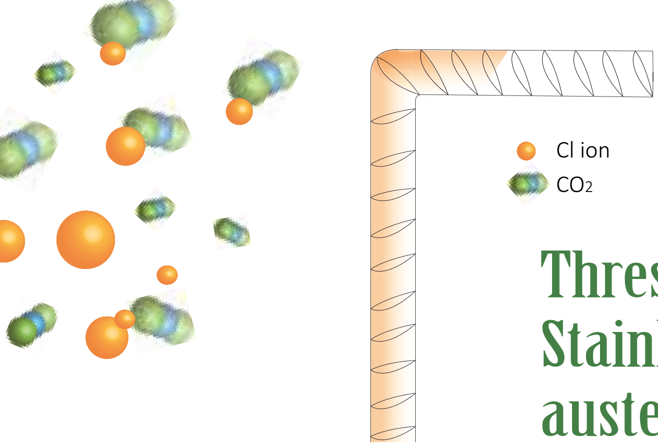

Threshold Concentration of Chlorides for Stainless Steels reinforcement : Classic austenitic and new duplex stainless steel

1. Introduction

The corrosion of steel reinforcements is one of the main causes of the reduction of durability in reinforced concrete structures. The main agents that cause corrosion are the carbonation of concrete due to the presence of CO2 and the entry of chlorides in the case of marine environments or de-icing salts. The latter have the greatest impact on the lifespan of the structures [1, 2].

The concern for the corrosion of the reinforcements due to the presence of chlorides has given rise to numerous studies for the case of carbon steel reinforcements with different approaches to the chemical part: i) some focus on the study of the concentration of free chlorides $[Cl^-]$, ii) others in the chloride / hydroxide concentration ratio $[Cl^-]$ / $[OH^-]$ and iii) others in total chlorides as percentage by weight of cement (% BWOC) [3]. There are also different approaches in terms of the methodology used, although mainly electrochemical tests have been performed, there are several studies that include techniques such as anodic polarization curves, corrosion rate measurements (Icorr), gravimetry, electrochemical impedance spectroscopy, etc. [3-18] In these studies, different values of critical concentration of chlorides are shown as the necessary value to initiate corrosion [3, 19], these values are different depending on the methodology study used and the exposure conditions, whether natural or laboratory tests [3-7, 9-18, 20]. In the case of the Structural Concrete Instruction (EHE-08), a 0.6% BWOC value is established for the critical concentration of total chlorides, a value that coincides with those obtained in previous studies carried out in the IETcc-CSIC [21].

The increasing use of stainless steel reinforcement has stimulated new studies on the chloride limit for different qualities. Studies in solution show that these limits are four to six times higher than that for carbon steel at pH values of 9 to 13 and at a standard temperature of 20°C [22]. Other authors have found that the critical chloride concentration is 10 times higher than for carbon steel in the case of austenitic stainless steel EN 1.4307 and EN 1.4404 [23]. However, there are no researches in mortar or concrete that established the critical thresholds of chlorides for different grades of stainless steel, since their corrosion resistances vary depending on the microstructure, type of alloy and composition [22, 24-27].

The Group of Corrosion of Reinforcement and Structural Safety of the IETcc-CSIC in collaboration with ACERINOX have carried out an investigation on the critical concentration of chlorides of 5 different qualities of stainless steel in mortar within the Integrated Research Project on Sustainable Islands (IISIS) [28].] In this project two grades of austenitic stainless steel have been studied: EN 1.4307 (AISI-304L) and EN 1.4404 (AISI-316L); and three duplex stainless steels grades: EN 1.4482 (2001), EN 1.4362 (2304) and EN 1.4462 (2205).

2. Methodology

The methodology followed in the investigation is based on the standard UNE 83992-2 "Durability of concrete. Test methods. Chloride penetration tests in concrete. Part 2: Accelerated integral method." The method is based on applying an external electric field perpendicular to the reinforcement embedded in the mortar/concrete specimen. The field is applied between a copper electrode located in a vessel on the test tube with a solution 0.6 M NaCl and 0.4 M CuCl2. In the lower part, a stainless steel mesh is placed. In this way, the electric field produces the migration of the Cl^- ions to the reinforcement, increasing its concentration progressively

EN/AISI	C	Si	Mn	Cr	Ni	Mo	P	S	N	PREn
1.4307/304L	0.028	0.308	1.376	18.099	7.978	0.243	0.033	0.034	0.07	19.6
1.4404/316L	0.020	0.291	1.363	16.797	10.481	2.025	0.035	0.03	0.045	23.5
1.4482/2001	0.018	0.687	4.175	20.124	1.815	0.166	0.029	0.0009	0.099	19.5
1.4362/2304	0.016	0.647	1.609	22.730	4.226	0.107	0.034	0.0008	0.143	25.8
1.4462/2205	0.032	0.395	1.616	22.408	4.695	3.341	0.03	0.002	0.173	37

Table 1. Quality, composition and PREn index of the reinforcements.

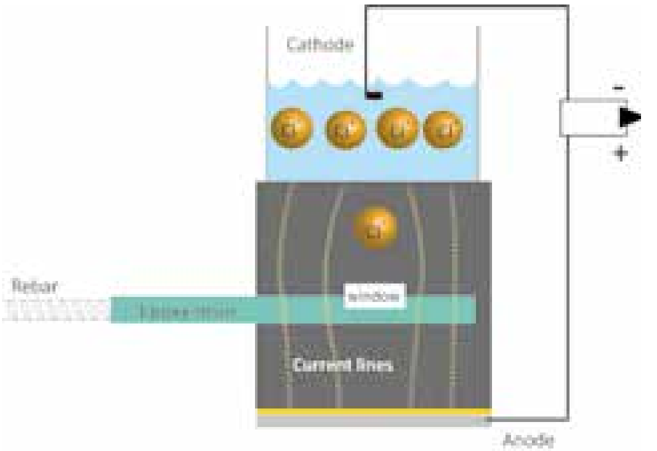

Figure 1. Scheme of the accelerated integral essay with the proposed modification.

until reaching the necessary one to cause the corrosion of the steel [30]. During the test the corrosion potential and the corrosion rate are measured to determine the time at which corrosion starts [2, 31]. Once the corrosion has started, the electric field is disconnected, the test piece is broken and the amount of Cl- is measured in the reinforcement environment.

Samples

Five types of diameter 12 mm reinforcement have been studied whose composition is shown in table 1. For each grade of stainless steel 6 samples of mortar of 7x7x7 cm^3 have been manufactured, using a cement type I, with a water/cement ratio of 0.5.

Modification of the test method to adapt it to stainless steel reinforcements.

In this accelerated test method the reinforcement is within an electric field that produces its polarization. This effect is negligible in the case of carbon steel reinforcements, which have no repassivation capacity [32]. However, the behaviour of stainless steel is very sensitive to said electric field which can lead to a start of non-"real" corrosion. To avoid this polarization the reinforcement has been coated with epoxy resin except for a window of approximate dimensions of 2x1 cm2 on the face exposed to the entry of Cl^-. In the work carried out in the framework of the project between IETcc-CSIC-ACERINOX it is shown how the current lines do not cross the reinforcement when applying this coating and it has been verified experimentally [28]. The following figure shows an outline of the essay.

Following the test procedure proposed in the UNE 83992-2 standard, the external electric field is connected for a few hours, it is disconnected and the sample is left approximately 1 hour before performing the measurements of corrosion potential (Ecorr) and corrosion rate (Icorr). The corrosion rate is measured by applying a linear polarization (LRP) around the corrosion potential [33-35].

Another of the modifications introduced in the test methodology is to set the depassivation limit when the corrosion rate is higher than 0.2 $\mu A/cm^2$. In this way, the external field is applied until that moment, and if for 10 days thereafter it remains in values above this limit, the test is concluded. Otherwise, if the corrosion rate decreases to values below this threshold, the electric field is reconnected until it returns to the previous situation.

Once a stable corrosion rate has been reached, the electrochemical test is dismantled and the test piece is broken by a plane perpendicular to the face containing the pool and passing through the bar. Samples are taken from the concrete near the reinforcement and their chloride content is analysed in accordance with the UNE 80213 standard. Additionally, the surface of the reinforcement is analysed and the type of corrosion that has occurred is studied.

3. Results

Figure 2 shows the time that the external field has been applied until reaching the depassivation of the reinforcement. It is observed that, qualitatively, the average test time increases according to the following order for stainless steel grades: 2001 (92 h) <304-L (117 h) <2304 (481 h) <316-L (608 h) <2205 (1909 h).

Figure 3 shows the values of corrosion rate (Icorr) after the chloride penetration test and the concentration of Cl^- (as % with respect to the weight of cement) at the depth of the reinforcement. Taking as a depassivation limit the value of 0.2 $\mu A/cm^2$, it can be observed that, qualitatively, 2001 and 304-L types exceed this threshold for concentrations of Cl- close to 1% (BWOC), while at the other extreme, 2205 type exceeds this threshold for concentrations above 4% to the weight of cement.

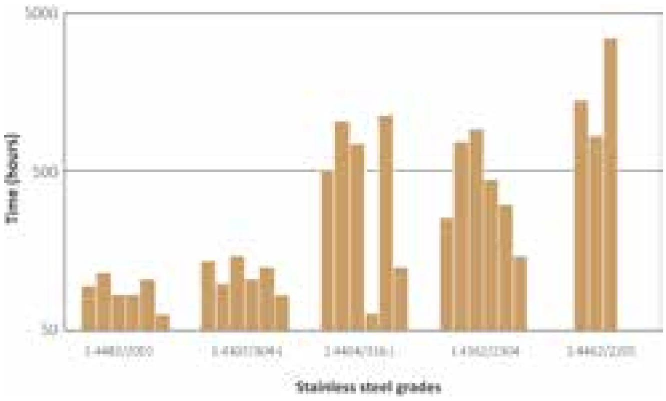

Figure 2. Depassivation time for different grades of stainless steel

4. Discussion of results.

In order to determine the useful life of these stainless steel reinforcements, it is necessary to determine the critical concentration of chlorides produced by the depassivation thereof. An indicator of the resistance to corrosion of a stainless steel type is the PREn index, which is defined by the following formula:

PREn=%Cr+3.3%wMo+30%wN-%wMn

Eq.1

As mentioned in the results (Figure 3), in some cases the depassivation of the reinforcement has not been reached, as is the case of some test pieces with the EN 1.4462/2205 duplex. Taking only into account the cases in which values of corrosion speed higher than 0.2 μA/cm2 have been reached, in Figure 4 the concentration of chlorides against the value of PREn has been represented. There is a linear correlation between both parameters (R2 = 0.92). Given the dispersion of the results inherent to the type of test, it is possible to calculate the critical concentration of chlorides considering or assuming a 10% risk normally used in the standards. This result allows us to assume that with a probability of 90%, any value obtained will be above the curve “confidence interval of 10%”.

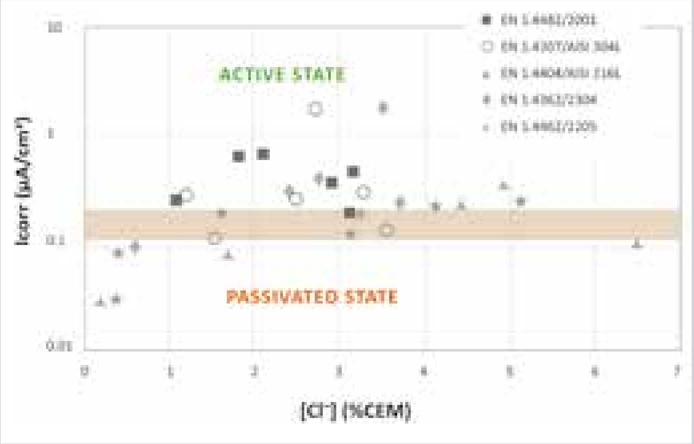

Figure 3. Results of Icorr and Cl$^-$ concentration for each of the stainless steel grades studied.

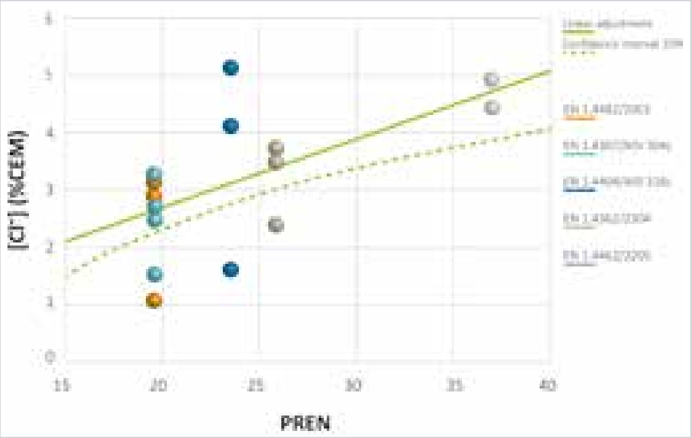

Figure 4. Concentration of Cl$^-$ against the PREn value.

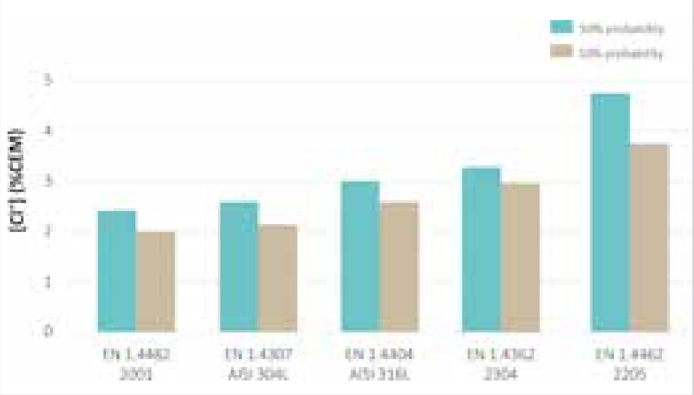

Figure 5. Critical concentration of Cl$^-$ for each of the stainless steel grades studied.

Figure 5 shows the results of the critical concentrations obtained by this method for 50% and 10% probabilities.

Case Study. Application for estimating the initiation period of corrosion in a reinforced concrete structure.

The following is the calculation of the corrosion initiation time of the reinforcements of a structure that is in a marine environment, IIIb according to EHE-08, which is the environment with the highest chloride surface concentration. Considering that the transport of chlorides is purely diffusive, the 2nd Fick Law is resolved:

$$\frac{dC}{dt} = D\nabla C$$

Eq.2

Where C is the concentration, t is the time and D is the diffusion coefficient. In turn, as expressed in Annex 9 of the EHE-08, it can be considered that the diffusion coefficient varies with time following the equation:

$$D(t) = D(t_0)\left(\frac{t_0}{t}\right)^n$$

Eq.3

Where D (t_0) is the chloride diffusion coefficient at age t, D (t0) is the chloride diffusion coefficient at age t0, and n is the age factor. In the calculations that have been made, it is considered that this age factor is applied during the first two years, considering that after this time the concrete does not continue to “age” or decreasing the diffusion coefficient.

The calculations have been made with a commercial finite element program taking into account the input parameters to the model shown in Table 2. The surface concentration of chlorides chosen is that proposed by the EHE-08 for a marine environment IIIb. The calculations have been made for two concrete types, with two different diffusion coefficients (table A.9.4, Annex 9, EHE-08) and the evolution of the chloride concentration has been obtained considering coatings varying between 20 and 50 mm.

Figure 6 shows the evolution of the concentration of chlorides for the different concrete covers together with the critical concentration of chlorides for different stainless steels considering a concrete with a diffusion coefficient of 5.6 10-12 m2/s. In the case when it has been calculated if carbon steel is used, whose critical concentration has been established at 0.6% weight of cement, it would be depassivated in 20 years for the largest of the covers considered, 50 mm.

In the case of duplex steel 2001 or austenitic 304-L, a 40 mm cover would suffice to achieve an initiation period of more than 100 years. The remaining grades of stainless steel (316-L, 2304 and 2205) could reach the 100-year initiation period with minimal cover. It must be borne in mind that in this exercise it is being considered that there are no other types of degradation.

C_s(%cem)	C_o(%cem)	r(mm)	D(m²/s)	n
3.2	0	20-50	$5.6\ 10^{-12}$-$1.4\ 10^{-12}$	0.5

Table 2. Parameters of entry to the model: surface concentration of chlorides (*Cs*), initial concentration of chlorides (*Co*), coating (*r*), diffusion coefficiente (*D*) an age afctor (*n*).

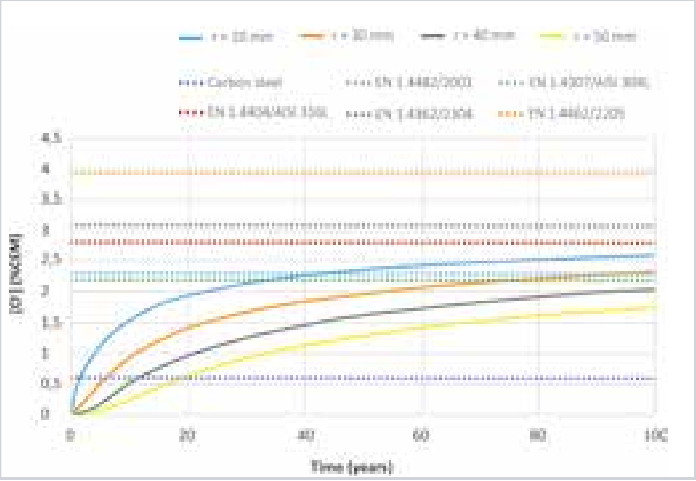

Figure 6. Evolution of Cl^- concentration for different concrete covers (r), and a diffusion coefficient of 5.6 10^{-12} m²/s. Critical concentration of different steels.

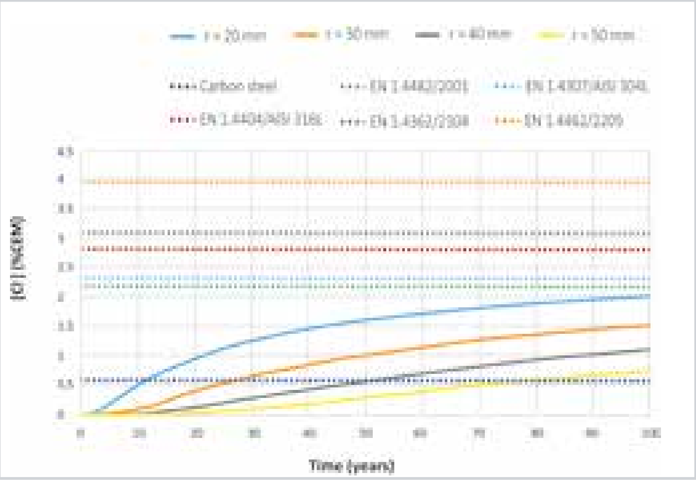

Figure 7. Evolution of the Cl^- concentration for different concrete covers (r) , and a diffusion coefficient of 1.4 10^{-12} m²/s. Critical concentration of different stainless steels.

In Figure 7 the previous exercise has been repeated for the case of a concrete with a lower diffusion coefficient, 1.4 10-12 m² / s. If carbon steel was used, it would be necessary to guarantee concrete covers greater than 50 mm throughout the structure so that the corrosion initiation time was 100 years.

However, depassivation would not be achieved in 100 years if a stainless steel was used, even if a minimum cover of 20 mm of concrete was used.

5. Conclusions

The main conclusions that are obtained from this study are:

- Based on the UNE-EN 83992-2 standard, a modification of the same is proposed to obtain a methodology that allows the calculation of the critical value of chlorides for the case of stainless steels. This study would be necessary to complete it with more tests that would allow to reduce the uncertainty due to the high dispersion of the results.
- A good relationship between the critical concentration of chlorides and the PREn value has been obtained, which would allow to estimate the critical concentration of chlorides for other stainless steel grades not studied.
- An application exercise of stainless steel reinforcement in a marine environment IIIb according to EHE-08 is shown. Maintaining a minimum concrete cover would achieve durability greater than 100 years.

Source:

J. Sánchez[a], N. Rebolledo[a], J. Torres[a], V. Matres[b]
[a]Grupo de corrosión de las Armaduras y Seguridad Estructural,IETcc-CISC, Madrid
[b]Acerinox Europa, S.A.U. (Cádiz)

⭳ references only on-line