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Chloride ion penetration in concrete: The reaction factor in the electrical resistivity model

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ABSTRACT

Several models have been published to calculate service life of reinforced concrete based on considering diffusion as the main ingress mechanism. However, these models have some limitations and involve destructive and time consuming testing. The authors have developed an alternative model based on electrical resistivity, which is a non-destructive test. When measured in concrete, electrical resistivity is an indication of its pore connectivity and also can be related to the concrete resistance to the penetration of gases and liquids. The main basis of the model has been already published. The present paper describes the calculation of the so-called "reaction or retardation factor" which is necessary for the model to take into account the amount of bound chlorides or carbon dioxide. The resistivity alone only appraises the available porosity which is equivalent to the effective diffusion coefficient. To consider the retardation in the ingress due to the chloride and carbon dioxide binding, it is necessary to include such an effect. In the model this is done by multiplying the resistivity measured at 28 days in water saturated concrete by a reaction factor, r_b, which will give the "apparent resistivity" equivalent to the apparent diffusion coefficient r_{Cl}. The value of r_{Cl} is calculated from the ratio between effective and apparent diffusion coefficients. This paper gives such values for several cement types.

1. Introduction

Chloride ions can penetrate through the concrete pore network, potentially leading to the corrosion of steel reinforcement. The penetration process is usually modeled by solving Fick's second law for certain boundary conditions, which gives the known error function equation [1]. However, this equation has important drawbacks that make very uncertain the prediction of chloride penetration into concrete. The main limitations of the equation can be summarized as follows: (a) it is based on assuming that the surface concentration of chlorides remains constant [2], which does not apply unless the concrete is fully submerged and the chloride concentration is expressed as free chloride in the pore solution, (b) the diffusion coefficient D is variable [3] and seems to decrease: with time, with higher external concentrations and with lower temperatures, (c) the D value cannot be compared for different surface concentrations C_s because D is a function of C_s and both parameters should be given together [4], (d) the error function equation does not take into account other mechanisms than diffusion [5], when absorption is also important in many real environments, (e) the skin of the concrete surface behaves usually different than the concrete bulk [6] and then the skin of the concrete may exhibit a different D value than the interior one modifying the profile and showing a maximum in the chloride concentration as the figure indicates. All these reasons explain why the models based on Fick's second law fail to offer accurate predictions in many occasions [4].

A model based on the concrete electrical resistivity [7,8] was developed as an alternative in view of these theoretical difficulties and, also, since resistivity measurement is of non-destructive character, avoiding the time-consuming operations of grinding and chemically analyzing chloride profiles. The resistivity value is proportional to concrete porosity when the material is water saturated and, therefore, can inform on the available space for the chlorides or the CO_2 gas to penetrate. Additionally, the resistivity is proportional to the steady state diffusion coefficient through the Einstein relation [7]:

$$D_{ef} = A/\rho_{ef} \qquad (1)$$

where D_{ef} is the effective diffusion coefficient and A is a factor, which depends on the external ionic concentration (for 0.5 M in chlorides a value of 23.5E−5 can be used), $_{ef}$ is the "effective" resistivity (in this case of concrete saturated with water).

However, this expression does not take into account the chloride binding [8] and therefore to use the resistivity to predict

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chloride penetration into concrete has to be complemented with the consideration of the binding with hydrated cement phases in order to model the retardation of the chloride front due to part of the chlorides are immobilized by the cement phases [9]. This reaction of chlorides with cement phases can be accounted in several manners. For the sake of simplifying the treatment, in the resistivity model is taking into account by means of introducing a new term: r_{Cl} = reaction or binding factor. This factor accounts for the slower chloride threshold advance, that is for the "retardation" of the penetration of chlorides. Then, the above Eq. (1) can now be re-formulated by proposing the "apparent resistivity" [8]:

$$\rho_{ap} = \rho_{ef} \cdot r_{Cl} \tag{2}$$

By analogy of the differences between the effective and apparent diffusion coefficients:

$$D_{ap} = \frac{A}{\rho_{ap}} = \frac{F_{Cl}}{\rho_e \cdot r_{Cl}} \tag{3}$$

Making $A = F_{Cl}$ to account for the differences in the environmental aggressivity, the model is completed by assuming that the relation of the resistivity with the time to the steel depassivation follows a diffusion law and then, the "square root law", which gives the following expression:

$$t_i = \frac{x_i^2 \cdot \rho_e \cdot r_{Cl}}{F_{Cl}} \tag{4}$$

where x is the depth of the chloride threshold, F_{Cl} is a factor which depends on the external ionic concentration or the exposure class [10]. The present paper illustrates how the reaction factor can be measured or calculated in the case of chlorides and gives values in function of the type of cement, which through its composition, is the controlling parameter of the binding ability.

2. Experimental program

A set of concretes has been fabricated and characterized by measuring different parameters at 28 days (Table 1): porosity in volume by MIP, the resistivity in cylindrical samples in saturated conditions, the D_{ap} by natural diffusion test at 90 days and the D_{ef} and D_{ap} by means of the Multiregime test [11]. The concrete mix proportions are given in Table 1.

The specimens tested were cylindrical of 15 and 30 cm in height. They were cured 24 h in the moulds and in a chamber with 21 °C and RH > 95%. After demoulded they were wet cured until 28 days. From theses specimens, slices of around 2 cm thick are cut removing the upper one because it has more paste due to the settlement of aggregate. The slices are tested by means of the multiregime test which enables the simultaneous determination of the steady and non-steady state diffusion coefficients [11].

The multiregime test method consists in the use of a migration cell with two compartments; the catholyte is filled with a solution 1 M of NaCl and the anolyte with distilled water. As electrodes are used steel bars. The steel bar immersed in the anolyte is corroded during the experiment which prevents the potential of the anode to go to the transpassive potential region and induce the evolvement of Cl_2 gas which would decrease the amount of chloride ions and introduce errors in their determination. Through the corrosion of the electrode in the anolyte, the potential is less anodic and avoids the chlorine evolution. The oxides do not disturb the correct determination of the conductivity of the solution from which the chloride concentration is determined. An aspect of the test is given in Fig. 1.

The steady state or effective diffusion coefficient, D_{ef}, is calculated from the slope of the increase of chloride concentration with time in the anolyte and the non-steady-state or apparent, D_{ap} from the time lag.

The porosity was determined by mercury intrusion with a Micromeritics Poresizer equipment folllowing the standard D4404. The sample is of around 1 cm^3 and the range of pores determined was between 400 and 0.006 m.

The resistivity was determined by the 4 point method (Fig. 2) by measuring in six of the bisectrices of the cylindical specimen.

3. Results

The values of D_{ef}, D_{ap} and porosity of the different concretes and their resistivity at 28 days, are given in Table 2. The reaction factor calculated through Eq. (6) given below is also shown in the table.

Table 1
Mix proportions studied.

Denomination	Cement type	Amount of cement (kg/m^3)	Additions	Water (l/m^3)	w/c Ratio
I-02	CEM I 42,5 R	355		180	0.51
I-03	CEM I 42,5 R	400		180	0.45
I-05	CEM I 52,5 R	300		180	0.6
I-06	CEM I 52,5 R	300		165	0.55
I-07	CEM I 52,5 R	300		150	0.5
I-10	CEM I 52,5 R	350		157.5	0.45
I-11	I 42,5 R/SR	400		180	0.45
I-13	CEM I 52,5 R	450		202.5	0.45
I-17	CEM I 52,5 R	350		129.5	0.37
I-19	CEM I 52,5 R	450		166.5	0.37
II-a-03	I 42,5 R/SR	364	D/16,1	163.8	0.45
II-a-04	CEM I 52,5 R	450	D/6	166.5	0.37
II-a-05	CEM I 52,5 R	450	D/9	166.5	0.37
II-a-06	I 42,5 R/SR	260	V/62,5	117	0.45
II-a-07	I 42,5 R/SR	224	V-D/62,5 (v) + 16,1 (D)	100.8	0.45
IIA-01	CEM II/A-P 42,5 R	310		175	0.56
IIA-02	CEM II/A-P 42,5 R	355		180	0.50
IIA-03	CEM II/A-P 42,5 R	400		180	0.45
IIA-16	CEM II/A-V 42,5 R	320		176	0.55
II + PN + SF-01	Type II (ASTM)	350	12%PN + 8%SF	105	0.3
II + PN + SF-02	Type II (ASTM)	350	12%PN + 8%SF	98	0.28
II + PN + SF-03	Type II (ASTM)	400	12%PN + 8%SF	136	0.34
II + PN + SF-04	Type II (ASTM)	400	12%PN + 8%SF	112	0.28
II + PN	Type II (ASTM)	375	25%PN	150	0.4
II + SLAG	Type II (ASTM)	375	50%slag	127.5	0.34

[*] PN = pozzolans; SF = silica fume.