Cement & Concrete Composites 31 (2009) 515–521

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Predicting the service-life of concrete structures – Limitations of simplified models

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ARTICLE INFO

Article history:
Received 8 September 2008
Received in revised form 8 January 2009
Accepted 12 January 2009
Available online 27 January 2009

Keywords:
Chloride ingress
Fick's law
Simplified models

ABSTRACT

North American civil infrastructure systems are deteriorating. Roads, bridges, overpasses, marine and airport facilities are all impacted. The primary causes of premature concrete deterioration are harsh climatic conditions and chemical attacks, particularly exposure to winter de-icing salts and seawater. Given the growing concern for concrete degradation, numerous computer-assisted tools have been developed to assist engineers in the prediction of the service-life of structures. Many of these models are based on simplified equations that significantly restrict the scope of their application. The limitations of these approaches for the design of new construction and rehabilitation of existing structures are discussed. The theoretical assumptions at the basis of these models are first reviewed. Special attention is paid to the consequences of these simplifying assumptions on the reliability of the models. The difficulties of using these simplified models for the treatment of actual structures exposed to natural conditions are then discussed.

1. Introduction

Hydrated cement systems (cement pastes, mortars, plain and fibre-reinforced concretes) are used in the construction of a wide range of different structures, many of which are being exposed in service to chemically aggressive environments. Deterioration mechanisms generally involve the penetration of external ions into the material pore structure and/or the dissolution of chemical species from its hydrated and unhydrated phases. Laboratory test results and field experience clearly indicate that the durability of cement-based composites is, in most cases, controlled by their ability to act as a tight barrier that can effectively impede, or at least slow down, the transport process [1].

Given the increasing importance of durability problems, transport phenomena in hydrated cement systems have received a great deal of attention over the past decades. Collaborations between physicists, electrochemists, materials science specialists and civil engineers have contributed to gradually refine our understanding of the basic mechanisms that control the movement of ions and moisture in these materials [1,2]. Theoretical advances on the subject have not only allowed improving existing standards and codes of practice but they have also led to the introduction of a variety of models developed to assist engineers in the design of durable concrete structures. If the scope of these tools was initially limited to the treatment of relatively simple problems, systematic innovations in the field of computer science have enabled engineers to tackle increasingly complex problems [3]. Specialists have now access to service-life models that can describe the coupled transport of moisture and multiple ions in concrete elements subjected to a wide range of fluctuating exposure conditions.

Despite the significant improvements in the sophistication of service-life models, many scientists and engineers still elect to rely on simplified approaches to predict the behavior of concrete exposed to chemically aggressive environments. The limitations of these approaches for the design of new construction and rehabilitation of existing structures are discussed in the next sections. After a brief historical review, the theoretical assumptions at the basis of these models are presented. Special attention is paid to the consequences of these simplifying assumptions on the reliability of the models. The difficulties of using these simplified models for the treatment of actual structures exposed to natural conditions are then discussed.

2. Brief historical review

Given the ubiquity of steel corrosion problems, investigations on mass transfer in concrete have been mostly focused on chloride transport mechanisms. In their pioneer paper published in 1966, Ost and Monfore [4] were among the first to emphasize the fact that the resistance of concrete to chloride penetration is greatly dependent upon the water/cement ratio of the mixture. Their conclusion was later confirmed by the study of Collepardi et al. [5] who also observed that the addition of natural pozzolans and a reduction of the ambient temperature could significantly decrease the kinetics of chloride diffusion in neat paste and concrete

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doi:10.1016/j.cemconcomp.2009.01.007

samples. Both papers concerned chloride penetration in mature mixtures that had been maintained fully saturated throughout the entire experiments.

From the standpoint of modeling, the contribution of Collepardi et al. [5] is of particular interest since it is probably the first paper on hydrated cement systems in which authors were attempting to quantify the kinetics of chloride penetration using a mathematical equation.[1] In this particular case, Collepardi et al. [5] analyzed their chloride profiles using the mathematical expression proposed by Fick in 1855 [6,7][2] to describe the diffusion of matter in permeable media:

$$\frac{\partial c}{\partial t} - D^* \frac{\partial^2 c}{\partial x^2} = 0 \tag{1}$$

In this expression, D^* stands for the diffusion coefficient (often called the apparent diffusion coefficient) and c the chloride concentration in the pore solution. In their paper, Collepardi et al. relied on an analytical solution of Fick's non-linear differential equation to fit their profiles:

$$c = c_0 \ \mathrm{erfc}\left(\frac{x}{\sqrt{4D^* t}}\right) \tag{2}$$

where c_0 is the chloride concentration in solution imposed at $x = 0$ and erfc is the complementary error function. As will be seen in the following section, the validity of this solution rests on a series of assumptions that will be discussed in more details. Collepardi et al. [5] reported chloride diffusion coefficients that ranged from 0.83 to 4.85×10^{-8} cm^2/s depending on the mixture composition and the test temperature.

Following the paper by Collepardi et al. [5], numerous authors relied on more or less complex (analytical or numerical) solutions of Fick's diffusion model to analyze chloride penetration profiles in saturated cement paste and concrete samples. It, however, appeared quickly that the diffusion coefficient calculated using this approach was not a property of the material under investigation. For instance, in their landmark paper published in 1974 in the proceedings of the VI International Congress of the Chemistry of Cement, Ushiyama and Goto [8] noted that the diffusion coefficient of chlorides in saturated neat paste samples was strongly affected by the composition of the salt solution used in the experiment, and particularly by the type of cation. Chloride diffusion coefficient calculated for a 0.5 N $MgCl_2$ solution was as much as three times higher than that obtained for a companion paste sample in contact with a 0.5 NaCl solution.

It was also noticed very early on that chloride penetration profiles measured on concrete samples do not have the typical smooth shape predicted by Fick's second law [9]. This appears to be particularly the case for curves obtained on specimen extracted from real-life structures that have been intermittently subjected to wetting and drying cycles. In many cases, the maximum chloride concentration is not measured at the surface of the sample (directly in contact with the solution) but a little deeper in the material as illustrated in Fig. 1. These results support the assumption made by many that diffusion in a saturated material is not the sole phenomenon involved in the penetration of chlorides in concrete structures and that capillary sorption may in certain cases have a significant influence on the kinetics of chloride transport. The peculiar shape of the chloride distribution curve at the vicinity of the surface also poses some practical problems for those who aim at reproducing the profile using a solution of Fick's model. This point will be discussed in more details in the following section.

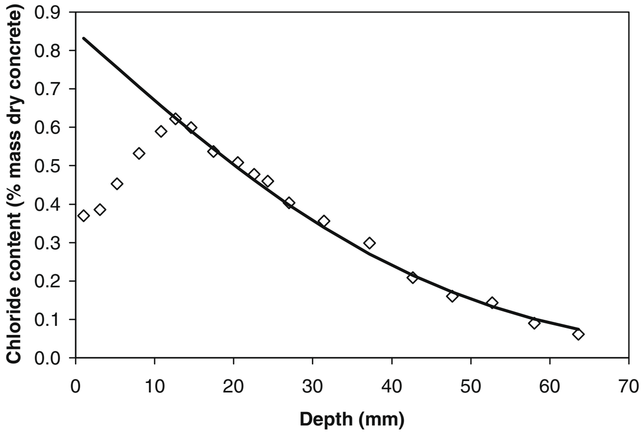

Fig. 1. Typical chloride profile obtained for field samples (shown by the symbols) and chloride distribution curve predicted by Fick's diffusion model.

Curiously, it is only in the early nineties that scientists and engineers dealing with the diffusion of ions in hydrated cement systems apparently took notice of the abundant work published on similar problems by electrochemists and physicists. Ion diffusion mechanisms in free solutions and in porous media have been the subject of a great deal of basic research for more than a century. Most of the early theoretical investigations devoted to the question were focused on the fact that ions, contrary to molecules, are charged particles that do not move independently of one another in solution [10].

In an ionic solution, the local electroneutrality shall be preserved at any point. The conservation of electroneutrality requires that the flows of all diffusing species should be equal in magnitude, since otherwise a net transfer of electric charge would result (i.e. that an electric current would be induced in the solution). During the diffusion process, all ions are not drifting at the same speed. The faster ions, of course, tend to diffuse at a higher rate. However, any excess charge transferred by the faster ions builds up a local electric field which slows down the faster ions, and reciprocally accelerates the slower ions. Thus, the electroneutrality is preserved. The local electric field which enforces the equality of the ionic flows is called the diffusion potential.

The determination of the diffusion potential is a well-known problem in electro-chemistry. The first solution of this problem was proposed by Planck in 1890 [11]. His solution combined with the mathematical expression for ionic mobility proposed by Nernst led to the following equation known as the Nernst–Planck equation for ionic diffusion in ideal electrolytes:

$$\overrightarrow{j_i} = \overrightarrow{j_{i,\mathrm{diff}}} + \overrightarrow{j_{i,\mathrm{el}}} = -D_i \mathrm{grad}(c_i) - \frac{D_i z_i F}{RT} c_i \mathrm{grad}(\psi) \tag{3}$$

where $\overrightarrow{j_i}$ is the total ionic flux [mol/m^2/s], $\overrightarrow{j_{i,\mathrm{diff}}}$ [mol/m^2/s] is the diffusion contribution to the flux, $\overrightarrow{j_{i,el}}$ [mol/m^2/s] is the portion of the flux associated with the electrical coupling, c_i is the concentration of species i in the pore solution [mmol/L], D_i is the diffusion coefficient [m^2/s], z_i is the valence number of the ionic species i, F is the Faraday constant [96485C/mol], ψ is the electrodiffusion potential [V], R is the ideal gas constant [8.3145 J/mol/K] and T is the temperature [K]. This relation holds true for all mobile species present in a very diluted electrolyte. The set of Nernst–Planck equations, one for each species, must be solved under the appropriate conditions. The latter requirement has direct consequences for engineers and concrete technologists interested in predicting the transport properties of cement-based materials. Even in the most simple

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[1] A preliminary version of the chloride analysis had been published in Italian by the authors in 1970.

[2] Fick's model was inspired from the early work of the mathematician Fourier who published in 1822 the first version of the heat transfer equation, see Fourier (1822), Analytical theory of heat. English translation by A. Freeman, Dover Publication, New York, 1955.

laboratory experiment, the determination of the diffusion coefficient of a specific species requires to monitor the flows of all the other species present in solution.

It should also be emphasized that the Nernst–Planck equation applies whenever an electric field exists. As underlined by Helfferich [10], it is totally irrelevant whether the field is generated by an external source or by a diffusion process within the system, since the individual ions have no means of knowing the origin of the electric field. Such a fact has often been overlooked by many researchers in the cement and concrete field who have had the tendency to limit the use of the Nernst–Planck equation to migration processes where an external electric potential is applied to the system.

3. Theoretical background

As previously emphasized, the Nernst–Planck equation was initially intended to describe the diffusion of ions in ideal electrolytes. It has been shown that its application could be extended to the treatment of ionic diffusion in unsaturated porous media involving concentrated electrolytes. A general expression for the mass conservation of ionic species in unsaturated porous materials is given by [12,13]:

$$\frac{\partial c_i^b}{\partial t} + \frac{\partial (wc_i)}{\partial t} - \operatorname{div}\Bigg(D_i w \operatorname{grad}(c_i) + \frac{D_i z_i F}{RT} wc_i \operatorname{grad}(\psi) + D_i wc_i \operatorname{grad}(\ln \gamma_i) + \frac{D_i c_i \ln(\gamma_i c_i)}{T} w \operatorname{grad}(T) + c_i D_w \operatorname{grad}(w)\Bigg) = 0 \tag{4}$$

where c_i is the concentration of species i in the pore solution [mmol/L], c_i^b is the concentration of species i bound to the solid phase [mol/m$^3_{\text{material}}$], w is the water content [m^3/m^3], D_i is the diffusion coefficient [m^2/s], z_i is the valence number of the ionic species i, F is the Faraday constant [96485 C/mol], ψ is the electrodiffusion potential [V], R is the ideal gas constant [8.3145 J/mol/K], T is the temperature [K], γ_i is the activity coefficient, and D_w is the water diffusivity [m^2/s].

The diffusion coefficient of each ionic species in a porous medium is expressed as [12]:

$$D_i = \tau D_i^o \tag{5}$$

where τ is the tortuosity of the saturated material and D_i^o is the diffusion coefficient of the species in free solution. The values for D_i^o are constant at a given temperature and can be found in the literature (see for instance Ref. [14]). The tortuosity characterizes the porous network of the saturated material. It is affected by the saturation level, the hydration of the binder and the chemical reactions that alter the hydrated cement paste microstructure [13].

As previously discussed, the electrodiffusion term in Eq. (4), involving the potential ψ, is mainly responsible for maintaining the electroneutrality of the pore solution. Its role is to balance each individual ionic mobility so that there is no net accumulation of charge at any location in the pore solution. The term associated with the chemical activity coefficient γ_i is responsible for nonlinear effect in transport at high concentrations [15]. Obtaining Fick's second law from Eq. (4) requires these terms to be neglected.

The same can be said from the terms involving gradients in temperature and water content. Neglecting the water content variations in a structure implies that Ficks's second law works only for saturated concrete. In that case, the water content is constant and corresponds to the porosity ϕ. Once all the previous terms are neglected, Eq. (4) can be simplified as:

$$\frac{1}{\phi}\frac{\partial c_i^b}{\partial t} + \frac{\partial c_i^b}{\partial t} - \operatorname{div}(D_i \operatorname{grad}(c_i)) = 0 \tag{6}$$

The first term in Eq. (6) represents the interactions between the pore solution and the hydrated cement paste. It is often calculated using a simplified approach according to which the amount of bound chloride is related to chloride in the pore solution. The relationship can be derived from experiments where small paste samples are immersed in sodium chloride solutions of different concentrations [16]. Results published in Ref. [16] clearly show the nonlinear nature of chloride binding. It is then assumed that the amount of bound chloride only depends on the chloride in solution. In that case, $c^b = f(c)$, where c^b is the amount of bound chloride and c is the amount of chloride in solution. The i index is dropped because neglecting the electrodiffusion coupling between the ions and assuming that the amount of bound chloride only depends on chloride in the pore solution decouples chloride from the other ionic species. Following these assumptions, Eq. (6) can be written as:

$$\left[\frac{1}{\phi}\frac{\partial c^b}{\partial c} + 1\right]\frac{\partial c}{\partial t} - \operatorname{div}(D\operatorname{grad}(c)) = 0 \tag{7}$$

To simplify calculations, it is assumed that the relationship between bound chloride and chloride in the pore solution is linear, which consequently yield a constant value for the term ∂c^b. In that case, Eq. (7) can be simplified as:

$$\frac{\partial c}{\partial t} - \operatorname{div}(D^* \operatorname{grad}(c) = 0) \tag{8}$$

where

$$D^* = \frac{D}{\frac{1}{\phi}\left[\frac{\partial c^b}{\partial c} + 1\right]} \tag{9}$$

Eq. (8) corresponds to Fick's second law with a linear diffusion coefficient. It describes the amount of chloride in the pore solution (c). It is important to remember that the equation is valid only if the following assumptions are verified:

- the effect of the electrical coupling between the ions is negligible,
- the influence of chemical activity gradients is minimal,
- the amount of chlorides bound by concrete is a sole function of their concentration in the pore solution and follows a linear relationship,
- the temperature gradients are weak in the material,
- the material is kept fully saturated and not subjected to any water movement.

It can be easily understood that most of these assumptions are rarely valid, particularly for concrete structures exposed to natural exposure conditions. The electrical coupling between the ions was shown to significantly influence the rate of ingress of species due to the strong concentrations in the pore solution [17]. The composition of the pore solution, especially the pH, was also found to significantly influence the binding of chloride [18]. Consequently, chloride binding is not simply a function of chloride in solution. Finally, except for specific cases such as immersed marine structures, concrete structures are most of the time exposed to various wetting and drying cycles which make the saturated assumption invalid.

Assuming 1D transport, which is suited for many chloride ingress cases, Eq. (8) becomes:

$$\frac{\partial c}{\partial t} - D^* \frac{\partial^2 c}{\partial x^2} = 0 \tag{1}$$

where c is again the chloride concentration in the pore solution. This equation has an analytical solution for semi-infinite domain ($0 \leqslant x < \infty$), under the assumption of constant boundary conditions:

$$c = c_o \ \mathrm{erfc}\left(\frac{x}{\sqrt{4D^* t}}\right) \tag{2}$$

where c_0 is the chloride concentration in solution imposed at $x = 0$ and erfc is the complementary error function. Again, the analytical solution was obtained assuming that D^* and c_0 are constant.

Eq. (1) is commonly used to analyze the long-term penetration of chloride in concrete structures. The previous paragraphs exposed the limitations of such an approach for actual structures. Even in that case, it has been used inappropriately for many years. The mathematical simplifications that gradually lead to Eq. (1) show that the concentration c corresponds to the chloride content in the pore solution. However, many papers (see for example [19,20]) were published where c was defined as the total chloride concentration, i.e. the sum of free and bound chlorides in the material, which totally violate the basic mass conservation equation at the origin of Eq. (1).

4. Typical examples of the limitations of simplified approaches

The intrinsic limitations of simplified approaches will be illustrated by three examples involving the transport of chlorides in hydrated cement systems. The first example concerns the diffusion of chloride ions in saturated paste samples. The second one is linked to the effect of moisture transport, particularly drying, on the redistribution of chlorides in contaminated concrete. The third and last one deals with the penetration of chlorides in the reinforced concrete slab of a parking structure.

4.1. Chloride diffusion in saturated neat paste samples

The first set of experimental results was obtained from neat cement paste samples exposed to a series of sodium chloride solutions prepared at different concentrations. The paste mixture was prepared with an ordinary portland cement (type GU according to the Canadian standard CSA A3001-03 *Cementitious Materials for Use in Concrete*) at water/cement ratio of 0.5. The paste was prepared under vacuum to prevent the formation of air voids. The paste mixture was then poured in plastic cylinders (diameter = 10.0 cm, height = 20 cm). The molds were sealed and rotated for the first 24 h to prevent bleeding. The paste cylinders were then demolded and placed in a fog room. Table 1 summarizes the characteristics of the neat paste mixture.

After 90 days of curing in the 100% relative humidity fog room, 50-mm thick samples were cut from the cylinders and sealed on the bottom and side surface with wax. They were then immersed in different sodium chloride solutions (see Table 2) for 200 days. The solutions were renewed on a regular basis to maintain a pH around 7 and constant chloride concentrations.

Table 1
Hydrated cement paste characteristics.

Properties	Values
Mixture characteristics	
w/c	0.5
Cement Type	CSA Type GU (Type 10)
Cement	1222 kg/m^3
Water	611 kg/m^3
Cement chemical composition (% mass)	
CaO	61.7
SiO_2	19.1
Al_2O_3	5.18
Fe_2O_3	2.27
SO_3	3.51
MgO	2.75
K_2O	0.94
Na_2O	0.28
LOI	3.58
Permeable voids @ 28d (ASTM C642)	46.4%

Table 2
Immersion solutions.

Series	Condition	Composition of solution
1	A	10 mmol/l NaCl
	B	10 mmol/l NaCl + 300 mmol/l NaOH
2	A	20 mmol/l NaCl
	B	20 mmol/l NaCl + 300 mmol/l NaOH
3	A	50 mmol/l NaCl
	B	50 mmol/l NaCl + 300 mmol/l NaOH
4	A	100 mmol/l NaCl
	B	100 mmol/l NaCl + 300 mmol/l NaOH
5	A	250 mmol/l NaCl
	B	250 mmol/l NaCl + 300 mmol/l NaOH
6	A	500 mmol/l NaCl
	B	500 mmol/l NaCl + 300 mmol/l NaOH

After the 200-day immersion period, one chloride profile was measured per test condition using a layer-by-layer acid dissolution technique similar to the ASTM C1152 standard procedure. Sample profiles are shown on Fig. 2.[3]

The results first confirm the influence of the chemical environment on the penetration of chloride ions in hydrated cement systems as discussed by Ushiyama and Goto [8]. In this case, the presence of Na^+ and OH^- ions in solution not only affects the kinetics of chloride diffusion in the neat cement paste but also influences the interaction of chlorides with the solid phases of the material as suggested by Tritthart [18].

Each of the 12 profiles was then fitted according to Eq. (2) to estimate the apparent diffusion coefficient D^*. The results are plotted on Fig. 3. They show that the apparent diffusion coefficient is not only affected by the presence Na^+ and OH^- ions in solution but also varies significantly with the chloride concentration of the test solution. Depending on the test conditions, the value of D^* was found to vary by a factor of 2.3 and 3.5. These results clearly invalidate the assumption at the basis of the erfc analytical solution according to which D^* is constant. In addition, results presented in Fig. 3 emphasize the intrinsic difficulty of using Fick's model to predict the service-life of concrete structures exposed to natural conditions. Since D^* is not, per se, a property of the material but rather a reflection of the impact of the material and the local exposure conditions on the kinetics of chloride penetration, any variation of the external environment should be explicitly taken into account in the calculations. This is hardly possible if not readily impossible in practice.

4.2. Influence of drying on chloride distribution in contaminated concrete

As previously mentioned, most simplified models based on a solution of Fick's diffusion model do not take into account the influence of moisture transport on the kinetics of chloride penetration in concrete. It is often argued that the impact of fluid transport is strictly limited to the surface of a concrete element and has no significant effect on the distribution of chlorides deeper within the material. It can be easily shown that this assumption is unfortunately invalid in most practical cases.

To illustrate the influence of moisture transport, a 0.45 water/cement ratio concrete was produced with CSA Type 10 cement.

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[3] All the chloride profiles presented in the paper were obtained from a single measurement series.

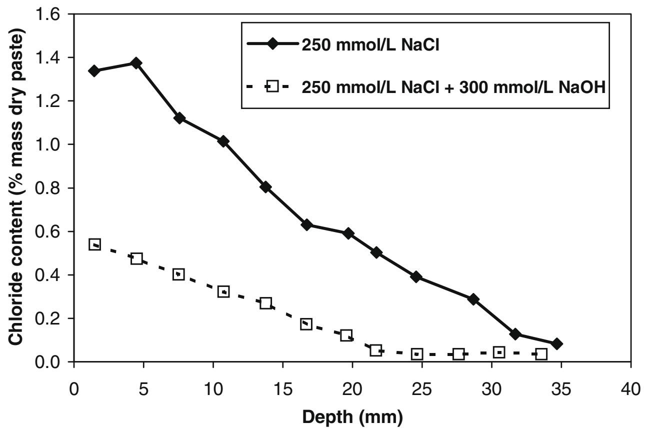

Fig. 2. Chloride profiles for the paste samples exposed to 250 mmol/L NaCl and 250 mmol/L NaCl + 300 mmol/L NaOH.

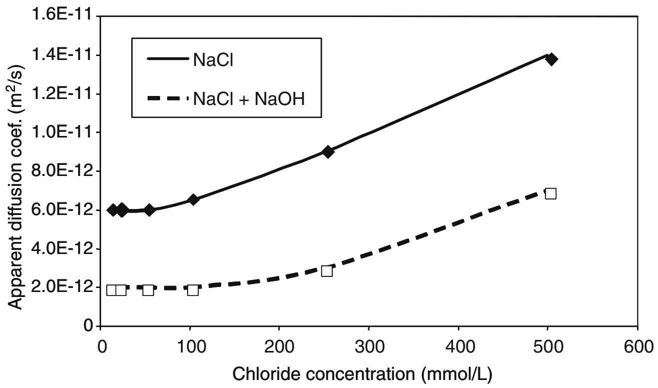

Fig. 3. Apparent diffusion coefficients evaluated from the chloride profiles on paste samples exposed to different chloride conditions.

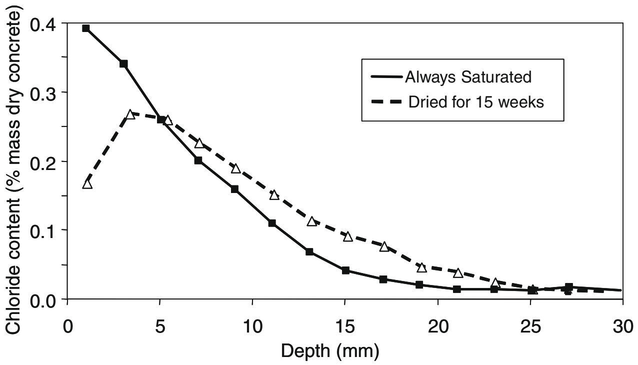

Fig. 4. Impact of drying on chloride distribution within concrete.

Mixture characteristics are given in Table 3. The concrete was cast in plastic cylinders (diameter = 10.0 cm, height = 20 cm) and demolded after 24 h. Cylinders were then placed in a fog room and cured for two years. At the end of the curing period, samples were cut from one cylinder, sealed with wax except for the cut surface, and exposed to a 500-mmol/L NaCl solution for 90 days. The chloride penetration profile was then determined on a first series of samples, always using the layer-by-layer acid dissolution technique. The profile is given in Fig. 4. Another series of samples were taken from the chloride solution and left to dry in a room kept at 23 °C and 50% RH for an additional 15 weeks. At the end of the drying period, a second profile was determined (see also Fig. 4).

Table 3
Characteristics of the 0.45 laboratory concrete mixture exposed to chloride and 50% RH.

Properties	Values
w/c	0.45
Cement Type	CSA Type 10
Mixture proportions (kg/m^3)	
Cement	380
Water	171
Fine aggregates	719
Coarse aggregates	1127
Cement chemical composition (% mass)	
CaO	62.1
SiO_2	20.4
Al_2O_3	4.3
SO_3	3.2
Fe_2O_3	3.0
Na_2O_{eq}	0.84

As can be seen, drying has several effects on the distribution of chloride within contaminated concrete:

- At the surface, the loss of water contributes to locally reduce chloride concentration which turns the profile into a bell-shaped curve quite distinct from what could be predicted by Fick's diffusion model. It should be emphasized that this reduction arises even if the sample has not been exposed to any leaching. The particular shape of the profile complicates the determination of the surface chloride concentration C_0 required to solve Eq. (2).
- In addition, the penetration of chlorides continues to diffuse deeper within the material, but at a reduced rate since the outside source is cut. This effect cannot be predicted by Fick's diffusion model since it involves fluctuating boundary conditions and the transport of moisture, two phenomena which are not taken into account by Fick's approach.

Similar profiles were reported in Ref. [21] in concrete cores taken from a 9-year-old highway exposed to deicing salts. Additional causes for the drop in chloride content near the surface were suggested, such as the periodic exposure to rain water on structures [21] or carbonation [22]. In any case, a durability analysis based on Eq. (2) cannot be expected to provide reliable results given the complexity of the phenomena involved.

4.3. Chloride penetration in the reinforced concrete slab of a parking structure

To further illustrate the intrinsic limitations of the simplified erfc-model to assess the service-life of reinforced concrete structures, another series of laboratory tests were performed on concrete samples and compared to results from the field. The test case concerns a 20 year-old parking structure in Quebec City (Canada). Cores were extracted from the structure to obtain the chloride profiles. Records indicate that the concrete had a water to cement ratio of 0.45 with a compressive strength in the 35–40 MPa range at 28 days. Parallel to this, a 0.45 concrete mixture was prepared in laboratory using an ASTM Type I cement. The mixture characteristics are given in Table 4. The concrete was cast in plastic cylinders (diameter = 10.0 cm, height = 20 cm) and demolded after 24 h. The cylinder were then placed in a fog room and cured for three years in a 100% RH environment. Given the long hydration period, the material can be considered to be well hydrated and the transport properties stable. After that period, samples were cut from one cylinder, sealed with wax except for the cut surface, and exposed to a 500-mmol/L NaCl solution

Table 4
Mixture proportions of the 0.45 laboratory concrete cured 3 years in a fog room.

Properties	Values
w/c	0.45
Cement Type	ASTM I
Mixture proportions (kg/m^3)	
Cement	375
Water	169
Fine aggregates	815
Coarse aggregates	925
Cement chemical composition (% mass)	
CaO	64.0
SiO_2	21.0
Al_2O_3	5.9
SO_3	3.3
Fe_2O_3	2.2
K_2O	0.41
Na_2O	0.22

for 90 days. Following this, chloride profiles were measured using the layer-by-layer acid dissolution technique. Then were then fitted to Eq. (2) to obtain c_0 and D^*, which gave: $c_0 = 0.47\%$ and $D^* = 14.5e{-}12$ m^2/s (see Fig. 5).

These parameters were used to simulate the profiles after 20 years on the parking structure. As shown on Fig. 6, even though similar materials are compared, the profile obtained on the basis of Eq. (2) using parameters from the lab samples vastly overestimate the chloride ingress in the structure.

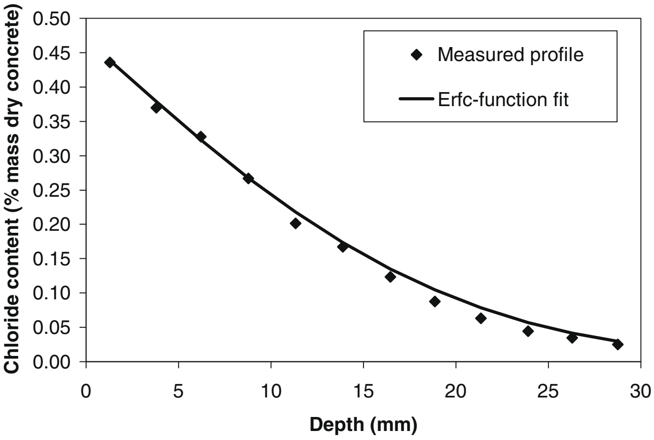

Fig. 5. Measured chloride profile in the 0.45 laboratory concretefitted with the erfc simplified model.

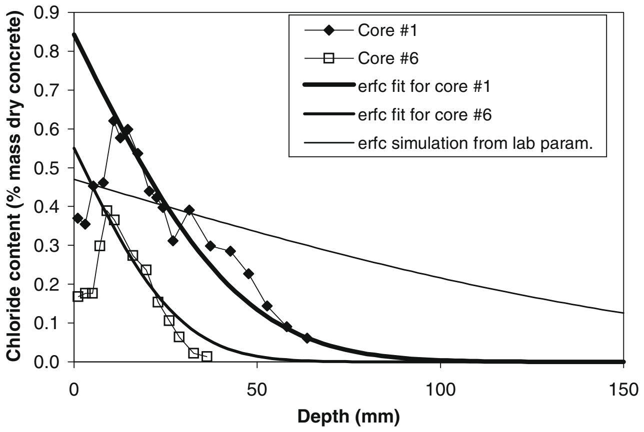

Fig. 6. Chloride profiles measured in cores from the parking structures compared to the estimations made on the basis of the simplified erfc approach.

The chloride profiles measured in the structure were also fitted with Eq. (2) to get c_0 and D^*. Following a commonly used (and accepted) approach, the fitting started at the maximum value of the profiles. It should be noted that neglecting the first few points certainly helps fitting the profiles with the erfc function but this is not supported by any scientific background. The fitting procedure gave $D^* = 1e{-}12$ m^2/s for core #1 and $4e{-}13$ m^2/s for core #6. As shown on Fig. 6, the three D^* values obtained yield very different estimated chloride profiles even though the results were obtained each time on very similar materials. Most importantly, similar materials showed a ratio of 36 between the highest and lowest values (14.5e−12/4e−13) of D^*. This again confirms that the use of the apparent diffusion coefficient in any durability analysis can hardly be considered safely.

5. Conclusion

The paper showed that using Fick's law of diffusion to analyze chloride ingress in concrete structure is inappropriate. From a theoretical standpoint, Fick's model is based on many assumptions such as saturated conditions and simplified chemical interactions that do not reflect the behavior of cementitious materials and the environment to which structures are exposed. Actual chloride profiles were presented that emphasizes the inadequacy of the simplified model.

The most glaring problem with the simplified approach occurs with the use of the analytical solution to Fick's second law for chloride ingress analyses. In most cases, the total chloride content in the material is directly substituted to the chloride concentration in the pore solution, which violates the mass conservation equation at the origin of the model. Most importantly, this leads to the determination of a parameter called the apparent diffusion coefficient which does not only characterize the material but also reflect the local exposure conditions. Many results were presented that emphasize the dependence of the chloride apparent diffusion coefficient on the external environment. Consequently, it is not possible to predict long-term service-life of structures on the basis of laboratory samples or to take apparent diffusion coefficients obtained for a given environment and use them for durability analyses in another environment. Any material database incorporating apparent diffusion coefficients for service-life predictions cannot be expected to provide reliable results given all the limitations outlined in this document.

Fortunately, other approaches have been proposed to predict chloride ingress in concrete structures. Some models are based on a single-ion approach but incorporate nonlinear chemical binding relationships, humidity and temperature variations (e.g. the model published by Saetta et al. [23]). More recently, multiionic approaches were developed to provide a more accurate prediction of the intricate interaction between ions and the hydrated cement paste (e.g. Samson and Marchand [13,17] and Johannesson [24]). These models incorporate more detailed transport and chemistry equations and require a larger number of input parameters but provide more reliable service-life predictions. In the field of contaminant transport in soils, these multiionic models are now standard and currently used. Going back to simpler approaches would never be considered because of their lack of reliability. Given the cost of building and managing concrete structures, these advanced numerical tools present numerous advantages.

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