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Limitations of Traditional Corrosion Detection Methods of Stainless-steel Reinforced Concrete

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ABSTRACT

Stainless steel (SS) reinforcement has been increasingly used in marine substructures due to its superior corrosion resistance over that of plain carbon steel (CS) despite its greater material cost. While investigations have thoroughly addressed the reliability of corrosion detection techniques of CS reinforcement, very little work has addressed the variations in the applicability of these techniques to stainless steel reinforcement. This study evaluates the sensitivity of traditional corrosion detection methods such as half-cell potential and electrochemical impedance spectroscopy to stainless steel corrosion in concrete. Reinforced concrete specimens incorporating either plain carbon steel or stainless steel were designed to promote macrocell corrosion. The specimens were monitored for corrosion activity using half-cell potential and electrochemical impedance spectroscopy without a guard ring. Corrosion detection sensitivity was assessed by comparison to experimental results of analog specimens in the form of small concrete cylinders in which the uncertainty in the measurement results is minimized. Additionally, finite element simulations are used to further specify the limitations of each method. As a result of this work, modifications to existing methods or recommendation for more suitable methods will be provided for corrosion detection of stainless-steel reinforced concrete.

Key words: Stainless steel, non-destructive techniques, half-cell potential, electrochemical impedance

INTRODUCTION

One of the main factors affecting the durability of reinforced concrete structures is the corrosion of the steel reinforcement. This factor becomes even more critical in structures exposed to aggressive environments. In an attempt to increase the durability of reinforced concrete structures, corrosion-resistant alloys, such as stainless steel (SS), have garnered attention over the past two decades. Different investigations have suggested that the higher material cost may be recovered throughout the service life of structures as the chloride threshold can be as much as an order of magnitude greater than that of carbon steel (CS) reinforcement.^{1-4,5} There may also be an added benefit to the corrosion propagation stage. While there is not much reported information on the stainless-steel propagation stage, it is

expected that the corrosion morphology may be highly localized, which may limit the feasibility of traditional non-destructive techniques (NDTs) to detect corrosion.

In theory, with the formation of an anode, the breakdown of the local stable passivity in passive materials results in a drop of the open circuit potential at that location. This is caused by the anode-cathode interaction wherein the increasing number of electrons can only be balanced by a drop of potential in the anode, assuming that the surface responsible for the cathodic reaction remains relatively the same as before. Although this has been proven for the case for CS, differences in corrosion behavior in the more corrosion resistant alloys may limit the applicability of this technique to SS reinforcement. Recent investigations suggest that corrosion of SS reinforcement is not only longitudinally limited by the length of the anode but also around the circumference of the steel reinforcement bar. The portion of the circumference subjected to corrosion was found to be $\sim 1/2$ and $\sim 1/3$ by investigations performed by Presuel and Hansson, respectively.^{7, 8} Furthermore, Presuel⁷ suggested that corrosion was observed to occur preferentially in the portion of the steel facing the concrete cover surface.

A traditional NDT that has been widely used to detect the corrosion condition in steel reinforcement is half-cell potential (HCP) mapping. The half-cell potential method (per ASTM C876 guidelines) provides potential ranges associated with different probabilities of corrosion serving as a reference to identify areas of high corrosion risk. Table 1 presents the HCP ranges, in reference to a Copper-copper Sulfate Electrode (CSE) and a Saturated Calomel Electrode (SCE), suggested by ASTM C876.⁹ A similar specification was proposed by RILEM¹⁰ technical committee on Electrochemical techniques for Measuring Corrosion of steel in concrete, 154 EMC. The RILEM technical recommendation on HCP, applicable to structures with ordinary or stainless-steel reinforcement, provides typical active corrosion potential ranges of normal steel reinforcement. According to the authors, stainless steel and carbon steel exhibit similar passive potentials.¹⁰

Table 1: Criteria to Evaluate the Corrosion Potential Results - ASTM C876.⁹

Probability of corrosion	CSE (mV)	SCE (mV)
90% - High	$V < -350$	$V < -276$
Uncertain	$-200 < V < -350$	$-124 < V < -276$
10% - Low	$-200 < V$	$-124 < V$

where "V" is Electrical Potential

It is important to note that HCP values are strongly influenced by the concrete resistivity, as an indicator of the saturation condition, and the concrete cover (X_c).¹⁰ The macrocell current that is formed due to action of the anode polarizing the passive regions yields a drop in potential that is easily detected in concretes with a low resistivity. Nevertheless, as the resistivity of the concrete increases, the electrical conductivity and macrocell current decrease, making it more difficult to detect corroding regions. Similarly, the HCP drops are more evident at the steel surface. Thus, as greater concrete cover values are considered, the more challenging it is to detect corrosion locations. The effect of these parameters on the reliability of the HCP technique is further exacerbated when highly localized corrosion is analyzed.

Several investigations have found that HCP results may provide reasonable correlations for passive and active corrosion regions of stainless-steel reinforcement in concrete. A previous investigation studied the corrosion performance at Progreso Pier, the oldest major structure reinforced with SS.¹¹ Field measurements showed highly negative HCP values (as much as ~ -550 mV CSE) suggesting active corrosion at particular regions. In addition, a recent investigation compared half-cell potential and LPR results for different types of stainless-steel reinforcement. This recent study included 2-year field-exposure experiments of ~ 11 mm diameter SS rebars embedded in mortar with very low cover (~ 7 mm) as well as bare bars, to a high-tide marine environment. After the two-year exposure period, the SS specimens exhibited potential values ranging between -100 mV and -200 mV which correlated to low corrosion current densities estimated using the LPR technique.¹² Although these HCP values have not

been correlated directly to corrosion severity, they provide some indication of the range of potentials that may be expected for SS reinforced concrete in field service.

Another investigation by Gonzalez et. al.¹³ found that although the HCP criterion should not be rejected, its results should be treated with high reservation. The authors found that the ASTM C-876 criterion was in theory correct to detect actively corroding regions, nevertheless, it ignores the possible presence of short-circuited passive and active areas.¹³ The latter could lead to severe misinterpretation when identifying active and passive regions in steel reinforcement. This issue could become more challenging when considering highly localized corrosion. A similar conclusion was drawn by a subsequent investigation performed in cracked reinforced concrete by Nijenhuis⁸ which questioned the applicability of the ASTM C876 in stainless steel reinforcement. The disagreement between authors and scarce available literature on SS reinforcement suggest that further investigation would be required to determine the correlation between the recommended HCP ranges for each corrosion probability category per ASTM and similar guidelines.^{9, 14}

Other NTDs, such as electrochemical impedance spectroscopy (EIS), have been proposed to assess corrosion condition in SS. The reliability of EIS is expected to be higher when compared to the HCP technique. While the HCP technique is limited to identifying the risk of corrosion at a certain location, EIS measurements may also be used to obtain information regarding the electrochemical state of steel in reinforced concrete. Wenger¹⁵ developed a model that allowed estimating the charge transfer resistance from the EIS data which could be later used to obtain corrosion rate estimations. A subsequent investigation by Wenger¹⁶ (1990) validated the model conclusion with experimental results from large reinforced concrete specimens and a small counter electrode. A spatial distribution of the electrochemical impedance was obtained. When local corrosion was considered, it was found that the EIS enabled the detection and location of corrosion, as well as quantitative data from ongoing corrosion mechanisms in the area of interest.¹⁶ Corrosion currents densities were estimated to range between $3 \mu\text{A}\cdot\text{cm}^{-2}$ and $7 \mu\text{A}\cdot\text{cm}^{-2}$ along an area of 25 cm^2 . These values were correlated to the electrical conductivity of the concrete and the inverse of the charge transfer resistance.¹⁶ One limitation that is important to note is that the method is based on a predetermined corroding area, however, this parameter is rarely known. Thus, the difficulty of obtaining accurate local corrosion current estimates should be considered. In addition, the detection of localized corrosion with the EIS technique could be limited by small values of the concrete resistivity, as well as, increased distance between the probe and the corroding region.

A finite difference model was successfully developed to analyze the d-c polarization phenomenon of reinforcing bars with a highly localized corrosion degree.¹⁷ It was suggested that the increased anode to cathode ratio resulted in smaller excitation currents than those of uniform electrodes. The a-c signal distribution was also considered. The authors concluded that methods used for uniform corrosion should be carefully considered in localized corrosion scenarios. It was also concluded that the electrochemical response was limited by the position of the reference electrode.¹⁷

The RILEM technical committee 154 EMC developed a set of specifications to obtain on-site corrosion rate measurements of steel reinforcement in concrete by means of the polarization resistance method. Although the EIS technique is not in the scope of the specification, it is suggested that the polarization resistance can be also obtained with this technique.⁶ A similar criteria to evaluate corrosion rates was developed in which values higher than $10 \mu\text{m}\cdot\text{yr}^{-1}$ could be associated with high corrosion levels. Likewise, corrosion for values smaller than $1 \mu\text{m}\cdot\text{yr}^{-1}$ were suggested as negligible.⁶ When the corrosion is limited to a small area, the authors suggested that the error could be minimized by either restricting the polarized area or identifying the corroding area.⁶ While the first solution could be implemented by using a guard ring to confine the current, the second one is often challenging since there is no accurate way to predict that parameter in real-size structures.

The present work includes a set of experiments and computational simulations to assess the reliability of traditional NTDs used to detect corrosion in stainless steel. Two sets of specimens, simulated concrete beams and mortar cylinders, reinforced with stainless and plain carbon steel are used to monitor and

compare traditional corrosion detection methods. Given the increased chloride threshold of stainless steel,⁷ chlorides were admixed to the concrete in the mid-region of the simulated beams and the mortar of the cylindrical specimens. A finite element model (FEM) is developed to analyze the detection limits of HCP and EIS technique considering different scenarios including several lengths of the anode and concrete cover, in addition to different corrosion morphology conditions. This analysis is expected to provide valuable information regarding existing NDTs specifications as well as recommendations to improve the reliability of these techniques to monitor the onset and intensity of corrosion in stainless steel reinforcement.

EXPERIMENTAL PROCEDURE

Two sets of concrete specimens reinforced with UNS S41000 SS and AISI1018 CS were prepared to study the corrosion behavior of stainless steel compared to that of carbon steel (CS), and to determine whether corrosion of stainless steel in concrete could be detected by methods traditionally used for carbon steel reinforcement. The plain-chromium SS alloy has only moderate pitting resistance. It was chosen based on it being more likely to result in an actively corroding regime without the need for impressed potential polarization. Concrete specimens were made in triplicate per type of reinforcing steel for each set.

Beams

The first set was cast as simulated reinforced concrete beams, exposed to conditions representative of wet service under marine or deicing salt environments. The specimens were 5 cm by 6.4 cm (Figure 1) ~180 cm long with a 1.5 cm concrete cover. The steel reinforcement consisted of 178 cm (~6-ft) long, ~1.27 cm (0.5-inch) diameter smooth round bars. The CS bars were smooth rolled bars of Type 1080 steel, in as-received rolled condition. The SS bars were also smooth rolled and annealed, with a pickled shiny surface condition. Two concrete mixture proportions were used: chloride-free concrete and chloride-contaminated concrete admixed with 5.84% of chloride ions by weight of cement. Both mix designs approximated the technical requirements provided by the FDOT for Class IV concrete with w/c= 0.41 and cement content 390 kg/m³.

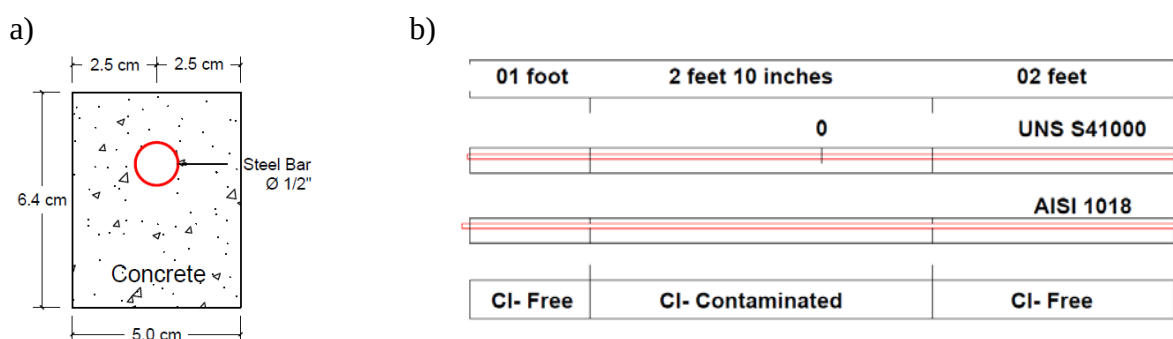


Figure 1: Schematic illustration of beams; (a) cross section and (b) longitudinal view with designation regions with and without admixed chlorides.

Half-cell potential and electrochemical impedance measurements were performed regularly to monitor the corrosion performance of the steel reinforcement bars at designated points along the beams. Starting from the center of the specimen, the spacing between these points was ~10 cm resulting in 19 measuring points per specimen. For the HCP technique, all nineteen points were measured while for the EIS technique about half of these were assessed (nine per specimen). Measurements were initiated at an age of ~60 days. The specimens were kept moist by spraying them periodically with deionized water. Despite the high level of chlorides admixed into the concrete, after ~245 days no indication of corrosion initiation of the SS steel specimens was observed. Due to the time constraints of this investigation, a combination of mild corrosion acceleration methods were employed to speed up the onset of corrosion.

At an age of ~245 days, acrylic reservoirs were placed on the top surface of SS specimens within the chloride contaminated region of the beam to perform cyclic ponding with a sodium chloride solution. Subsequently, low-high heat cycles were initiated at an age of ~300 days, with temperatures ranging between ~22 °C and ~38 °C, to further promote corrosion initiation.

The HCP data was acquired using a Multimeter (Fluke 289) with an input resistance of 10 MΩ, and a reference saturated calomel electrode (SCE) fitted with a small sponge on its tip. The EIS measurements were obtained using a Gamry Reference 600+ potentiostat/galvanostat with a potential perturbation of 10 mV. A three-electrode array in which the steel reinforcement served as the working electrode, a ~10 cm long hollow rectangular titanium mesh on top of a moist sponge was used as the counter electrode, and a SCE electrode with a small moist sponge on its tip placed in the middle served as the reference electrode. An initial range of frequencies between 10 mHz to 100 kHz with 10 points per decade was selected, nevertheless, the lower bound was later adjusted to 1 mHz at the end locations of the SS specimens to observe the change of behavior in the low frequency portion of the impedance response.

An estimate of the polarization resistance (R_p) was acquired from the EIS data using a measurement model software¹⁸ in which a series of Voight elements is fit to the data and an extrapolation is made to the high and low frequency limits of the impedance. Subsequently, the Stern-Geary equation was employed to estimate the values of corrosion current density as a function of position. The corrosion current was calculated assuming a value of Stern-Geary constant (β) for iron (Fe) equal to 26 mV. A finite element model was used to obtain estimates of the polarized area of the steel reinforcement at each measurement point. While this provides a reasonable estimate of the polarized area, the model did not consider changes in steel corrosion rates which would also influence this parameter.

Cylinders

The second set of specimens comprised small reinforced mortar cylinders with a 5 cm (2 in) diameter and 5 cm (2 in) high. The steel reinforcement was the same as that used in the beams. The mixture proportions were comparable to the chloride contaminated concrete used for the first set of specimens. Given the small dimensions of the specimens, mortar was used instead of concrete. Furthermore, a novel placement of embedded electrodes was proposed to improve the sensitivity of the corrosion detection and monitoring techniques. A titanium wire, placed a few millimeters away from the steel reinforcement to avoid direct contact, acts as a reference electrode, and a titanium mesh surrounding the steel reinforcement as well as the wire would act as the counter electrode, shown in Figure 2.

All samples were cured within the casting mold which was placed in a humidity chamber, with controlled humidity (85% RH) and temperature (20 ± 2 °C), for 28 days. Following the curing period, specimens reinforced with stainless steel were heated intermittently inside an enclosed glass tank with controlled humidity (~85% RH) and a heat lamp set to 38°C (~100°F) to promote corrosion initiation.

HCP and EIS were performed periodically. These tests proceed in a similar manner as those described for the first set of specimens while differing in reference and counter electrode arrangement. The potential of the Ti wire was periodically calibrated with respect to an SCE. Contrarily to the first set of specimens, these were designed to promote a uniform polarization of the steel over a known surface area. Hence, the computation of the corrosion rates did not require the implementation of a finite element model but rather a value for A_{pol} . ~20 cm² per the bar and specimen dimensions.