

4.   Comparison between Diffusion Coefficients

The D_s values are dependent mainly on the external concentration of chlorides and on the concrete porosity. As figure 7 shows, the more the external solution is concentrated, the slower the movement of ions due to the ion-ion interactions. The difference in D_s value with external concentration of chlorides is depicted by figure 8 for the case of a migration test. Around one order of magnitude of difference can be found for concentrations from 0.1 M to 1M NaCl.

Providing this fact is borne in mind, the comparison of D_s between different concretes would inform on the different porosities of them, as the transport is the main controlling parameter affecting D_s.

The situation is not so favourable when trying to compare D_{ns} from different concretes as D_{ns} is very much affected by the C_s value, which varies with time (4). Thus figure 9

shows theoretical examples (10) in which in a) with the same C_s, higher D_{ns} provides higher chloride concentration at a certain depth, but the case in b) illustrates that the same D_{ns} with different C_s values, give dramatically different Cl$^-$ concentration at a certain depth. The case shown in c) is an extreme case where the profiles reverse. Therefore, the comparison between D_{ns} is completely misleading unless the C_s values are specified. This means that current practice of designing for a D_{ns} is as well misleading without assuming a C_s.
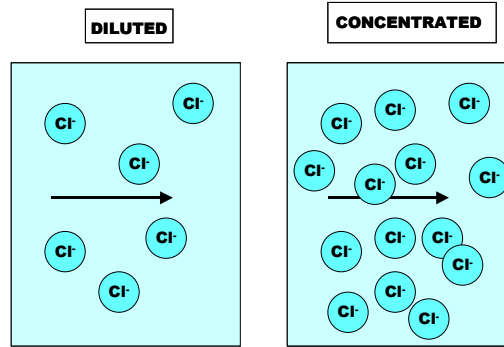

Figure 7. A simulation of diluted and concentrated chloride solutions visually indicating that the most concentrated aims into a lower D due to the ion-ion interaction.
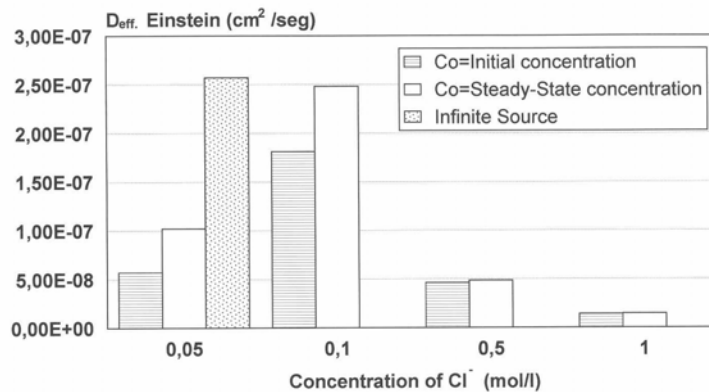

Figure 8. Values of steady-state D obtained in a migration experiment ( ) and calculated by Einstein equation. The D values are lower for higher chloride concentrations, providing a large reservoir (infinite source) is used in the upstream chamber.

A further difficulty when using D_{ns} values for comparative purposes is that they usually are fitted to the profile of total chloride content. Figure 10a gives another theoretical example where profiles are plotted with the same D_s and C_s but different binding ratios

(10). The trend is logical, although it shows how much different the profiles can be with the same porosity but different binding abilities. However, figure 10b presents the case where the situation reverses being the lower Diffusion Coefficient giving the higher chloride concentration at a certain depth. This is obtained when C_s and the binding capacities differ.
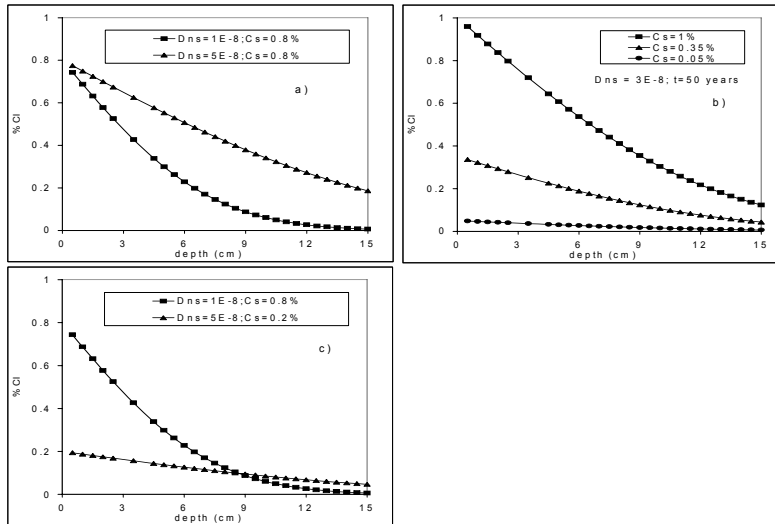

Figure 9. Profiles of chloride with concrete depth, a) the same C_s and two D_{ns}, b) the same D_{ns} and three different C_s and c) different D_{ns} and C_s ( )
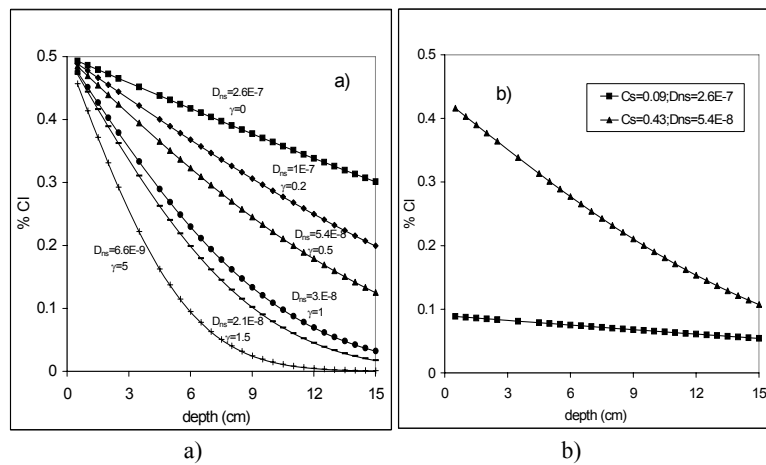

Figure 10. Profiles of chloride with concrete depth, a) same D_{ns} and C_s with different binding ratios and b) different C_s and binding ratios lead into D_{ns} lower for higher chloride concentration at the same concrete depth ( ).

In consequence, comparison between D_s and D_{ns} should not be made unless equations [2,3,4] are used for making coherent the units. Comparison between D_s is possible providing the external concentrations are similar. However, the comparison between D_{ns} is very controversial and misleading if C_s is not specified, and the binding capacity unknown. Opposite to what is assumed related to D_{ns}, this parameter is not a material characteristic. In fact, the same concrete can present several D_{ns} values depending on exposure aggressivity.

5.   Variability of Diffusion Coefficients

Apart from the influence of external concentration or the C_s, and the binding capacity, the D values (D_s and D_{ns}) vary with time. This effect has been emphasized by different authors (13-14), although the causes of this variation have not been univocally identified. In general it is accepted that:

$$D(t) = D_o \left[\frac{t}{t_o} \right]^n \tag{8}$$

where D_o is the initial D (without clear reference to the time where the test has to be made) and n is the exponent indicating the decreasing trend of D (t) value.

The decrease in D_{ns} with time may be due to the refinement of pore structure or a higher binding ratio in more mature concretes, however it can be due as well to an increase in C_s values as illustrated in Figures 9 and 10.

Regarding the time dependence of D_{ns} observed another aspect to consider is the sequence of events shown in figure 11. Assuming 3 profiles obtained at times $t_1 < t_2 < t_3$ and plotting in the figure arbitrarily the maximum concentration of free chlorides and of total chlorides (at saturation of the sample), it results evident in the following:

1) At t_1 only reaching regions I in the figure, a significant part of the chlorides arriving are free and almost any are combined.
2) At t_2 the amount of free chlorides remains at its maximum in region I while the combined chlorides proportionally increase, but in region II there are similar free chlorides to those at t_1 in region I.
3) At t_3, saturation of total chlorides is reached in region I. While in region II the situation is similar to what happened at t_2 in region I. The "front" of the profile has almost free chlorides.

That means that binding affects differently the rate of transport in function of the proportion of bound/free chlorides and, in consequence, the D_{ns} value is not a single one, but represents the slowest step. In the example given it seems logical to be t_3, that is when the concrete is saturated. This situation aims at a slowering of the whole process with time, although in the front of the profile (region III) the chlorides may move much more quickly.
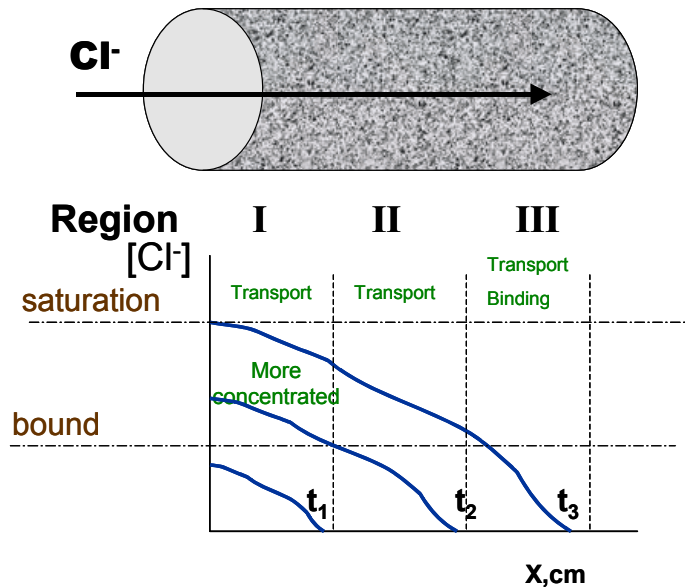

Figure 11. A simulation of chlorides profiles in which it is shown that the binding ratio should affect the D_{ns} value.

Skin effect

Another source of variation of D_{ns} is the building-up of a shape in the chloride profile of the type shown in figure 12, indicating that the skin (external layers) of concrete behave differently than the internal (bulk) ones (13). It the D_{ns} value is obtained from this kind of profiles by extrapolating back to the surface, the D_{ns} value so obtained is different than that obtained rigorously applying the solution named "skin effect". A simple manner of obtaining the correct D_{ns} value consists in rescaling to zero the maximum of the profile, as shown in the figure.
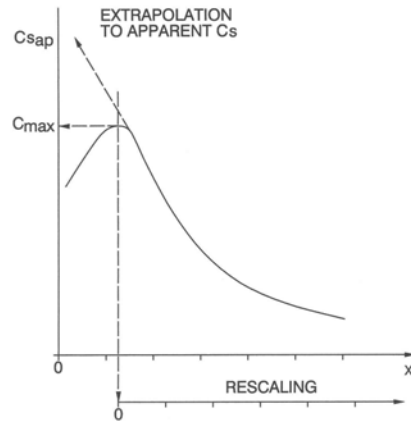
Figure 12. Procedure of rescaling for obtaining a correct D_{ns} when a maximum in concentration appears beyond the concrete surface ( ).

6.   Test types to determine the diffusion coefficients

At present, D_s values are obtained in diffusion or migration cells composed of two compartments, while D_{ns} is obtained from the time lag of these cells or from a ponding (natural or accelerated with an electrical field) test.

Tang and Nilsson recommended the use of the migration cell to obtain the D_{ns} value before reaching the time lag (14). It was explained before that this practice may lead to D_{ns} values in which the chloride binding has not been fully taken into account due to the fact that the external testing solution is 0.5 M NaCl. Care has to be taken therefore of the further use of the D_{ns} even for comparative purposes, as different cement types may produce different proportion of chloride binding and, therefore, make the comparison miss useless.

In any case, from testing, the first thing to emphasize is to prevent the use of D values obtained in short-term experiment for predicting long-term behavior. The variabilities above-commented and the uncertainty of evolution of D with time should prevent this kind of extrapolation.

D_s values can be used for comparative purposes as this type of diffusion coefficient accounts for transport characteristics. However, the use of D_{ns} values for comparative purposes, can only be correct if: a) they are obtained from a natural diffusion test, or b) they are from a migration one in which the external concentration is $\geq$ 1M NaCl.

Proposal of a multiregime method

The most comprehensive may be the use of a "multiregime" method in which both D_s and D_{ns} are obtained. This is possible from a diffusion or migration cell in which D_s is obtained from the slope of the chloride flow and D_{ns} from the time lag. From analyzing for water soluble and total chloride content the concrete sample after testing it is possible as well to obtain a "binding factor". The detailed description of the test can be found in (15).

7.   Proposal of Nomenclature for D values

In order to unify the understanding of diffusion coefficient values, the following nomenclature and definitions are proposed:

D_s –   value calculated from a steady-state experiment and in which the chloride concentration, [Cl⁻] is *expressed in g/l or mol/l of the solution.*

D_e –   value in steady-state conditions with [Cl⁻] expressed in *% of cement or concrete weight*

D_{ns} –   value in non-steady state conditions obtained from fitting error function equation to *test samples* and with [Cl⁻] expressed in % of cement or concrete weight

D_{ap} –   value obtained when fitting error function equation to cores drilled from *real structures* with [Cl⁻] expressed in % of cement or concrete weight

D_{rep} – value to be used in *prediction models*

8.   Conclusions

The main conclusions that can be drawn up from the present considerations are:

1) The diffusion coefficient can be expressed in different units referring to the cement or concrete weight or to the chloride concentration in the pore solution. Attention has to be paid to the translation from one to the other one.
2) Attending to the diffusion regime, the D values can be as well calculated in steady or in non steady-state conditions. In steady state conditions, chloride binding is not taken into account. Resistivity values can be transformed into D_s values and therefore either D or resistivity do not account for binding.

3) Comparison between D values obtained in different testing conditions has to be made with care, because D values are not constant (they are not a material characteristic). D values vary with: the external concentration, time and degree of chloride binding.
4) When using the so-called "error function equation" care has to be taken as well for comparative purposes, because profiles obtained from the same D_{ns} value with different C_s ones aim at very different chloride concentrations for the same concrete cover depth.
5) Values of D_{ns} suppose an integral of the process of transport and binding.
6) The proposal of a multiregime test to calculate both D_s and D_{ns} is made, as well as that of a nomenclature for the different types of D values.

9. References

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