RECLAMATION

Managing Water in the West

Self-Healing Coatings to Mitigate Corrosion and Impact Damage

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Mission Statements

The U.S. Department of the Interior protects America's natural resources and heritage, honors our cultures and tribal communities, and supplies the energy to power our future.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

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Executive Summary

The goal for this research project was to perform a background review, testing, and analysis to identify the pros and cons for using Battelle's self-healing oligomer filled microcapsule additives within the PPG Amerlock 2 coating system used in the Bureau of Reclamation (Reclamation).

This report consists of the following sections:

- Background review on novel self-healing oligomer filled microbeads manufactured by Battelle and their capacity to mitigate corrosion and impact damage.

- Discussions and challenges related to ease of use, applicability, and feasibility of using Battle's self-healing oligomer filled microcapsule additives within a coating system.

- Testing and analysis including methods and materials, sample preparation, visual inspection, scanning electron microscopy (SEM), stereoscopic microscopy, and electrochemical impedance spectroscopy (EIS).

Experimental results showed that coatings containing microbeads supplied by Battelle did not fully prevent corrosion of the exposed metal substrate after impact over the exposure time period for this study. However, these coatings showed less coating degradation and corrosion on the metal substrate compared to the coatings without the microbeads.

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Introduction

The primary mission of the Bureau of Reclamation (Reclamation) is the delivery of water and power. Dams, pipelines, and canals are among the structures that are used for this purpose. In order to mitigate corrosion associated with metals and concrete, protective coatings are used. However, coatings can experience impact damage. This causes additional maintenance and repair, which can become costly.

Self-healing oligomer filled microcapsule coating additives, also called microbeads, may provide additional options in the protection of Reclamation's coated infrastructure. Although this technology has been around for a decade and has been published in many academic journals, there have been many challenges, particularly associated with the catalyst activated version of this technology. Battelle has developed a non-catalyst version that appears promising. In support of a project funded by Office of Naval Research, Battelle demonstrated this technology on several Humvee doors as well as on coupons that were mounted on the back bumper of two Humvees located at Camp Lejeune, NC. They also did beachfront exposure testing at their Florida Materials Research Facility in Daytona Beach, FL. Results showed that coatings with microbeads demonstrated improved performance in these tests.

This scoping study aims to investigate if the new self-healing coating technology offered by Battelle can address the challenges with protecting Reclamation infrastructure in harsh and corrosive environments. This study also aims to determine if this technology is a viable solution to reduce Reclamation's infrastructure coating maintenance.

Background

NACE International estimates that the annual cost of corrosion in the United States (U.S.) is $451 billion – 2.7 percent of the nation's gross domestic product (GDP) [1]. Many methods can be used to protect infrastructure from corrosion, including: organic, inorganic, and metallic protective coatings, corrosion inhibitors, and cathodic protection. For many situations, applying protective coatings is the most cost effective mitigation strategy. However, in practice, coatings degrade over time, and when corrosion starts, it spreads and can be located in areas that are difficult to access. Corrosion can cause damage that can be costly to repair.

Battelle uses the microencapsulation concept in the development of their self-healing microbeads. Encapsulation is a process in which an active ingredient is enclosed inside of a polymer capsule core. Encapsulation allows for reactive chemical compounds to be stored until they are released by some type of trigger, such as: pressure, temperature, pH level, ultraviolet light, or chemical and biological signals (figure 1) [2]. Encapsulation also protects active ingredients from degradation and ensures that activation occurs at a desired time when they are needed [2, 3].

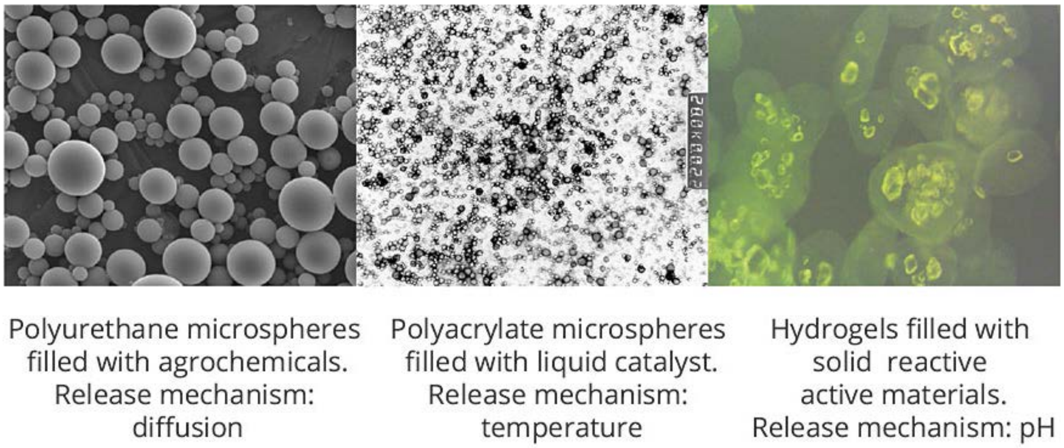


Figure 1.—Different microcapsule responses to various release mechanisms, reprinted from "The Science of Corrosion-Busting Smart Coatings," Paint and Coatings Industry [2].

Typically self-healing coatings have been designed with two microcapsules occupying the same space. When both capsules release their contents then the reaction can take place. This method is challenging to implement. According to Battelle, the ultimate development in self-healing coating technology depends on the stability of the self-healing core, its transport to the defect site, and its cure without the need of a catalyst [2, 4]. By removing the need for two microcapsules some of the difficulties in obtaining a reaction are removed. Battelle's new oligomer filled microcapsules are able to provide a self-healing reaction to the metal ions present in a corrosion initiation site. The microbeads release chemicals to fill the corrosion microcracks that form [5].

Battelle's self-healing microbeads consist of two parts: shell and core. The shell material must be insoluble in the polymer core material as well as the coating. It must not be reactive to the coating system and it must be resilient under typical performance and application pressures. It must break open easily when encountering microfractures due to corrosion. The polymer core must be compatible with the coating for adequate adhesion, flow by capillary action in order to fill the cracks, form a film which is resistant to corrosive materials, and remain stable. The polymer core is composed of a proprietary thermoplastic material in which a catalytic curing agent is not required (figure 2) [2, 4].

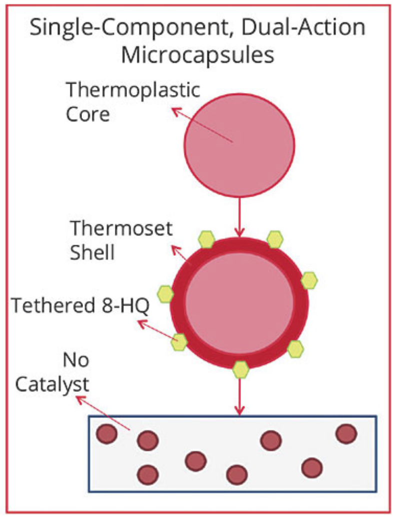


Figure 2.—Schematic diagram of Battelle's version of microbeads using a thermoplastic healing material with no catalyst required, reprinted from "The Science of Corrosion-Busting Smart Coatings," Paint and Coatings Industry [2].

The microbeads resemble a fine white powder (30-50 µm in diameter) designed to be mixed into paints and coatings [2, 6]. A self-healing coating releases a chemical when the coating is damaged and automatically fixes the microcracks (figure 3) [2, 4].

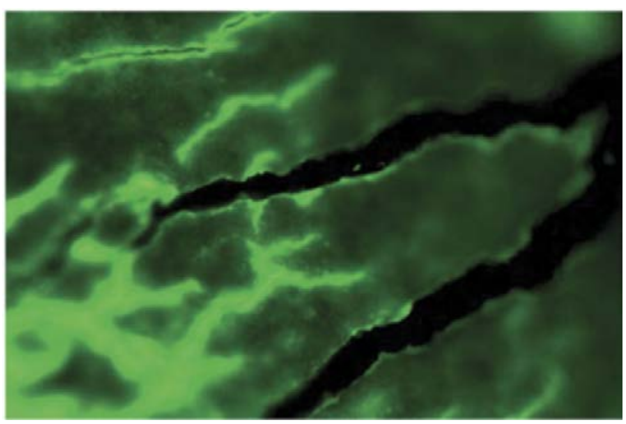


Figure 3.—Fluorescent microscope image demonstrating the flow of self-healing materials into cracks, reprinted from "The Science of Corrosion-Busting Smart Coatings," Paint and Coatings Industry [2].

The stability of the polymer inside of the microcapsule core remained functional and was not lost. It was observed that the low viscosity as well as the overall stability of the self-healing polymer could fill the microcracks more effectively. The corrosion performance of the microcapsule filled coatings showed improvement, demonstrated by the results of SAE J2334 cyclic corrosion tests (figure 4) [4].

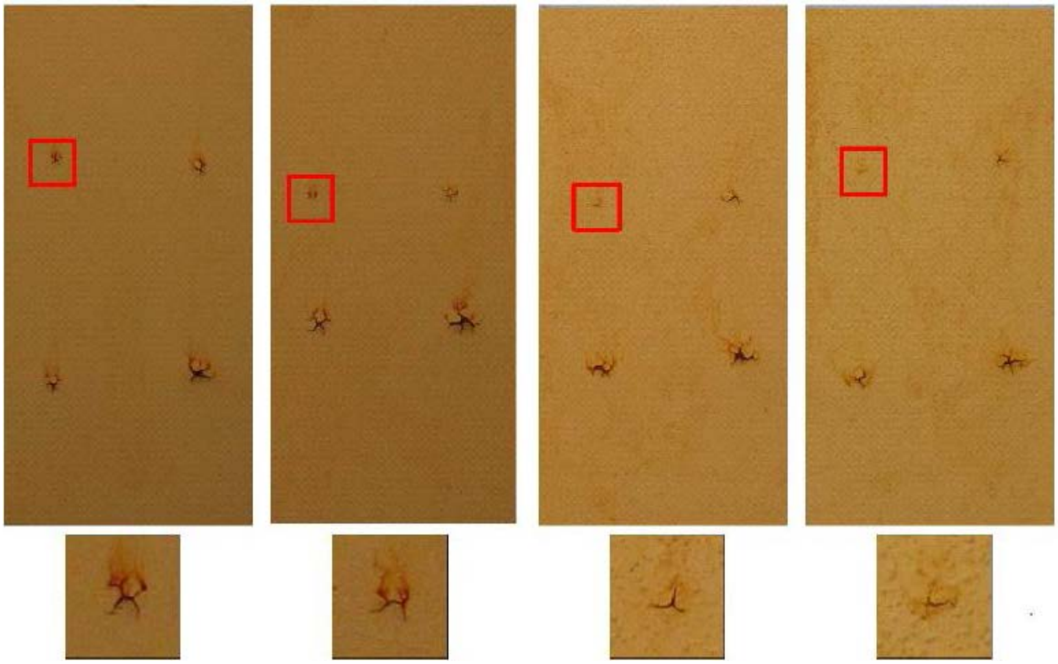


Figure 4.—Panels exposed to cyclic corrosion test (7 days): (a) Control panel with no capsules; (b) Panel with Paraloid/toluene capsules, (c) Panel with PSMATG capsules, one coat; (d) Panels with PSMATG capsules, two coats. Reprinted from Muzynski et al. "Development of Corrosion Resistant Coatings Using Novel Self-Healing Oligomer Filled Microcapsules," [4].

Materials and Methods

Battelle provided Reclamation with 200 grams of self-healing oligomer filled microcapsule coating additives, called microbeads, with a median particle size of 30 to 50 microns in diameter. They were a mixture of a proprietary polymer used as a healing agent along with a corrosion inhibitor (8-hydroxyquinoline). During impact (a physical impact using a steel mass, intended to cause mechanical damage through the protective coating) the self-healing polymer is released, reacts with metal ions present in a corrosion reaction, and cures into a hard thermoset material.

Steel coupon samples were abrasive blasted and solvent cleaned for proper adhesion of the PPG Amerlock 2 epoxy coating. Ninety grams of the coating were mixed with 10 grams of the microbeads and applied to samples by brush application. Three coats of PPG Amerlock 2 epoxy were applied to each sample, with the first two coats containing the microbeads in a 10 percent weight ratio. The PPG Amerlock 2 coating with the microbeads was mixed using a mixer attachment for a drill by using the 1:2 weight ratio specified per manufacturer instructions. Samples were prepared in triplicate (some only had duplicates due to available metal coupons) for four exposure conditions (air-dry (control), salt fog, immersion, and ultraviolet) without and with microbeads, shown in table 1.

Table 1.—Sample Exposure Conditions

Coating	**Exposure Condition**			
	Air Dry (Control)	**Salt Fog**	**Immersion**	**Ultraviolet (UV)**
without microbeads	xx	xx	xxx	xxx
with microbeads	xxx	xxx	xxx	xxx

* xx denotes two samples prepared.
* xxx denotes three samples prepared.

Samples were prepared, air dried for a week, and then exposed to accelerated weathering in their respective environments for a week before commencing Electrochemical Impedance Spectroscopy (EIS) testing.

Microscopy involved using a JEOL JSM-5800LV SEM and an OLYMPUS Stereoscope Model SZH10. SEM was used to identify the presence of the microbeads inside the coating. Pieces of the coating with microbeads present were cut into 5 mm x 5 mm squares, mounted on studs with double-stick carbon tape, and coated with a 2 nanometer thick layer of gold prior to imaging.

For EIS testing a Gamry Instruments FAS2 Femtostat was used. The frequency range was from 10^{-2} to 10^{5} Hz. A saturated calomel electrode (SCE) attached to the white wire, platinum mesh electrode attached to the red wire, and the metal substrate attached to the green wire were connected to the Gamry instrument as the reference, counter, and working electrodes, respectively. The EIS test cell is shown in figure 5.

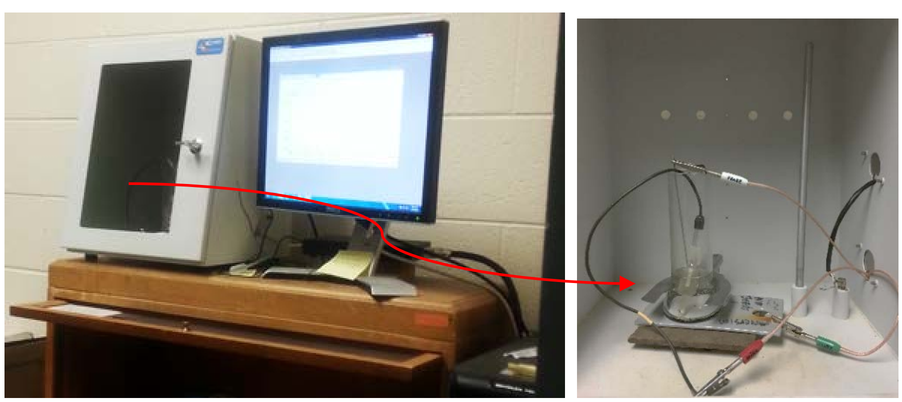


Figure 5.—EIS test cell setup: working (green), reference (white), and counter (red) electrodes.

Air dried samples (figure 6) were used as control samples to determine the effect of the microbeads without the added effect of accelerated weathering. Samples were left on a benchtop in the lab under ambient conditions.

Figure 6.—Air dried control samples.

Salt fog accelerated weathering test required the use of the Q-FOG model SSP600 apparatus manufactured by Q-Lab Corporation in Ohio. ASTM D5894 [6] was the standard used for this accelerated weathering condition. The corrosive electrolyte used during exposure was a dilute Harrison's solution (DHS) consisting of 3.5 weight percent ammonium sulfate ($(NH_4)_2SO_4$) and 0.5 weight percent sodium chloride (NaCl). Figure 7 shows the Q-FOG apparatus and samples used for testing.

(a) **(b)**

Figure 7.—Salt fog testing (a) apparatus and (b) samples.

Immersion accelerated weathering test consisted of constant immersion in DHS (figure 8). The immersion tank used in the lab follows standard described in ASTM D870 [7]. The samples remained in this immersion exposure at all times and were only removed for EIS testing.

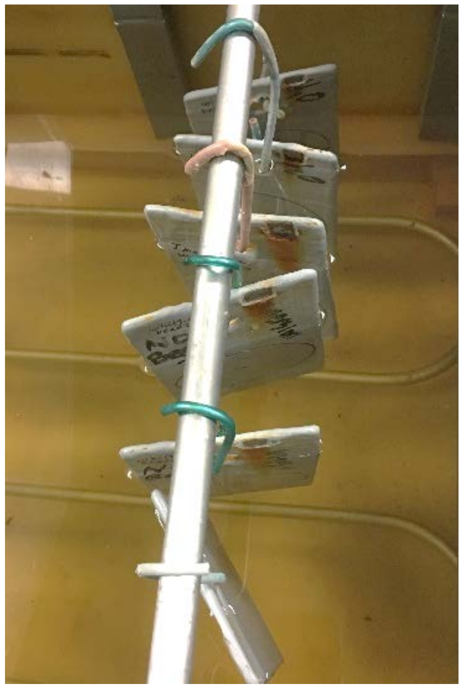


Figure 8.—Immersion testing tank including samples.

Ultraviolet accelerated weathering test required the use of the QUV apparatus (Q-Panel Company, Ohio). The samples were exposed following the standard described by ASTM D4587 [8]. Figure 9 shows the QUV apparatus and samples used for testing.

(a) (b)

Figure 9.—QUV testing (a) apparatus and (b) samples.

Samples were impacted after two months of accelerated weathering exposure using the drop weight impactor, shown in figure 10, with an impact force of 40 inch-pounds. The drop weight impact test followed ASTM D2794 [9]. After impact testing the samples were re-conditioned for a week in their respective environments before resuming EIS testing. The results obtained for one pre-impact test and all of the post-impact tests are discussed in this report.

Figure 10.—Drop weight impact test apparatus and sample.

Results and Discussion

There were a number of challenges associated with sample preparation that affect ease of use, potential applicability, and feasibility of using the microbeads in future coatings systems here at Reclamation. We hire many of our coating jobs out to various contractors. Can the contractor add this extra step without significant risk to our final product? If we are predominantly using these additives for corrosion protection then perhaps it's unnecessary to worry about aesthetics in the final product. But if aesthetics are important then the microbeads may create some barriers to that end goal.

Brush application was chosen because the beads were too large to pass through a spray nozzle. Spray equipment requires a particle size below 10 microns, so as to prevent clogging of the nozzle during application. The brush application is not a desired method as it creates aesthetically inferior coatings as opposed to spray applications. The sizes of the microbeads limit the use of spray applications, unless they are specifically designed to be smaller than 10 microns in diameter. Battelle has indicated that they can make the microbeads in many sizes to accommodate various equipment needs. Then questions arise of whether or not the smaller bead sizes can produce enough of the self-healing material to be useful, or if significantly more (by weight percent) has to be mixed into the coating. A larger weight percentage will make the coating surface rougher.

Another potential challenge is the process of mixing the microbeads into the coating. Battelle has indicated that high speed centrifugal mixing can be used with the microbeads. But the primary concern, in our opinion, is the premature rupture of the microbeads if the mixing is too forceful. Without proper mixing, dispersion could be problematic. Uneven dispersion will create areas that are not as protected from corrosion if an impact event occurs in part of that location. It is also not ideal to have clumps created by uneven dispersion throughout the coating and these clumps could present problematic situations if the coatings are being used in certain environments requiring smoother surfaces. For example, the clumping could create friction or disrupt the hydrodynamic surface requirements for a coating inside of a pipe. Future testing may involve the examination of this challenge. Can the beads withstand forceful mixing and is even dispersion accomplished through a standard mixer attachment for a drill? If the standard drill attachment is sufficient enough for even dispersion then high speed mixing can be avoided, depending on a coating system that is used.

In all coating applications the coating film thickness is very important. This helps determine if the coating was applied adequately and if standards were met. The microbeads add bulk to the film thickness and create a rougher surface. This is not aesthetically ideal and can be a problem for most coating requirements in the field. The microbeads could also be imparting defects into the coating film due to the extra voids they may create. The coating film thickness was not examined during the course of this experiment but was visually determined to be rougher and thicker for the PPG Amerlock 2 coating with the microbeads. It is recommended that future testing examine the film thickness.

Assuming the above challenges can be overcome, the following sections present the laboratory based testing results obtained during this research.

Visual Inspection

Visual inspection of the impacted samples after three months of exposure showed corrosion in the impact zone. Based on visual inspection, the microbeads did not fully protect the impacted samples from corrosion in their respective conditions of exposure. However, the microbeads reduced the amount of corrosion present in the damage zones of each sample set in a given accelerated weathering condition, as compared to samples without microbeads present. Figure 11 shows the samples in all four test conditions without and with the microbeads.

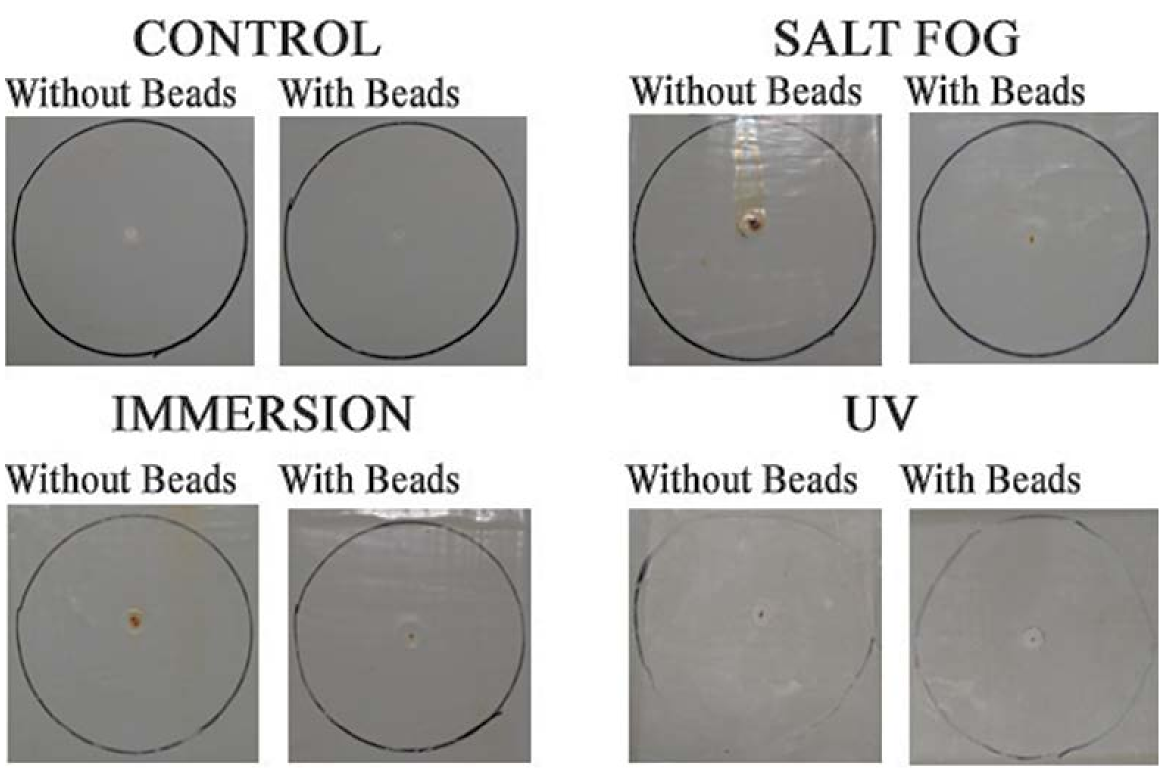


Figure 11.—Visual inspection of samples without and with microbeads in each test condition for about three months exposure after impact.

It is important to note that the dry film thicknesses were not determined in this experiment and slight variations in film thicknesses of each sample can potentially alter the degree of corrosion seen. The general trend demonstrates less corrosion seen in the samples with the microbeads compared to the samples without the microbeads.

Microscopy

SEM showed a cross section of a microbead within the Amerlock 2 coating system. The size of the microbead correlates with the 30-50 micron size ranges mentioned in the background section of this report. There are spheres present inside the microbead that are potentially indicative of leftover self-healing material adhered or was absorbed into the microbead surface. This material is potentially a solid sphere or just liquid that “dislikes” the microbead’s thermoset shell.

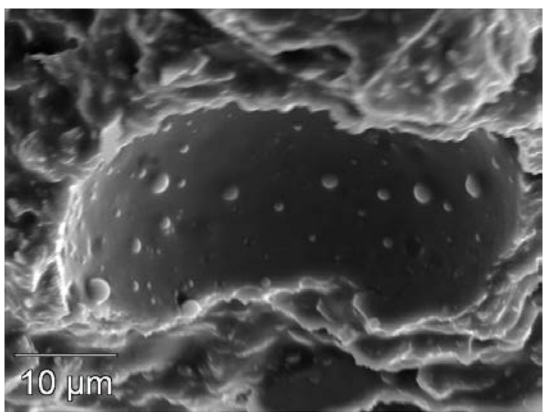


Figure 12.—SEM cross sectional image of a microbead seen inside the PPG Amerlock 2 coating.

Figures 13 to 15 show images of the impacted samples without and with microbeads one week after exposure in testing conditions, taken by the stereoscope. These images confirm healing in the wound impact region present with the use of microbeads as compared to those without use of microbeads in the coating. It should be noted that corrosion is not visually detected in these images, with the exception of figure 15, because of the short duration of exposure post impact. These images serve to identify impact zone closing.

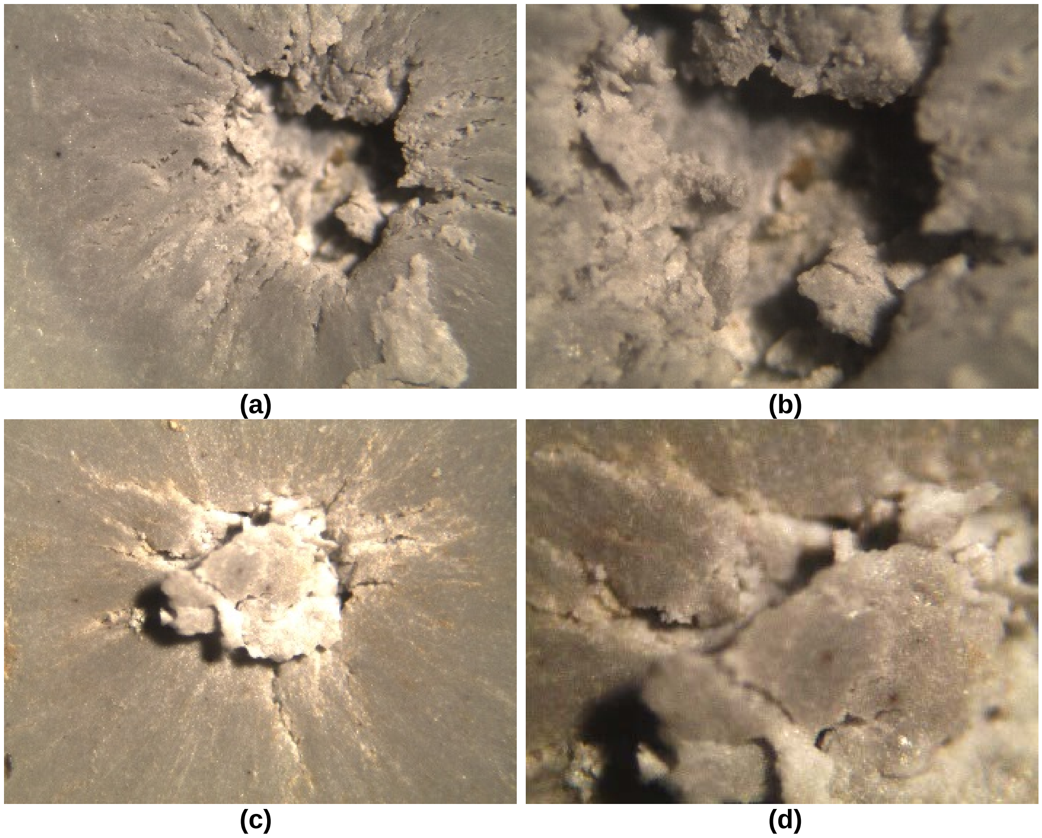
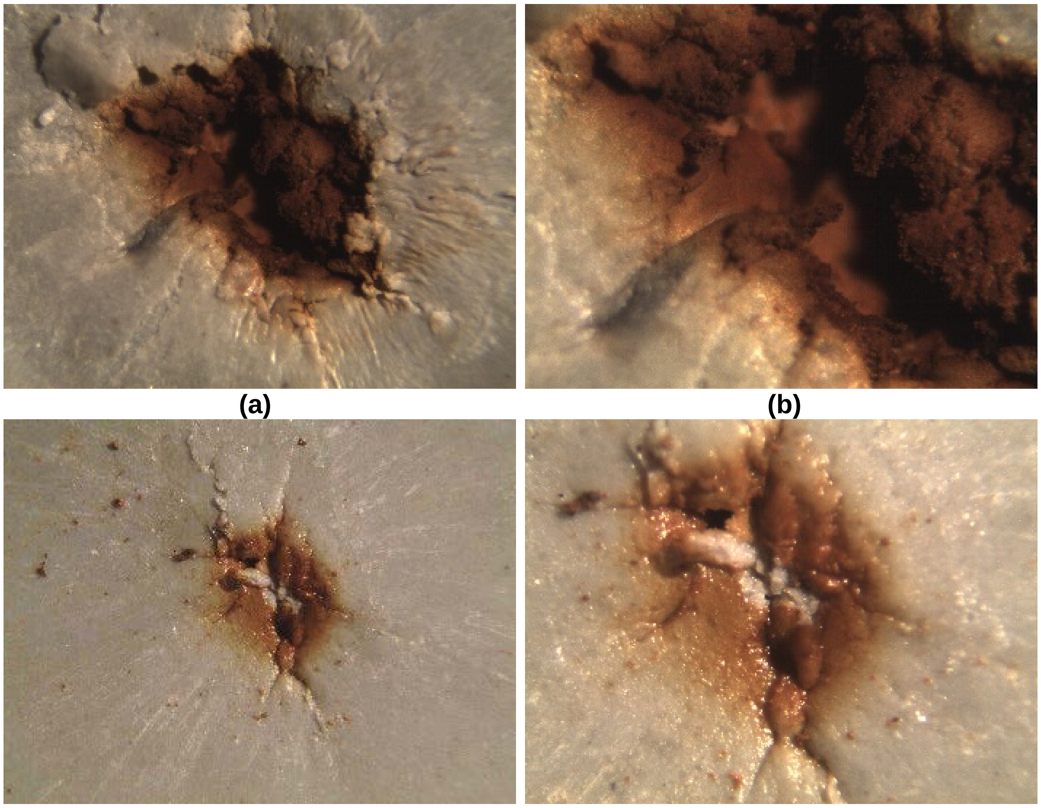


Figure 13.—Salt fog stereoscope images of impacted samples (a) without microbeads at 3x magnification, (b) without microbeads at 6x magnification, (c) with microbeads at 3x magnification, and (d) with microbeads at 6x magnification.



(a) **(b)** **(c)** **(d)**

Figure 14.—Immersion stereoscope images of impacted samples (a) without microbeads at 3x magnification, (b) without microbeads at 6x magnification, (c) with microbeads at 3x magnification, and (d) with microbeads at 6x magnification.

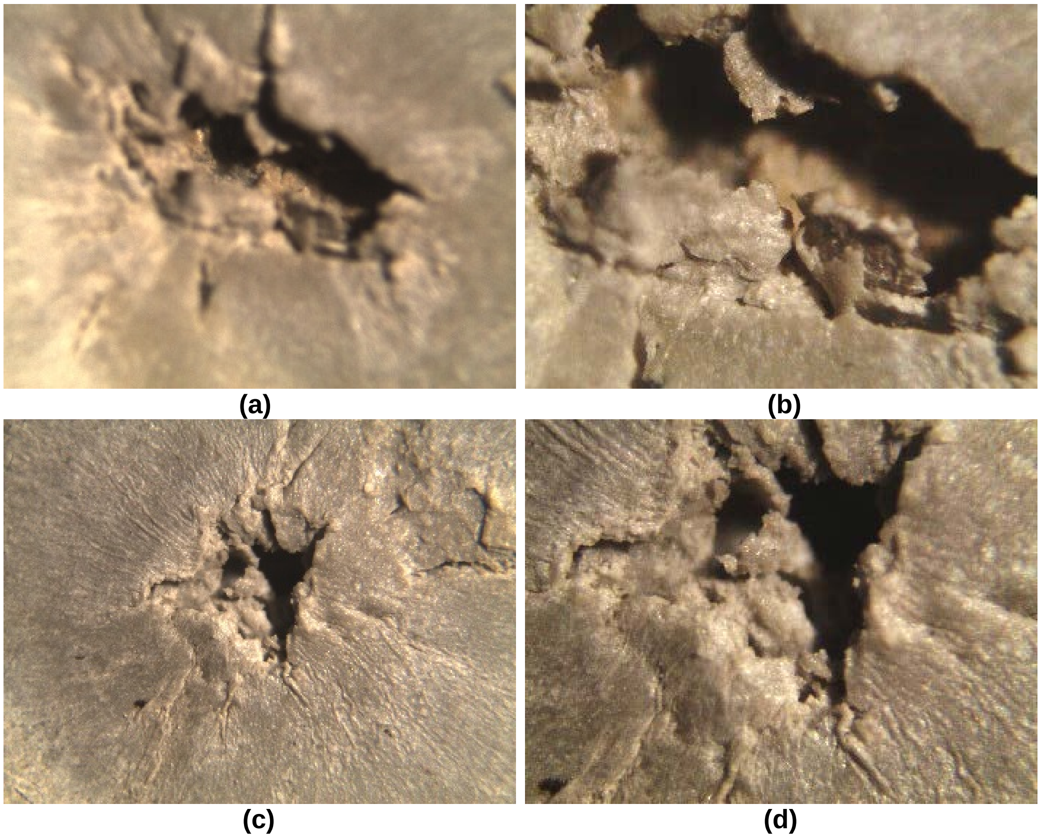


Figure 15.—UV stereoscope images of impacted samples (a) without microbeads at 3x magnification, (b) without microbeads at 6x magnification, (c) with microbeads at 3x magnification, and (d) with microbeads at 6x magnification.

From the images in figure 13 it appears that corrosion products can be produced over the impacted region by salt fog test exposure. These products could perhaps act as barriers to mitigate corrosion. Therefore, corrosion is not visible in these images as compared to those seen in figure 14 for samples in immersion test condition. In figure 15, no corrosion is visible in the impacted region of the samples after exposure in UV test condition; for both without and with microbeads in the coating.

These images demonstrate that there is a significant difference between the samples with the microbeads compared to the samples without the microbeads. It is obvious that the microbeads are playing a role in closing the impact damage zone, which in theory should help reducing the spread of corrosion.

Electrochemical Impedance Spectroscopy

EIS is a test method used to determine coating performance over time. It can be used to compare the degradation seen in the coating systems with microbeads versus the coating systems without microbeads. EIS can indicate coating degradation along with potential causes of the degradation [10].

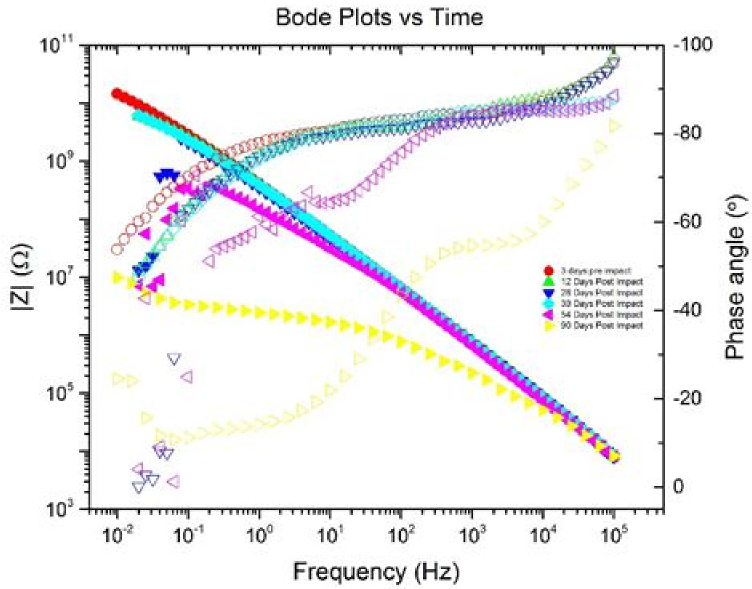
The EIS data are plotted by impedance magnitude |Z| on the left y-axis and the phase angle on the right y-axis, versus the frequency on the x-axis. The solid colored data points represent the impedance and the outlined data points are for the phase angle. Each set of data within each figure shows the results of a single experiment, indicated in the legend by the number of days relative to impact.

Merten describes how EIS uses a broad range of frequencies to make the following interpretation [10, 11]:

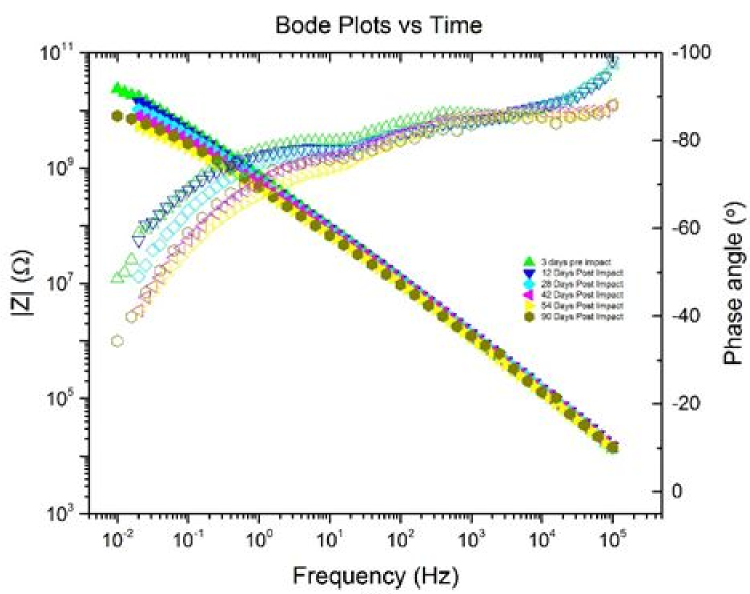
- Corrosion reactions at the coating/metal interface can be captured at low frequency measurements.
- The solution resistance between the coating surface and the counter electrode is the only process observed at high frequency measurements.
- Impedance at the low frequency region indicate "resistive behavior" for horizontal line and phase angle of 0° and indicate "capacitive behavior" for 45 degree line and phase angle of -90°.
- Increased resistive behavior is representative of coating degradation and the presence of corrosion.

See Reclamation reports "Re-evaluating Electrochemical Impedance Spectroscopy (EIS) for the Field Inspector's Toolbox: A First Approach," and "Coating Evaluation by Electrochemical Impedance Spectroscopy (EIS)" [10, 11] for a more in depth discussion.

Figure 16 shows test results for coating samples without and with microbeads in the control samples pre- and post-impact. In figure 16(a), it took 54 days to show a significant decrease in |Z|. This increase in resistive behavior confirms a decrease in corrosion protection. The data in this figure show scatter in the testing runs. The results in figure 16(b) for the coating sample with the microbeads show only a slight decrease in |Z| and phase angle at low frequency over time of exposure. This demonstrates that microbeads inside the coating could perhaps increase the resistance of the coating to degradation and corrosion in atmospheric exposure.



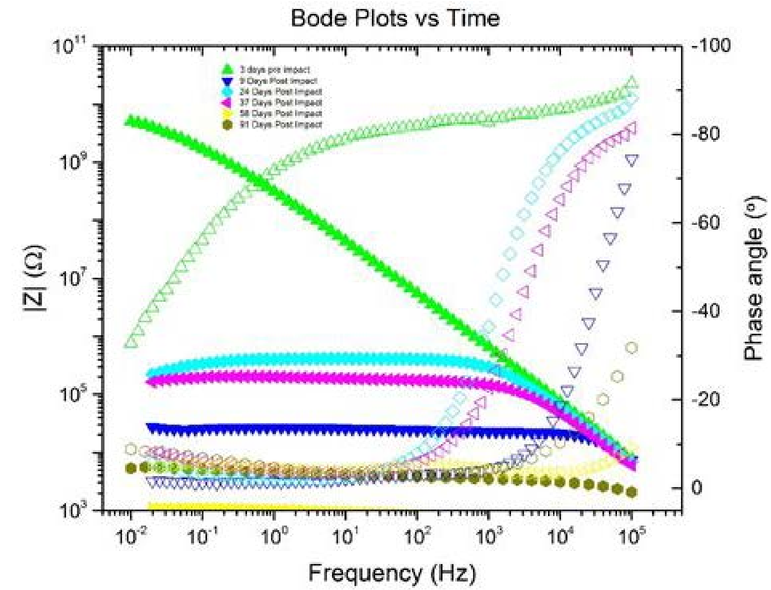
(a)



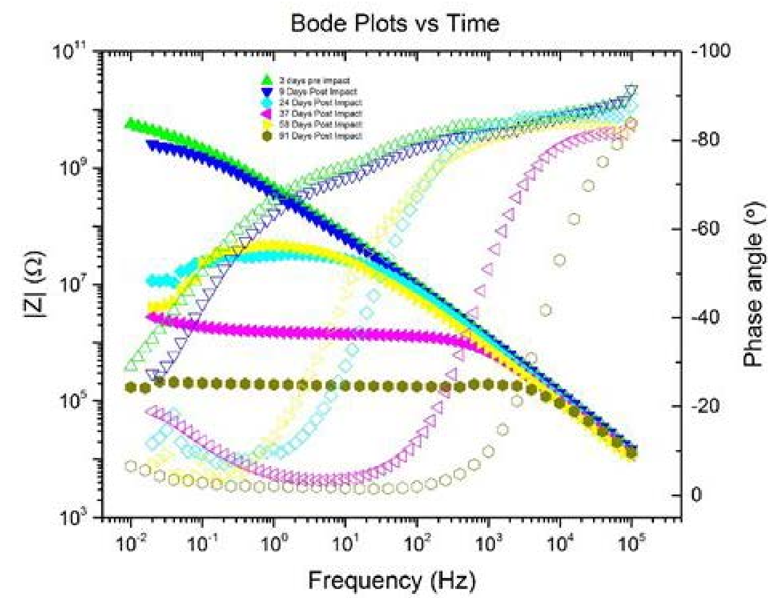
(b)

Figure 16.—EIS control test results for coating (a) without microbeads and (b) with microbeads pre- and post-impact.

Figure 17 shows test results for coating samples without and with microbeads in salt fog exposure pre- and post-impact. It appears that degradation / corrosion happens rapidly for both samples without and with microbeads. However, the presence of microbeads in the coating slows down coating degradation and subsequent corrosion. |Z| does not drop as low in figure 17(b) as compared to that in figure 17(a), but it is clear that corrosion is significant.



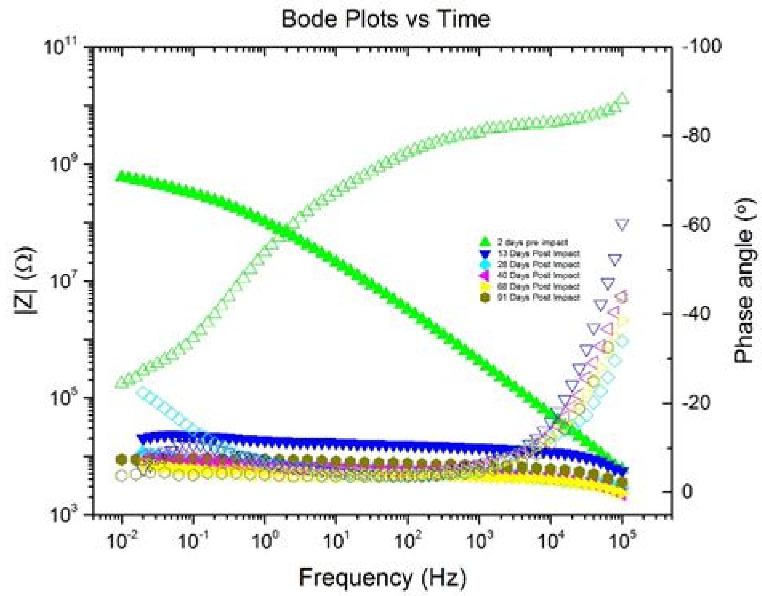
(a)



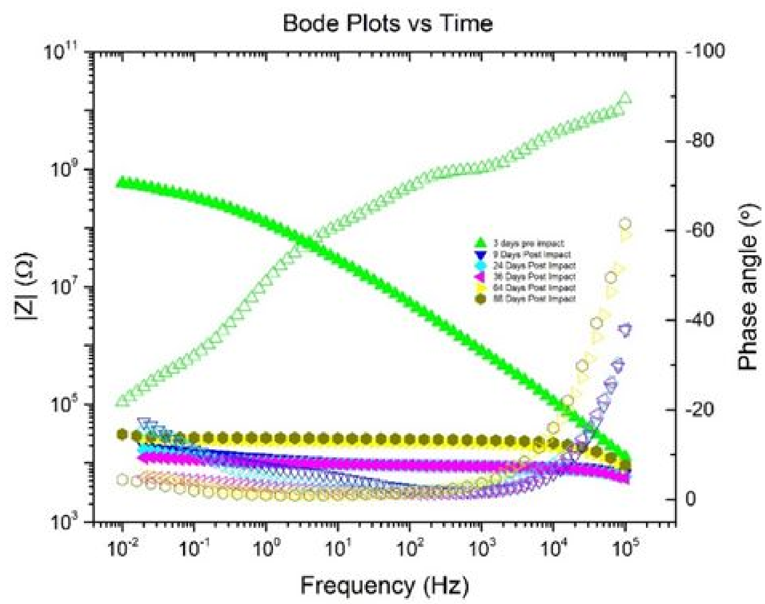
(b)

Figure 17.—EIS salt fog test results for coating (a) without microbeads and (b) with microbeads pre- and post-impact.

Figure 18 shows test results for coating samples without and with microbeads in immersion exposure pre- and post-impact. These results indicate no corrosion protection in either the coating without the microbeads or the coating with the microbeads. From these plots no significant difference in |Z| and phase angle measurement over time of exposure could be seen without and with presence of the microbeads in the coating. The microbeads contain a water soluble portion within them that could be washing out or dissolving into the DHS in immersed and salt fog exposure. This would drastically affect curing rates, curing chemistry, and corrosion inhibition.



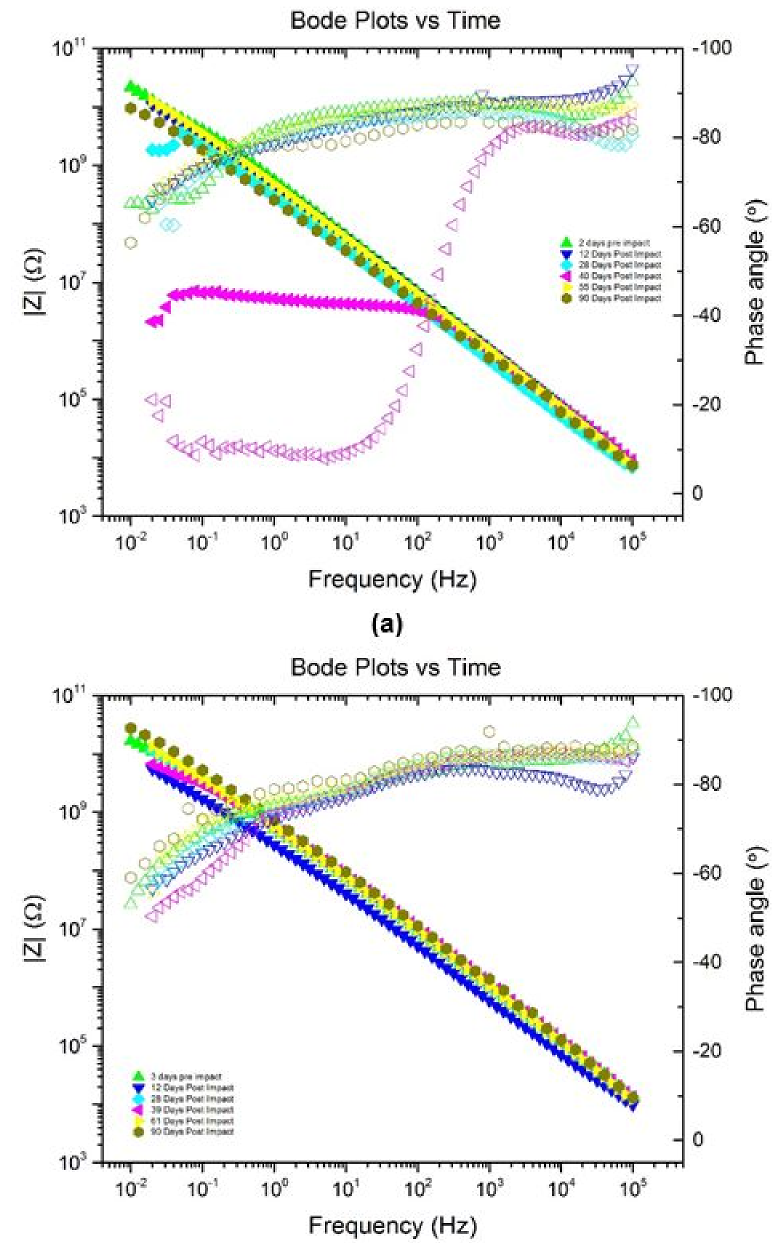
(a)



(b)

Figure 18.—EIS immersion test results for coating (a) without microbeads and (b) with microbeads pre- and post-impact.

Figure 19 shows test results for coating samples without and with microbeads in UV exposure pre- and post-impact. In figure 19(a), |Z| decreases at low frequency for coating without the presence of microbeads indicating a slight degradation. Note that the sudden drop in |Z| for 40 day post-impact is likely a testing error and is ignored in this analysis. On the other hand, figure 19(b) shows a slight resurgence in |Z| over the time of exposure due to presence of microbeads.



(b)

Figure 19.—EIS UV test results for coating (a) without microbeads and (b) with microbeads pre- and post-impact.

Conclusions

The goal of this investigation was to examine the effect of self-healing microbeads in PPG Amerlock 2 coatings to mitigate corrosion and impact damage and its applicability in Reclamation projects. Samples were prepared in triplicate or some in duplicates for four exposure conditions (air dry (control), salt fog, immersion, and ultraviolet) without and with microbeads produced by Battelle.

Based on visual observations alone, the microbeads supplied by Battelle did not fully protect the impacted samples from corrosion in conditions they were exposed to. However, the microbeads reduced the amount of corrosion present on each sample set over the time of exposure.

Stereoscope images of the samples exposed to testing conditions for about one week after impact also confirm healing in the impact zone with the use of microbeads as compared to those without use of microbeads in the coating. Salt fog exposure produces corrosion products inside the impact zone which can perform as a barrier to prevent corrosion. Samples with the presence of microbeads in the coating in UV exposure show some healing in the impact region as well.

EIS test results demonstrate that the presence of microbeads could decrease coating degradation and corrosion in air dry exposure. For salt fog exposure it appears that degradation / corrosion happens rapidly for both samples without and with microbeads. However, the presence of microbeads in the coating slows down this degradation and subsequent corrosion. In the case of immersion exposure and salt fog exposure, EIS test results indicate no corrosion protection in either the coating without the microbeads or the coating with the microbeads. In atmospheric (control) and UV exposures, EIS shows a slight reduction in the rate of corrosion over the time of exposure due to presence of the microbeads. Atmospheric and UV exposures are two potential exposure conditions in which the presence of microbeads would be beneficial.

Battelle's microbeads used for this project show the self-healing effect in coating by slowing down degradation / corrosion on samples after impact over the time of exposure to specified conditions. However, at the end of exposure period defined for this project, corrosion mitigation is not fully obtained.

This research helped to identify performance of the microbeads inside of the Amerlock 2 coating system, but it did not fully address issues related to ease of use and applicability. Other questions not addressed by this research include stability of the microbeads in a coating system for a long period of time and cost of implementation. It is recommended for the future research to examine these additional questions along with laboratory testing of other coating systems in atmospheric and UV exposures.

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