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Corrosion Initiation Period for Stainless Steel Reinforcement in Concrete Structures

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Abstract. *The designed service life of reinforced concrete structure is often shortened when disposed in aggressive environments. In certain situations, stainless steel reinforcement may be an appropriate replacement to attain a higher level of durability. This paper presents the findings of an experimental study conducted to determine the critical chloride threshold for two types of stainless steel reinforcement (UNS S40977 and UNS S32001). For each steel grade, a prediction model for the corrosion initiation period was obtained, applying the electrochemical test data in a Monte Carlo analysis. Results show that if the initiation period is taken as the corresponding for a 7% corrosion probability, that will occur at 6.5 years of age for carbon steel and over 150 years for UNS S32001 stainless steel.*

Keywords: *Stainless Steel, Corrosion, Chloride-threshold, Monte Carlo Simulation.*

1 Introduction

Corrosion is the main reason for durability reduction of reinforced concrete structures (Andrade, 2015; Cairns et al., 2005). Even though reinforced concrete is the most used material in construction, it has its limitations regarding its durability in aggressive environments (L. Bertolini, 2008; Green, 2020; Pachón-Montaño et al., 2018; Rodrigues et al., 2021; Val & Stewart, 2003).

The deterioration of these structures can occur by carbonation-induced corrosion or chloride-induced corrosion. The latter have a greater impact on the useful life of structures and it is prone in marine environments or with the use of de-icing salts (García-Alonso et al., 2007; Garcia Alonso et al., 1998; Hussain et al., 1995; Lambert et al., 1991a).

Chloride (Cl^-) penetration into reinforced concrete is aggressive due to its ability to depassivate the steel bar and initiate the corrosion process, which will reduce the service life of the structure (L. C. T. Bertolini & Redaelli, 2009; Mangat & Molloy, 1992). The chloride-induced corrosion process starts after the chloride concentration reaches a certain limit around the rebar. The oxidation of the metal causes not only a loss of base metal and adhesion in the steel-concrete interface, but also an increase in volume that leads to the appearance of tractions in the coating of the structural element (U. Angst et al., 2009; L. Bertolini et al., 2016; Lollini et al., 2016; Otieno et al., 2011; Torres Martín et al., 2022).

Spanish structural concrete code establishes a threshold chloride concentration of 0.6% by weight of concrete, for passive carbon steel reinforcement. As other authors have pointed out, the substitution of carbon steel for stainless steel can lead to a ten times higher critical chloride levels needed to cause pitting corrosion, since these alloys ensure a passive state in highly aggressive environments (L. Bertolini et al., 1996; L. Bertolini & Pedeferri, 2002; Gastaldi et al., 2015; Lollini et al., 2019; Pachón-Montaño et al., 2018).

This paper presents the data of chloride penetration test on concrete with accelerated migration method, called "Integral Test". It intends to determine the relation between chlorides concentration near the reinforcement and the corrosion rate. Based on these results it is possible to obtain critic chloride thresholds, which trigger corrosion, comparing three different types of reinforcement: carbon steel and two stainless steel alloys.

2 Methodology

2.1 Samples and materials

The tests were conducted on fifteen cubic concrete specimens for each rebar type, with the rebar placed in the centre of the specimen. The concrete was prepared with type I 42.5R cement, batched at approximately 350 kg of cement per m^3 of concrete and the water/cement ratio was 0.55. Corrugated Φ20 mm samples of stainless steel UNS S40977 (DIN EN 1.4003), stainless steel UNS S32001-2001 (DIN EN 1.4482) and carbon steel B 500 SD were used.

2.2 Test method

The methodology followed in the research was based on the accelerated electrochemical chloride penetration test, which is described in the UNE 83992-2 EX standard "*Chloride penetration test in concrete. Part 2: Accelerated Integral Method*". This methodology allows the study of corrosion of the reinforcement and its progress by measuring the corrosion potential and the corrosion rate.

The method consists on applying an external electric field perpendicular to the reinforcement embedded in the mortar/concrete specimen. The electric field is applied between a copper electrode located in a container on the specimen with a 0.6 M NaCl and 0.4 M $CuCl_2$ solution, and a stainless steel mesh put on the bottom of the sample. The electric field produces the migration of Cl ions to the rebar, progressively increasing their concentration until reaching the necessary one to cause corrosion of the reinforcing bar (Pachón-Montaño et al., 2018).

In this accelerated test method, the reinforcement is inside an electric field that generates its polarization. Stainless steel is very sensitive to that electric field and to avoid its polarization an epoxy resin coat was applied in the rebar, leaving an exposed area of approximately 3 cm^2 (Sánchez-Montero et al., 2019).

The measurements were conducted daily through electrochemical techniques. The corrosion potential (E_{corr}) and the polarization resistance (Rp) were obtained by non-destructive methods such as Linear Polarization Resistance (LRP) and Electrochemical Impedance Spectroscopy (EIS) aiming the continuous monitoring of the specimen without affecting it (Andrade & Izquierdo, 2022; U. M. Angst, 2019; Lambert et al., 1991b; Yang & Cho, 2004). These values allow the calculation of the corrosion rate. The Rp is related to the corrosion rate (Icorr) by means of a constant *B* denominated by Stern et al. (Stern & Geary, 1957), associating anodic and cathodic Tafel constants.

$$I_{corr} = \frac{B}{R_p} \tag{1}$$

The readings were executed and recorded on a Metrohm Autolab potentiostat-galvanostat (Alonso et al., 2000; Izquierdo et al., 2004). The electrochemical cell used was composed of saturated concrete as the medium, a steel bar as the working electrode, a copper foil as the auxiliary electrode, and saturated Ag/AgCl solution as the reference electrode (Garcia Alonso et al., 1998).

After the electrochemical measurements, the specimens were broken in half and samples of the mortar were taken immediately above the rebar. These samples were analyzed by X-ray fluorescence test (XRF) to obtain the limit value of chlorides, in percentage by weight of cement, which is taken as the necessary concentration to depasivate the reinforcement (C_{crit}) (Chinchón-Payá et al., 2021; Dehghan et al., 2017).

3 Results and Discussion

The data obtained with daily measurements allows the calculation of corrosion rate of the reinforcing bars.

Concerning the connection time of the electric field, it is observed that the time necessary to achieve depassivation for the carbon steel is lower than the one for UNS S40977 stainless steel, which is lower than the one for UNS S32001 stainless steel. In a qualitative way, since the connection time is related to the migration time of the ions, these results are related to the chloride corrosion resistance capacity of each type of steel. Figure 1 shows in a box and whisker plot the comparison between the connection times mentioned, in which time has been represented on a logarithmic scale on the x-axis.

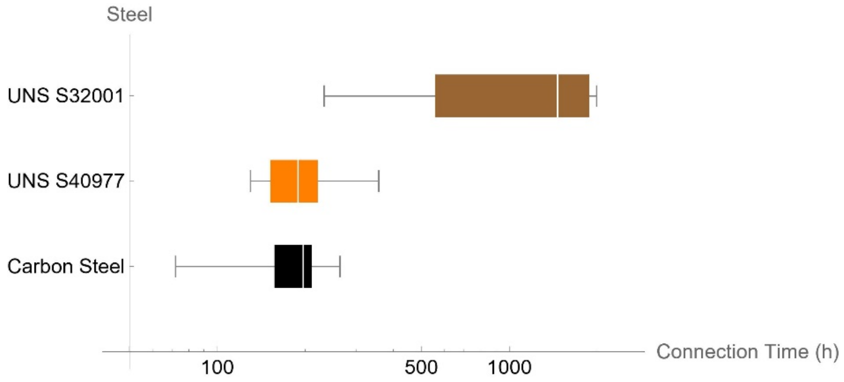

Figure 1. Connection time during the accelerated migration test.

The chloride threshold that produced corrosion can be seen in Figure 2, also in a box and whisker plot, in which the x-axis represents chloride concentration expressed in percentage by cement weight (%cem). The concentration needed to affect the carbon steel is lower than the one for UNS S40977 stainless steel, which is lower than the one for UNS S32001 stainless steel.

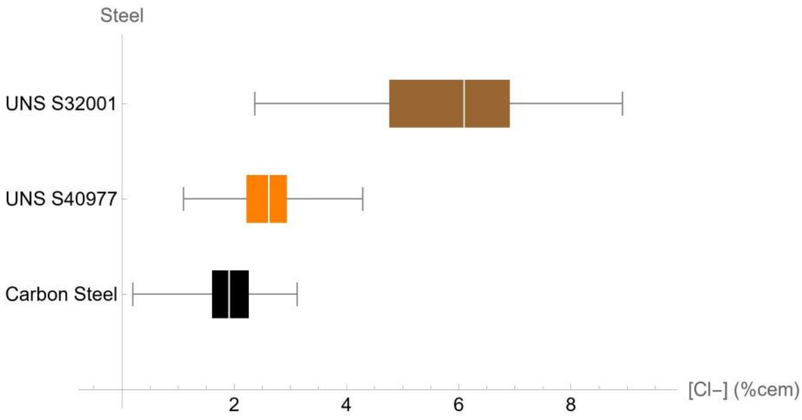

Figure 2. Chloride concentration near the rebar.

In order to quantify the critic chloride threshold that produced depassivation of the steel, the data has been adjusted to a probability distribution. After performing different tests it has been concluded that the Log-normal distribution is the most appropriate to fit the experimental data. Following this methodology, Figure 3 shows the probability density function (PDF) obtained for each type of steel. It is shown that the chloride concentration needed to initiate corrosion, with a given probability, is higher for UNS S32001 stainless steel, followed by UNS S40977 stainless steel and finally carbon steel.

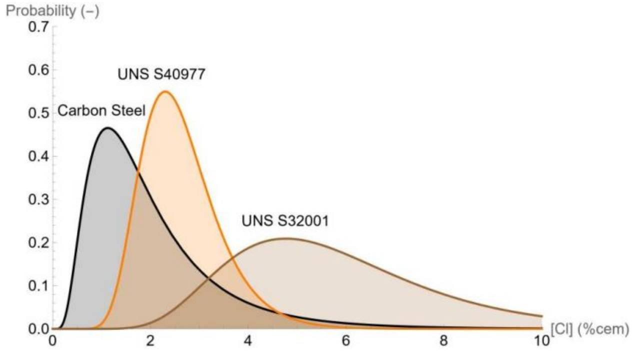

Figure 3. Probability density function comparing the chloride concentration in the reinforcement for each type of steel studied.

Table 1 shows a summary of the critic chloride thresholds that cause depassivation of the different types of steel studied, at a 90% confidence interval. The value obtained for carbon steel of 0.60%cem coincides with the one established by the regulations. The corresponding value for UNS S40977 stainless steel is 1.5%cem and 3.0%cem for UNS S32001 stainless steel, which represents a significant resistance increase with important repercussions on the durability of reinforced concrete structures.

Table 1. Critic chloride threshold.

Steel Grade	Lower value at a 90% confidence interval
Carbon steel	0.6
UNS S40977 stainless steel	1.5
UNS S32001 stainless steel	3.0

3.1 Application to the durability calculation of an existing structure

A durability evaluation of a concrete structure exposed to marine environment was carried out, based on the published case study by Torres-Martín *et al*. The corrosion initiation period was estimated considering the materials studied in this article and the chloride diffusion process without aging effect hypothesis.

In order to consider all possible scenarios that can be reached in the structure, an analysis has been carried out using a Monte Carlo simulation, taking into account the variability of the diffusion coefficient and the surface concentration of chlorides (Chinchón-Payá et al., 2021; Kalos & Whitlock, 2008; Torres Martín et al., 2022). In these calculations, 10^5 simulations have been performed.

The chloride concentration profile was fitted to Fick's second law (Andrade et al., 2012; Li et al., 2016). The fit was performed under the assumptions that the surface concentration (Cs) and diffusion coefficient (D_{ns}) are constant.

$$C_x = C_i + (C_s - C_i)\left(1 - erf\left[\frac{x}{\sqrt{D_{ns} \cdot t}}\right]\right) \quad (2)$$

Where C_x is the chloride content corresponding to depth x after time t; C_s is the calculated chloride content corresponding to the exposed concrete surface; C_i is the initial chloride content; x is the depth from each analysis point to the surface; D_{ns} is the diffusion coefficient in non-steady state; t is the age of the structure. The condition for passive state is that the chloride concentration must be lower than the critical one defined in the previous section, $C(t) < C_{crit}$.

Figure 4 shows the kernel histograms for the probability density function (PDF) at 15 and 40 years.

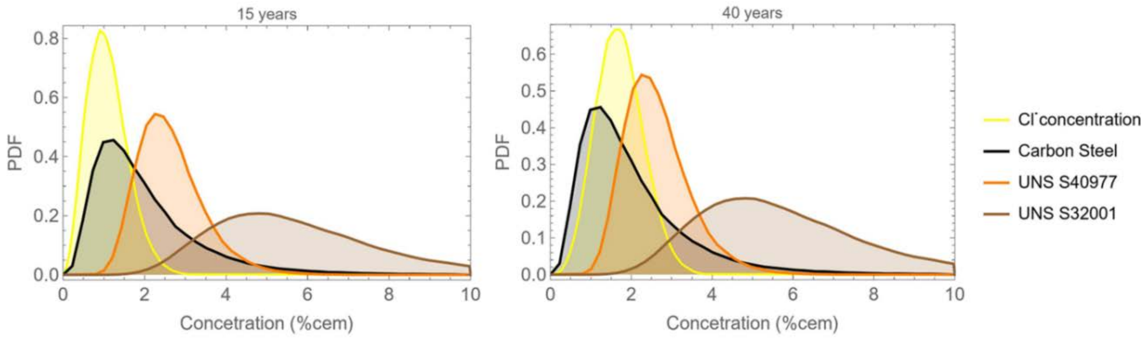

Figure 4. Smooth kernel histogram for the PDF of the chloride concentration and critical chloride concentration for each steel grades. Left: t = 15 years; Right: t = 40 years.

For each time, the evolution of the chloride concentration at the reinforcement position is compared with the chloride concentration resulting in the depassivation of the reinforcement for each steel grade. While the chloride concentration at the reinforcement position changes over time, the chloride concentration that causes depassivation of the reinforcement for each steel grade remains constant. As a conceptual approach, the initiation of corrosion will occur when both distributions become similar causing the critical concentration of chlorides in the reinforcement to be exceeded.

Each concentration value obtained, $C^i(t)$, is compared with the critical concentration, C^i_{crit}, both obtained randomly according to the Monte Carlo method.

Therefore, the probability of corrosion occurring can be estimated at each age, taking into account that this will happen once the chloride concentration reaches a higher value than the critical concentration. Figure 5 shows the evolution of this probability for the different steel grades studied.

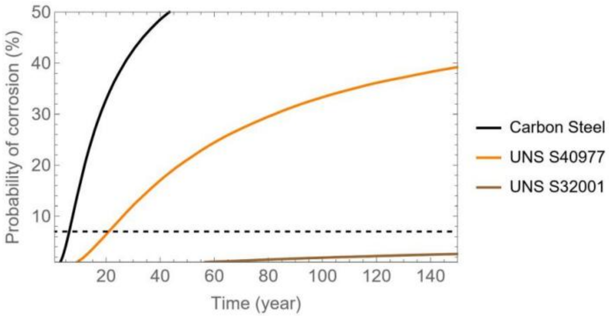

Figure 5. Corrosion probability and initiation period.

Taking the initiation period as the corresponding for a 7% probability, it will occur at 6.5 years of age for carbon steel, 21 years for UNS S40977 stainless steel and over 150 years for UNS S32001 stainless steel.

4 Conclusions

The chloride threshold that causes depassivation of two types of stainless steel and carbon steel has been obtained through accelerated migration test. Defined as the lower value for a 90% confidence interval, the C_{crit} for carbon steel is 0.6%cem, for UNS S40977 stainless steel is 1.5%cem and for UNS S32001 stainless steel is 3.0%cem. In conclusion, the grades of stainless steel tested have shown greater resistance against chloride-induced corrosion than carbon steel.

Structures exposed to aggressive environments are susceptible to deterioration. Under these conditions, the implement of protection methods or corrosion-resistant material, such as stainless steel, is needed. This paper presents a methodology for evaluating existing structures, which is also applicable for new structures design.

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