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# Corrugated stainless steels embedded in carbonated mortars with and without chlorides: 9-Year corrosion results

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## HIGHLIGHTS

- 5 corrugated stainless steels are studied in carbonated mortars.
- Corrosion synergies between carbonation and chlorides are analyzed.
- S32205 duplex shows no corrosion even at high polarizations.
- Partial immersion promotes higher corrosion rates than in non-carbonated mortars.

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## ABSTRACT

The corrosion behavior of 5 corrugated stainless steel bars was evaluated in carbonated mortars: UNS S20430, S30400, S31603, S31635 and S32205. The tests were carried out under 3 different exposure conditions: at high relative humidity (C-HRH); partially immersed in 3.5% NaCl (C-PI); and with $CaCl_2$ added during mortar mixing and exposed to high relative humidity (C-HRHCl). Corrosion potential ($E_{corr}$) measurements and electrochemical impedance spectroscopy (EIS) were used to monitor the behavior during the first 8 years of exposure. Then, anodic polarization tests were carried out and the exposure was extended for another additional year. Stainless steels do not corrode in carbonated conditions without chlorides, but some grades can suffer localized corrosion if they are submitted to high anodic polarizations. Low-Ni, austenitic S20430 corrugated bars are especially prone to suffer a low-intensity corrosive attack in carbonated mortars with chlorides. Moreover, the corrosion rate of S20430 bars can easily increase under moderate anodic polarizations. Duplex S32205 is immune to corrosion in the carbonated mortar with chlorides, even in partial immersion conditions and under high anodic polarizations.

## 1. Introduction

Corrosion of reinforcements often limits the durability of reinforced concrete structures. The corrosion of steel bars is caused by chlorides and/or $CO_2$ from the environment. The carbonation of concrete is associated to the $CO_2$ penetration through the pores. Initially, the concrete is highly alkaline ($pH \approx 12–14$) due to the presence of $Ca(OH)_2$ and often of other hydroxides in the pore solution. The $CO_2$ that comes from the atmosphere, in presence of water, reacts with the $Ca(OH)_2$. As $Ca(OH)_2$ is consumed, the alkalinity of the solution inside the pores decreases. A $CO_3^{2-}/HCO_3^-$ buffer is often formed, and the pH of the solution decreases to pH values of about 9. At these pHs, carbon steel bars suffer uniform corrosion, because the passive layer that protects the steel at a higher pH is dissolved.

The carbonation process progresses from the surface of the concrete, advancing usually as a quite uniform front. The carbonation rate depends on the diffusion of the gases in the concrete porous network. The penetration rate of the carbonation front is affected by the environmental conditions such as the $CO_2$ concentration [1] and the humidity [1,2], but also on concrete characteristics, such as the size of the aggregates [3], the water/cement ratio [4] or the composition of the cement [5–7].

It has been foreseen that the increasing generation of $CO_2$ emissions will increase the carbonation rate of concrete structures [8]. A reduction in service lifespan due to carbonation of 15–20 years has been calculated for concrete structures constructed in 2030, in areas with moderate humidity and high temperatures [1]. Hence, carbonation resistant conditions should be especially kept in mind nowadays while designing reinforced structures.

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Substitution of the traditional carbon steel bars by stainless steel bars in the most exposed regions of the concrete structure [9] is an alternative increasingly in use to avoid damages caused by corrosion. Relevant results about the mechanical and structural behavior of corrugated stainless steels in comparison to that of traditional carbon steel reinforcements have been recently published [10]. Moreover, a long-term study has analyzed the behavior of different stainless steel corrugated bars in non-carbonated mortars with chlorides and their susceptibility to pitting corrosion [11], offering reliable results about the in-service behavior of these materials. However, it is also interesting to know in depth the behavior of stainless steel corrugated bars in carbonated concretes. The nature of the passive layers formed on stainless steel at pH 9 is different from that formed at more alkaline pHs [12]. Passive layers of less protective nature are formed in carbonated than in non-carbonated solutions [13]. Nevertheless, previous studies in solutions that simulate those contained in the pores of the concrete have proved that no corrosion takes place in stainless steels in carbonated solutions without chlorides [14], suggesting that they can be a good option to assure the durability of structures with a high-risk of carbonation.

Moreover, it is interesting to know the response of stainless steels in highly aggressive environments resulting from the simultaneous effect of chlorides and carbonation. This circumstance is not very usual in coastal areas, where low-$CO_2$ concentrations and high humidity are typical [4], but it can easily appear in other environments, for example, where the use of de-icing salts is common or where contaminated sand is used as aggregate.

The effect of carbonation and chlorides in the corrosion behavior of carbon steel in reinforcements has been studied in solution [15], showing a great dependence not only on the chloride content, but also on the concentration of the $CO_3^{2-}/HCO_3^{-}$ buffer. Although a common way to express critical chloride threshold to initiate corrosion in reinforced structures is the $[Cl^-]/[OH^-]$ ratio [16], some authors [17,18]have proved that the inhibiting effect of hydroxide ions becomes weaker with decreasing pH. Hence, the carbonation of chloride contaminated structures is an especially dangerous situation if carbon steel reinforcements are used in the most exposed parts. A meaningful fraction of the chlorides that penetrate into the concrete can be chemically and physically bounded to constituents of the cement paste. The degree of chloride binding depends on many factors as the water/cement ratio, the porosity and fineness of the aggregates, the age of the concrete or the cation associated with the chlorides. The key factor for the chloride binding capacity of a concrete is the binder chemical composition (mainly $C_3A$ and $C_4AF$ content) [16,19]. $C_3A$ and $C_4AF$ form chloride bearing salts during their hydration [20]. Reducing the pH in concrete may destabilize the chloroaluminates and thus reduce the percent of bound chlorides [21]. So, carbonation potentially increases the risk that chloride implies for reinforced concrete structures.

Results of stainless steels in carbonated simulated pore solutions with chlorides have also been published. These results show that stainless steels are susceptible to pitting corrosion under these conditions. Their resistance to localized corrosion and the morphology of the attack depend on the composition of the stainless steels [14] and on the processing method of the corrugated bars [22,23]. It has been reported that the thickness of the passive layer formed on stainless steel in carbonated solution decreases as the chloride concentration increases, thus leading to a reduction in the corrosion resistance [24].

Anyway, it has been proved for carbon steels that the critical chloride concentrations that cause corrosion are different when they are obtained from solution tests than when they are obtained using concrete samples [16]. The main reasons for this difference have been previously commented in other article [11]. However, it should be mentioned that there is no significant difference in the critical chloride concentrations obtained in mortar and in concrete tests [16]. Up to now, results of two years have been published about the behavior of a couple of stainless steels in activated fly-ash mortar, considering the dual effect of chlorides and carbonation [25], but long-term results of corrugated steel in carbonated mortars (with and without chlorides) can offer very interesting, complementary information.

## 2. Experimental

Five different corrugated stainless steels were considered in the study. The bars have been manufactured by Roldán (Acerinox Group) to be used as reinforcements in concrete structures. The diameter of the bars and their mechanical properties can be seen in Table 1. The chemical compositions of the stainless steels (given by the manufacturer) are shown in Table 2. Traditional carbon steel corrugated bars were included in some parts of the study as reference.

The corrugated bars were partly embedded in mortar with a cement/sand/water ratio of 1/3/0.6 (w/w). CEM II/B-L 32.5N was the cement type used to prepare the mortar. The sand was standardized CEN-NORMSAND (according to DIN EN 196-1 standard).

Part of the samples was manufactured with 3% $CaCl_2$ (1.9% Cl), weighed in relation to the cement amount. As a reference, it can be considered that, in European countries and in North America, it has become common practice to limit the tolerable chloride content to around 0.4% of the weight of cement [26].

Cylindrical mortar samples were used (Fig. 1), the thickness of the mortar cover always being 1.5 cm. The length of the bar exposed to the mortar was always 3 cm. The corrugated surfaces of the bars were studied in as-received condition. All cross-sections of the bars embedded in mortar were previously polished to 320# and passivated with $HNO_3$ in the laboratory, in order to reproduce the passivizing process carried out on the corrugated surfaces of the bars in the industry. The surface area exposed to mortar of bars was delimitated using an isolating tape. Ti-activated electrodes [27] where embedded close to the corrugated bars to allow the monitoring of the carbonation front in a subsequent step. Other details about the samples can be found in a previous work [11].

After their manufacturing, the reinforced mortar samples were cured for 30 days at 20 ± 1 °C at high relative humidity (HRH), about 92–93%, and then, the mortar was carbonated. The carbonation process was carried out in a chamber where 10% $CO_2$ enriched air was injected. The temperature in the chamber was 18 ± 1 °C and the relative humidity was between 75% and 80%. The potential of the Ti-electrode was monitored periodically using a saturated calomel electrode (SCE) placed in the outer part of the sample (on the upper surface of the mortar sample). To assure good contact between the mortar and the reference electrode, a small wet pad was used, as it has been plotted in Fig. 1. The carbonation of each sample was determined individually by an abrupt increase in the potential (of about 0.2 V) that corresponds to a change in the pH [28]. In this way, all samples were completely carbonated and errors due to dispersion in the advance of the carbonation front caused by the placement in the chamber were avoided.

After carbonation, the samples were divided into 3 groups and exposed to different aggressive conditions:

- C-HRH: Half of the carbonated samples manufactured without chlorides were exposed at HRH.
- C-PI: The other half of the carbonated samples manufactured without chlorides were partially immersed in 3.5% (w/w) NaCl solution and at HRH. In this case, the level of the solution was kept coinciding with the middle of the exposed length of the bars embedded in the mortar.
- C-HRHCl: The samples manufactured with chlorides were exposed to HRH.

The electrochemical monitoring of the corrosion behavior during the 8-year exposure period was carried out using corrosion potential ($E_{corr}$) and electrochemical impedance spectroscopy (EIS) measurements. To obtain the $E_{corr}$ values, a SCE was used. For the EIS measurements, a three-electrode configuration was used. The surface of corrugated bar exposed to the mortar acted as a working electrode, the reference electrode was a SCE and the counter-electrode was a copper cylinder,

**Table 1**
Mechanical properties and diameter of the five studied stainless steels.

| UNS stainless steel | Diameter (mm) | Tensile strength (MPa) | Yield strength (MPa) | Elongation (%) |
|---|---|---|---|---|
| S20430 | 5 | 918 | 756 | 32 |
| S30400 | 8 | 1035 | 923 | 21 |
| S31603 | 10 | 805 | 521 | 26 |
| S31635 | 12 | 860 | 726 | 22 |
| S32205 | 12 | 1156 | 968 | 12 |