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Chloride-binding isotherms in concrete submitted to non-steady-state migration experiments

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Abstract

Chloride binding is an essential step in the determination of the chloride transport across concrete. The binding ability has been previously modelled in different ways, among which is that of assuming an adsorption process and fitting to the mathematical expression of an isotherm from data obtained from natural diffusion tests. In the present paper, chloride concentration profiles from non-steady-state migration tests have been fitted to a Brunauer, Emmett, Teller (BET) isotherm general equation to model chloride binding under these conditions and to compare it with natural diffusion results. The results indicate that chloride ions remains unbound until the concentration in the pore solution exceeds about 28 g/L and that interactions in the chloride/cement matrix could be similar to those of natural diffusion when the chloride external concentration is higher than 1 M in Cl^-. In addition, it has been found that the "chloride isotherm" is of type V with a BET characteristic constant $C < 2$.

Keywords: Chloride binding; Migration tests; BET isotherm; Chloride diffusion coefficients

1. Introduction

The calculation of chloride apparent diffusion coefficients (D_{app}) from chloride profiles is a common practice because this parameter reflects the resistance of the concrete to the transport of chlorides. However, as the evaluation of D_{app} from diffusion tests is extremely slow, the application of an electrical field, which accelerates ionic transport, could reduce the testing time if it can be demonstrated that D_{app} can be calculated from the results. The application of an external electrical field to force ionic transport through concrete was first used in the late seventies, but the theoretical basis for its interpretation has only recently begun to be studied [1].

One concern is that the interactions between chloride ions and cement matrix may be modified by the application of the electrical field. Considering the fact that D_{app} also depends on the interactions between chloride ions and the cement matrix, if the application of current modified these interactions, D_{app} obtained from migration experiments would be different from those obtained from diffusion ones.

Although numerous studies exist on the subject, the mechanisms of chloride binding in cement paste are not yet well understood, because the ability of combination or binding of cement matrix depends on a variety of parameters, among which are: chemical composition of pore solution, type of cement, kind of binder used, associated cation and concentration [2–6].

Ramachandran [2] stated that chlorides may be in different forms in hydrated cement paste: some of the chlorides are free ions dissolved in the pore solution and the rest are chemically combined or physically adsorbed on pore walls. Although the binding of chloride ions by cement paste seems to take place as the result of both chemical combination and physical adsorption on the gel, due to the great difficulty in the distinction among them, the term "binding isotherms" has been adopted in literature [7]. They describe the quantitative relationships between free and combined chlorides at constant temperature, assuming that local equilibrium is instantaneously achieved.

Different mathematical expressions have been given to chloride isotherms. A lineal relationship was used by Tuutti [8] and Arya and Newman [9]. However, experimental data of most researchers [7,10–18] do not fit this kind of relationship. In most cases, relationships between free and combined chlorides are not linear.

With the aim of fitting this nonlinear relationships, other researchers [7,14,15] used the Langmuir isotherm to describe chloride binding. Tang and Nilsson [17] found that a Langmuir isotherm does not fit experimental data when free chloride concentration is higher than 0.05 M, while a Freund-

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Table 1
Chemical analysis of the cement used

		%									
L.I.	I.R.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Free CaO	Cl^-	Na_2O	K_2O
3.45	1.97	19.37	6.12	3.13	62.86	1.78	3.23	1.28	0.013	0.18	1.00

L.I. = Loss of ignition. I.R. = Insoluble residue.

lich isotherm can be applied in the range of free chloride concentration from $0.01 < C_l < 1$ M. Bigas et al. [19] and Delagrave et al. [20] also used this kind of isotherm to fit their experimental data.

Xu [21] proposed a modified Brunauer, Emmett, Teller (BET) isotherm that was also used by Tang and Nilsson [22], which fit their own data and data from Page et al. [23]. The values of the BET characteristic constant that they found were above 50 in all cases.

The results discussed above were based either on adding the chlorides in the mixing water or on natural diffusion tests where the contact time between chloride and cement matrix is relatively long. In all of these cases, the isotherms were of type I or IV, and they were "concave" to the x-axis.

There are chloride extraction data in concretes submitted to electrolytic migration experiments [24–26]; this suggest that after the electrical field application, the amount of bound chlorides may decrease depending upon the voltage applied and the duration of the treatment.

Only Hauck [27] and Ollivier et al. [28] have given data on free and combined chlorides obtained from migration experiments in steady-state conditions. No data have been found in the literature on non-steady-state conditions.

In the present paper, a chloride-binding isotherm calculated from non-stationary migration experiments is given. Its shape is convex to the x-axis and therefore the calculation of a D_{app} from these types of experiments is questionable unless certain testing conditions are fulfilled.

2. Methods

2.1. Materials and preparation of specimens

The specimens were made of concrete (water/cement ratio = 0.4) and were cylinders 75 mm in diameter and 150 mm in height. They were demoulded at 24 h and cured for 28 days underwater. They were then stored until testing time in a $Ca(OH)_2$-saturated solution.

The chemical analysis of the cement employed is shown in Table 1, while Table 2 contains the mix proportion of the concrete fabricated.

Table 2
Concrete dosage used

Cement (kg/m^3)	Sand (kg/m^3)	Coarse aggregate (kg/m^3)	Water (kg/m^3)	Water/cement ratio
380	771	1177	152	0.4

2.2. Techniques and procedures

Two series of non-steady-state migration tests (see Fig. 1) at constant voltage were carried out. One of them used different chloride concentrations in the external solution, and in the other the migration time was changed. The conditions were:

1. Series with different chloride concentrations: The catholyte containers (300 mL in volume) were filled with 0.05, 0.1, 0.5, and 1 M NaCl solutions. The test lasted 21 days. The voltage applied was 12 V.
2. In another set of experiments, containers were filled with 0.5 M solution of NaCl. A voltage difference of 12 V was applied during 7, 14, 21, and 28 days.

At the end of each experiment, the specimen was cut in slices (about 5–10 mm thick) that were analysed by X-ray fluorescence to obtain the total amount of chlorides. Free chlorides were also determined by a leaching method in an alkaline solution. This was made by putting 3 g of the sample (crushed to a particle size between 3 and 4 mm) in contact with 2 mL of NaOH 0.3 M solution (prepared with de-

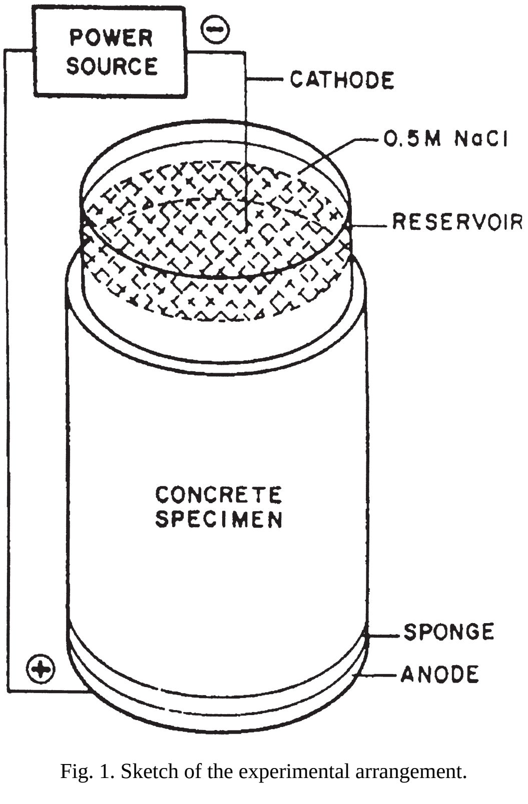


Fig. 1. Sketch of the experimental arrangement.

carbonated water) in an inert atmosphere for 24 h. Chloride concentration was then analysed in the filtrated solution. Another fraction of the sample was used to calculate the pore free water by introducing it in a stove at 105°C for 24 h.

In the determination of the free chlorides, the establishment of the equilibrium between the leaching and the pore solutions is assumed. This method has been calibrated by the pore pressing technique [29].

3. Results

Fig. 2 shows the chloride profiles (total and free chlorides) obtained after the test for every concentration and duration of the experiment (percentage with respect of dry total sample).

Values of chlorides at depth $x = 0$ represent the surface concentration obtained by smooth erasing of the first mm of the specimen. It usually resulted as much higher than the rest of the profile. It has not been used in the further work, although their values are included in the figure for the sake of illustration of the results obtained.

Figs. 3a and b show the resulting values of the integration of each curve of Fig. 2.

In Fig. 3a it can be seen that with cathodic solutions of 0.05 and 0.1 M NaCl, all chlorides remained free in the aqueous phase of the pores, while when increasing the concentration to 0.5 and 1 M NaCl some of chlorides got combined.

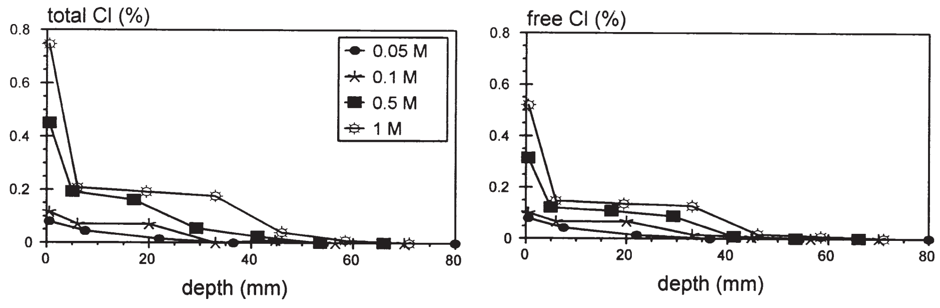
In the case of different testing times with an external concentration of 0.5 M NaCl, Fig. 3b shows that for the smallest testing times (7 and 14 days), as happened for different concentrations, all chlorides remained free in the aqueous phase. For the longest periods, some of chlorides got combined.

Fig. 4a shows the relation between free chlorides in the pore solution and total chlorides in the different slices analysed (percent with respect of the total sample). The figure indicates that initially all chlorides remain dissolved and do not bind to the solid phases until the total chloride amount reaches about 0.14%. By subtraction of free from total chloride, the combined chlorides are depicted in Fig. 4b.

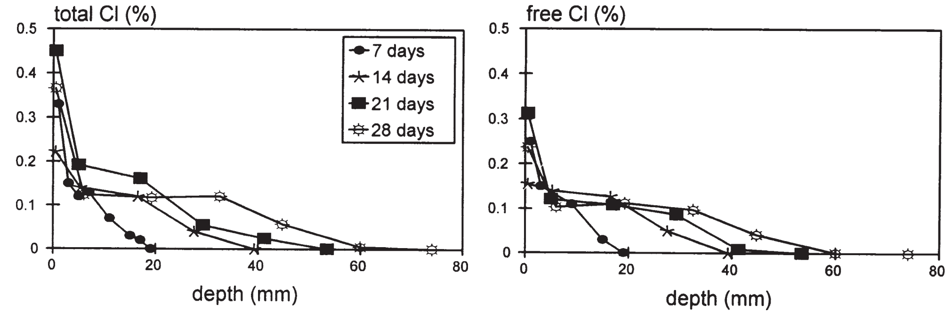
It is also important to point out that even in the samples that retain more chlorides, the combination is below 20% of what would be expected if all of the aluminium and iron phases of the cement had reacted with chlorides to form mono-chloro-aluminates and ferrates of the Friedel's salt type: $C_3A \cdot CaCl_2 \cdot 10H_2O$ and $C_3F \cdot CaCl_2 \cdot 10H_2O$ [30].

3.1. Chloride-binding isotherm calculation

To quantify the ability of the cement matrix to bind chlorides, the results of total and free chlorides obtained from the different experiments have been fitted to the general BET adsorption isotherm. Adaptation for adsorption from a liquid was made following Tang and Nilsson [22], replacing the ratio of pressures by the concentration ratio. Modelling the chloride binding by an isotherm was aimed at compar-



different chloride concentrations



different times of contact

Fig. 2. Chloride profiles obtained at the end of each experiment.

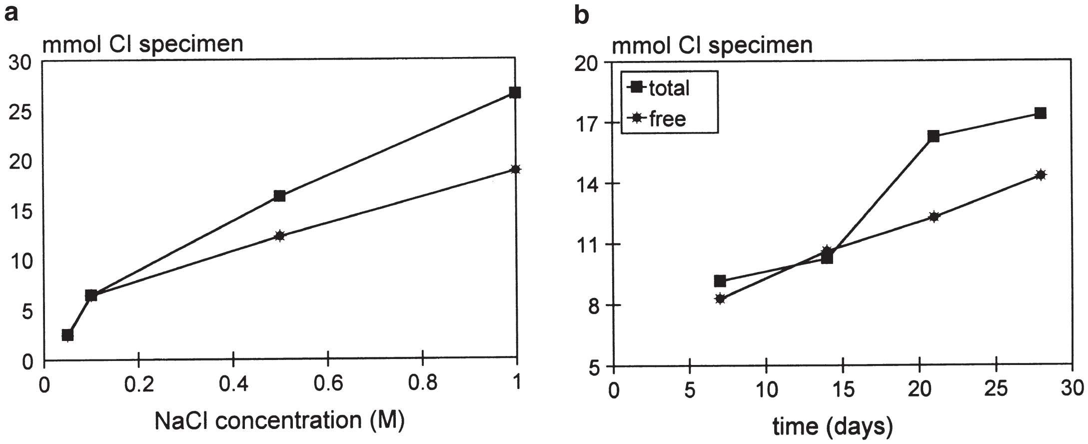


Fig. 3. Total amount of chlorides in the specimens at the end of each experiment. (a) Different NaCl concentrations, 21 days. (b) Different testing times. [NaCl] = 0.5 M.

ing the result with previous literature, and does not imply the authors support any particular mechanism. The mechanism for adsorption and/or reaction with the hydrated cement matrix is not discussed in the present work.

To fit the experimental data into the BET equation, the ratio *V*/*Vm* has been substituted by %/%*m*. Thus, instead of obtaining *Vm* (the volume of adsorbate needed to cover the surface of the cement matrix with a monolayer), what is calculated is the percentage of combined chlorides equivalent to cover this surface with a monolayer. The other parameters obtained are the BET characteristic constant *C* and the number of monolayers *n*.

Therefore, resulting chloride isotherm equation is shown in Eq. (1):

$$\frac{V}{V_m} = \frac{Cx}{(1-x)}\frac{1-(n+1)x^n+nx^{n+1}}{1+(C-1)x+Cx^{n+1}} \quad (1)$$

In this equation all the parameters have the original meaning (BET) except for *x*, which now is the ratio between C_f = free chlorides in the pore solution (g/L) and C_{sat} = chloride concentration of a saturated NaCl solution at the temperature T (g/l) [see Eq. (2)]:

$$x = C_f/C_{\text{sat}} \quad (2)$$

To translate data of percentage of free chlorides (%) into concentrations (g/l), it is necessary to measure the volume of pore solution per weight of the sample. This has been done by mercury porosimetry analysis of the concrete being the averaged value of 2.9*E* − 5 m^3 (solution)/Kg (sample). Complete saturation of the concrete has been assumed.

The fitting of the experimental data to the Eq. (1) is given in Fig. 5. Although the fitting has a correlation factor of only 0.818, it should be appreciated that all data lie between the margin of 95% confidence and the residues are in the range of ±0.03 units, which is good, considering the intrinsic heterogeneity of the concrete.

The parameters obtained from the fitting were:

%*m* = 0.257 (percentage of chlorides needed to cover with a monolayer the internal surface of the cement matrix),

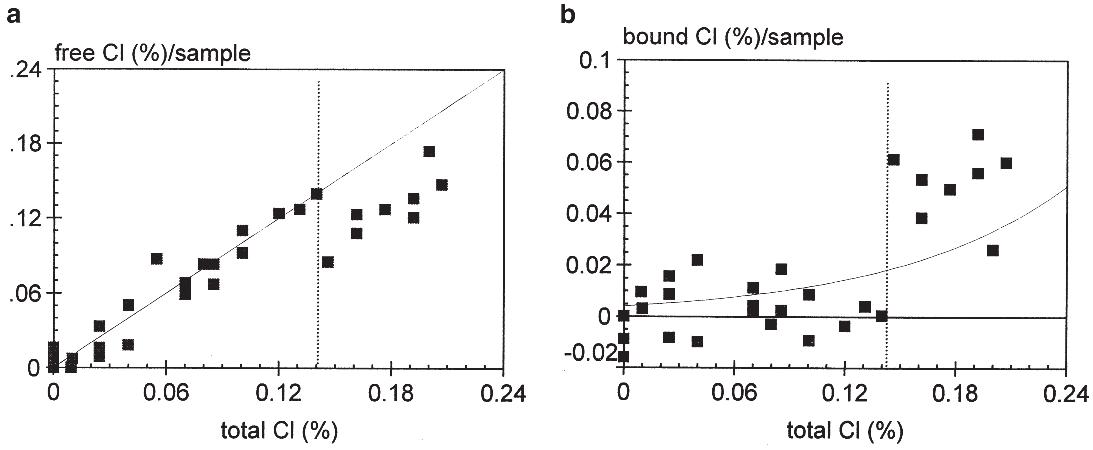


Fig. 4. Percentage of free and combined chlorides vs. total chlorides in the sample. (a) Free chlorides. (b) Bound chlorides.

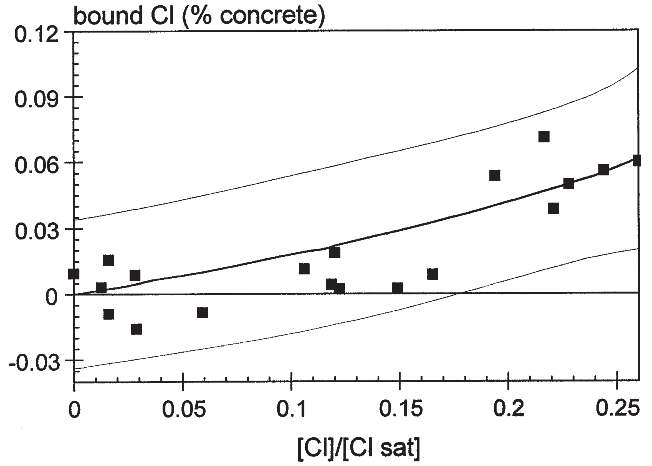


Fig. 5. Fitting of the experimental data to a BET isotherm. (Dotted lines show the 95% confidence interval.)

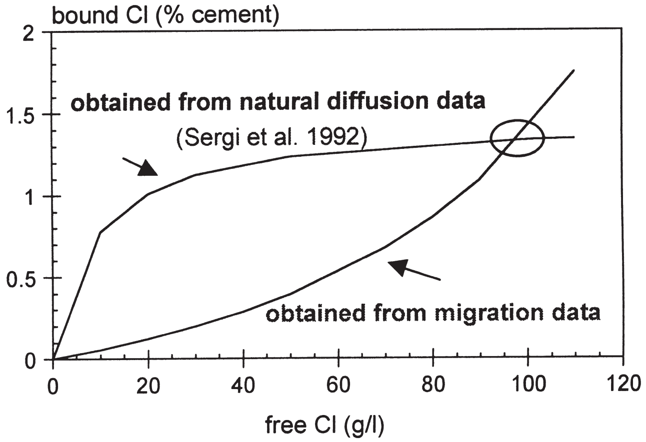


Fig. 6. Chloride-binding isotherms from migration and diffusion experiments.

$C = 0.597$ (BET characteristic constant), and
$n = 1078$ (number of monolayers).

It is important to point out that the most important data obtained from the fitting is the BET characteristic constant, *C*. Concerning the other parameters, they do not have a practical significance except that the very high value for *n* confirms the non-Langmuirian behaviour of the isotherm; that is the particular case for $n = 1$.

It is also important to remark that the shape of this isotherm can be ascribed to an isotherm of type III or V. In the type III, the convex character persists all along the x-axis, while in the type V an inflexion point appears for high enough *x* values. The range of values C_f/C_{sat} obtained does not enable discrimination of whether the isotherm is type III or type V.

The value of the BET constant *C* lower than 2 also confirms that the isotherm is of type III or V, both characteristics of weak and nonfavourable interaction between the adsorbate and the substrate. The values of *C* previously obtained by Tang and Nilsson [22] from natural diffusion experiments were above 50, which indicates a strong interaction between adsorbate and substrate.

To clarify further the differences in chloride-binding ability between diffusion and migration experiments, Fig. 6 presents the curve of combined chlorides (percentage by cement weight) in function of the chloride concentration in the pore solution calculated in the present experiment together with the Langmuir isotherm proposed by Sergi et al. [14] for diffusion experiments in ordinary Portland cement paste. Even though extrapolation of both isotherms can be mechanistically misinterpreted, it is necessary to proceed in this manner, because comparison of both curves enables some interesting observations. Extrapolating both isotherms, a chloride concentration is found in which combined chlorides are similar. This meeting point of both curves corresponds to a 0.48% of total chloride with respect to the weight of sample, a value that can only be reached at high chloride concentrations in migration experiments.

From Fig. 6 it seems reasonable to think that a limit in the percentage of combined chlorides should exist, which enables the statement that the chloride isotherm in migration experiments should be of type V.

4. Discussion

First, it has to be pointed out that the isotherm obtained here is not in contradiction with that found by Ollivier et al. [28] from migration experiments in steady-state conditions. The isotherm found in by Ollivier has a similar shape of that found by Sergi et al. [14] in natural diffusion conditions. This is attributed to the length of the contact time between the penetrating solution and the concrete. In a steady-state experiment, equilibrium may be achieved if the time of contact is long enough, while in the present experiments, a nonsteady state is operating and that equilibrium seems not to be achieved unless high amounts of chlorides are used in the external solution.

The differences accounted for migration and diffusion experiments in the ratio between free and combined chlorides, mathematically figured in the form of an isotherm, enable us to deduce a different type of interaction between the chlorides and the cement matrix. There may be two reasons for this difference:

1. On reason, as previously mentioned, is the duration of the contact time. In natural diffusion the reaction time is relatively much quicker than the transport step; however, in migration tests it seems that the transport rate is so rapid that the binding does not occur in the same extension. In other words, there is a change in the controlling step of the global process and it seems that the equilibrium of the binding is not instantaneously achieved, as it is assumed to be in the isotherm representation.

2. A second reason, more hypothetical, is the effect that the electrical field could induce in the double layer of the pore walls. That is, it is possible that the electrical field applied could alter the double layer potential and, in consequence, induce a different interaction between the chlorides and the substrate.

To be able to discriminate between both mechanisms, it is necessary to carry out specific experiments. For example, to calibrate the importance of the second argument, it would be necessary to perform parallel oxygen diffusion tests, as was developed elsewhere [31,32]. Both kind of actions or mechanisms seem to hold until a determined value of free chloride in the pore solution is reached, which happens at quite high external chloride concentrations (⩾1 M NaCl). This comment needs further theoretical elaboration, together with a more thorough study of the fundamentals of the chloride-binding mechanism.

4.1. Calculation of D_{app} from migration experiments from chloride profiles

For external chloride concentrations <1 M NaCl (in this case chloride concentration near the concrete surface reaches the diffusion and migration isotherm meeting point), an accordance between diffusion and migration experiments seems doubtful. Providing that the experimental conditions would enable reaching similar surface concentrations [33], the differences in the binding ability will lead into different chloride profiles and, in consequence, different D_{app} values.

In fact, the profiles of chlorides in migration experiments (see Fig. 2 and Andrade et al. [34]) are different in their "shape." This may now be explained as due to the different binding ability. The "front" or shape with a low enough chloride concentration remains as it was with unbounded chlorides, and reaches a longer distance than when chlorides penetrate by diffusion. The migration profiles do not advance as an abrupt front [35], rather the opposite occurs: the shape of the profile extends beyond that when diffusing [36].

Fig. 7 depicts the variation of combined chlorides in function of free chlorides ($\partial C_b/\partial C_f$) for the same isotherms shown in Fig. 6 (from Sergi et al. [14] and calculated from present experiments). In diffusion experiments, the highest variations in binding ability take place for the smallest chloride concentrations (almost constant above about 50 g/L), while the opposite happens in migration experiments. In these last tests, the variation in binding ability is negligible for the smallest chloride concentrations.

Hence the constancy range of D_{app} coefficients calculated from migration and diffusion experiments with regard to concentration will be different. This indicates again that they will not give the same diffusion coefficient value until the chloride concentration is high enough to equal the percentage of combined chlorides. However, an opposite deduction can also be derived, that the D_{app} calculated from migration experiments using low chloride concentrations can be constant since all the chlorides will remain free, if the testing conditions are the appropriate.

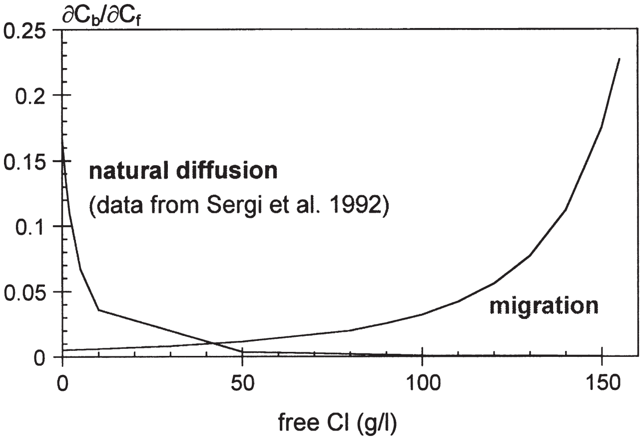


Fig. 7. Variation of combined chlorides vs. free chlorides.

In this last case, the relation proposed by Atkinson and Nickerson [37] is fulfilled [see Eq. (3)]:

$$\alpha = \frac{D_{\text{eff}}}{D_{\text{app}}} = \varepsilon \tag{3}$$

where ϵ is the porosity of the concrete and D_{eff} is the coefficient in steady-state conditions, which enables the calculation of the highest D_{app} if D_{eff} and ϵ are known. ϵ could be calculated as well if D_{eff} and D_{app} are known.

A further practical deduction from the present results is that a reduced binding will be produced in short tests of the type ASTM C1202-91 [38,39] and therefore their results should not be applied to calculate the behaviour of chloride penetration in real non-steady-state conditions. They may serve to calculate the resistivity of the specimen and from it the D_{eff}, but they cannot give information on the D_{app}.

5. Conclusions

Chloride migration experiments were carried out using ordinary Portland concrete with low water/cement ratio, and results were compared with published data on natural diffusion. The main conclusions are as follows:

1. The amount of free and combined chlorides is different in non-steady-state migration and diffusion experiments. This implies a different rate or mechanism of interaction between chlorides and cement phases in the two types of test. For the cement tested, the combined chlorides are similar in diffusion and migration experiments for external chloride concentrations above 1 M NaCl (0.25–0.30% free chlorides by sample weight).
2. The opposite of what happens in diffusion, in a non-steady-state migration experiment the shape of the chloride isotherm is convex with respect to the x-axis.

The value of the BET characteristic constant was calculated to be <2, which indicates an unfavourable interaction between the adsorbate and the substrate. This type V of BET isotherm appears to be due to the limited binding ability of chlorides in a migration experiment, attributed to a change in the controlling step of the global process. It seems that the instantaneous equilibrium assumed in an isotherm is not fulfilled during migration experiments with low external chloride concentration.

3. Provided the testing conditions enable a similar surface chloride concentration, C_s, the differences in the binding ability make the calculation of the apparent diffusion coefficients, D_{app}, from migration experiments uncertain unless external chloride concentrations (about 1 M) are used. On the other hand, the fact that at low chloride concentrations all chlorides remain free in the pore solution enables the calculation of the maximum D_{app} possible for any particular concrete, which in turn enables the calculation of D_{eff} (steady-state conditions) if the concrete porosity is known or vice versa.

Acknowledgments

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