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

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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.

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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

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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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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:

$$c = c_0 \operatorname{erfc}\left(\frac{x}{\sqrt{4D^*t}}\right)$$
(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} cm²/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 MgCl₂ 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



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

aim at reproducing the profile using a solution of Fick's model. This point will be discussed in more details in the following section.

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:

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

where \vec{j}_i is the total ionic flux $[\text{mol}/\text{m}^2/\text{s}]$, $\vec{j}_{i,\text{diff}}$ $[\text{mol}/\text{m}^2/\text{s}]$ is the diffusion contribution to the flux, $\vec{j}_{i,el}$ $[\text{mol}/\text{m}^2/\text{s}]$ 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 $[\text{m}^2/\text{s}]$, 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

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.

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