

# Corrosion behaviour of new duplex stainless steel reinforcements embedded in chloride contaminated concrete

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## Summary

The use of reinforcing stainless steels (SS) in concrete have proved to be one of the most effective methods to guarantee the passivity of reinforced concrete structures exposed to chloride contaminated environment. The present research studies the corrosion behaviour of a new duplex SS reinforcements with low nickel content (LND) (more economically compatible) is compared with the conventional austenitic AISI 304 SS and duplex AISI 2304 SS. Corrosion behaviour of ribbed SS reinforcements was studied in mortars with chloride content (0, 0.4, 2 and 4% Cl<sup>-</sup>) using linear polarization resistance and potentiostatic pulses technique,  $E_{\text{corr}}$  and  $R_p$  values were monitored over the exposure time. The obtained  $i_{\text{corr}}$  data for the new duplex stainless steel LND no afforded passivity breakdown after one year exposure.

## 1 Introduction

The annual consumption of SS has increased at a compound growth rate of 5% over the last 20 years, surpassing the growth rate of other materials. It is estimated that in 2006, approximately 4 million tones of SS went into construction applications worldwide, 14% of the total quantity consumed.

Perhaps the most significant recent advance impacting the construction sector has been the use of duplex grades for structural applications, which offer a combination of higher strength than the austenitics (and also the great majority of carbon steels) with similar or superior corrosion resistance. Duplexes have tremendous potential for expanding future structural design possibilities, enabling a reduction in section sizes leading to lighter structures. It is worth noting that although they have good ductility, their higher strength results in more restricted formability compared to the austenitics [1].

Toghether with cathodic protection, corrosion inhibitors, galvanized steel and new alternative cementitious matrix, stainless steel reinforcements are a reliable way to guarantee service life of reinforced concrete structures in chloride containing environments [2-5].

SS reinforcements passivate in concrete because its high alkalinity, usually within a pH range of 12-13 [6]. The stability of the passive film formed depends on the alloy composition, temperature, passivation time and working environment. Passive film

breakdown has been reported to occur non-uniformly on the surface of SS rebars, starting from a number of activated sites where the reaction products are a voluminous non-protective hydroxide compounds [7].

Reinforcing SS is distinguished by its corrosion resistance against the attack of chloride ions. Types austenitic and duplex are the most recommended for use in reinforced concrete structures (RCS). Austenitic is the most used, and their tolerance to chloride is 5 to 10 times higher than that of carbon steel [8]. Duplex is cheaper than austenitic, due to its lower nickel content, and yet has a higher resistance to chloride pitting corrosion [9]. Both SS grades allow to increase the durability of RCS, compared with to protect carbon steel reinforcement [10, 11].

However, with time, severe corrosion may occur in RCS. Corrosion is most frequently induced by the entry of chloride ions, which leads to local destruction of the oxide layer. Chloride ions are commonly found in construction materials and may originate from contamination of the water used in concrete production, from contaminated aggregates, or even from the external environment, as in the case of marine environments [5].

SS reinforcements were first used many decades ago and have proved their ability to prevent corrosion for a very long time, even in very aggressive environments. SS offers exceptional advantages for certain applications in construction, combining intrinsic durability with aesthetics, strength, ductility and formability. However, their use has been limited due to the high cost of SS compared to carbon steel. For this reason, new SSs, in which the nickel content has been lowered by replacement with other elements, nickel is subject to considerable price fluctuations due to stock market factors, are being evaluated in the literature as possible alternatives to conventional carbon steel [12].

The aim of this paper is to study the corrosion behaviour of a new type of duplex SS, with a low nickel content, embedded in ordinary Portland cement (OPC) mortar with different chloride additions. Conventional austenitic AISI 304 SS and duplex AISI 2304 SS are also studied for comparative purposes. Corrosion potential, linear polarisation resistance, and potentiostatic pulses measurements have been performed to evaluate the corrosion behaviour of new duplex SS reinforcements, up to 1 year of experimentation.

## **2 Experimental**

Experiments were performed on small prismatic specimens measuring 8×5.5×2 cm, as depicted in Figure 1. Two 8 mm wide and 85 mm length low-nickel duplex SS (LND), AISI 304 austenitic SS, and AISI 2304 duplex SS rebars (Table 1), symmetrically embedded in the prisms, were used as working electrodes (WE) during the measurements, with an external SS cylinder of 7 cm diameter acting as a counter electrode (CE) provided with a central hole to place a saturated calomel electrode (SCE) as reference electrode (RE). A pad soaked in water was used to enable the electrical conductivity measurements using a three electrode configuration (Fig. 2). An active surface area of 10 cm<sup>2</sup> was marked on the working electrodes with adhesive tape, thus isolating the triple mortar/steel/atmosphere interface to avoid possible localised corrosion attack due to differential aeration.

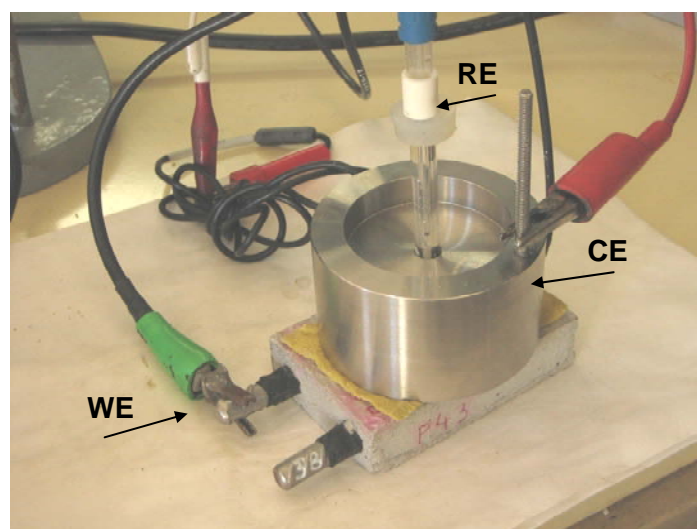


**Figure 1:** Reinforced concrete specimen embedding two stainless steel reinforcements Ø8 mm wide.

**Table 1:** Chemical composition (wt.%) \* of the tested stainless steels.

Acero	C	Si	Mn	P	S	Cr	Ni	Cu	N	Mo
LND	0.023	0.661	4.153	0.025	0.01	19.98	1.80	0.032	0.129	0.214
AISI 304	0.07	0.75	2.00	0.075	0.015	18.50	9.00	-	-	-
AISI 2304	0.03	1.00	2.00	0.035	0.010	23.00	3.50	0.20	0.10	0.20

[\*] Balance: Fe



**Figure 2:** Three electrodes configuration used for reinforced concrete corrosion electrochemical monitoring: RE, CE and WE.

Mortar specimens were prepared with a cement/sand/water ratio of 1/3/0.5 and chloride additions of 0, 0.4, 2 and 4%, relative to cement weight. These specimens were exposed in a very wet atmosphere with a relative humidity of approximately 95%.

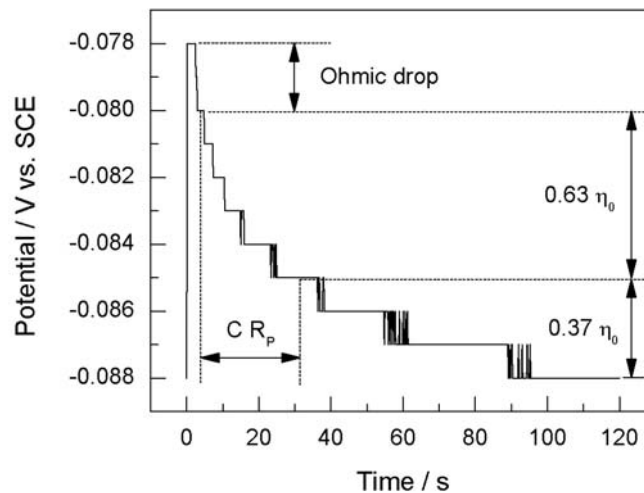
Steel corrosion over time was monitored using two techniques: (i) corrosion potential ( $E_{corr}$ ) values; (ii) linear polarization resistance ( $R_p$ ) values ( $R_p = \Delta E / \Delta I$ ). The steel corrosion rate can be calculated from the Stern-Geary equation [13]:  $i_{corr} = B / R_p$ , applying  $\Delta E \pm 15$  mV at a scan rate of  $0.16 \text{ mV s}^{-1}$ , and adopting a tentative value of 52 mV or 26 mV for the B constant for steel in the passive or active (corroding) state, respectively [14]. An EG&G PARC potentiostat model 273A was utilised for DC measurements. Electrochemical monitoring was performed periodically during one year exposure.

After  $R_p$  measurements, pulse technique was applied to determine the time constant of the corrosion process. Figure 3 shows typical pulse shapes obtained applying potentiostatic pulses signal of +50 mV for about 2 s duration and recording the potential decay over time by the probe for 120 s.

Under potentiostatic conditions, the potential response of a system, approximated by a simple Randles circuit, to a current step  $\Delta I$  is given by:

$$\eta_T = \Delta I R_\Omega + \Delta I R_p \left( 1 - \exp\left(-\frac{t}{C R_p}\right) \right) \quad (1)$$

Where  $\eta_T$  is the polarization at a given time of the working electrode (WE),  $\Delta I R_\Omega$  is the ohmic drop in the concrete between the reference electrode and the working electrode,  $\Delta I R_p$  is the effective polarization at 2 s charging time,  $R_p$  is the polarization resistance of the rebar,  $C$  is the double layer capacitance of the interface and  $C R_p$  is the time constant  $\tau$  for the corrosion process.



**Figure 3:** Potentiostatic pulse plot and layout of the direct calculation of the time constant for a concrete-embedded reinforcement.

For a given time

$$\tau = CR_p \quad (2)$$

Eq. 1 is reduced to:

$$\frac{\eta_\tau}{\eta_0} = e^{-1} = 0.37 \quad (3)$$

Where  $\eta_\tau$  is the polarization at time  $t$  from current interruption, and  $\eta_0$  is the maximum polarization at the time of interrupting the current. Thus, it is possible to directly determine  $\tau$  by measuring the time in which  $\eta_t$  is reduced to 37% of its initial value.

As  $C$  is directly proportional to the surface area of the WE and  $R_p$  is inversely proportional,  $\tau$  is independent of this magnitude. Consequently, if  $C$  corresponding to the unit of surface area is inserted in the Eq. 1, the  $R_p$  of the rebars per unit of surface area will be estimated, without their number or their diameter being of importance.

In order for things to happen this way, the possible interference of other partial processes besides corrosion must be of little importance, or must occur in very different times to those used in the measurements, in order not to mask the potential decay due to the corrosion process [15].

The direct measurement of  $\tau$  to determine  $R_p$  applying potentiostatic pulses was advocated in a highly interesting work by Glass [16]; though previously determining the interfacial capacitance from the charge injected, the potential shift achieved, and the surface area of the steel. The interfacial properties of the steel-concrete system have been also studied by using galvanostatic pulses, thus allowing rapid determination of the corrosion activity of the steel and readily yielding values for the polarization resistance and interfacial capacitance [17].

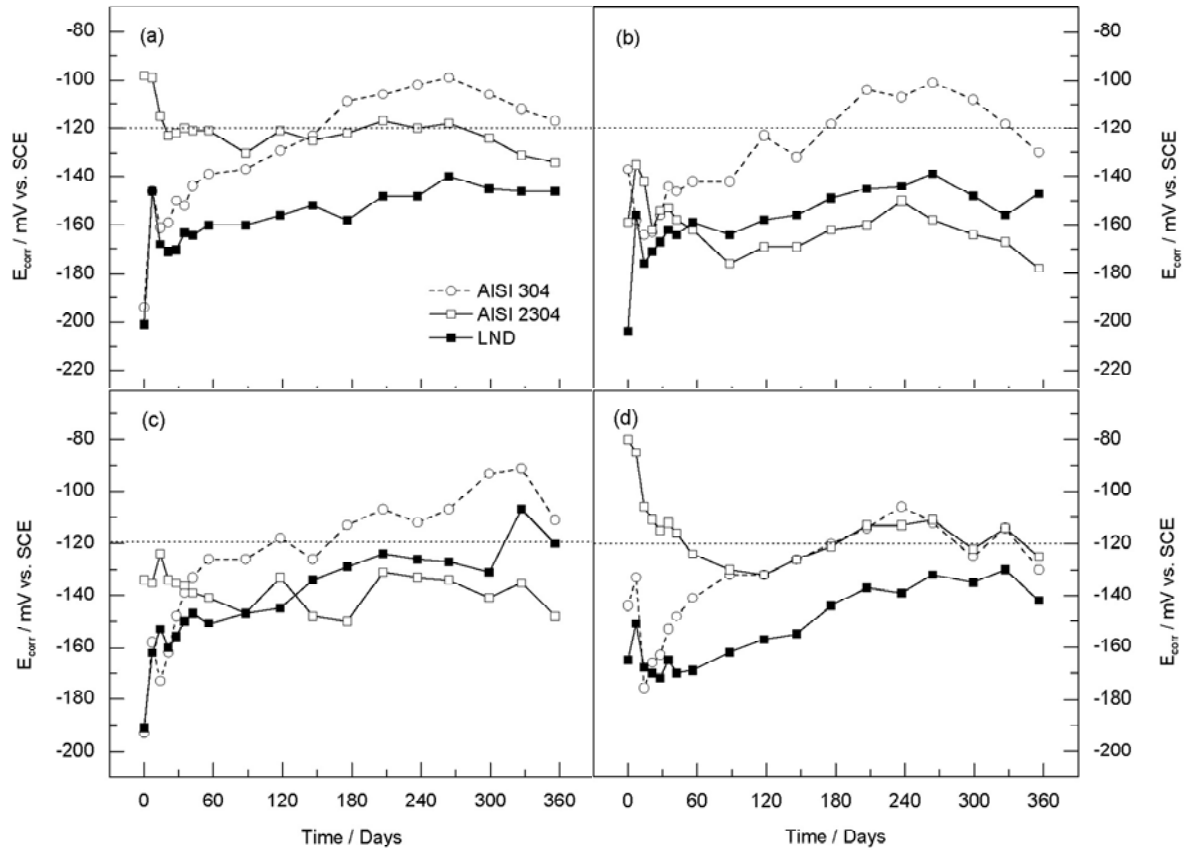
With potentiostatic pulses is possible to estimate reliable values of  $R_p$  in RCSs without the need to know the surface area of the rebars, assuming an approximate value of the capacitance ( $C$ ) [18].

### 3 Results and discussion

Figure 4 shows  $E_{\text{corr}}$  versus time (one year) for LND low-nickel duplex SS, AISI 304 SS, and AISI 2304 SS embedded in mortars with different chloride additions: (a) 0%, (b) 0.4%, (c) 2% and (d) 4%. As can be seen, all SS exhibited  $E_{\text{corr}}$  values around  $-120$  to  $-180$  mV vs. SCE, slightly higher for both duplex SS than the austenitic, regardless of the chloride content.

After forming the passive layer during the first weeks, the  $E_{\text{corr}}$  parameter is stabilized in the range of values that are considered likely to be uncertain for metal corrosion (between  $-120$  and  $-270$  mV for carbon steel) [19].

Fig. 5 shows the  $i_{\text{corr}}$  values, estimated from the  $R_p$  measurements, versus time for LND SS, AISI 304 SS, and AISI 2304 SS embedded in mortars with different chloride additions: (a) 0%, (b) 0.4%, (c) 2% and (d) 4%.



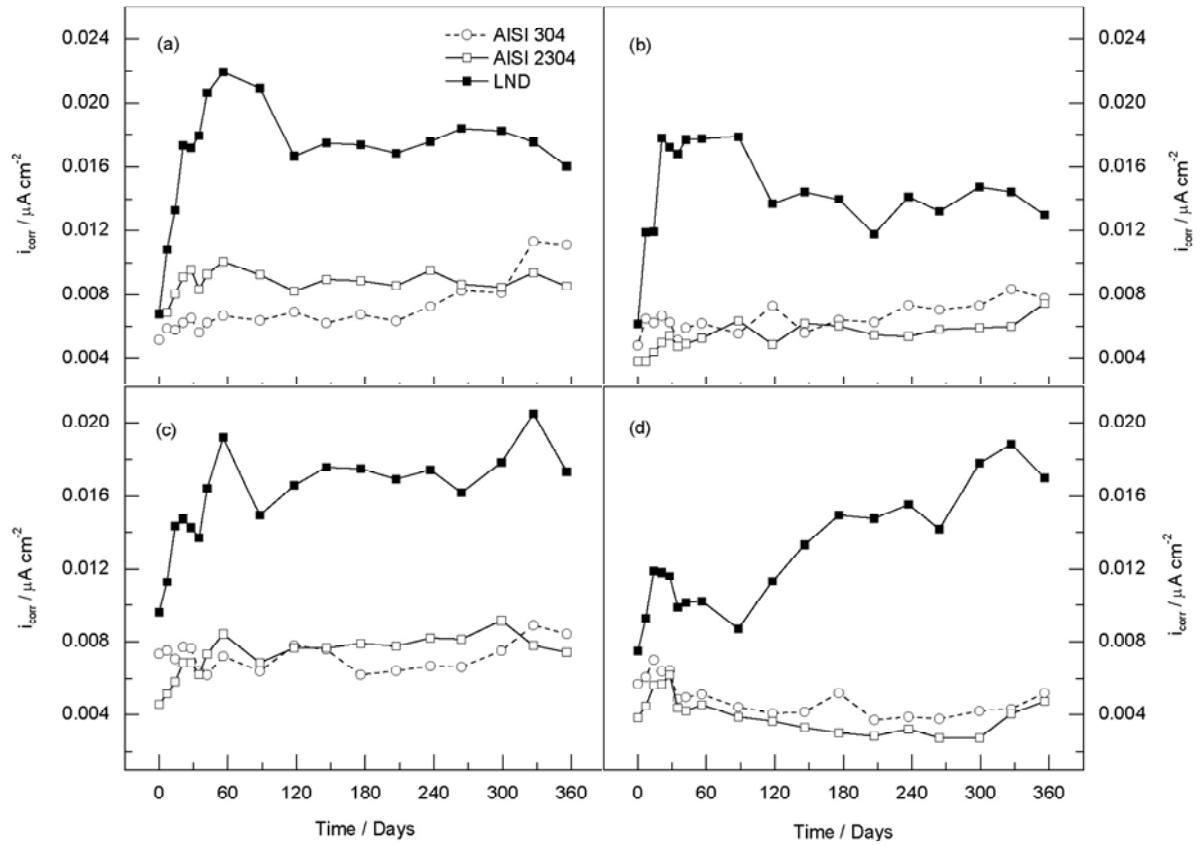
**Figure 4:** Corrosion potential ( $E_{\text{corr}}$ ) recorded for the three stainless steel studied over 1 year exposure, AISI 304, AISI 2304 and LND, with chloride addition of (a) 0%, (b) 0.4%, (c) 2% and (d) 4%  $\text{CaCl}_2$ .

The  $i_{\text{corr}}$  values of LND increase have only  $0.004$  to  $0.012 \mu\text{A cm}^{-2}$  respect AISI 304 y 2304 SS, regardless of chlorides content. In an attempt to compare these results with the behaviour of OPC mortar/carbon steel, the Durar Network Specification indicates [20]: for  $i_{\text{corr}} < 0.1 \mu\text{A cm}^{-2}$  passivity, for  $0.1 \mu\text{A cm}^{-2} < i_{\text{corr}} < 0.5 \mu\text{A cm}^{-2}$  low corrosion, for  $0.5 \mu\text{A cm}^{-2} < i_{\text{corr}} < 1.0 \mu\text{A cm}^{-2}$  high corrosion, and for  $i_{\text{corr}} > 1.0 \mu\text{A cm}^{-2}$  very high corrosion. After a year of exposure, the  $i_{\text{corr}}$  values of the three stainless steels are below the limit threshold between the passive and the active state.

$R_p$  data obtained by the polarization resistance method, and the time constant values of the corrosion process  $\tau$  obtained by the potentiostatic pulse technique (Eq. 1), enable to estimate (Table 2) the C values after one year of exposure of the specimens.

## 4 Conclusions

Figs. 4-5 showed a similar trend of the corrosion behaviour of low-nickel duplex SS, AISI 304 austenitic SS and AISI 2304 duplex SS, after one year of exposure, in the absence of chlorides or with contents of 0.4, 2 and 4 % of chlorides in the mortar. The three SS exhibited  $E_{\text{corr}}$  values around  $-120$  to  $-180$  mV vs. SCE and  $i_{\text{corr}}$  values of the order of  $0.01 \mu\text{A cm}^{-2}$ .



**Figure 5:** Corrosion current density ( $i_{\text{corr}}$ ) recorded for the three stainless steel studied over 1 year exposure, AISI 304, AISI 2304 and LND, with chloride addition of (a) 0%, (b) 0.4%, (c) 2% and (d) 4%  $\text{CaCl}_2$ .

**Table 2:** Double layer capacitance of the interface C [ $\mu\text{F}/\text{cm}^2$ ] recorded after 1 year exposure using the potentiostatic pulse technique and the polarization resistance method

Stainles Steel	$\text{CaCl}_2$			
	0%	0.4%	2%	4%
LNSS	10	10	10	8
AISI 304	4	4	4	3
AISI 2304	5	5	5	3

According to the results, the evolution of  $i_{\text{corr}}$  values during the first year of exposure of the specimens does not present significant differences at different chloride content in mortar. The  $i_{\text{corr}}$  values of the LND are in the same order of magnitude as  $i_{\text{corr}}$  values of AISI 304 or AISI 2304, and always below the limit threshold of  $0.1 \mu\text{A cm}^{-2}$  established for carbon steel.

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