

Prediction of chloride ingress into saturated concrete on the basis of a multi-species model by numerical calculations

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Abstract. A multi-species model based on the Nernst-Planck equation has been developed by using a finite volume method. The model makes it possible to simulate transport due to an electrical field or by diffusion and to predict chloride penetration through water saturated concrete. The model is used in this paper to assess and analyse chloride diffusion coefficients and chloride binding isotherms. The experimental assessment of the effective chloride diffusion coefficient consists in measuring the chloride penetration depth by using a colorimetric method. The effective diffusion coefficient determined numerically allows to correctly reproduce the chloride penetration depth measured experimentally. Then, a new approach for the determination of chloride binding, based on non-steady state diffusion tests, is proposed. The binding isotherm is identified by a numerical inverse method from a single experimental total chloride concentration profile obtained at a given exposure time and from Freundlich's formula. In order to determine the initial pore solution composition (required as initial conditions for the model), the method of Taylor that describes the release of alkalis from cement and alkali sorption by the hydration products is used here. Finally, with these input data, prediction of total and water-soluble chloride concentration profiles has been performed. The method is validated by comparing the results of numerical simulations to experimental results obtained on various types of concretes and under different exposure conditions.

Keywords : chloride; durability; multi-species; predictive model; concrete.

1. Introduction

Chloride ion contamination is the major cause of steel corrosion in reinforced concrete structures. Chlorides may penetrate in the concrete cover from the external environment or may be present in the original mix compounds. Consequently, for example, chloride contamination in marine environments has resulted in significant corrosion in jetty substructures. Likewise, the use of deicing salts has induced corrosion problems in bridge decks, and calcium chloride added as a set accelerator has caused problems to many buildings (Frederiksen 1996). Chloride ions, which are present in the environment, diffuse through the pores of the concrete cover to the embedded

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reinforcing steel. When the chloride concentration reaches a critical level at the first layer of steel rebars, depassivation of the reinforcement occurs and the corrosion process can begin, reducing thereby the structure service lifetime and affecting its load bearing capacity/structural integrity, functionality, and aesthetics. In addition, decontamination of concrete from energy facilities, or the remediation of soils, is a major concern in environmental engineering (Hausmann 1967). Hence, significant efforts have been made in order to understand the processes associated with chloride ingress in concrete structures exposed to aggressive environments, and to predict their service life. Chloride penetration is governed by a standard diffusion process slowed down by the binding of ions onto the solid matrix. The durability of reinforced concrete structures strongly relies upon the location of the penetration front. The propagation of the penetration front mainly depends upon two key material properties: the diffusion coefficient and the binding isotherm, the latter governing the interaction between the solid phase and the species in solution. Depending on reaction enthalpy and mechanism, chloride binding seems to result from both chemical reactions and physical adsorption (Bigas 1996, Francy 1998).

Many research works have been devoted to the modelling of isothermal chloride ingress into concrete, ranging from empirical to physically and chemically-based models (Nilsson 2005). Within the framework of physical models, the LCPC model (Nguyen, *et al.* 2006) has been developed according to a multi-species approach. This model allows to describe the transport of various ionic species in cement-based materials. As a superimposed electrical field can be taken into account, both diffusion and electrical migration simulations can be performed. The electrical coupling between the different species is computed by assuming spatial electroneutrality within the pore solution. This model will be described in the present paper. The main input data of the model are the effective diffusion coefficients of the species present in solution, the chloride binding isotherm and the pore solution composition. The method of assessment of these data will be discussed in the paper.

2. Model and basic equations

2.1. Governing equations

Within the framework of physical models, the LCPC model has been developed according to a multi-species approach, on the basis of the works reported in Marchand, *et al.* (2002) and Truc, *et al.* (2000a), which include the species Cl^- , OH^- , Na^+ , K^+ , along with their influence on chloride diffusion. When sodium and chloride ions are present in solution, chlorides will diffuse faster than sodium ions, as a result of the difference in magnitude of the respective diffusion coefficients. However, chlorides are charged negatively, whereas sodium ions are charged positively. As a consequence an electrical field therefore develops, which slows down the faster ions and accelerates the slower ones. In water saturated concrete, the contribution by convection can be neglected. The transport of each ion i is then described by the Nernst-Planck equation, as in Truc, *et al.* (2000a):

$$J_i = -D_i \left[\text{grad} c_i + c_i \text{grad}(\ln \gamma_i) + \frac{z_i F}{RT} c_i \text{grad} \psi \right] \quad (1)$$

where J_i , D_i , c_i , γ_i and z_i are the flux (in $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), the effective diffusion coefficient (in $\text{m}^2\cdot\text{s}^{-1}$), the (“free”) concentration in the pore solution (in $\text{mol}\cdot\text{m}^{-3}$), the chemical activity coefficient and the valence number of each ionic species i , respectively. F is the Faraday constant ($9.64846 \times 10^4 \text{ C}\cdot\text{mol}^{-1}$),

R the ideal gas constant ($8.3143 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T the absolute temperature (in K) and ψ the local electrical potential (in V).

On the basis of such an analysis, the set of mass balance equations for each species either present as an ion or included in a solid compound is as follows:

$$\frac{\partial n_i}{\partial t} + \text{div} J_i = 0 \quad (2)$$

where J_i is the flux given by Eq. (1) and n_i ($i = \text{O}, \text{H}, \text{Cl}, \text{Na}$ and K) denotes the total molar content of i in the ionic species or solid compounds. For example, $n_{\text{Cl}} = \phi c_{\text{Cl}} + s_{\text{Cl}}$, where ϕ is the porosity, c_{Cl} (in $\text{mol}\cdot\text{m}^{-3}$ of pore solution) is the chloride concentration of the aqueous phase (free chloride) and s_{Cl} (in $\text{mol}\cdot\text{m}^{-3}$ of material) denotes the amount of bound chlorides.

To complement the system of equations, another relation is needed to account for the electrical potential that is locally induced by ion movements. Truc, *et al.* (2000a) and Li and Page (1998) solved the Nernst-Planck problem by using the nil current assumption. In a more general case, Marchand, *et al.* (2002) instead have used Poisson's equation. In this paper, the electrical interactions between ions are computed by assuming electroneutrality of the pore solution (Helfferich 1962):

$$\sum c_i z_i = 0 \quad (3)$$

In order to validate the computation with Eq. (3), the three approaches (nil current, Poisson's equation and electroneutrality condition) were compared. Fig. 1 compares the chloride concentration profiles and the potential distributions obtained with these three approaches. A good agreement is observed. From a numerical point of view, computation is complicated because the Poisson equation, which relates electrostatic potential to space charge density, contains a small parameter (i.e. the dielectric permittivity of the medium is of the order $10^{-12} \text{ F}\cdot\text{m}^{-1}$). Furthermore, it is found that the electroneutrality condition is a consequence of Poisson's equation when a certain dimensionless parameter is small (the small parameter can be interpreted as the ratio of a Debye length and the sample thickness). Thus, the analysis suggests that the assumption of electroneutrality in the pore solution, which can drastically simplify the computations, gives rise to very little error under usual conditions. Therefore, this assumption is taken chemical activity into account.

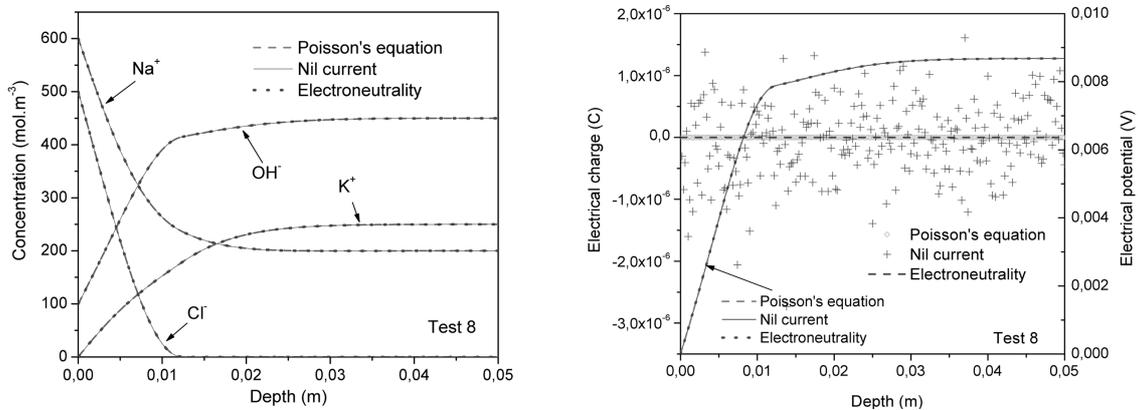


Fig. 1 Computed results of the Nernst-Planck problem with different approaches (see Table 3 for input data)

2.2. Chemical activity

The effect of the activity of the species in solution on ion transport, within the range of the concentrations observed in concrete, is still a subject of discussion. Some authors (e.g. Truc, *et al.* 2000a and Tang 1996a) conclude from their investigations that activity has a negligible effect, while others (e.g. Samson and Marchand 1999a and Li and Page 1998) consider it to have a significant effect. By using the modified version of the Davies equation that follows with very good accuracy the experimental data on the chemical activity coefficient of a sodium hydroxide solution, the chemical activity coefficients appearing in Eq. (1) can be calculated as follows (Samson, *et al.* 1999b):

$$\ln \gamma_i = -\frac{Az_i^2\sqrt{I}}{1+a_iB\sqrt{I}} + \frac{(0.2-4.17\times 10^{-5}I)Az_i^2I}{\sqrt{1000}} \quad (4)$$

where I ($\text{mol}\cdot\text{m}^{-3}$ of solution) is the ionic strength of the solution while A and B are temperature dependent parameters. The parameter a_i varies with the type of ionic species i . More information on this approach can be found in Samson, *et al.* (1999b).

The influence of the activity coefficient on the transport process has been investigated here through some examples. In these examples, the potential difference across the sample is assumed to be equal to zero. Therefore, a pure diffusion process is considered. Indeed, it is in this case (without external electrical field) that the non-ideality of the solution will have the stronger effect on the results. As shown in Fig. 2, the non-ideality of the solution affects the chloride concentration profiles only when the ionic strength of solution is very high. In the following it is assumed that the activity coefficients are all equal to 1 primarily because the concentrations of the ions studied are not high.

2.3. Binding isotherm

Interactions occur between the ionic species and the solid phase. Data in the literature suggest that chloride binding in hardened cement paste is a reversible process, which tends to equilibrium.

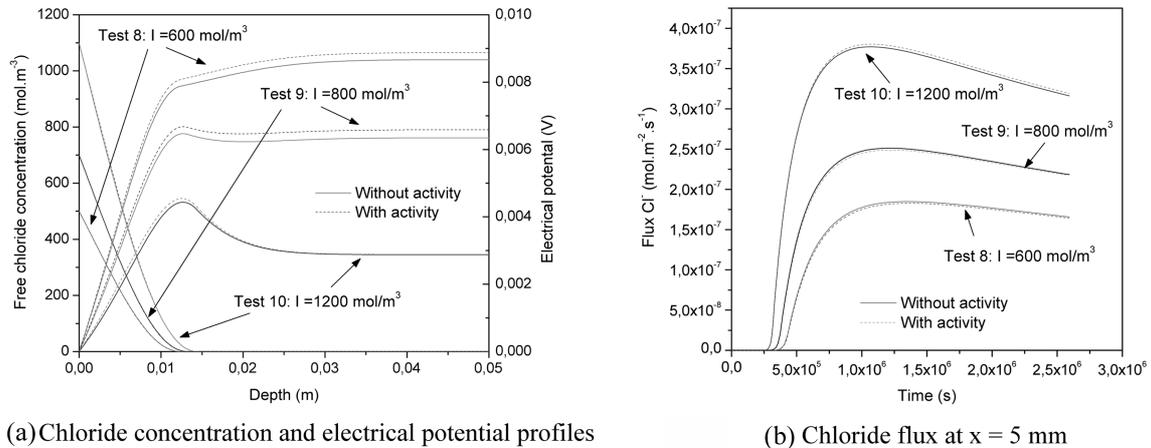


Fig. 2 Influence of the activity of the solution (see Table 3 for input data)

Chloride ions are adsorbed onto calcium silicate hydrate (C-S-H) and onto the other constituents of hardened hydrated or unhydrated cement paste (Beaudoin, *et al.* 1990). They also chemically react with the C_3A and C_4AF constituents of the cement and with the products of their hydration, and thus produce so-called Friedel's salt (Birnin-Yauri and Glasser 1998, Suryavanshi, *et al.* 1996). The most usual way to describe chloride binding in numerical models is to fit chloride binding isotherms obtained from experiments. In the proposed model, two possibilities are offered: global binding according to Freundlich's isotherm (cf. Eq. (5b)) or physical adsorption according to Langmuir's isotherm (cf. Eq. (5a)) depending on which provides the best correlation to the data.

$$\text{Langmuir's isotherm: } s_{Cl} = \frac{\alpha c_{Cl}}{1 + \beta c_{Cl}} \quad (5a)$$

$$\text{Freundlich's isotherm: } s_{Cl} = \mu c_{Cl}^\gamma \quad (5b)$$

where α , β , μ and γ are the Langmuir and Freundlich isotherm parameters, respectively, which vary according to the concrete binder composition.

In addition, the adsorption of ions present in the pore solution, except Cl^- , is neglected. In order to maintain the electroneutrality of the solid phase, chloride binding is balanced by the dissolution of negatively charged hydroxyl ions from the solid phase. The model is based on the following assumption: the local thermodynamic equilibrium is maintained during the diffusion process (instantaneous reaction). The influence of the hydroxyl ion concentration on the binding phenomena is neglected (Masi, *et al.* 1997).

2.4. Chloride concentration dependency of effective diffusion coefficient

Several investigations have demonstrated that the effective chloride diffusion coefficient, determined by using Fick's first law in case of diffusion tests or the simplified Nernst-Planck equation in the case of migration tests, is not a constant, but is a function of the concentration (Bigas 1996, Francy 1998). However, in reality, for one specific material, there should be only one effective diffusion coefficient for each species. This effective diffusion coefficient is a constant depending solely on the ion and on the material.

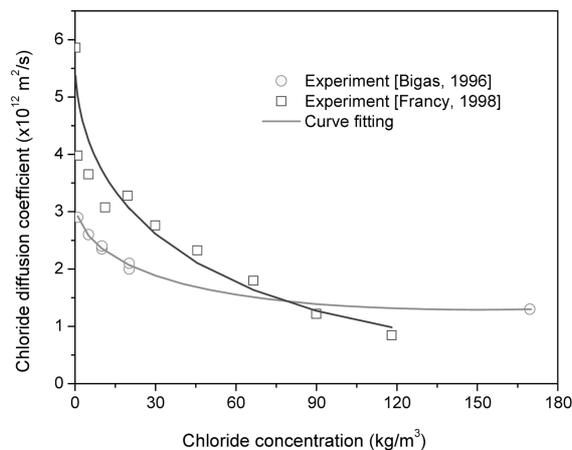


Fig. 3 Variation of chloride diffusion coefficient with the chloride concentration

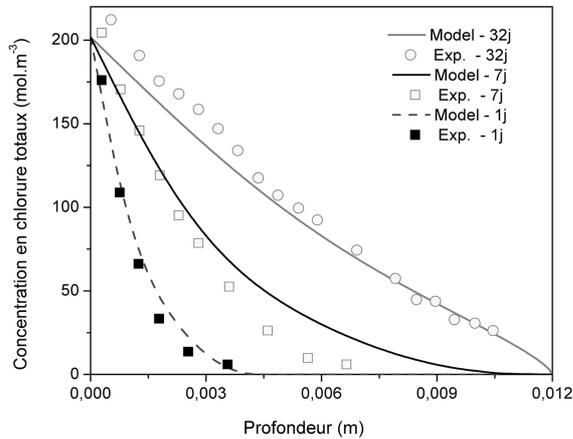


Fig. 4 Total chloride concentration profiles. Comparison between calculations and experiments on mortars from Francy (1998)

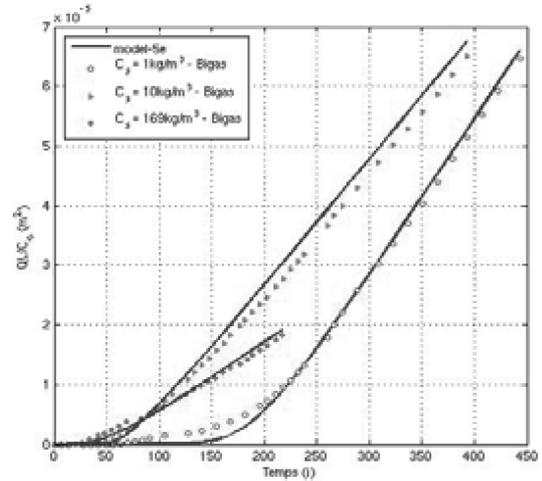


Fig. 5 Cumulative mass Q of ions arriving in the downstream compartment vs. time. Comparison between calculations and experiments on mortars from Bigas (1996)

Bigas (1996) measured the flux of chlorides for steady-state conditions and the diffusion coefficient was then determined by using Fick's first law whereas Francy (1998) determined the diffusion coefficient by using chloride concentration profiles in non-steady-state by using Fick's second law. The dependency obtained in both cases is illustrated in Fig. 3. It appears that chloride diffusivity decreases as the chloride concentration in the pore water increases, as predicted by certain authors, and reaches its maximum for very low concentrations. The diffusion coefficient corresponding to a chloride concentration equal to zero will be called intrinsic diffusion coefficient. The term intrinsic refers to a characteristic property of the material for a particular species. With very low concentrations, the electrical field auto-induced by the movement of the different species becomes negligible. It is thus assumed that the coefficient only depends on the microstructure of the material and on the chloride species.

The intrinsic diffusion coefficient was introduced in the multi-species model. Figs. 4 and 5 show the comparison between the results from the model and the experiments. It is essential to highlight that the numerical simulations made with the LCPC model were performed with constant diffusion coefficients for all the species whatever the experimental conditions were. It can be noticed that the simulations made with the LCPC model are in good agreement with the experimental results (cf. Figs. 4 and 5). Therefore, the dependency that is found experimentally is another evidence of the influence of other species on chloride transport through cement-based materials. As a matter of fact, when Fick's first law is used to calculate the diffusion coefficients instead of the Nernst-Planck relation, the electrical field created by all the species (multi-species effects) is neglected. As a result, by using a constant intrinsic diffusion coefficient and the multi-species model, it is thus possible to explain experimental observations for which the analysis would be complicated with models based on Fick's first law. These remarks clearly demonstrate that the chloride diffusion coefficient determined experimentally from diffusion tests by using the Fick's laws cannot be directly introduced in a predictive model for chloride ingress into reinforced concrete structures. Indeed, this parameter strongly depends on the experimental conditions and the method used to calculate it.

2.5. Numerical solution

A numerical algorithm has to be used to solve such a complex system of non-linear equations (Eq. (1) to Eq. (4)). The spatial discretization of this coupled system is well performed here through the finite volume method, since the discrete form of the mass balance laws (Eq. (2)) is strictly satisfied. The four unknown variables in the adopted discretization scheme are the chloride, sodium, potassium, hydroxyl concentrations and the electrical potential. An implicit approximation of the normal derivative ensuring the best stability of the scheme is used. The nonlinear set of equations is solved with a standard Newton algorithm (Eymard, *et al.* 2004).

3. Required input data

In order to solve the problem by means of the finite volume method procedure, some input data are required: the effective chloride diffusion coefficient and the chloride binding isotherm. In addition to boundary conditions, the initial pore solution composition (initial conditions) is also a property that has to be provided. This section is therefore devoted to the presentation of the methods used to assess these parameters.

3.1. Pore solution composition (initial conditions)

In this paper, the chemical composition of the pore solution is calculated by using Taylor's method (1987), which describes the release of alkalis from the cement and alkali sorption by the hydration products. The total numbers of moles of Na^+ and K^+ present per m^3 of pore solution can be computed from the corresponding mass fractions and molar masses. For Na^+ , the computation is as follows:

$$[\text{Na}^+]_T = 2 \frac{C \varphi_{\text{Na}_2\text{O}}}{\phi M_{\text{Na}_2\text{O}}} \quad (6)$$

where $[\text{Na}^+]_T$ denotes the total Na content ($\text{mol}\cdot\text{m}^{-3}$), $\varphi_{\text{Na}_2\text{O}}$ the Na_2O fraction ($\text{g}\cdot\text{g}^{-1}$), $M_{\text{Na}_2\text{O}}$ the molar mass of Na_2O ($\text{g}\cdot\text{mol}^{-1}$), ϕ the porosity and C the cement content deduced from the mix-composition ($\text{kg}\cdot\text{m}^{-3}$).

Alkalis in cement are partly present in readily soluble sulphate phases and partly bound in the major clinker minerals (Taylor 1987). The alkalis present in sulphate phases will dissolve instantaneously and will be in solution before hydration of silicates takes place. The remaining fractions of alkalis are released during the hydration process. It is assumed that the alkalis bound in the major clinker minerals are evenly distributed over major clinker phases, and will be released into the pore solution as soon as the clinker reacts and dissolves. The amount of Na^+ released from the clinker is thus linearly proportional to the degree of hydration of the cement. The total number of moles of Na^+ released per volume of pore solution is the sum of Na^+ released from sulphates and from clinker minerals. This sum is:

$$\begin{aligned} [\text{Na}^+]_{\text{Released}} &= f_{\text{Na,sulphate}}[\text{Na}^+]_T + (1 - f_{\text{Na,sulphate}})\alpha[\text{Na}^+]_T \\ [\text{K}^+]_{\text{Released}} &= f_{\text{K,sulphate}}[\text{K}^+]_T + (1 - f_{\text{K,sulphate}})\alpha[\text{K}^+]_T \end{aligned} \quad (7)$$

where $f_{\text{Na,sulphate}}$ and $f_{\text{K,sulphate}}$ are respectively the fraction of Na^+ and K^+ present in sulphates as taken

from (Pollitt and Brown 1969) ($f_{\text{Na,sulphate}} = 0.35$; $f_{\text{K,sulphate}} = 0.55$), while α is the degree of hydration of the cement.

Taylor (1987) proposed that the amount of each alkali cation taken up by the hydration products C-S-H and AFm is proportional to the concentration present in the solution and the quantity of these hydration products formed. The linear relationship between the amount of alkalis in solution and the amount adsorbed by hydration products has been confirmed by Hong and Glasser (1999), who report that C-S-H contributes the most to the apparent sorption, as it is a good sorbent and the most abundant reaction product. The use of their concept of binding yields:

$$[\text{Na}^+] = \frac{\phi[\text{Na}^+]_{\text{Released}}}{\phi + R_d m_{\text{CSH}}} \quad [\text{K}^+] = \frac{\phi[\text{K}^+]_{\text{Released}}}{\phi + R_d m_{\text{CSH}}} \quad (8)$$

where R_d ($\text{cm}^3 \cdot \text{g}^{-1}$ -CSH) is the binding factor. In the present study, binding factors of 0.4 and 0.38 were assumed for Na^+ and K^+ , respectively (Hong and Glasser 1999). For mixtures with silica fume, R_d of 0.7 for both Na^+ and K^+ were chosen (Brouwers and van Eijk 2003). m_{CSH} ($\text{g} \cdot \text{cm}^{-3}$ -concrete) is the C-S-H content in the concrete, deduced from the mix composition and the hydration kinetics of the cement by using the analytical formula proposed in Mounanga, *et al.* (2004) (see also Papadakis 2000), when supplementary cementing materials are used).

Numerical predictions of the alkali concentrations are compared with the experimental results reported by Larbi, *et al.* (1990) and Baroghel-Bouny (1994). These experimental results are obtained on hardened cement pastes. More information on the mineral composition of the cement used can be found in Larbi, *et al.* (1990, Baroghel-Bouny (1994). Samples of pore solution were obtained at different ages by using pore fluid expression. Then, $[\text{Na}^+]$ and $[\text{K}^+]$ in extracted pore solution were determined by means of flame emission spectroscopy (cf. Table 1). The alkali concentrations computed by the proposed method are presented in Table 1 (α , ϕ , m_{CSH} calculated by using a cement hydration model (Mounanga, *et al.* 2004)). From Fig. 6 it can be seen that the predicted alkali concentrations are in correct agreement with the measured ones. This agreement is very good after 7 days of hydration. The difference between measured and calculated values can be attributed

Table 1 Computed and measured alkali concentrations

Times (days)	α	ϕ (%)	m_{CSH} (g/cm^3)	Na^+ concentration ($\text{mol} \cdot \text{m}^{-3}$)				K^+ concentration ($\text{mol} \cdot \text{m}^{-3}$)				References
				Total	Rele.	Calc.	Meas.	Total	Rele.	Calc.	Meas.	
0.25	0.22	48.85	0.091	181.11	89.29	83.25	50	466.44	302.72	282.76	270	OPC (Larbi, <i>et al.</i> 1990)
0.5	0.30	46.66	0.147	189.61	103.34	92.06	50	488.33	334.51	298.84	310	
1	0.40	44.6	0.220	198.37	121.13	101.58	50	510.89	373.18	314.23	330	
2	0.51	42.52	0.300	208.07	141.80	111.18	60	535.88	417.72	329.34	340	
3	0.57	41.4	0.346	213.70	153.97	116.14	70	550.38	443.88	336.93	350	
7	0.70	38.87	0.452	227.61	183.22	126.06	110	586.20	507.06	351.67	360	
14	0.78	37.21	0.520	237.76	203.76	131.84	130	612.35	551.73	360.25	380	
28	0.83	36.09	0.568	245.14	218.05	135.08	140	631.35	583.05	364.76	390	
14	0.79	41.19	0.599	122.74	105.98	67.62	51.61	431.75	390.95	251.77	245.96	C (Baroghel-Bouny 1994)
90	0.91	38.81	0.719	130.26	122.64	71.20	51.61	458.23	439.67	258.02	272.34	
12	0.79	32.4	0.695	156.03	134.73	73.36	64.14	548.88	497.01	273.81		CO (Baroghel-Bouny 1994)
26	0.86	30.96	0.760	163.29	148.43	75.83	64.58	574.41	538.23	278.44		

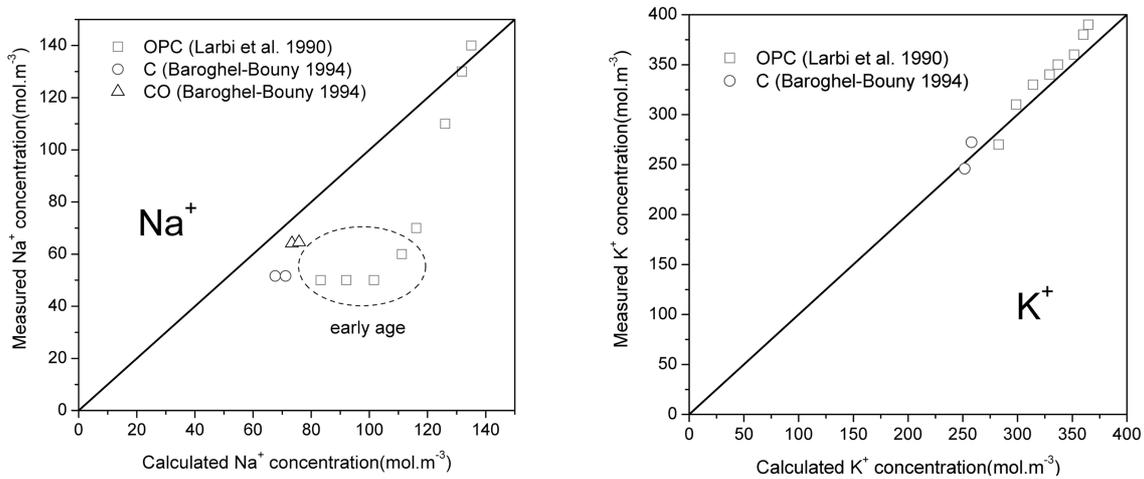


Fig. 6 Comparison between calculated and measured (Larbi, *et al.* 1990, Baroghel-Bouny 1994) alkali concentrations

to the absence of equilibrium at very early ages.

The initial chloride concentration is assumed to be equal to zero. Thus, the hydroxyl concentration is calculated by adopting the electroneutrality condition of the pore solution:

$$[\text{OH}^-] = [\text{Na}^+] + [\text{K}^+] \quad (9)$$

3.2. Effective chloride diffusion coefficient

The effective chloride diffusion coefficient is a major input data. In general, effective chloride diffusion coefficients determined from different test methods are not directly comparable. Even, when the same method is used, different exposure solutions may also result in different diffusion coefficients (Andrade, *et al.* 2000, Baroghel-Bouny, *et al.* 2004a). Non-steady-state migration tests under an electrical field are now commonly used to estimate the diffusion coefficients of cement-based materials (Tang and Nilsson 1992). In this case chloride binding is neglected, as the duration of the test is short (10-60h) and as the transport rate is very fast. Therefore, this method seems to be an efficient way to assess the effective diffusion coefficient. Over the past decade, various approaches have been proposed to analyze migration test results. In many cases, the interpretation of test data is based on a series of simplifying assumptions. However, a thorough analysis of the various transport mechanisms that take place during a migration experiment suggests that some of them are probably not valid (Samson and Marchand 2003). In addition, the effective diffusion coefficient obtained from this method can vary with experimental conditions. This is of course not satisfactory, since there is only one effective chloride diffusion coefficient for a given concrete. Consequently, a more rigorous approach to analyze migration test results is needed.

In an attempt to assess apparent chloride diffusion coefficients, Tang and Nilsson (1992) proposed an analysis of non-steady-state migration tests. According to Tang and Nilsson's approach (1992), the potential gradient across the sample is assumed to be constant and to correspond to the externally applied electrical field. For semi-infinite media, the analytical solution of the chloride

concentration can be found in Tang (1996b) and in Samson and Marchand (2003). According to this approach, the value of the apparent chloride diffusion coefficient is obtained by fitting the chloride profile calculated numerically to one measured during the migration test. Many authors found the diffusion coefficient value derived from this approach to be sensitive to the boundary conditions (McGrath and Hooton 1996). But as previously mentioned the diffusion coefficient should be an “intrinsic” property of the material and of the ionic species considered and thus should be independent of the boundary conditions. The apparent sensitivity of the diffusion coefficient values questions the validity of the constant field assumption. In order to solve this question, several migration tests were simulated by using the proposed numerical model. It has to be underlined that these simulations were performed by using a constant voltage and not a constant current density. The boundary conditions correspond to the concentration in both upstream and downstream compartments as well as the imposed potential difference across the sample. The boundary conditions were assumed as constant, as the duration of the test was short enough to neglect the variations of the concentrations in the both upstream and downstream compartments. In the papers dealing with the analysis of non-steady-state migration test data, it is assumed that chemical reactions can be neglected. This hypothesis is, at least partially, justified by the fact that non-steady-state migration tests have a shorter duration than steady-state experiments. In addition, the high velocity of the ions being transported through the sample tends to greatly attenuate the influence of chemical reactions (Castellote, *et al.* 1999). Neglecting the chemical reactions also implies that there is no change in the microstructure of the material during the whole duration of the test, which is equivalent to the assumption that the porosity and tortuosity remain constant.

The concrete indicated by BO has been chosen for the simulations (Baroghel-Bouny, *et al.* 2004a). The mix composition and the main characteristics of the tested concrete are summarized in Table 2. The set-up for the migration test is presented in Fig. 7(a). The input data used for the numerical simulations are given in Table 3. Condition No. 1 is in accordance with the LCPC test method, while conditions No. 2 to No. 7 are modifications of No. 1.

Typical results for non-steady-state migration test simulations are presented in Fig. 7(b). The figure reveals only slight differences between the potential profiles predicted by the model and that predicted by the constant electrical field assumption. However, the slight differences in the potential profiles lead to significant differences in chloride concentration profiles, as shown in Fig. 7(b) when

Table 2 Information on concrete BO

Properties	Values
Gravel (G) (min/max grain size in mm)	1192 (4/20)
Sand (S) (min/max grain size in mm)	744 (0/5)
Cement (C)	353
Water (W)	172
Water to Cement ratio (W/C)	0.49
Total aluminate content of the cement (% by unit mass of cement)	10.9
App. Density of the dry concrete ($\text{kg}\cdot\text{m}^{-3}$)	2292
Porosity accessible to water (%)	12.1
28-day compressive strength (MPa)	49.7

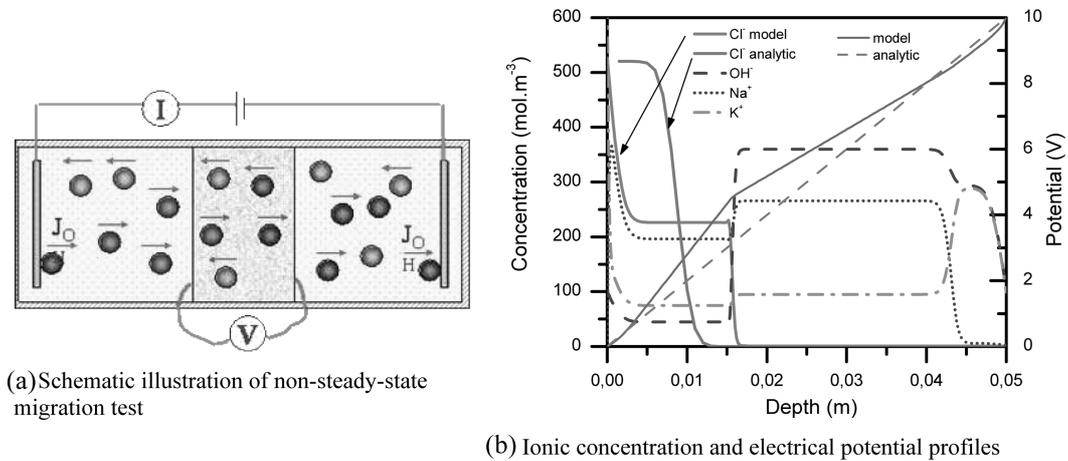


Fig. 7 Setup and typical results of simulation of non-steady-state migration tests

comparing the profile obtained by the analytical formula (“Cl⁻ analytic”) under the assumption of constant electrical field and the one predicted by the numerical model (“Cl⁻ model”). This result indicates that the weak local electrical field induced by ion-ion interactions has a strong influence on the penetration of the ions during a non-steady-state migration test, as shown by the computation performed by Samson and Marchand (2003). Indeed, it can be seen in Fig. 7(b) (where considering the slopes of the potential curve) that the electrical field is larger upstream than downstream since the conductivity of the pore solution is lower upstream. The conductivity is lower, since, chlorides penetrate the concrete sample, while hydroxyl ions go out. As the chloride diffusion coefficient is smaller than the one for hydroxyls, the conductivity decreases.

Non-steady-state migration test results obtained on BO are given in Fig. 8 (Baroghel-Bouny, *et al.* 2004a) for different test conditions. The chloride profiles are similar in shape to those usually found in the literature for non-steady-state migration tests (Tang and Nilsson 1992, Tang 1996a). The major problem for the simulation of non-steady-state migration tests is that the pore solution

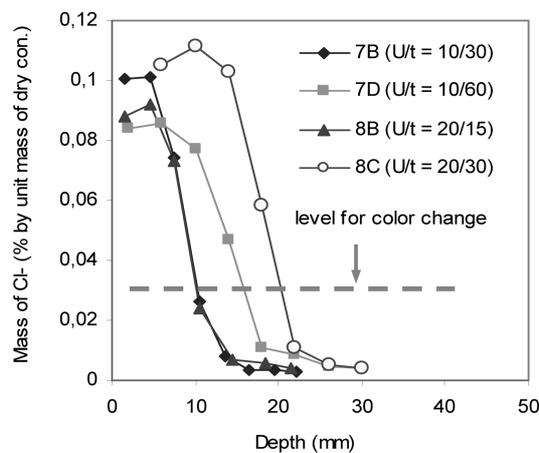


Fig. 8 Chloride concentration profiles measured on concrete BO (non-steady-state migration tests)

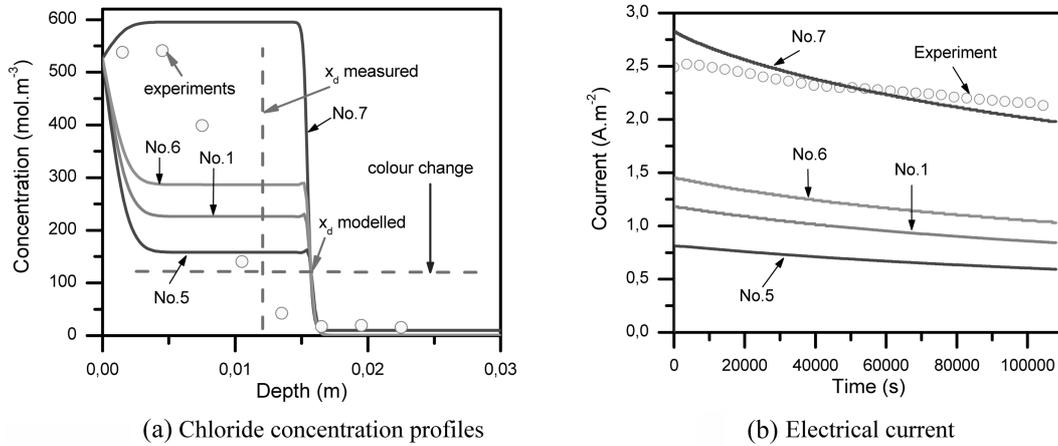


Fig. 9 Sensitivity of the model (non-steady-state migration tests): effect of the pore solution composition

Table 3 Simulation conditions for non-steady-state migration and diffusion tests

No	U (V)	t (h)	Upstream solution (mol·m ⁻³)				Pore solution (mol·m ⁻³)			Downstream solution (mol·m ⁻³)		
			Cl ⁻	OH ⁻	Na ⁺	K ⁺	OH ⁻	Na ⁺	K ⁺	OH ⁻	Na ⁺	K ⁺
1	10	30	523.2	100	623.2	0	360	95	265	100	100	0
2	-	60	-	-	-	-	-	-	-	-	-	-
3	20	15	-	-	-	-	-	-	-	-	-	-
4	-	30	-	-	-	-	-	-	-	-	-	-
5	10	30	-	-	-	-	200	95	105	-	-	-
6	-	-	-	-	-	-	450	200	250	-	-	-
7	-	-	-	-	-	-	800	400	500	-	-	-
8	0	10 ³	500	100	600	0	450	200	250	450	200	250
9	-	-	700	100	800	0	-	-	-	-	-	-
10	-	-	1100	100	1200	0	-	-	-	-	-	-

composition is not known in detail. Therefore, it was decided to take four different pore solution compositions for these calculations and to study the sensitivity of the results (concentration profiles and electrical current) to the variation of the pore solution composition. The first composition (Test No.1) is obtained by the method proposed in section 3.1, while compositions in Test No.5 to No.7 are variations of the first composition. The compositions are given in Table 3. These pore solution compositions were used as initial conditions for the simulations of the non-steady-state migration tests. The comparison of the profiles calculated by the model and the measurement results (see Fig. 9a) illustrates the difficulty of calculating diffusion coefficients by fitting the calculated profiles to the one measured during the migration test.

As shown in Fig. 9, the initial pore solution composition strongly influences the simulation results. Given the marked difference between the shapes of two curves and the sensitivity of the chloride concentration profiles on the pore solution composition, it can be deduced that a reliable assessment of the diffusion coefficient requires an accurate determination of the pore solution

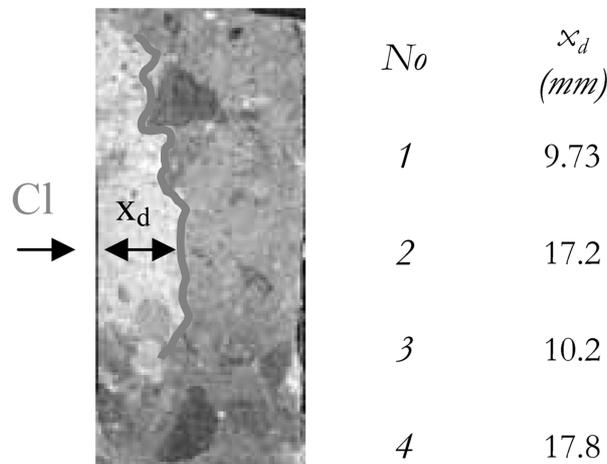


Fig. 10 Colorimetric method and results on concrete BO

composition. Samson and Marchand (2003) have proposed a new method to calculate diffusion coefficients using migration test results. The test procedure is relatively simple and consists in measuring the evolution of the electrical current passing through the sample. Experimental results are then analyzed using a numerical model based on the Nernst-Planck/Poisson set of equations. Chemical reactions are neglected. For each experiment an algorithm is used to determine the chloride diffusion coefficient that allows to best reproduce the current curve measured experimentally. Such a method requires a sophisticated calculation and as previously mentioned the detailed composition of the pore solution (see Fig. 9b).

Another type of method is proposed here for the assessment of the effective chloride diffusion coefficient. It is based on the measurement of the chloride penetration depth by using a colorimetric method (AgNO_3 spray test) and on the fitting of the chloride penetration depth calculated numerically to the one measured (Baroghel-Bouny, *et al.* 2004a) (see Fig. 10). This choice results from the observation that the initial composition of the pore solution does not significantly influence the chloride penetration depth results (same x_d are found in the four cases, as displays in Fig. 9a).

Here the threshold detection concentration of the colorimetric method is assumed to be $160 \text{ mol}\cdot\text{m}^{-3}$ (Baroghel-Bouny, *et al.* 2004a). The effect on the migration results of the experimental conditions such as the applied potential and the test duration is presented in Fig. 11. The effective diffusion coefficient D_e obtained is slightly dependent on the external potential applied to the sample (see Fig. 11b). It can be noted that the maximum error on D_e is about 15%. This is an acceptable discrepancy, given the usual experimental variations recorded. As shown in the Fig. 11b, the values determined from this method agree rather well with the ones directly measured by steady-state migration tests (Baroghel-Bouny, *et al.* 2004a). In addition, a good relevance has already been reported in the literature for the assessment of the effective chloride diffusion coefficient by using the steady-state migration tests (see for example Truc, *et al.* 2000b). Therefore, it could be concluded that, in the non-stead-state migration test the limited information on the composition of the pore solution and the experimental conditions do not result into a large measurement uncertainty. From these observations, it is now possible to calculate the chloride diffusion

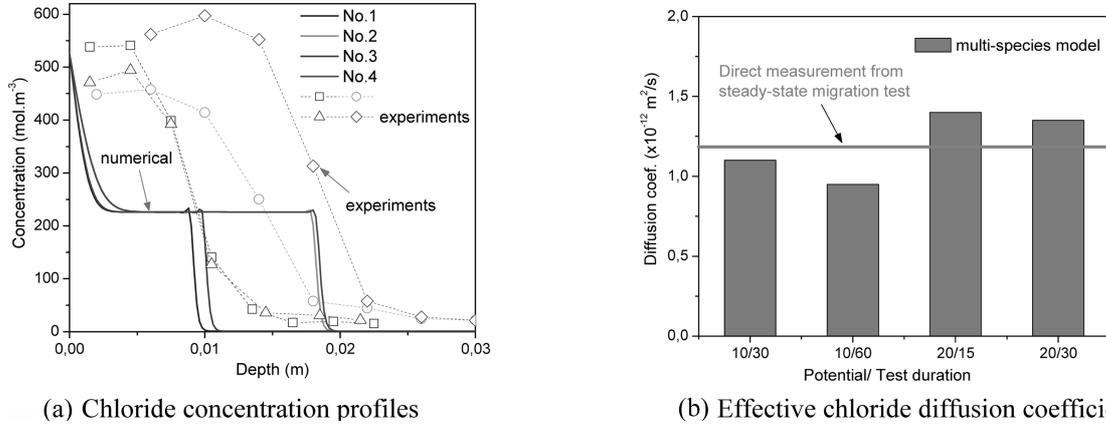


Fig. 11 Chloride concentration profiles and effective chloride diffusion coefficients. Measurements and numerical simulations

coefficient on the basis of the average chloride penetration depth x_d in the material after the migration test and by using the numerical model.

3.3. Effective diffusion coefficient of the other species

In order to apply the multi-species model, the effective diffusion coefficients of all the species, which are taken into account in the model, have to be known. Several studies have indicated that hydrated cement affects the diffusion of cations to a greater extent than that of anions (Goto and Roy 1981, Atkinson and Nickerson 1984). In other words, tortuosity seems to affect differently cation and anion movements. Such effects may result from the surface charge of the pore walls, which may partly result in the binding of chloride ions previously discussed. Thus, it has been argued that the typical hydration products of Portland cement will tend to adsorb anions that replace desorbed hydroxyl surface groups. In this case the pore surface will exhibit a positive charge and will act as an anion exchange membrane. In reality, the sign and value of the surface charge have been found to depend on the electrolyte composition and pH, as well as on the binder type and composition of the hydration products. However, to make up for any lack of experimental data, in this model the effective diffusion coefficients of the other species D_i will be estimated from the ratio, as proposed in Truc, *et al.* (2000a), according to Eq. (10):

$$\frac{D_{eff}}{D_i} = \frac{D_{cl}^o}{D_i^o} \quad (10)$$

where D_{cl}^o and D_i^o are the coefficients in an infinitely diluted solution, for each ion i .

3.4. Chloride binding isotherm

Data on chloride binding data are highly important, as bound chlorides do not directly participate in ionic transport processes and do not alter the pore solution concentration. Thus chloride binding strongly influences the rate of chloride penetration into concrete exposed to external chloride source, the net effect being to slow down the rate of penetration. Several techniques exist to assess binding

isotherms. The profile method proposed by Baroghel-Bouny (2004b) is based on the measurement of total and “free” chloride concentration profiles obtained from a non-steady-state diffusion test. The amount of bound chlorides is calculated in this case as the difference between the total and the “free” chloride ones at each depth. In the equilibrium method developed by Tang and Nilsson (1993), the measurement of the decrease in chloride concentration in a solution in contact with the crushed material leads to a relation between bound and “free” chlorides when equilibrium is reached. Larsen (1998) also proposed to use an immersion test, until equilibrium. The extraction of the pore solution combined with the quantification of the total chloride content by chemical analysis, also leads to a relation between bound and “free” chlorides. The various methods have advantages and drawbacks. The first method requires only one sample but there is a difficulty for the measurement of the “free” chloride concentration (condensation phenomenon at the surface Nagataki, *et al.* 1993). The two latter methods require a sample of material for each point of the binding isotherm. Furthermore, all concentration measurements require sample crushing and, as a consequence do not account for the actual microstructure of concrete in service.

Consequently, an indirect method called “numerical inverse method” is proposed. It consists in measuring a total chloride concentration profile after a non-steady-state diffusion test, which is the data most often available. The experimental results are analyzed by using the proposed numerical model (see section 2). A simple algorithm is used to determine the binding isotherm for each experiment, which results in the best reproduction of the experimental total chloride concentration profiles.

Here, the complicated chloride binding phenomenon is described globally by means of Freundlich’s non linear isotherm (see Eq. (5b)). With the initial conditions and the effective chloride diffusion coefficient determined by the methods proposed in section 3.1 and 3.2 respectively, the equations are solved with different m and g values, which are adjusted in an iterative manner in order to minimise the χ function, as described in the following. The χ function is calculated at each measurement time:

$$\chi = \sqrt{\sum_{k=1}^M [c_k^{\text{mes}}(x_k) - c_k^{\text{num}}(x_k)]^2} \quad (11)$$

where c_k^{mes} and c_k^{num} are the measured and predicted chloride concentrations at depth x_k , respectively, and M is the total number of measurements.

The values of the isotherm parameters, which lead to the smallest error with respect to the measurement, yield the best estimate of the binding isotherm for the material considered. This analysis procedure is performed automatically by using the downhill simplex method of Nelder and Mead (1965). The method only requires function evaluations, not derivatives. It is not very efficient in terms of the number of function evaluations that it requires. It is important to apply the minimization procedure several (5-10) times by using different initial values for the fitting parameters, in order to ensure that the global minimum of the χ function has finally been located. Note that the relevance of the proposed method can be evaluated a posteriori through its accuracy to fit a lot of experimental plots, thanks to the identification of two material binding parameters.

Estimation results of chloride binding isotherm by inverse analysis are shown in Fig. 12. The binding isotherm parameters μ and γ are identified by “numerical inverse method” from an experimental total chloride concentration profile obtained at 44 days with the hardened cement pastes CO and CN (CEM I 52.5; W/C = 0.35 and 0.45 respectively) (Chaussadent, *et al.* 2000). The

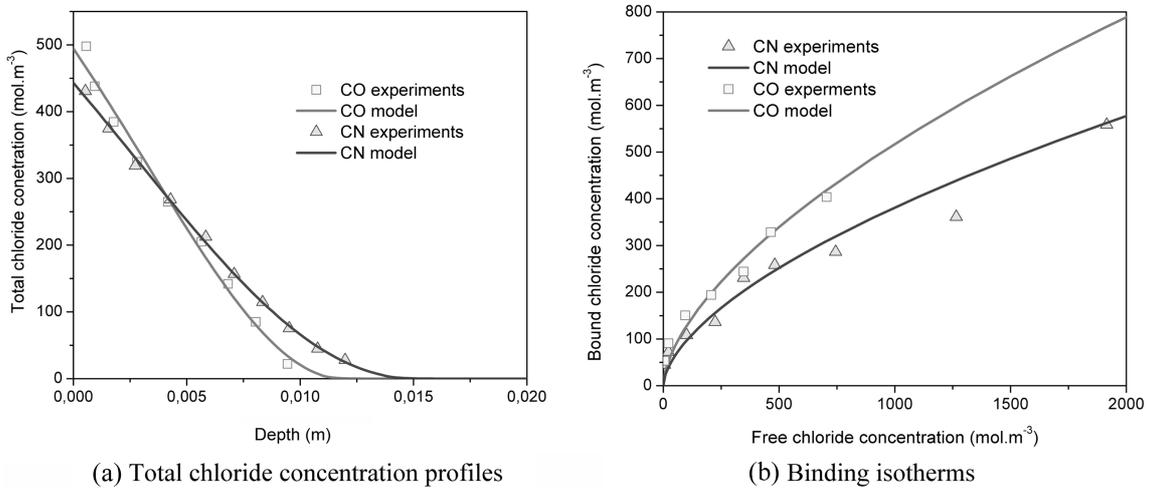


Fig. 12 Chloride concentration profiles and binding isotherm in the case of non-steady-state diffusion tests. Measurements obtained by immersion tests and numerical estimated chloride binding with the LCPC model

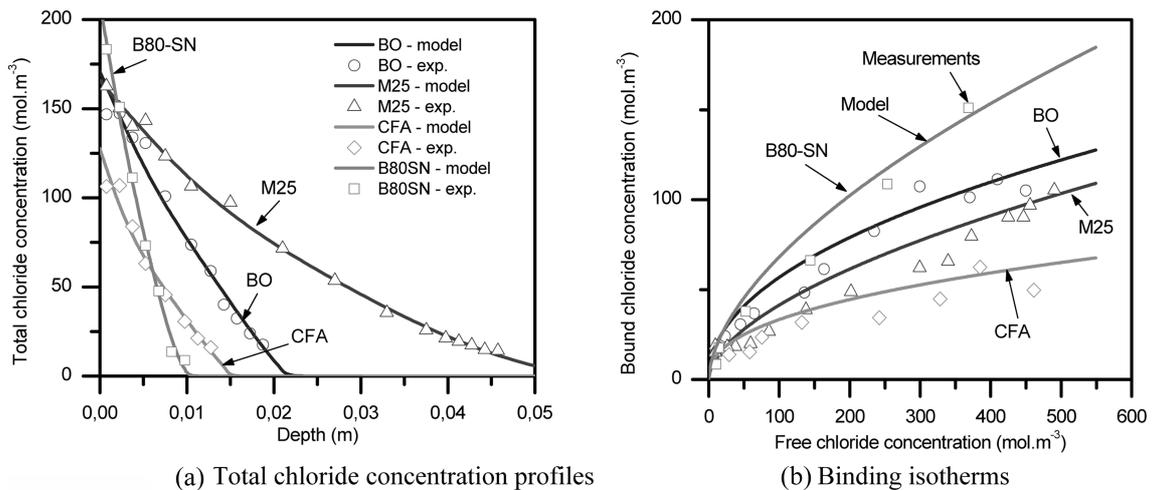


Fig. 13 Some examples of fitting results for concentration profiles by using the reverse analysis method

experimental binding isotherm was determined by using the equilibrium method on crushed pastes particles. Fig. 12(b) shows the comparison between the results from the present method and the experiments. It can be noticed that the results obtained from the experiments and numerical inverse method are almost in good agreement. In addition, it shows that the numerical model predict very well the binding capacity at high chloride concentration for the paste CN.

Simulations with various concretes were performed to test the method reliability in predicting chloride-binding isotherm (see Fig. 13). As shown in Fig. 13(a), good fitting results were obtained in every case with correlation coefficient higher than 0.97. As depicted in Fig. 13(b), the good correlation between isotherms obtained numerically and isotherms deduced from the profiles (non-steady-state diffusion test) is a good argument to validate the proposed method. In addition, the

method can easily be applied to concretes with different water-to-binder ratios and which incorporate supplementary cementing materials (concretes B80-SN and CFA). From these analyses, the estimated non-linear binding parameters estimated by the “inverse method” in this study are thought to be appropriate.

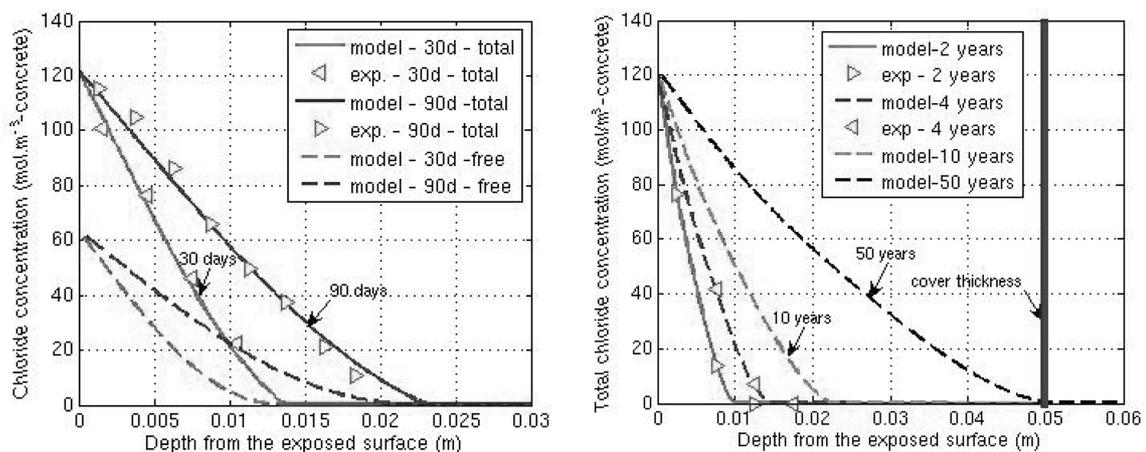
However, the dependence of the binding on the condition of ionic concentration in the pore solution and the conditions in solid phase of concrete are very important and cannot be directly included in the non-linear binding model suggested here. When additional data are available on a chloride binding mechanism, the semi-empirical Freundlich’s relation could be replaced by a more chemically-based factor. For example, the role of chemical binding (formation of Friedel’s salt) has been presented recently in Nguyen, *et al.* (2006).

4. Modelling of chloride ingress into the concrete

4.1. Comparison with the experiments

The initial conditions are determined according to the method described in section 3.1. The effective chloride diffusion coefficient is calculated from the measurement of the average chloride penetration depth by the colorimetric method, as explained in section 3.2. The binding isotherm parameters m and g are quantified by the “numerical inverse method” from an experimental total chloride concentration profile obtained at a given exposure time with the studied material (see section 3.4). Once these data are included in the multi-species model, it is then possible to predict “free” or/and total chloride concentration profiles at longer exposure times for the same material.

This method has been applied to a diffusion test carried out on concrete BO under non-steady-state conditions in the laboratory. The experimental total (acid soluble) chloride concentration profile has been measured by grinding and chemical analysis (Baroghel-Bouny, *et al.* 2004a), after 30 days and 90 days in $30 \text{ g}\cdot\text{L}^{-1}$ NaCl and NaOH 0.1 M (Baroghel-Bouny 2004b). The “numerical



(a) Concrete BO – Non-steady-state diffusion test in laboratory (b) Concrete M120FS – Marine environment (La Rochelle)

Fig. 14 Chloride concentration profiles. Measurements and numerical simulations with the LCPC model

inverse method” has been applied at time 30 days, while the comparison between model and experiment has been performed at 90 days, indicating a good agreement (see Fig. 14a).

The method has also been applied to a RC structural element (high-performance concrete M120FS: CEM I 52.5; W/C=0.26; SF/C=0.12) in a marine environment (tidal zone in La Rochelle (Baroghel-Bouny, *et al.* 2004c)). The experimental total chloride concentration profile after 2-year exposure has been used to identify the input data. It was then possible to predict the profiles after 4-, 10- and 50-year exposure. A good agreement with the available experimental profile at 4 years is obtained (see Fig. 14b). In addition, Fig. 14(b) shows that chlorides will not reach the level of the reinforcement steel in sufficient amounts to cause depassivation for a cover thickness of 50 mm within 50-year exposure.

The quality of the numerical prediction seems sensitive to the variables of the model (i.e. ϕ , D_e , μ and γ). Thus, the influence of these parameters on the results of the model is studied in the following section.

4.2. Sensitivity of the modelling to material properties

This section analyses the influence of the material properties on the modelling of chloride penetration into water saturated concrete. Four parameters (total porosity ϕ ; effective chloride diffusion coefficient D_e ; parameters μ and γ of chloride binding isotherm; initial alkali concentrations Na^+ , K^+) were selected to study the sensitivity of the numerical calculations. Uncertainty values of the parameters are given in Table 4. The effects of these parameters are studied independently. This means that only one single parameter changes at a given time and the three others remain fixed. The effect of these parameters is observed on the chloride penetration depth at 3 months in $30 \text{ g}\cdot\text{L}^{-1}$ NaCl and NaOH 0.1 M (here, a chloride threshold concentration $160 \text{ mol}\cdot\text{m}^{-3}$ of pore solution was assumed).

The results in Fig. 15 show that a variation of the porosity or the alkali concentrations has a small influence on the results of the mathematical model. In fact, variations of 20% of the initial alkali concentrations and 10% of the porosity induce a variation of the numerical prediction lower than 2.5% around the prediction obtained with the reference values. The variations are even lower than 1% for the initial alkali concentrations. The effective chloride diffusion coefficient plays an important role in the results. A variation of 15% in the effective chloride diffusion coefficient induces a large variation in the penetration depth (7.5%). The most important parameters are the chloride binding isotherm parameters. In fact, variation of 10% of these parameters leads to a variation of 9% in the numerical results. As shown in Fig. 15, the results of the numerical simulation appears to be in good agreement with the experimental results. The discrepancy observed between the experimental data (Baroghel-Bouny, *et al.* 2004a) and the numerical prediction of the chloride penetration depth can be explained by an underestimation of the effective chloride diffusion coefficient or overestimation of the binding isotherm. In fact, reducing binding capacity or increasing

Table 4 Data for sensitivity study

Parameter	1	2	3	4	5	6
	ϕ	D_e	μ	γ	Na^+	K^+
Reference value	0.121	1.2×10^{-12}	5.6	0.48	95	265
Uncertainty	$\pm 10\%$	$\pm 15\%$	$\pm 10\%$	$\pm 10\%$	$\pm 20\%$	$\pm 20\%$

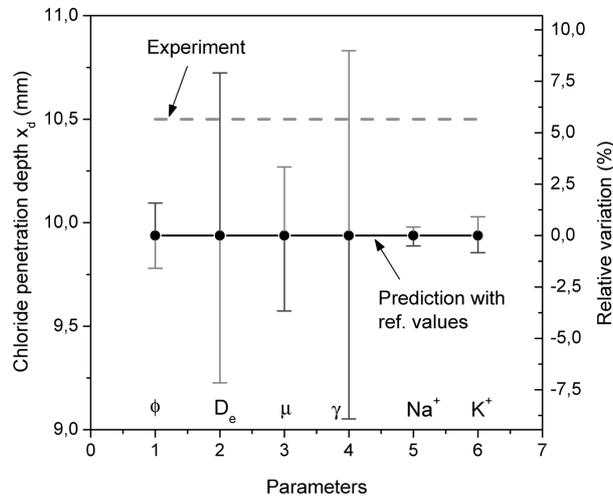


Fig. 15 Concrete BO: Effect of uncertainties of the material parameters on the chloride penetration depth at 3 months

effective chloride diffusion coefficient will lead to a faster ingress of the penetration front.

5. Conclusions

In this work, an approach is proposed for predicting chloride ingress into concrete. A multi-species model considering the electrical coupling between ions is applied. The numerical method requires the knowledge of the porosity, the effective chloride diffusion coefficient, the binding isotherm and the pore solution composition. Methods of assessment of these parameters are presented in the paper. Then, the finite volume method has been used for the numerical resolution. Due to its conservative properties, this method can accommodate high nonlinearities and ensures a good prediction of the kinetics of chloride penetration or total and “free” (i.e. water-soluble) chloride concentration profiles. Engineers can use these numerical solutions as a predictive tool for the estimation of the service life of reinforced concrete structures in the design stage, thus reducing costly on-site experimentation.

The simulations reported in this paper point out that chloride penetration in concrete can be predicted “a priori” if the proper parameters are correctly estimated. The alkali concentrations and the pH can be assessed from the mix composition and an analytical model for cement hydration. The predicted results agree well with the experimental ones reported in the literature. In addition to boundary conditions, a set of two characteristics is required: effective chloride coefficient and binding isotherm. The proposed approach to assess these parameters is based on an analysis of diffusion and migration tests within the non-steady-state regime with a multi-species model. The chemical reactions are neglected in the analysis of the migration used to determine the chloride diffusion coefficient. The diffusion test is used to identify the binding isotherm and to validate the simulation. Although the proposed method requires a more sophisticated calculation, it also offers some advantages: it is based on chloride penetration depth measurement, which is cheap and easy to perform and on a total chloride concentration profile which is the data most often available. By

using the estimated parameters from an experiment obtained at a given exposure time with the studied material, “free” or/and total chloride concentration profiles at longer exposure times were predicted and compared with experimental results. A good agreement was obtained. Furthermore, it has been shown that the influence of chloride binding is important, whereas porosity and pore composition have negligible effects on service life predictions. The understanding of the binding properties of a given cementitious system enables to better estimate chloride penetration depths and therefore, the depassivation time of reinforcing steel.

References

- Andrade, C., Castellote, M., Alonso, C., and Gonzalez, C. (2000), “Non-steady-state chloride diffusion coefficients obtained from migration and natural diffusion test-Part I: Comparison between several methods of calculation”, *Mater. Struct.*, **33**, 21-28.
- Atkinson, A. and Nickerson, A.K. (1984), “The diffusion of ions through water-saturated cement”, *J. Mater. Sci.*, **19**, 3068-3078.
- Baroghel-Bouny, V. (1994), “Caractérisation des pâtes de ciment et des bétons-Méthodes, analyse, interprétation”, *Laboratoire Central des Ponts et Chaussées*.
- Baroghel-Bouny, V., and al. (2004a), “Which toolkit for durability evaluation as regards chloride ingress into concrete? Part I: Comparison between various methods for assessing the chloride diffusion coefficient of concrete in saturated conditions”, *Proc. of the 3rd Int. RILEM Workshop “Testing and modelling chloride ingress into concrete”*, Sept., Madrid, Spain (Ed. By C. Andrade & J. Kropp, RILEM Publ., Bagneux, 2004), **PRO 38**, 105-136.
- Baroghel-Bouny, V. (2004b), “Which toolkit for durability evaluation as regards chloride ingress into concrete? : Part II. Development of a performance approach based on durability indicators and monitoring parameters”, *Proc. of the 3rd Int. RILEM Workshop “Testing and modelling chloride ingress into concrete”*, Sept., 2002, Madrid, Spain (Ed. By C. Andrade & J. Kropp, RILEM Publ., 2004), 137-163.
- Baroghel-Bouny, and al. (2004c), “Ageing of concretes in natural environments: an experiment for 21st century. IV-Results on cores extracted from field-exposed test specimens of various sites at first times of measurement”, *Bul. Lab. Ponts & Chaus.* **249**, 49-100.
- Beaudoin, J.J., Ramachandran, V.S., and Feldman, R.F. (1990), “Interaction of chloride and C-S-H”, *Cement Concrete Res.*, **20**, 875-883.
- Bigas, J.P. (1996), “La diffusion des ions chlore dans les mortiers”, Ph.D thesis, Génie civil, Toulouse (in French).
- Birmin-Yauri, U.A. and Glasser, F.P. (1998), “Friedel’s salt: Its solid solution and their role in chloride binding”, *Cement Concrete Res.*, **28**, 1713-1723.
- Brouwers, H.J.H. and van Eijk, R.J. (2003), “Alkali concentration of pore solution in hydrating OPC”, *Cement Concrete Res.*, **33**, 191-196.
- Castellote, M., Andrade, C., and Alonso, C. (1999), “Chloride binding isotherms in concrete submitted to non-steady-state migration experiments”, *Cement Concrete Res.*, **29**, 1799-1806.
- Chaussadent, T., Baroghel-Bouny, V., Care, S., Perrin, B., Bonnet, S., François, R., Francy, O. (2000), Transferts dans les bétons et durabilité des ouvrages. Analyse des interactions physico-chimiques entre les chlorures et le béton, Thème de Recherche OA9-Sujet n° 3-Programme 3.1, Rapport de synthèse LCPC/LETHEM/LMDC, 41 p.
- Eymard, R., Gallouet, T., Herbin, R., in: P. Ciarlet, J.L. Lions (Eds.) (2004), *Handbook of Numerical Analysis: The Finite Volume Method*, in press.
- Francy, O. (1998), “Modélisation de la pénétration des ions chlorures dans les mortiers partiellement saturé en eau”, Ph.D thesis, Génie civil, Paul Sabatier, Toulouse (in French).
- Frederiksen, J.M. (1996), “Chloride penetration into concrete state-of-the-art”, Report No. 53, The Danish Road Directorate, 118-123.
- Goto, S. and Roy, D.M. (1981), “Diffusion of ions through hardened cement pastes”, *Cement Concrete Res.*, **11**, 751-757.
- Hausmann, D.A. (1967), “Steel corrosion in concrete: How does it’s occur”, *Materials Protection*, **4**,

- 19-25.
- Helferich, F. (1962), *Ion Exchange*, McGraw-Hill, New York.
- Hong, S.Y. and Glasser, F.P. (1999), "Alkali binding in cement paste: Part I. The C-S-H phase", *Cement Concrete Res.*, **29**, 1893-1903.
- Larbi, J.A., Fraay, A.L.A., and Bijen, J.M. (1990), "The chemistry of the pore fluid of silica fume-blended cement systems" *Cement Concrete Res.*, **20**, 506-516.
- Larsen, C.K. (1998), "Chloride binding in concrete, effect of surrounding environment and concrete composition", PhD thesis, Norwegian University.
- Li, L.Y. and Page, C.L. (1998), "Modelling of electrochemical chloride extraction from concrete: Influence of ionic activity coefficient", *Comput Mat. Sci.* **9**, 303-308.
- Masi, M., Colella, D., Radaelli, C., and Bertolini, C. (1997), "Simulation of chloride penetration in cement-based materials", *Cement Concrete Res.* **27**, 1591-1601.
- Marchand, J., Samson, E., Maltais, Y., Lee, R.J., and Sahu, S. (2002), "Predicting the performance of concrete structures exposed to chemically aggressive environment-Field validation", *Mater. Struct.*, **35**, 623-631.
- McGrath, P.F. and Hooton, R.D. (1996), "Influence of voltage on chloride diffusion coefficient from the migration tests" *Cement Concrete Res.*, **23**, 1329-1244.
- Mounanga, P., Khelidj, A., Loukili, A., and Baroghel-Bouny, V. (2004), "Prediction Ca(OH)₂ content and chemical shrinkage of hydrating cement pastes using analytical approach", *Cement Concrete Res.* **34**, 255-265.
- Nagataki, S., Otsuki, N., Wee, T.H., and Nakashita, K. (1993), "Condensation of chloride ion in hardened cement matrix materials and on embedded steel bars", *ACI Mater. J.*, **90**(3), 323-332.
- Nelder, J.A. and Mead, R. (1965), *Comput J.*, **7**, 308-313.
- Nilsson, L.O. (2005), "WP4 report-modelling of chloride ingress", Report, 112p.
- Nguyen, T.Q., Baroghel-Bouny, V., Dangla, P., and Belin, P. (2006), "Multi-level modelling of chloride ingress into saturated concrete", *Proc. of Int. RILEM Workshop "Performance based evaluation and indicator for concrete durability"*, Madrid, Spain, Mar.
- Papadakis, V.G. (2000), "Effect of supplementary cementing materials on concrete resistance against carbonation and chloride ingress", *Cement Concrete Res.* **30**, 291-299.
- Pollitt, H.W.W. and Brown, A.W. (1969), 5th ISCC, vol. 1, p. 322.
- Samson, E. and Marchand, J. (1999a), "Numerical solution of the extended Nernst-Planck model", *J. Colloid Interf. Sci.* **215**, 1-8.
- Samson, E., Lemaire, G., Marchand, J., and Beaudoin, J.J. (1999b), "Modelling chemical activity effects in strong ionic solution", *Comput. Mater. Sci.* **15**, 285-294.
- Samson, E. and Marchand, J. (2003), "Calculation of ionic diffusion coefficients on the basis of migration test results", *Mater. Struct.*, **36**, 156-165.
- Suryavanshi, A.K., Scantlebury, J.D., and Lyon, S.B. (1996), "Mechanism of Friedel's salt formation in cements rich in tri-calcium aluminate", *Cement Concrete Res.* **26**, 717-727.
- Tang, L. (1996a), "Chloride transport in concrete-measurement and prediction", PhD thesis, Building Materials, Chalmers, Gothenburg.
- Tang, L. (1996b), "Electrically accelerated methods for determining chloride diffusivity in concrete-Current development", *Mag. Concrete Res.*, **48**, 173-179.
- Tang, L. and Nilsson, L.O. (1993), "Chloride binding capacity and binding isotherms of OPC pastes and mortar", *Cement Concrete Res.* **23**, 247-253.
- Tang, L. and Nilsson, L.O. (1992), "Rapid determination of the chloride diffusivity in concrete by applying an electrical field", *ACI Mater. J. Technical paper*, 49-53.
- Taylor, H.F.W. (1987), "A method for predicting alkali ion concentration in cement pore solution", *Adv. Cement Res.*, **1**, 5-16.
- Truc, O., Ollivier, J.P., and Nilsson, L.O. (2000a), "Multi-species transport in saturated cement-based materials", *Proc. of the 2nd RILEM Workshop "Testing and modelling chloride ingress concrete"*, Sep., Paris, France 1995 (Ed. By C. Andrade & J. Kropp, RILEM Publ., 2000), 247-259.
- Truc, O. and Ollivier, J.P. (2000b), Carcasses, M., "A new way for determining the chloride diffusion coefficient in concrete from steady-state migration tests", *Cement Concrete Res.*, **30**, 217-226.