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Chloride induced corrosion of reinforcing steel evaluated by concrete resistivity measurements

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Abstract

The chloride threshold (Cl_{TH}) concentration for rebar corrosion initiation has received extensive attention over the last years. The chloride threshold concentration depends on several factors involving concrete composition and quality, exposure conditions and rebar surface characteristics. As a consequence, many researchers have proposed Cl_{TH} ranges that take into account the relative influence of each of these many factors. On the other hand, the electrical resistivity of concrete has proven to be an effective parameter that can be used to estimate the risk of reinforcing steel corrosion, particularly when corrosion is induced by chloride attack. The present study is based on a correlation of electrochemical parameters such as corrosion potential (E_{corr}) and current density (i_{corr}) together with concrete resistivity of concrete quality) is proposed. A relationship between chloride threshold values for rebar corrosion initiation and resistivity values (indicative of concrete quality) is proposed. According to this correlation, when the electrical resistivity of concrete increases from 2 to 100 k Ω cm, the value of Cl_{TH} increases from 0.44 to 2.32% relative to the weight of cement.

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1. Introduction

It is widely accepted that chloride ions are responsible for causing local passive layer breakdown and subsequent corrosion of reinforcing steel bars (rebars). This can be the case when concrete is either exposed to marine environment or deiceing salts and also when concrete is prepared with contaminated aggregates. The chloride-induced corrosion mechanism has been, and continues to be, extensively investigated. There is a general agreement in the existence of a certain value representing the chloride threshold (Cl_{TH}) concentration that must be reached at the rebar surface in order to initiate the corrosion process [1–4]. The chloride threshold value is of great importance when evaluating the service life of reinforced concrete structures, as it determines how long it takes to initiate the corrosion process [5,6]. Many investigations have focused in determining the

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E-mail address: mvazquez@fi.mdp.edu.ar (M. Vázquez). ¹ ISE member. Cl_{TH} value [7–10], although the results that can be found in the literature show great variability.

As discussed by Alonso et al. [10], there are many variables that affect the Cl_{TH} value. Some of these depend on the concrete mix properties, such as the cement type content, the water to cement ratio [11–15] and the pore solution pH [16,17]. Other variables are related to the reinforcement: the rebar composition and surface condition [18] should be considered. The environment also plays an important role, determining temperature and relative humidity [19–22], eventually also being the source of chloride penetration [23]. The oxygen availability at the rebar surface as well as its polarisation potential [1,2,16,24] also need to be taken into account. The great number of variables involved in the chloride-induced corrosion process explains the reason why the Cl_{IH} values reported in the literature present such wide range of variability.

Another important issue still under discussion is the most appropriate way to define the chloride threshold value in concrete. Glass and Buenfeld [9] carried out an extensive review of chloride threshold levels published in the literature. They concluded that chloride threshold levels are best presented as a total (bond plus free chlorides) content expressed relative to the weight of cement. The values of Cl_{TH} reported in that review varied within a wide range (0.17–2.5% relative to the weight of cement). Alonso et al. [10] argue that chloride to hydroxyl ion ratio would be the best way of defining the value of Cl_{TH} , although it is also suggested that either free or total chlorides expressed relative to the cement content in concrete are appropriate ways of defining Cl_{TH} . According to them, the chloride threshold may vary from 1.24 to 3.08% when considering total chlorides which, in turn, would represent a variation from 0.39 to 1.16% when only free chlorides are taken into account.

Further than the aspects addressed above, and accepting that Cl_{TH} depends on many factors, one more question arises that needs a practical answer: how to establish an appropriate Cl_{TH} value for a given structure exposed to a particular environment.

In a previous publication [25], the electrical resistivity of concrete was proposed as an effective parameter to evaluate the risk of reinforcing steel corrosion, particularly when corrosion is induced by chloride attack. Likewise the Cl_{TH} value, the resistivity of concrete is strongly dependent on the concrete quality and on the exposure conditions, such as the relative humidity. Also, temperature affects the degree of concrete pore saturation [19,26,27] and so the resistivity values. Therefore, the idea of finding a relationship between concrete resistivity and Cl_{TH} values would seem quite feasible. In order to determine the existence of such correlation, certain electrochemical parameters as the corrosion potential (E_{corr}) and current density (i_{corr}) are investigated together with concrete resistivity and chloride concentration data.

2. Experimental data

The results evaluated in this work were taken from previous investigations conducted by the authors [25,28,29].

The performance of four different concrete proportioning was investigated over a period of 1000 days of exposure to seashore and immersion conditions. Chloride concentrations varied from 0.16 to 1.6% relative to the cement content. A detailed description of the experimental set-up can be found in a previous publication [25].

2.1. Samples design

Cylindrical concrete test specimens (15 cm diameter, 22 cm height) were prepared. Each contained four rebar segments positioned in such a way that a 1.5 cm concrete cover was achieved (see Fig. 1). The rebar segments present an exposed area of 40 cm^2 .

Table 1 presents the mix proportioning selected for the study. Mixes A and B were prepared using sea sand of the same type of that used by the local construction industry (siliceous, fineness modulus = 2.7 ± 0.3 and specific



Fig. 1. Schematic representation of the cylindrical concrete samples used in the study.

gravity = 2.7). Mixes C and D were prepared using river sand (fineness modulus = 2.7 and specific gravity = 2.65) containing less than 0.1% per weight of chloride ions. In the case of mix design C, NaCl was incorporated in a known proportion to reproduce the case of reinforced concrete structures heavily contaminated. Prepartion D has no admixed chlorides. The total initial chloride concentration (ASTM C-1152), expressed in percentage by weight of cement is presented in Table 2.

2.2. Exposure conditions

Two exposure conditions, referred as seashore and immersed, were evaluated. Four specimens per each mix design were prepared (totalling 16). Two samples per each mix were placed at the terrace of a 40-floor building located at less than 100 m from the seacoast in Mar del Plata city (latitude S: 3756; longitude W: 5735). These samples are labelled as seashore specimens and were directly exposed to rainfall, sea spray and wind. The other eight specimens

Table	1
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Concrete mix proportioning, slump test results and sample identification

Mix proportioning identification	A	В	С	D
Water/cement ratio (w/c) Cement content (kg m ⁻³)	0.60 300	0.40 400	0.60 300	0.60 300
Fine aggregate (FA) River sand (kg) Sea sand (kg)	_ 858	_ 789	851	858 _
River rock MAS = 10 mm (kg)	1003	1042	1003	1003
Sodium chloride (kg)	-	-	7.4	-
Superplastisizer (%)	1.0	2.5	-	-
Slump test (cm)	3.0	3.0	6.5	8.0

Table 2 Compressive strength ($f_{\rm C}$), porosity (P = % of air voids) and the total initial chloride concentration ($[{\rm Cl}^-]_0$) in the concrete mixes selected for the study

Concrete mix	f _C (Mpa)		P (%)	[Cl ⁻] ₀ (%)	
	7 days	28 days			
A	14.4	21.3	18.3	0.78	
В	21.5	31.4	12.1	0.43	
С	16.2	21.0	17.7	1.65	
D	14.0	22.5	18.5	0.16	

The compressive strength was determined after 7 and 28 days of curing. Chloride concentration is expressed as percent by weight respect to cement content. The concrete porosity and the total initial chloride concentration (acid soluble) were determined after approximately 100 days of casting the specimens. Values are average results of duplicate measurements.

were partially immersed in aerated saline solution containing 3.5% of NaCl by volume.

2.3. Mechanical and chemical analysis

Standard size concrete specimens were also prepared following the ASTM C-39 standard in order to characterise the mechanical properties of the concrete mixes. Compressive strength was evaluated (ASTM C-617) at 7 and 28 days after casting the specimens. In order to determine the total chloride ions concentration and the percentage of air voids (porosity of hardened concrete, ASTM C-642), another group of concrete specimens was also prepared.

The results of these characterisation analyses are presented in Table 2. Replicate specimens were tested for each analysis.

Chloride concentration profiles were obtained from concrete cylindrical cores (2 cm diameter, 5 cm long) extracted from the test specimens using a drilling machine. The extraction procedure was carried out after 850 days of exposure to both, seashore and immersed conditions. Cores extracted from the seashore specimens were drilled from the side that was facing the sea. Fig. 2 illustrates the cores extraction method and the chloride profile determination Table 3

Chloride effective diffusion coefficient (D_{eff}) and surface concentration (C_s) obtained from the mathematical curve fitting of the chloride content in-depth profiles [25]

Concrete mix	Immersed condition		Seashore environment	
	$\overline{D_{\rm eff}}~({\rm cm}^2{\rm s}^{-1})$	C _s (%)	$D_{\rm eff}({\rm cm}^2{\rm s}^{-1})$	C _s (%)
A	5.09×10^{-8}	3.2	4.83×10^{-8}	1.9
В	1.88×10^{-8}	2.4	1.79×10^{-8}	1.5
С	5.95×10^{-8}	3.8	4.53×10^{-8}	2.8
D	4.84×10^{-8}	3.2	3.88×10^{-8}	1.2

procedure. In order to analyse the chloride transport mechanism within the concrete specimens, the effective diffusion coefficient (D_{eff}) was determined by solving Fick's second law [25]. D_{eff} values are summarised in Table 3. The chloride profiles in the two exposure conditions under analysis are presented in Fig. 3. The chloride concentrations are expressed in percentage of total chlorides by weight of cement.

2.4. Electrical and electrochemical measurements

The electrochemical parameters normally used to characterise the corrosion behaviour of reinforcing steel in concrete were monitored periodically. These parameters included the corrosion potential, the corrosion current density obtained from polarisation resistance measurements (R_p) and the electrical resistivity of concrete (ρ) determined from resistance measurements between the two uncoated rebar segments.

The electrical resistance (R, in Ω) between two rebars bars was measured using a Nilsson 400 soil resistivity meter. This instrument uses a square wave of 97 Hz, preventing polarisation of the electrodes. The values of ρ were calculated as: $\rho = kR$, where k is a geometrical factor that depends on the shape of the sample. In this case, k = 7.5 and 12 cm for the dry and wet condition, respectively.

Experimental procedures and the equipment employed to evaluate the electrochemical parameters can be found in detail elsewhere [25].



Fig. 2. Cores extraction and chloride profile determination procedure.



Fig. 3. Chloride concentration profiles obtained from concrete specimens after 850 days of exposure to the immersed condition (left) and seashore environment (right). Vertical lines show the location of the rebars in the concrete sample.

The data reported in the figures correspond to average values of four independent measurements (two samples containing two rebars each one).

3. Results and discussion

On the basis of the compressive strength and porosity results, the concrete mixes can be classified in two groups according to their quality. On one hand, mixes A, C and D represent examples of standard quality concrete. They were prepared with the higher water to cement ratio (w/c = 0.6) and chloride contents ranging from 0.16 to 1.65%. The compressive strengths values (fc) at 28 days varied between 21 and 22.5 MPa and porosity (*P*) values between 17.7 and 18.5%. On the other hand, mix B, prepared with w/c = 0.4 and sea-sand, presented a fc value of 31.4 MPa and a porosity of 12.1%, values typical of a good quality concrete.

As a result of an extensive investigation [25,28,29], it was found that rebars in contact with a good quality concrete exposed for 1000 days to the seashore environment and prepared with a high content of admixed chlorides (0.43%) remained in the passive state, even when its surface chloride concentration reached 1% with respect to cement content (specimen B). Also, a standard quality concrete prepared with a w/c = 0.6 and 0.78% of admixed chlorides (sample A) would provide a protective environment for steel bars as long as the specimens were kept in a dry environment [25]. The evolution in time of the corrosion potential and the corrosion current density support these statements and are presented in Figs. 4a and 5a.

When immersed in a saline solution, all rebar segments achieved an active corrosion state, although the good quality concrete (samples B) showed a less active rebar corrosion behaviour than the standard quality one [25]. The results of corrosion potential and corrosion current density for this condition can be seen in Figs. 4b and 5b.

The different quality of the concrete mixes under study can be clearly distinguished by observing the electrical resistivity data (see Fig. 6a and b). Mix B (good quality concrete) presents resistivity values that are approximately three



Fig. 4. Variation of the rebar corrosion potential (E_{corr}) with time on mix designs A ([Cl⁻]₀ = 0.78%, w/c = 0.6); B ([Cl⁻]₀ = 0.43%, w/c = 0.4); C ([Cl⁻]₀ = 1.65%, w/c = 0.6); and D ([Cl⁻]₀ = 0.16%, w/c = 0.6). Horizontal lines define a region of active corrosion where $E_{corr} < -0.35$ V and a passive corrosion region where $E_{corr} > -0.2$ V vs. CSE [30]. Vertical lines show the day of exposure to each environment, after a conditioning period indoors. (a) Samples were exposed to seashore environment; (b) samples were partially immersed in aerated saline solution.





Fig. 5. Variation of the apparent rebar corrosion rate (CR) and the corrosion current density (i_{corr}) as a function of time on mix designs A (w/c = 0.6, [Cl⁻]₀ = 0.78%); B (w/c = 0.4, [Cl⁻]₀ = 0.43%); C (w/c = 0.6, [Cl⁻]₀ = 1.65%); and D (w/c = 0.6, [Cl⁻]₀ = 0.16%). Horizontal lines define a region of active corrosion where $i_{corr} > 0.2 \,\mu\text{A cm}^{-2}$ and a passive corrosion region where $i_{corr} < 0.1 \,\mu\text{A cm}^{-2}$ [31]. (a) Samples were exposed to seashore environment; (b) samples were partially immersed in aerated saline solution.

times higher than the values observed on mixes A, C and D (all of them of standard quality). The difference is evident both in seashore and immersed environments. As could be expected, the resistivity of the specimens exposed to the seashore environment are approximately three times greater than the corresponding values measured in the immersed condition.

immersed

The results of the rebar corrosion measurements ($E_{\rm corr}$ and $i_{\rm corr}$) together with the calculated values of rebar surface chloride concentration and the concrete resistivity values were reorganised to calculate chloride threshold values. The corrosion potential, the corrosion current density and the resistivity were measured at the same date. The chloride concentration at the rebar surface was calculated at each particular date using the data in Table 3.

Figs. 7 and 8 present a correlation between corrosion potential and corrosion rate values with respect to the concrete



Fig. 7. Correlation between corrosion potentials (E_{corr}) and concrete resistivity (ρ) values measured at the same time on specimens exposed to seashore and immersed conditions. Data points represented by hollow symbols (\bigcirc) where taken from reference 28.



Fig. 6. Variation of the electrical resistivity of concrete (ρ) as a function of time on mix proportions A (w/c = 0.6, [Cl⁻]₀ = 0.77%); B (w/c = 0.4, [Cl⁻]₀ = 0.43%); C (w/c = 0.6, [Cl⁻]₀ = 1.65%); and D (w/c = 0.6, [Cl⁻]₀ = 0.16%). Horizontal lines define a region of active corrosion where $\rho < 10 \text{ k}\Omega \text{ cm}$ and a passive corrosion region where $\rho > 30 \text{ k}\Omega \text{ cm}$ [25]. Vertical lines show the day of exposure to each environment, after a conditioning period indoors. (a) Samples were exposed to seashore environment; (b) samples were partially immersed in aerated saline solution.



Fig. 8. Correlation between corrosion rates (CR) and concrete resistivity (ρ) values measured at the same time on specimens exposed to seashore and immersed conditions. Data points represented by hollow symbols (\bigcirc) where taken from reference [28].

resistivity values measured at the same time [25]. From these it was concluded that rebars are likely to achieve an active state of corrosion when resistivity is lower than $10 \text{ k}\Omega \text{ cm}$, and likely to present a passive behaviour when concrete resistivity is higher than $30 \text{ k}\Omega \text{ cm}$.

The Cl_{TH} can be defined as the chloride concentration that would induce an active state of corrosion given by $E_{\rm corr} < -0.35$ V versus CSE and/or $i_{\rm corr} > 0.2 \,\mu\text{A}\,\text{cm}^{-2}$ [30,31]. Those samples in the transition region are assumed to have the threshold concentration value for chloride content. Fig. 9 presents the correlation between chloride content and concrete resistivity that results from this analysis. Two separated regions can be distinguished. There is an "active corrosion zone" where $E_{\rm corr} < -0.35$ V versus CSE and/or $i_{\rm corr} > 0.2 \,\mu\text{A}\,\text{cm}^{-2}$). Those samples have known values for chloride concentration and resistivity and are represented by filled squares in Fig. 9. In contrast, there is a "passive corrosion zone" (hollow square symbols), where $E_{\rm corr}$ values are



Fig. 9. Correlation between chloride threshold value (Cl_{TH}) and resistivity (ρ) for concrete mixes prepared with type I Portland cement. The filled and hollow symbols correspond to rebars undergoing active ($E_{\rm corr} < -0.35$ V vs. CSE and $i_{\rm corr} > 0.2 \,\mu$ A cm⁻², see Figs. 7 and 8) and passive corrosion, respectively ($E_{\rm corr} > -0.2$ V vs. CSE and $i_{\rm corr} < 0.1 \,\mu$ A cm⁻², see Figs. 7 and 8). The crosses correspond to those samples that fall in the transition region between active and passive corrosion (data between dot lines in Figs. 7 and 8).

more positive than -0.2 V versus CSE and i_{corr} values are lower than 0.1 μ A cm⁻² (~1 μ m year⁻¹). These last range of values is generally taken as representative of passive steel. Further than those, there are nine samples falling in the transition zone between active and passive regions (delimited by dot lines in Figs. 7 and 8). The values of the resistivity and the [Cl⁻] for these nine samples are represented by crosses in Fig. 9. These values are then used to derive correlation between the chloride content (assumed as the threshold value, Cl_{TH}) and the resistivity (ρ in k Ω cm). The best line fit which can be expressed by the following expression:

$$Cl_{TH}(\%) = 0.019\rho + 0.401$$
 (1)

This correlation is in good agreement with results published in the literature, where E_{corr} , i_{corr} , ρ and chloride concentration data are reported [14,26].

According to this correlation, when the electrical resistivity of concrete increases from 2 to $100 \text{ k}\Omega \text{ cm}$, the limit above which chlorides induce corrosion (Cl_{TH}) increases from 0.44 to 2.32% relative to the weight of cement. The resistivity of concrete appears to be a good indicator of its quality, so that for better quality concrete, higher threshold values can be accepted. These findings are also supported a paper recently published by Poupard et al. [32] where the results presented by the authors highlight the influence of the w/c ratio (porosity, in their words) on the chloride threshold level. They observe an increase in Cl_{TH} with the decrease of the w/c ratio.

Lower resistivity values could be associated with higher concentrations of free chlorides, which is supported by many authors as a variable with strong impact on the threshold value [10,19,33,34]. These chloride ions would be available for nucleating localised corrosion. Also, lower resistivity values could be associated with pore solution compositions with an optimum buffering capacity, so as to restrict local falls in pH to values below that which guarantees passivity. This view would adjust to the findings of another group of researchers who advocate the use of total chloride content to indicate threshold levels [9]. Finally, low resistivity values could be associated with low degrees of pore saturation, as defined by Lopez and Gonzalez [26] in such a way that low conductance in the pore solution prevents active state corrosion of reinforcements as effectively as passivating layers of steel in the absence of Cl⁻. Any of these mechanisms could explain the results presented in this paper. On the basis of our results, it is impossible to favour one against the others and could be regarded as highly speculative. This fact does not invalidate the usefulness of the relationship proposed in Eq. (1).

It should be taken into account that the correlation is valid within the frame imposed by the experimental design, i.e. for standard concretes prepared with type I Portland cement and no further additions. The cement composition and amount of blended material influence the chloride binding and the pH pore solution of concrete [11–13,35–37].

4. Conclusions

The chloride threshold concentration depends on several factors mainly involving, concrete composition and quality, exposure conditions and rebar surface characteristics. As a consequence, the Cl_{TH} reported in the literature presents a wide range of variation.

Based on the correlation of rebar corrosion parameters such as corrosion potential and current density together with concrete resistivity and chloride concentration data, a relationship that can be used to estimate chloride threshold values for rebar corrosion initiation from the measured resistivity values was proposed.

The results presented above show that the risk for chloride-induced corrosion and the chloride threshold value that will initiate the corrosion process can be estimated using a simple and non-destructive technique, such as concrete resistivity. When evaluated in context and compared with more standard E_{corr} and i_{corr} measurements, this parameter should surely contribute to establish a more accurate prediction of the service life of concrete structures exposed to chloride contaminated environments.

Further investigations are currently undertaken so as to take into account the effect of mortars and concretes of varying compositions.

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