Electrochemical characteristics of antifouling coated steel structure submerged in Florida natural waters to mitigate micro- and macrofouling

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HIGHLIGHTS

- Localized corrosion associated with MIC and fouling on steel H-piles was detected.
- Antifouling coating tested at three natural water test sites.
- Antifouling coating provided mitigation of fouling.
- EIS identified coating degradation associated with fouling.

ABSTRACT

Recent findings in a Florida bridge indicated that there are synergistic effects of surface fouling to facilitate biocorrosion. Coatings that have anti-microbial, anti-fouling and barrier-characteristics are applied to steel elements in natural waters to mitigate degradation including corrosion and marine fouling. Electrochemical impedance spectroscopy (EIS) was utilized to identify the performance of a commercially-available anti-fouling coating exposed in three test sites for ~200 days. The results showed that complete prevention of fouling was not attained. EIS showed impedance dispersion associated with surface heterogeneities indicating the coating degradation and biofilm formation as result of reduced coating biocide efficacy.

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1. Introduction

Steel structural elements exposed in natural waters can be subject to the deleterious effects of naturally occurring physical-, chemical-, and biodegradation processes. Among these degradation processes, corrosion and marine biofouling can cause the loss of steel section in elements submerged in natural waters [1–4]. Marine biofouling of steel occurs due to the accretion of marine organisms such as barnacles, mussels, and other hard fouling sedentary fauna. Barnacles are the primary foulers in many industries and are the primary targets for anti-fouling mitigation technologies including anti-fouling coatings [5–7]. Localized corrosion related to the fouling may develop if the non-uniform attachment and coverage of fouling organisms creates oxygen concentration cells and crevice environments [8–11]. Furthermore, steel in marine environments can be subject to microbiologically influenced corrosion (MIC) [1–4,12]. Recent findings indicated that there are synergistic effects of surface fouling to facilitate the biocorrosion [13–15]. Steel bridge piles in a Florida bridge showed severe localized corrosion that was associated with microbial activity under the marine fouling organisms [4,15]. Sulfate-reducing- (SRB), acid-producing- (APB), iron-reducing- (IRB), and slime forming- (SFB) bacteria were detected on the steel surface under the fouling marine flora and sedentary marine fauna.

Biofouling formation starts with the development of a conditioning film (by adsorption of the available organic molecules and ions in the water) leading to microfouling and then macrofouling [16–18]. Microorganisms such as bacteria can colonize on the conditioning film and form a biofilm [18–19]. Some have suggested that the biofilm [20–23] and surface properties such as roughness are important for site selection by fouling organisms [24–26].
Mitigation technologies include protective coatings and antifouling coatings. Antifouling coatings have a long history and have an important impact on managing macrofouling [16,23,27-28]. These coatings are categorized by its self-polishing and foul-release characteristics [16,29-30]. Much research has been conducted regarding the performance of different coatings exposed to biologically active environments, and antifouling coatings with biocides have been shown to be effective to reduce the growth of marine fouling organisms such as bacteria, fungi, algae, plants, and mussels [31-38]. Antifouling coatings utilizing copper as a biocide have been widely used for the last 200 years; however, due to the concerns about their negative environmental impacts, biocides are subject to regulatory restrictions [39-40]. Antifouling coatings with metal-free biocides were developed and are commercially available. Antifouling coatings with biocides that mitigate bacteria growth would have the benefits to impair the formation of the conditioning film and biofilm that is required for the attachment of macrofouling organisms as well as to suppress any subsequent deleterious effects of sessile bacteria and biofilm that can be associated with MIC.

Due to the development of severe localized steel corrosion, with a high population of bacteria associated with MIC under the marine fouling observed in a Florida bridge, it was of interest to identify mitigation technologies that may be applicable to mitigate the fouling and associated corrosion. Previous research detailed by Permeh et al., 2019 [37–38], described the characterization of biofilm formation on antifouling coated coupons by Electrochemical Impedance Spectroscopy (EIS) in a controlled laboratory test setup. Antifouling coated steel coupons were in contact with test solution consisting of isolated SRB inoculated in a modified Postgate B (MPB) nutrient broth. The impedance data generally showed varied responses that reflected the different surface and interfacial characteristics. The impedance of the steel with degraded antifouling coatings subjected to the inoculated test solution showed characteristic impedance responses of a polymer coated steel but also showed impedance dispersion that was related to the heterogeneities of the coating. That dispersion was associated with the biofilm on the surface. A calculation approach was developed to isolate the convoluted impedance dispersion at the intermediate frequencies. Distinct impedance associated with film development was apparent for the specimens inoculated with SRB, indicating the effect of microbial activity as well as the efficacy of EIS for testing and monitoring.

The results of the laboratory study allowed for the basis of testing of field exposed steel specimens to identify formation of surface layers and coating degradation due to natural exposures described here. Here, EIS was utilized to identify the performance of a commercially-available anti-fouling coating exposed in three remote field test sites for ~200 days.

### 2. Methodology

Steel coupons (dimensions: 12.7 cm × 7.6 cm × 0.3 cm and composition of 0.02%C, 0.16%Mn, 0.006% S, 0.03% Si and balanced Fe) coated with a commercially available water-based copper-free antifouling coating (chemical constituents included organic metal-free biocide1, ZnO, TiO2, and zinc pyrithione) were installed at three Florida bridge site locations with different environmental and water release characteristics [16,28]. These coatings are categorized by its self-polishing and foul-release characteristics. The impedance of the steel with degraded antifouling coating (chemical constituents included organic metal-free biocide1, ZnO, TiO2, and zinc pyrithione) were installed at three Florida bridge site locations with different environmental and water release characteristics. Much research has been conducted regarding the performance of different coatings exposed to biologically active environments, and antifouling coatings with biocides have been shown to be effective to reduce the growth of marine fouling organisms such as bacteria, fungi, algae, plants, and mussels [31-38]. Antifouling coatings utilizing copper as a biocide have been widely used for the last 200 years; however, due to the concerns about their negative environmental impacts, biocides are subject to regulatory restrictions [39-40]. Antifouling coatings with metal-free biocides were developed and are commercially available. Antifouling coatings with biocides that mitigate bacteria growth would have the benefits to impair the formation of the conditioning film and biofilm that is required for the attachment of macrofouling organisms as well as to suppress any subsequent deleterious effects of sessile bacteria and biofilm that can be associated with MIC.

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Eight coated specimens were installed at each of the three test sites, aligned vertically by depth in a single column. Specimen placement was measured relative to the marine growth line, identified as distance below the marine growth line (BMG). Even though the position of the test racks of each test site relative to the water surface varied due to the variation of the bridge sub-structural elements as well as due to variation in tidal levels at each test site, general exposure depths were similar and the test specimens were considered replicates for material subjected to tidal as well as submerged exposure depths. Table 1 shows the range of depths that the steel specimens were placed (for both tidal and submerged regions) for each test site.

The antifouling coating consisted of a metal primer, two coats of a tie coat and one coat of the anti-fouling coating following the manufacturer’s recommendations. The surface of the steel plates was ground to a uniform 60 grit size (265 μ) finish to SSPC-SP11 surface standards [42] prior to the application of the coating. The average coating thickness of the samples after surface preparation are shown in Table 1. Eight uncoated plain steel coupons were also similarly installed as a control set at all three sites. Furthermore, reference as-received coated coupons were tested in the laboratory as well.

The sessile bacteria levels on the coated steel surface were tested by localized sampling under portions of the fouling encrustation. Marine growth was removed from a small portion (~6.45 cm²) of the coupons where swabs were collected for the microbiological analyses. Microbiological testing adopted the Biological Activity Reaction Test (BART) kits for practical field testing of four common MIC related bacteria (SRB, IRB, SFB, and APB). The swabs were placed into the test vials for reaction with the reagents. Environmental aggressivity of the bacteria activity was categorized following guidelines by the test kit manufacturer. After the field exposure, the specimens were transported in river water to the laboratory to minimize disturbance of the fouling organisms.

EIS was conducted on all test specimens in the laboratory after field extraction without disturbance to the surface fouling, using a three-electrode configuration. The test coupon working electrodes were placed 8.9 cm deep, immersing a nominal ~335.5 cm² steel surface area, in the collected river water solution. Electrical connections were made by connecting a copper wire to the steel exposed on the top portion of the coupon made by filing. A saturated calomel electrode (SCE) was used as the reference electrode, and an activated titanium mesh was used as the counter electrode. The EIS testing was conducted at the open-circuit potential (OCP) condition with 10 mV AC perturbation voltage from frequencies 1 MHz > f > 1 Hz at 10 points per decade.

Visual photo-documentation of the coated steel coupon surface conditions was made immediately after removal from solution and after surface cleaning. The outer-shell of the hard foulers and marine flora were removed, and the specimens were rinsed with tapwater and surface dried. Metallographic cross-sections from representative specimens from the three sites were prepared to verify the extent of the coating degradation under the fouling. Sections were mounted in epoxy resin and were ground and polished following typical metallographic procedures (3 and 0.05 μm polishing steps using polycrystalline diamond and colloidal alumina with oil-based lubricants and extenders). X-Ray diffraction of the coated specimens were made to identify degradation of the biocide

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Table 1

Experimental field test conditions.

<table>
<thead>
<tr>
<th>Test Site</th>
<th>Water Type</th>
<th>No. of Test Coupons</th>
<th>Exposure Depth (m BMG)</th>
<th>Tidal Region (m BMG)</th>
<th>Submerged Region (m BMG)</th>
<th>Coating Thickness Front/Back (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site I Matanzas R. (intracoastal)</td>
<td>Brackish (30–35)</td>
<td>8</td>
<td>-0.8–2.5</td>
<td>-0.8–1.4</td>
<td>&gt;1.5</td>
<td>0.15/0.18, 0.18/0.23, 0.15/0.15, 0.20/0.20, 0.15/0.18, 0.13/0.10, 0.18/0.20, 0.18/0.13</td>
</tr>
<tr>
<td>Site II Alafia R. (downstream)</td>
<td>Brackish (15–20)</td>
<td>7</td>
<td>-0.1–1.6</td>
<td>-0.1–0.6</td>
<td>&gt;0.7</td>
<td>0.15/–, 0.18/–, 0.18/–, 0.15/–, 0.20/–, 0.15/–, 0.10/–</td>
</tr>
<tr>
<td>Site III Alafia R. (upstream)</td>
<td>Fresh (10–15)</td>
<td>8</td>
<td>-0.1–1.8</td>
<td>-0.1–0.6</td>
<td>&gt;0.8</td>
<td>0.30/–, 0.33/–, 0.13/–, 0.18/–, 0.23/–, 0.15/–, 0.15/–, 0.15/–</td>
</tr>
</tbody>
</table>

1 BMG: Below marine growth.

constituents in the coating. Testing was made at a range of 29 from 20 to 80 degrees with a 0.02 degree/min scan rate.

3. Results and discussion

3.1. EIS

Representative results of EIS testing of the coated specimens (presented in Nyquist diagrams) from the general test depths (tidal and submerged regions) for the three test sites are shown in Fig. 1. The results generally showed multiple impedance loops associated with the various time constants for the different system components. The presence of the multiple time constants indicated that the coatings, after field exposure, did not have strong barrier characteristics, in contrast to the large impedance (characteristic of a capacitor) of the control undamaged coating freshly immersed in solution [37]. The impedance at the intermediate frequencies showed varying extents of impedance dispersion by a distribution of time constants due to surface heterogeneities (that can be associated with the dielectric behavior of the surface layers). As described by Permeh et al., 2019 [37], that dispersion was observed in lab testing in the presence of the sessile bacteria and not in control non-inoculated tests. It was posited that the presence of biofilm (likely heterogenous in coverage and makeup) create conditions for the impedance dispersion there. In the field specimens, that surface heterogeneity can be attributed to a variety of additional reasons including the sporadic macrofouling and the coating degradation that occurred during the exposure period.

Variants of the circuit analog, including that proposed by Abdoli et al., 2016 [43] for biofilm on an aluminum coated steel metal surface (Fig. 2a), did not consistently yield good data fitting for the measured impedance spectrum of the field-exposed coated steel specimens. Treatment of the intermediate frequency dispersion by a parallel R and C elements (Fig. 2b), such as that presented by Chen et al., 2017 [44] was considered here but with the resolved terms nominally ascribed to an apparent heterogeneous surface film for discourse. As such, the impedance of the antifouling coating that have coating surface heterogeneity (degradation and formation of surface deposits) was posited to be characterized by the equivalent circuit analog shown in Fig. 2c and described by Equation 1 as a function of angular frequency \( \omega \). The circuit analog characterizes an idealized degraded coating with a coating pore resistance, the dispersion relating to the surface heterogeneities, and the impedance of the double-layer capacitance and polarization resistance for the exposed steel interfaces.

Constant phase elements, CPE, with pre-exponential admittance \( Yo \) and \( n \) terms were used to provide a mathematical expression for impedance that exhibit capacitive-like behavior including the dielectric behavior of the coating (subscript \( C \)), the surface film (subscript \( f \)), as well as the double-layer capacitance (subscript \( dl \)) at the steel interface. The impedance of a CPE is given as \( Z_{CPE} = 1 / Yo(j\omega)^n \). Resistance terms \( R \) relate to the bulk solution resistance \( (R_s) \), coating pore resistance \( (R_p) \), surface film resistance \( (R_f) \) and the polarization resistance \( (R_p) \) of the steel interface.

\[
Z(\omega) = R_s + \left( \frac{1}{Yo(j\omega)^n + \frac{1}{R_f}} \right) + \left( \frac{1}{Y_f(j\omega)^n + \left( \frac{1}{Yo(j\omega)^n + \frac{1}{R_p}} \right)} \right)
\]  

(1)

\[
C = Yo \cdot (2\pi f_m)^{n-1}
\]  

(2)

Generally, good curve fitting of the EIS data to the impedance described by the equivalent circuit analog was made. Following the approach by Permeh et al., 2019 [37], the impedance for each fitted R-CPE pair was decoupled with analysis of each parallel R-CPE circuit independently. The treatment of the EIS data was used to parse the general behavior and other complicating factors relating to non-uniform current distribution on degraded coatings and non-homogeneous surface films. An example of this approach for coated coupons from Site I is shown in Fig. 3. The capacitance for each CPE term was estimated following approaches developed by Hsu and Mansfeld using Equation 2, where \( f_m \) is the frequency of the maximum imaginary component of impedance [45]. As shown in Fig. 4, the resolved \( f_m \) for each time constant was shown to visually coincide with the breakpoint of capacitive and resistive behavior in the Bode plots as well as local maxima of \( -Z' \), even for the complicated total impedance spectra with convoluted time constants.

Based on the resolved impedance terms from the equivalent circuit fitting and the numerical treatment described above and detailed elsewhere [37–38] separation of impedance time constants \( (\tau = 1/RC) \) representative of the various system processes was evident as shown in Fig. 5. Similar to the resolved \( \tau \) values described for the coating, the steel interface, and the surface films that developed in bacteria inoculated solutions in laboratory testing in reference [37], low \( \tau \) values for the coating, high values for the steel interface, and intermediate values for the apparent surface film were resolved for the test specimens exposed in the three field test sites. Similar \( \tau \) values were also resolved for the control as-received coated specimen. The results showed impedance that would relate to heterogeneous surface film formation at Sites I and II. The impedance results on only one of the specimens from Site III showed a similar indication.

Comparisons of the resolved impedance components, fit using Equation 1 and 2, are shown in Fig. 6. The calculated coating capacitance for all three test sites was similar and in the range of \( 1 \times 10^{-8} \) and \( 1 \times 10^{-7} \) F (Fig. 6A). The capacitance of the coating is characterized by \( C_C = \varepsilon_r \varepsilon_0 A/d \). Assuming the submerged steel area,
A, the average original coating thickness, \( d \), and the dielectric of free space \( \varepsilon_0 = 8.8 \times 10^{-12} \text{F/m} \), the apparent coating dielectric \( \varepsilon \) would be in the order of 10–100, consistent to that of wet polymeric coatings [46]. The resolved \( \varepsilon \), assuming the initial \( d \), some-

![Fig. 1. Nyquist diagrams from EIS for antifouling-coated coupons at three sites. 1 MHz < f less than 1 Hz, 10 points/decade. Lines show fitted curves. (A) Site I, (B) Site II, (C) Site III.](image)

![Fig. 2. Electrochemical impedance equivalent circuit analogs. a) Circuit analog proposed by Abdoli et al., 2016 [43] for biofilm on an aluminum coated steel metal surface, b) Circuit analog proposed by Chen et al., 2017 for an apparent heterogeneous surface film, c) Circuit analog proposed by Permeh et al., 2019 [37] for biofilm on antifouling coated steel metal surface.](image)
times exceeded 100 for some of the permanently submerged specimens. This was in part due to the fact that those specimens had greater coating degradation and reduction of the coating thickness. The calculated coating capacitance for the coatings after field expo-

Fig. 3. Example of decoupled fitted and calculated impedance response for coated coupon exposed at Site I at 0.9 m and 2.5 m. (A) Coatings; (B) Surface Film; (C) Double Layer.

Fig. 4. Bode and $Z''$ plots of measured impedance for coated coupon exposed at Site I at (A) 0.9 m and (B) 2.5 m.
sure (particularly for the continuously submerged specimens) was consistently larger than that resolved for the control lab specimens attesting to that coating degradation and the increased moisture presence after prolonged immersion in the river water.

The resolved coating pore resistance (in the order of 1 to 10^2 O) for the specimens at Sites I and II (Fig. 6B) was lower than that of the control lab specimens (~10^4 O) consistent to wetting of the coating pore spaces and general coating degradation. The resolved pore resistance for the specimens at Site III was higher, in the order of 103 O, corroborating with earlier observations of more benign fouling environments there and better coating conditions (ie less depletion of the biocides and topcoat degradation). The resolved pore resistance of test specimens in the submerged region was consistently lower than that for the intermittently immersed specimen at all three test sites for similar reasons of prolonged wetting and more aggressive fouling in the former.
The capacitive and resistive impedance parameters for the apparent surface film were resolved for the test specimens in the submerged regions at the test sites (Fig. 6C and 6D). As previously introduced, the impedance dispersion that manifests as these characteristic capacitive and resistive parameters [44] are due to surface heterogeneities that can form due to a multitude of reasons. The sporadic placement of hard shelled foulers and the coating degradation (especially at Sites I and II) would have an effect as well. The lower resolved capacitance for the specimens at Site I than Site II could be indicative of a thicker surface layer within the range as reported elsewhere [47]. If that surface layer can be attributed to uniform coverage of biofilm and assuming a dielectric coefficient of 70 [48], the film thickness would be in the order less than 10^{-4} mm, comparable to biofilm thickness reported elsewhere [47]. The impedance associated with a surface film was not consistently resolved for all specimens at Site III, attributing to the better coating condition in the more benign exposure environment there to mitigate both micro- and macrofouling.

The resolved polarization resistance for the specimens at Site III was generally two magnitudes of order larger than specimens at Sites I and II (and similar to the control lab specimens), in general agreement with earlier observations of less coating damage in the former and thus better barrier characteristics during the time of testing (Fig. 6F). The polarization resistance of the coatings in Site I and II were in the order of 10^{2} to 10^{3} O corresponding to a corrosion current, \(i_{corr}\), in the order of 10^{-102} A, following the relation

\[Rp \omega \approx \frac{1}{2 \pi f i_{corr}}\]

where the Stern-Geary coefficient, \(\omega\), was assumed to be 26–54 mV/decade. In comparison, the polarization resistance was in the order of 10^{4}–10^{5} O for the Site III and control lab specimens, corresponding to a corrosion current in the order of 10^{-1}–1 \(\mu\)A. Uniform corrosion is not expected to develop with the presence of the polymer coating, but the steel corrosion would develop in localized regions with respect to coating defects and degradation.

3.2. Visual observations and surface degradation

In Site I, significant tidal action occurs, exposing surfaces above 1.6 m BMG during low tide. Below this level, the surfaces were continuously submerged, and heavier growths of marine flora and sedentary fauna were sustained on the uncoated concrete and steel bridge elements as well as the plain steel reference test specimens. At Sites II and III, the tidal action was not as severe as at Site I, and growth of hard foulers on the concrete bridge piles and on the plain steel specimens were similar at test depths deeper than 0.6 m BMG. Fouling at the three sites were of different species and the modality of fouling accretion differed. In addition to the growth of tunicates, hydroids, sponges, mussels, and other marine fauna at Site I, large diameter acorn barnacles with tight cementation on the steel surface formed. At Sites II and III, wide coverage of small diameter bay barnacles that conglomerated into loose outward-forming interlayers of barnacle plates and mantles formed. The general activity of barnacle in the upstream river Site III location was lower than the site II downstream location, but the barnacles still widely cover the plain steel coupons.

Fig. 7 presents the surface appearance of the water-based copper-free antifouling coated coupons and reference plain steel coupons at Sites I, II and III. By the end of testing at day ~200, it was evident that the antifouling coating retained some level of mitigation as there was less barnacle growth on the anti-fouling coated steel specimens than the comparative plain steel specimens. Although showing benefits in terms of the reduced level of fouling, the antifouling agents in the coating did not prevent attachment and growth of the barnacle species at the three test sites. The observation of early coating degradation (ie dissolution of the topcoat) in accordance with the trends in impedance characteristics and the visual surface marine flora and barnacle development would indicate that the anti-fouling agents and biocides of the coating became less effective as the topcoat diminished. Similar to the plain steel coupons, there was significantly less barnacle formation at the Site III upstream location, as can be expected in the freshwater where less nutrients are available. The more benign exposure environment in Site III would provide lower fouling tendency where anti-fouling agent concentrations (such as Zn and Ti oxides) would remain at effective levels for longer service times. In such conditions, the anti-fouling coating would be effective for prolonged periods as shown by the higher coating resistance and higher polarization resistance resolved by EIS.

Fig. 8 shows the cross-sections of the field exposed steel specimens coated with the antifouling coating for Site I, II and III compared with the control lab specimen. Different layers including the tie-coat, the topcoat and calcareous layer of barnacle can be identified. The thicker tie-coat bulk material remained mostly intact during exposure. In agreement with the EIS assessment of coating degradation and the visual observation of the onset of marine fouling, reduction in topcoat thickness was observed on coated specimens after exposure in all three sites (with significant top coat loss in Sites I and II). Fig. 8B and 8C also showed the degraded coating below the base of localized attached barnacles on specimens from Site I and II. Fig. 9 shows details on the placement of the barnacle base plate on the coated steel surface. The loss of topcoat material would correspond to a decrease in total coating thickness, corresponding to the larger coating capacitance and smaller pore resistance resolved by EIS. The tie coat remained intact for all cases, and no indication of steel corrosion was evident regardless of the level of coating degradation and onset of marine fouling.

3.3. Summary of bacteria activity

X-ray diffraction measurements (Fig. 10) on the surface of the exposed antifouling coated test specimens showed that the inorganic biocidal components such as zinc oxide, titanium oxide, and barium sulfate were retained despite the topcoat degradation, although the extent of biocide loss was not ascertained. XRD also does not provide indication of the concentrations of other biocide components that have amorphous structures. It was apparent that marine foulers could be inhibited early in the exposure time but prolonged exposures could diminish the level of mitigation. The loss of topcoat material with the biocide pigments and the intrinsic self-polishing characteristic of the coating would suggest the progressive loss of performance.

Table 2 shows the range of the measured population of SRB, IRB, APB, and SFB under marine growth layers for the antifouling coated specimens and the control plain steel specimens through the exposure time. In general, aggressive environmental conditions were identified by populations of SRB, IRB, APB, and SFB on the surface of the control uncoated steel specimens. Application of the antifouling coating showed that there was a positive effect of the coating and its constituent biocides for bacteria commonly associated with MIC such as SRB and IRB but not necessarily for all bacteria. The cause of this coincidence was not further explored but the role of the constituent biocides, surface effects, and local environments created as the coating ages can be factors of interest in future study. Zero SRB bacteria counts were measured at all three sites and only sometimes showed levels associated with moderate aggressivity.

It was noted that Site III generally had lower measured SRB sessile populations overall (even though high planktonic populations were present [49]) and was in part attributed to the lower density of marine foulers there and less isolated regions under fouling organisms that would provide protective environments for the microorganisms. As discussed in other research [13,49], the macrofouling provide conditions such as low-oxygen environments,
reduced convection, and access to nutrients that can support SRB proliferation. The presence of large surface bacteria populations coincided with the settlement of fouling organisms and subsequent heavy surface fouling. For example, as described by Dong et al., 2020 [50] bacteria associated with macrofouling also contribute to corrosion. Antifouling coatings thus would have beneficial qualities to not only reduce fouling but also to minimize the growth of SRB that can support biocorrosion.

The residual antifouling coating was shown to retain some presence of biocide as shown by XRD but depletion due to the topcoat degradation (in part related to the self-polishing of the topcoat, macro-fouling settlement, and microfouling metabolic activity) can allow for less effective protection. EIS showed that the coating degradation and biofilm development can occur in the aggressive environments (such as at Site I and II) and that the coating has greater longevity in less aggressive environments (such as at Site III). The coating degradation and biofilm formation on specimens in Site I and II were coincident with the onset of marine fouling on the coated steel specimen. Effective coating primers and midcoats are needed to enhance coating durability, but continued exposure without coating maintenance would allow for greater levels of marine fouling and subsequent damage to the steel piles.

The antifouling coating did show some benefit to mitigate the sessile growth of SRB and IRB, but the effect of the antifouling coating to mitigate the secondary effect of macrofoulers to support MIC as described by Permeh et al., 2020 should be addressed in future research [38]. The extent of required coating maintenance to control the macro- and micro-fouling should be assessed as well [51–53]. EIS was shown to provide good charac-
terization of the coating degradation and heterogeneities that can include surface film formation. Its use as an in-situ monitoring technique may be of interest especially for submerged steel substructure where detailed surface inspections are difficult due to dangerous underwater currents, low visibility, and heavy accumulation of surface fouling.

4. Conclusions

The antifouling coated test specimens exposed at three natural water field test sites were subjected to different levels of natural fouling tendencies where different fouling organisms proliferate and have varying modalities for surface accretion. Sites I and II exhibited heavier fouling than Site III in part due to the greater salinity in the former. As such, the performance and durability of the antifouling coating can differ. Mitigation of fouling afforded by the antifouling coating was apparent in comparison to non-coated surfaces; however, complete prevention of fouling was not attained during the ~200 days of testing. Coating maintenance is typical in these applications and would be appropriate for prolonged use. Marine flora and sporadic large diameter acorn barnacles developed at Site I. Wide coverage of small diameter bay barnacles developed at both Sites II and III although much less in the latter. Surface populations of SRB were apparently reduced on the antifouling coating in comparison to non-coated steel specimens, but other bacteria still abound. EIS following a deconvolution calculation approach was shown to be useful to separate impedance responses associated with coating degradation and development of surface films. In congruity with the visual observations of fouling and coating degradation, EIS showed that the degradation of the coatings at Sites I and II allowed for reduced efficacy of coating biocides, resulting in impedance dispersion associated with the formation of surface films that can be related to the onset of surface fouling. Coating performance at the less aggressive test Site III was shown to be better.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 2

<table>
<thead>
<tr>
<th>Test Sites</th>
<th>SRB</th>
<th>IRB</th>
<th>APB</th>
<th>SFB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site I</td>
<td>0 (NA)</td>
<td>500 (M)</td>
<td>14,000 (A)-475,000 (A)</td>
<td>13,000 (A)-440,000 (A)</td>
</tr>
<tr>
<td>Site II</td>
<td>0 (NA)- 6,000 (M)</td>
<td>0 (NA)- 9,000 (M)</td>
<td>14,000 (A)- 475,000 (A)</td>
<td>13,000 (A)- 1,750,000 (A)</td>
</tr>
<tr>
<td>Site III</td>
<td>0 (NA)- 1400 (M)</td>
<td>140,000 (A)</td>
<td>475,000 (A)</td>
<td>1,750,000 (A)</td>
</tr>
<tr>
<td>Uncoated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site I</td>
<td>75 (M)- 500,000 (A)</td>
<td>2,200 (M)- 115,000 (A)</td>
<td>14,000 (A)- 475,000 (A)</td>
<td>1,750,000 (A)</td>
</tr>
<tr>
<td>Site II</td>
<td>5 (NA)- 27,000 (A)</td>
<td>150 (M)- 9,000 (M)</td>
<td>82,000 (A)- 475,000 (A)</td>
<td>1,750,000 (A)</td>
</tr>
<tr>
<td>Site III</td>
<td>20 (NA)- 1,400 (M)</td>
<td>35,000 (A)-140,000 (A)</td>
<td>475,000 (A)</td>
<td>1,750,000 (A)</td>
</tr>
</tbody>
</table>

Aggressivity. (NA) Not Aggressive, (M) Moderately Aggressive, (A) Aggressive (General guidelines for BART test for corrosion).
Acknowledgment

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