The Prediction of Long-term Coating Performance from Short-term Electrochemical Data, Part II. Comparison of Electrochemical Data to Field Exposure Results for Coatings on Steel

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ABSTRACT

The pace of coatings development is limited by the time required to assess their corrosion protection properties. This study takes a step forward from Part I in that it correlates the corrosion performance of organic coatings assessed by a series of short-term electrochemical measurement with 18-month beachside exposure results of duplicate panels. A series of 19 coating systems on A36 steel substrates were tested in a completely blind study using the damage tolerance test (DTT). In the DTT, a through-film pinhole defect is created, and the electrochemical characteristics of the defect are then monitored over the next 4 to 7 days while immersed in 0.5M NaCl. The open circuit potential, anodic potentiostatic polarization tests and electrochemical impedance spectroscopy were used to study the corrosion behavior of the coating systems. The beachside exposure tests were conducted at the Kennedy Space Center according to ASTM D610-01. It was found that for 79% of the coatings systems examined, the 18 month beachside exposure results could be predicted by two independent laboratory tests obtained within 7 days.

INTRODUCTION

Significant field exposure time is often needed to differentiate the corrosion protection provided by a coating, particularly for high performance systems. This time for testing, which can be on the order of years, can be shortened by accelerated methods such as salt spray, but still may require as much as 3000 h or more to differentiate sample performance. In all cases, these field exposure and accelerated methods yield qualitative results that can vary as a function of testing site, testing chamber, or individual scoring the results, and require significant time for testing that ultimately provides a bottleneck to coating development.

A faster method that can provide accurate, quantitative results is needed for practical screening of the millions of new coating and surface treatment options that are created each day. Kendig and coworkers developed a 24 h electrochemical approach to determine the time-to-failure of an automotive coating on mild steel [1]. In these tests the barrier properties of the undamaged coating were assessed for 24 hours using electrochemical impedance spectroscopy (EIS) and the cathodic delamination characteristics were subsequently assessed by scribing the panels, polarizing them cathodically to -1.05 V_{NHE} and performing a tape test. These results were then compared to salt spray outcomes. The outcome of such approach was an empirical formula that predicted the relative time to failure (TTF) of the coatings as a function of the corrosion resistance measured after 24 hours, the disbond rate and the water uptake of the coating systems. The TTF was found to be directly proportional to the time to failure observed during the salt spray tests. Suay et al. subsequently used a different cycle to accomplish the same goal for coating systems on steel [2], while Poelman extended the same approach to aluminum substrates [3].

The present study combines the ideas of previous researchers [1-3] with the Damage Tolerance Test (DTT) discussed in Part I, so that the attention is now focused to the investigation of the damaged area and interface, and not on the barrier properties of the undamaged coating. In addition to examination of interfacial changes under ambient conditions, the present study also uses EIS in conjunction with DC-driven delamination to further delineate coating performance. Furthermore, this study builds on Part I by blindly comparing laboratory results to actual field data, *i.e.*, 18-month beachside exposure results, rather than salt spray performance data. This provides a more definitive performance metric.

EXPERIMENTAL METHODS

Field Exposure Evaluation

Both flat and "composite" coupons (4"x 6"x 3/16", KTA-Tator) were fabricated from ASTM A36 hot rolled carbon steel (Figure 1) and used as the substrate for each coating system investigated. Composite panels consisted of an A36 panel with a 1" C-channel welded on the front (see Figure 1). This C-channel panel incorporates many common surface irregularities (*e.g.*, welds, crevices, and sharp edges) that must inevitably be protected by a coating system (Figure 1), and thus provides a more challenging but realistic situation than the conventional flat panel. All panels were abrasively blasted to a white metal finish (SSPC-SP-5) to remove any mill scale and weld slag. The anchor profile created by the abrasive blasting is approximately 2.0 mils as measured by the Test-X replica tape method.

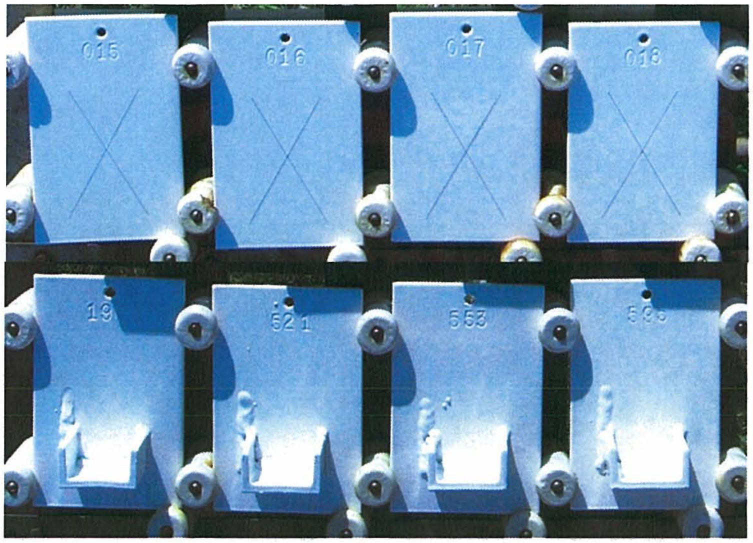


Figure 1. Example of Flat and Composite Panels.

The exposure site is located approximately 1.5 miles south of Launch Complex 39A at the Kennedy Space Center (Figure 2). The coated test panels were installed on stainless steel racks that use porcelain insulators as standoffs. The racks were installed on galvanized pipe test stands which oriented the samples at a 30° angle facing the ocean. The distance of the test stands from the mean high-tide line was approximately 30 meters (100 feet) from the Atlantic Ocean. After eighteen months of exposure, ASTM D 610 was used to rate the degree of corrosion on a scale from 0 to 10 (worst to best), in which each rating number represented the amount of rusted area (Table 1).

Figure 2. KSC Beach Corrosion Test Site

TABLE 1. ASTM D 610-01 Rating Scale at 18 months

Rating	Description
10	No rusting or less than 0.01% of surface rusted
9	Minute rusting, less than 0.03% of surface rusted
8	Few isolated rust spots, less than 0.1% of surface rusted
7	Less than 0.3% of surface rusted
6	Extensive rust spots, but less than 1% of surface rusted
5	Rusting to the extent of 3% of surface rusted
4	Rusting to the extent of 10% of surface rusted
3	Approximately 1/6 of the surface rusted
2	Approximately 1/3 of the surface rusted
1	Approximately 1/2 of surface rusted
0	Approximately 100% of surface rusted

Electrochemical Test Methods

The same coating systems were tested with the DTT for a more rapid and quantitative measure of coating protection. The DTT generally consists of observing the corrosion behavior of the panels immediately before and immediately after a defect is created through the coating. In a first set of experiments, a pinhole was made using a carbide scribe at time 0, and open circuit potential (OCP) measurements and impedance spectra (EIS) were recorded 30 minutes after the defect was made and then at 24 hours intervals for 7 days. The second set of experiments was aimed at consuming any sacrificial anodic pigments via a series of anodic potentiostatic polarizations (Figure 3). To this scope, after the defect was created, the impedance spectra at OCP were first collected immediately following the defect. This was followed by a series of four, one-hour potentiostatic polarizations at -0.5 V_{SCE} with 30 minute periods between each polarization in which the sample was left at OCP for EIS testing. A fifth polarization was carried out for 3 hours followed by 12 hours of OCP conditions and a final EIS spectrum was collected. EIS spectra were collected in a three-electrode potentiostatic mode using a 10 mV rms sine wave excitation from 50 kHz to 0.01 mHz. A barnacle-type cell was used to expose 7.2 cm^2 of sample surface area in each experiment. All EIS results were normalized to the surface area of the defect which was measured for each sample. The test solution was 0.5M NaCl at room temperature and ambient aeration conditions. The potentials were referenced to a saturated calomel electrode (SCE). A platinized niobium mesh was used as a counter electrode.

Coated steel panels having 19 different coating systems were supplied to the electrochemical testing laboratory. No information about the coating systems was known by this laboratory except that they were applied to steel. Three to four replicates of each coating system were tested to provide a mean and standard error for each data point.

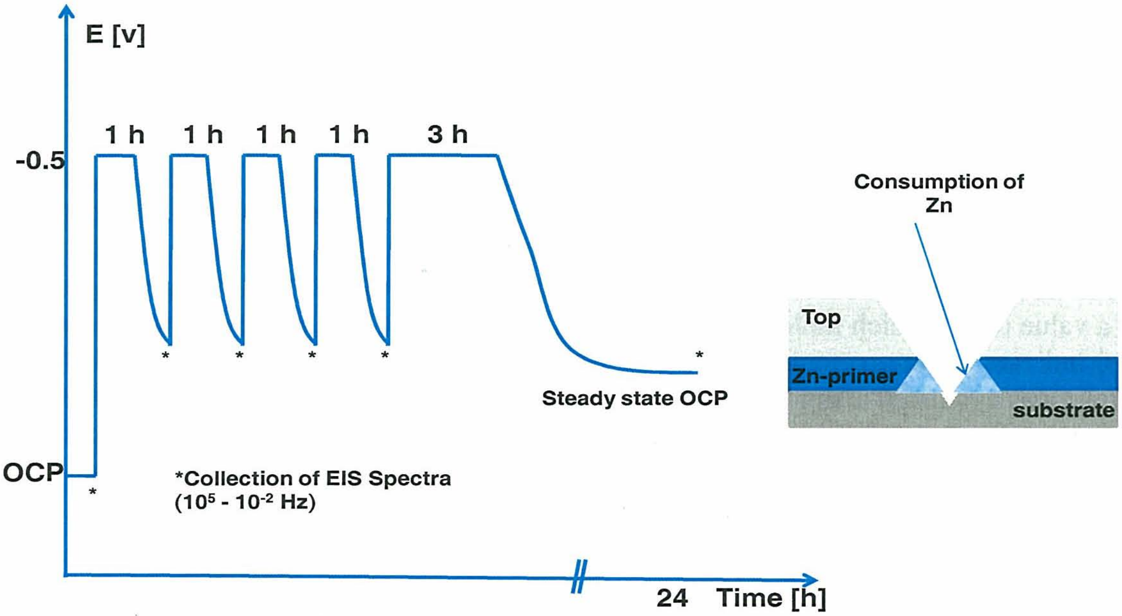


Figure 3. Schematics of the second series of tests.

RESULTS AND DISCUSSION

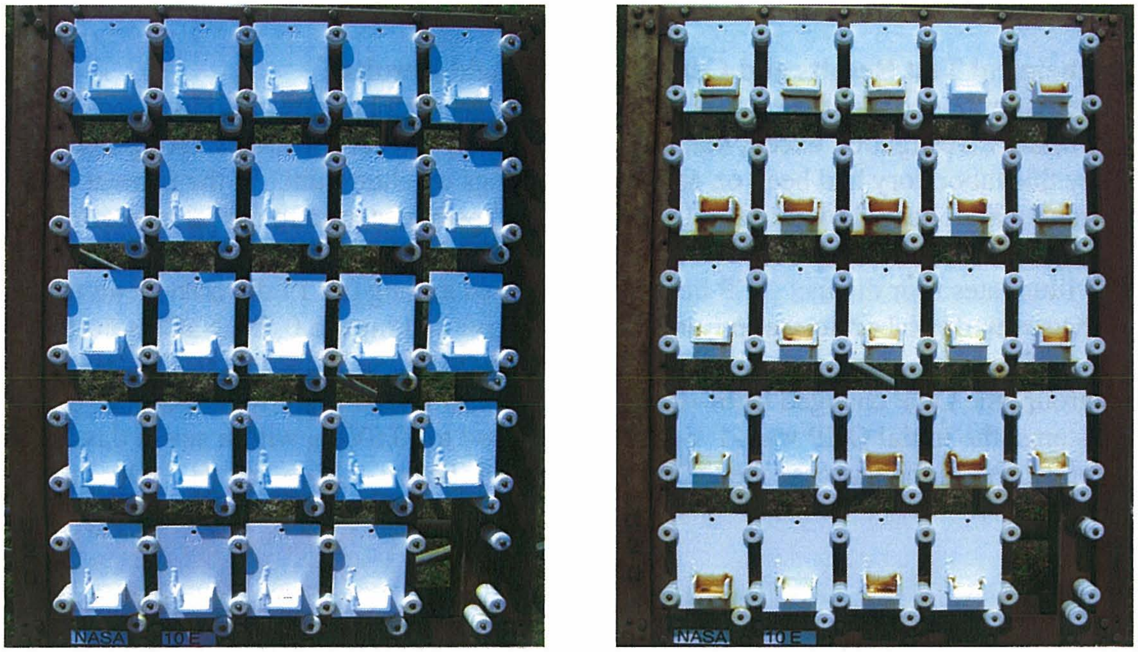
18-month Field Exposure Results

As stated above, nineteen different coating systems from three different studies were submitted to the University of Texas for a blind study. The coated panels used by the University of Texas were coated at the same time, using the same coating batches and panel lots as the panels used in the outdoor exposure studies. The three different coating studies were performed over a span of five years, from 2004 to 2009 (Table 2). When coating studies are performed at KSC, extra panels are prepared and archived in an indoor humidity controlled storage room. These panels are used as controls for each study. Samples from these archived lots were used for the electrochemical tests.

TABLE 2. NASA Panel Matrix

Study	Start Date	End Date	Acronym	System
1	5/1/2004	10/31/2005	TT	S1
			TT	S2
			TT	S3
2	4/20/2005	10/20/2006	AIU	S1
			AIU	S2
			AIU	S3
			AIU	S6
			AIU	S7
			AIU	S8
			AIU	S9
			AIU	S10
3	2/15/2008	8/16/2009	N10	S1
			N10	S2
			N10	S3
			N10	S4
			N10	S6
			N10	S7
			N10	S8
			N10	S10

The coated panels in each study were visually inspected and rated at the end of the exposure period, respectively (four coated panels per coating system). Photo documentation of the coated coupons, for each study, was performed prior to exposure, and after 18-months at the beach site to maintain a visual record of the results (Figure 4). The ASTM D 610 general rust grading scale runs from a value of 10, which indicates that less than or equal to 0.01% of the surface rusted, to a value of 0 indicating that greater than 50% of the surface is rusted (Table 1). Each panel from the set of four was evaluated using this standard and averaged using a simple arithmetic mean to give a final rating for that coating system (Table 3). In cases where the one panel's individual rating was substantially below the others in the group, its rating was not used in the average due to the possibility of application or preparation defects and not an issue with the coating.



Initial exposure **18 months of exposure**

Figure 4. Example of sample support for field exposure.

TABLE 2. NASA Panel Matrix Ratings

Study	System	Ratings Panel 1	Panel 2	Panel 3	Panel 4	Average
1	TTS1	7	8	7	7	7.3
	TTS2	8	9	8	8	8.3
	TTS3	8	8	9	9	8.5
2	AIU S1	8	8	7	8	7.8
	AIU S2	8	8	8	8	8.0
	AIU S3	7	9	7	7	7.5
	AIU S6	8	10	10	9	9.3
	AIU S7	9	8	9	8	8.5
	AIU S8	8	8	8	8	8.0
	AIU S9	1	1	1	1	1.0
	AIU S10	9	8	8	8	8.3
3	N10 S1	9	9	9	10	9.3
	N10 S2	8	8	8	9	8.3
	N10 S3	9	9	9	9	9.0
	N10 S4	9	10	9	9	9.3
	N10 S6	9	9	9	9	9.0
	N10 S7	10	9	9	8	9.0
	N10 S8	9	9	8	8	8.5
	N10 S10	10	10	9	8	9.3

Electrochemical Test Results and Comparison to Field Results

The reader is reminded that the electrochemical testing laboratory knew nothing about the coatings under investigation except that they were applied to steel substrates. All previous testing by this laboratory had been on aerospace coatings on aluminum. In the present study, the OCP, which was collected for all samples prior to EIS testing, started to reveal interesting clues about the possible corrosion protection mechanism of the coating systems under investigation. Figure 5 illustrates four distinct OCP behaviors observed among the 19 different coating systems during the seven day laboratory exposure of the defective coatings to 0.5M NaCl solutions. In one group of coating samples, the OCP remained around -0.6 V_{SCE} throughout the exposure. In a second group, the OCP changed from -1V_{SCE} to -0.6V within one day after the defect. For the other systems, the initial OCP was -1 V_{SCE}, but increased to -0.6V_{SCE} within seven days (behavior 3), and in the last case the OCP remained at or below -1 V_{SCE} for all 7 days (behavior 4).

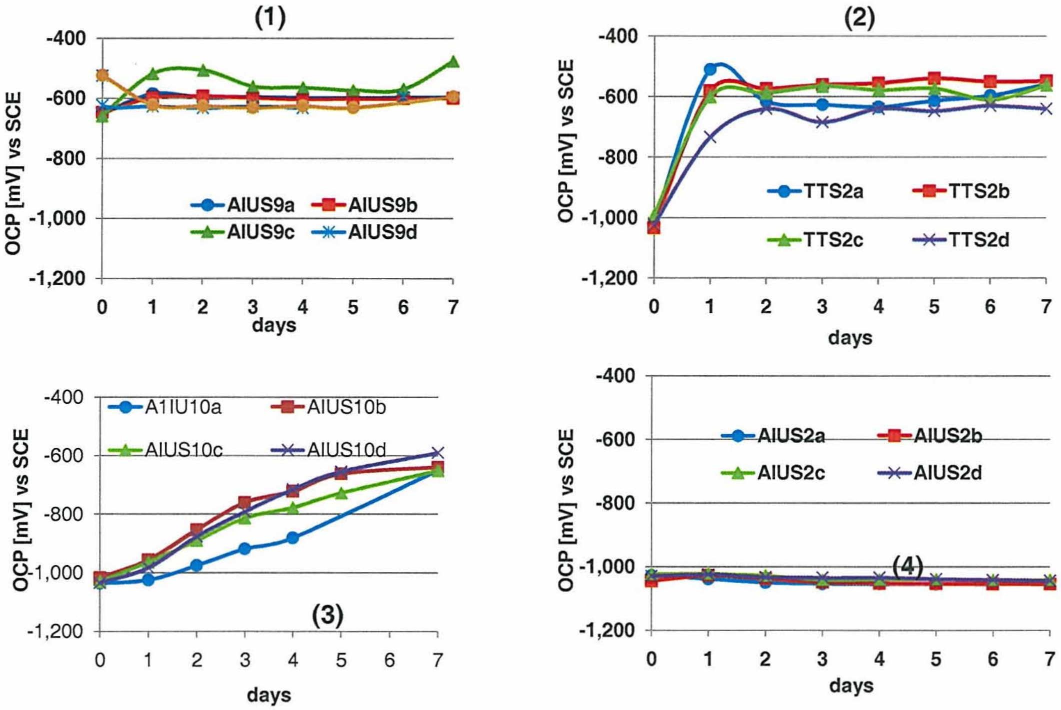


Figure 5. Time dependence of the open circuit potential of defective coatings.

The low initial OCP (*ca*. -1.0 V_{SCE}) indicated that the coating systems under investigation contained a sacrificial material (*e.g.*, zinc) and thus required possible modification to the original DTT testing approach which was developed for inhibited aerospace coating systems. The different OCP trends allowed grouping the coating systems into two distinct sets: those containing anodic sacrificial pigments (systems that showed potential of -1V) and those that did not contain active sacrificial material (or sufficient amounts of sacrificial materials needed to be conductive) as indicated by an OCP that was typical of corroding steel in NaCl solution (*ca.* -0.6 V_{SCE}). Moreover, the coating systems that showed a progressive increase in the OCP were thought to undergo a depletion of the sacrificial pigments. It was postulated that the faster the increase in the OCP, the faster the consumption of the sacrificial pigments and therefore, the shorter the life-expectancy of the coating systems.

An initial comparison of electrochemical results to field data simply correlated the observed rates of the OCP changes with the ASTM visual corrosion ranking of the coatings. Figure 6 compares the difference between the OCP observed at day 4 (OCP_4) and day 0 (OCP_0), with the ASTM ranking obtained by the exposure laboratory for the same coating systems (but obviously different individuals). It was observed that 76% of the samples clustered into two distinct groups: (1) coatings characterized by a rating of 9 or above did not show a significant change in the OCP which remained at -1 volt and (2) coatings characterized by a rating of 8.5 or lower showed a

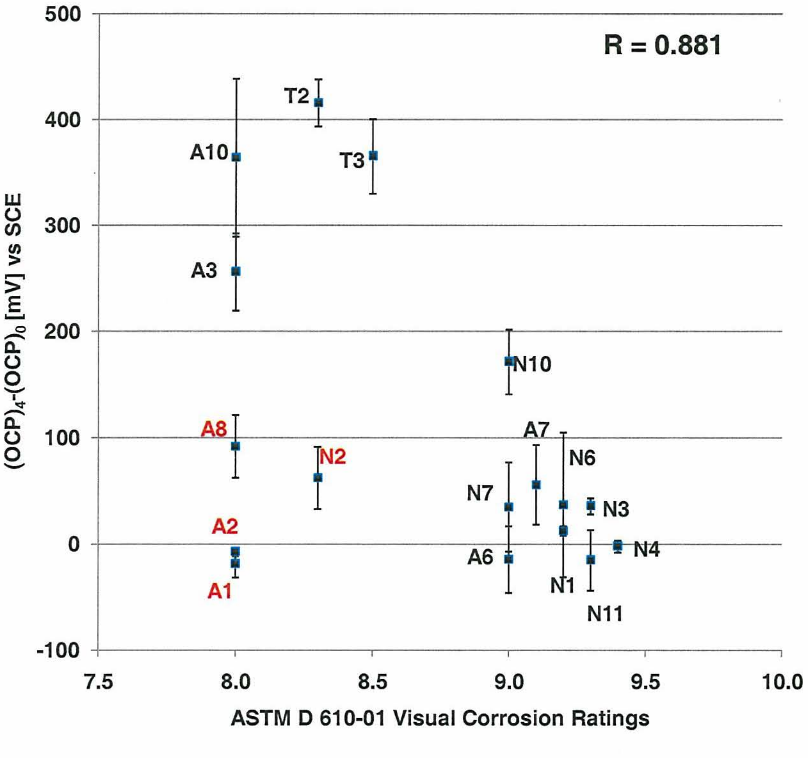


Figure 6. Correlation between the ASTM D 610-01 corrosion ranking at 18 months and the difference between the OCP at day 4 and day 0.

dramatic increase in the OCP due possibly to the progressive inactivation or consumption of the sacrificial pigments. Four out of 19 coatings fell out of this scheme. These four systems received a rating lower than 8.5 even though their OCP remained around -1 throughout the 7 days of exposure time. Two coating systems followed the behavior illustrated in figure 3 (trend 1). Their ratings was lower than 8, which confirmed the finding whereby the closer the OCP to the corrosion potential of steel, the lower the rating. Taking into consideration these two additional coatings systems, a correlation of 79 % was found between the ASTM visual corrosion rating and the observation of the corrosion potential over 4 days of immersion time. It is important to keep in mind that outdoor exposure, particularly at this site, includes significant UV and may be the source of deviation between the field results and the current DTT results. Subsequent analysis of these samples may suggest that further augmentation of the DTT protocol is needed for correlation to beachside results. It is possible that longer- term exposure results (*e.g.*, 5 years) may reveal different field results than the 18 month results presented here. It will be interesting to re-examine the field ranking and correlation between the laboratory results and field data at this time mark.

The impedance spectra collected at 24 hour intervals resulted in a significant lack of reproducibility with regards to the number of time constants. However, the low frequency impedance magnitude which is representative of the polarization resistance of the bared defect area showed systematic variations as illustrated in Figure 7. Most coatings displayed an increase in the impedance magnitude over time, whereas only a few were characterized by a decrease in the impedance magnitude. The percentage change in the impedance observed at day 0 and day 7 was plotted against the ASTM corrosion ranking and reported in Figure 7. The lack of correlation was expected because it was understood that for coating systems that contained sacrificial pigments, the impedance magnitude would depend on the corrosion rate of the sacrificial material and not be representative of the interfacial region between the coating and substrate.

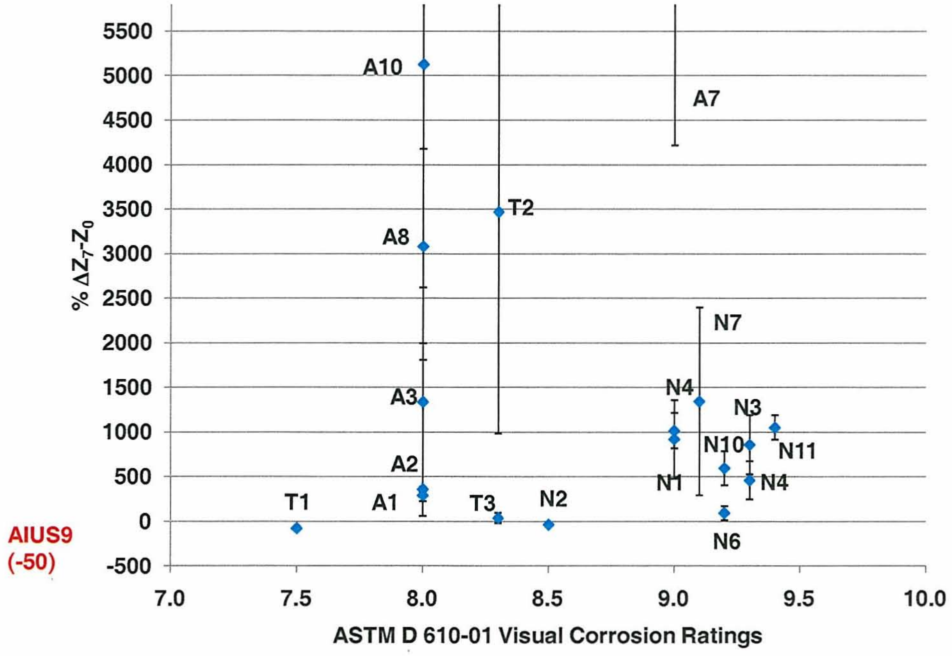


Figure 7. Correlation between the ASTM D 610-01 corrosion ranking at 18 months and the percentage change in the low frequency impedance magnitude from day 0 to day 7.

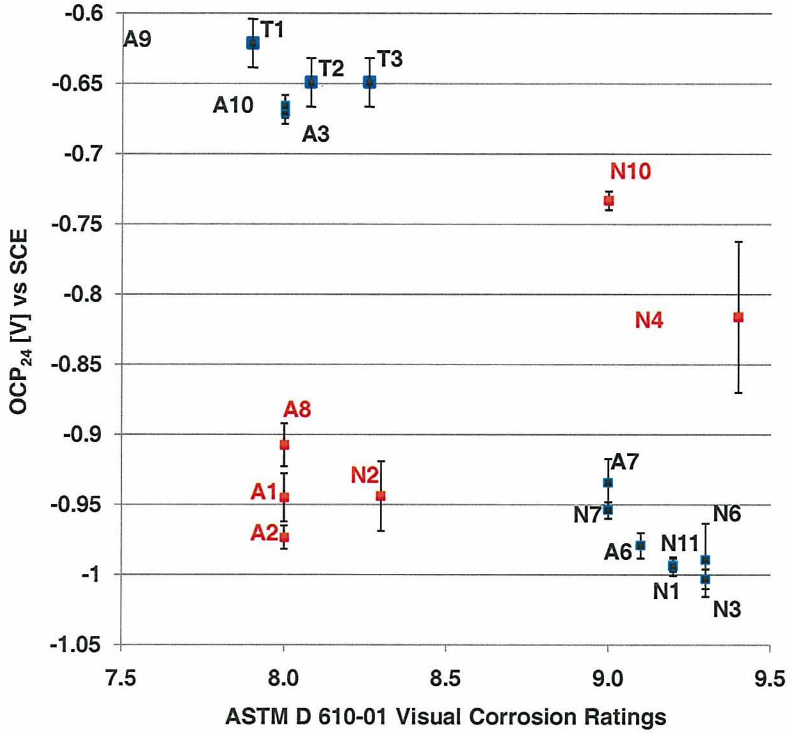


Figure 8. Correlation between the ASTM D 610-01 corrosion ranking at 18 months and the OCP observed 24 hours after the anodic polarization cycles.

It was now apparent from the OCP characteristics that the coating systems contained some level of sacrificial material. Therefore, a second phase of experiments was aimed to consume and quantitatively measure the amount of sacrificial material, and concomitantly cause and measure the amount of anodic undermining.

The samples were subjected to the polarization and testing cycle discussed previously and shown in Figure 3. The first parameter extracted from the polarization cycles was the steady state OCP values after 24 hours (OCP_{24}). The correlation between the ASTM corrosion ranking and the OCP_{24} is shown in Figure 8, note that the sample A9 is out of scale on the x axis because it received a rating of 1. It was observed that 68% of the coatings systems obeyed an inverse relationship between the OCP_{24} and the ASTM ranking. This relationship was expected because the more anodic the steady state potential after the anodic polarization, the easier the consumption of the sacrificial inhibitors and therefore, the faster the field degradation. A similar trend was obtained when the percentage change in the interfacial capacitance was plotted versus the ASTM ranking as shown in Figure 9. The anodic polarization was thought to cause anodic undermining which in turn would result in increasing values of the interfacial capacitance.

Therefore, an increase in the interfacial capacitance was anticipated to correlate with lower ASTM ranking.

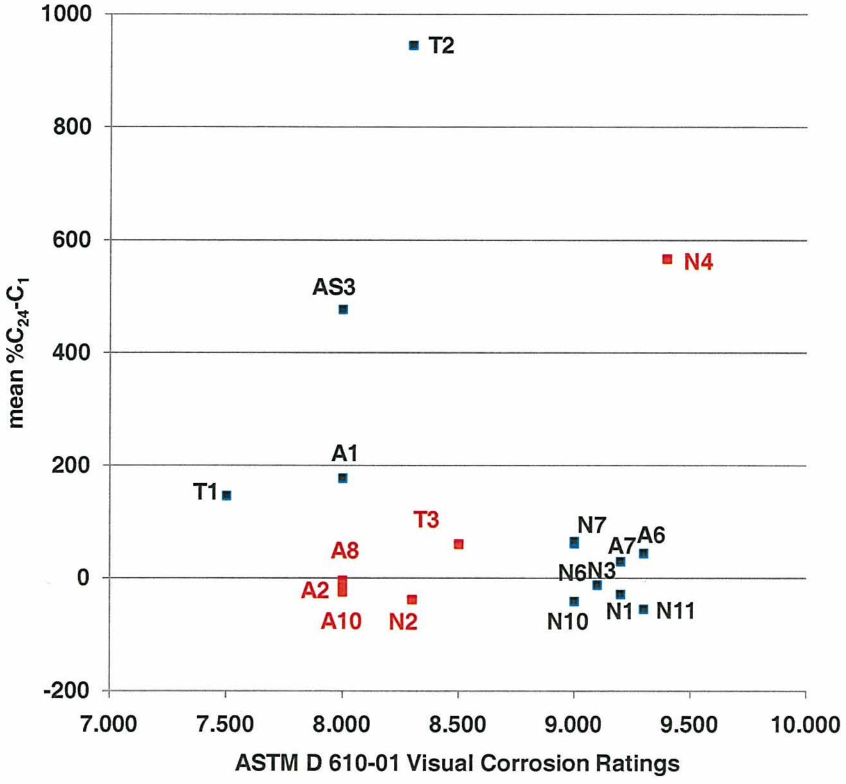


Figure 9. Correlation between the ASTM D 610-01 corrosion ranking at 18 months and the percentage capacitance change caused by the anodic polarization

Another parameter that was examined for these systems was the charge passed during each potentiostatic polarization. As illustrated in Figure 10, for some coating systems the charge decreased exponentially as a function of increasing polarization time; for other coatings, the charge increased over the polarization time. Finally, there were a few coating systems that showed both behaviors with consequently large variability in the charge values. The percentage change in the charge values were plotted as a function of the ASTM corrosion ranking and the results are shown in Figure 11. As with the initial OCP comparisons, it was found that that for 79% of the coating systems a decrease in the charge corresponded to a ranking of 9 or above, while an increase in the charge values correlated with a ranking lower than 9. These authors believe that the charge delivered at -0.5 V_{SCE} polarization was a very informative parameter. A decrease in the charge could be due to the presence of enough oxide material (*e.g.*, ZnO) to prevent further oxidation of both the sacrificial pigment and the iron substrate. On the other hand, the charge was expected to increase for those coating systems where the oxides formed did not slow down the corrosion process.

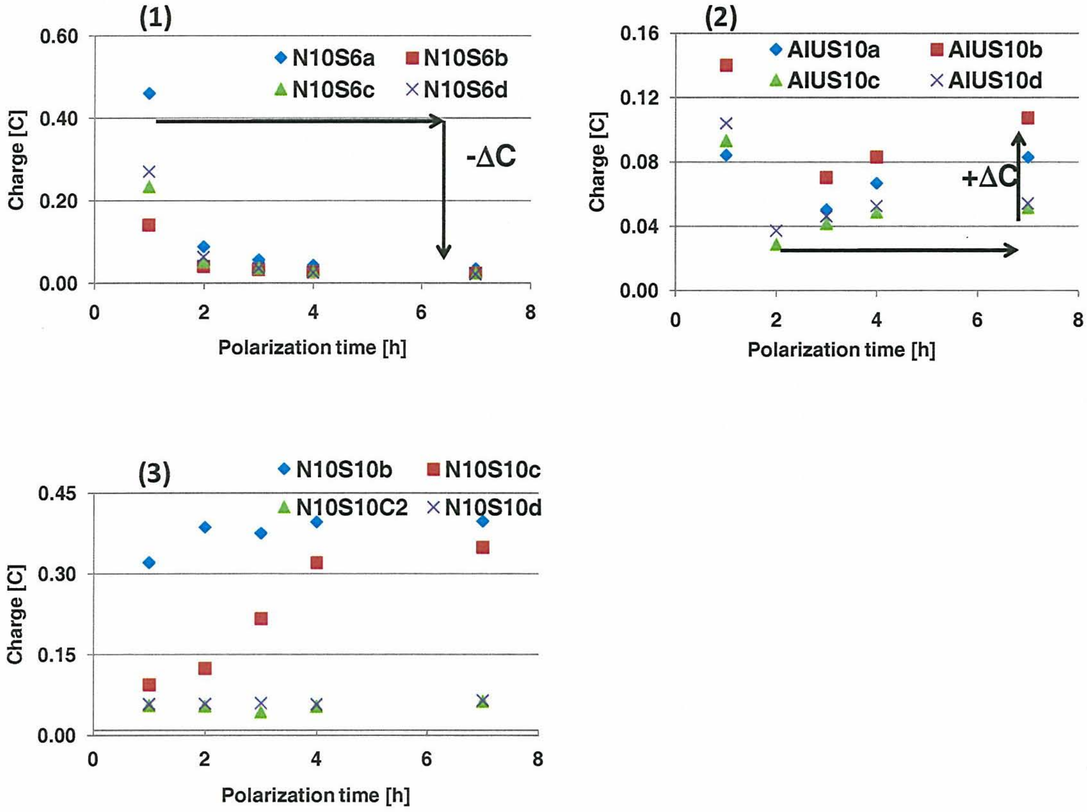


Figure 10. Variation of the charge measured during potentiostatic anodic polarization at -0.5 V.

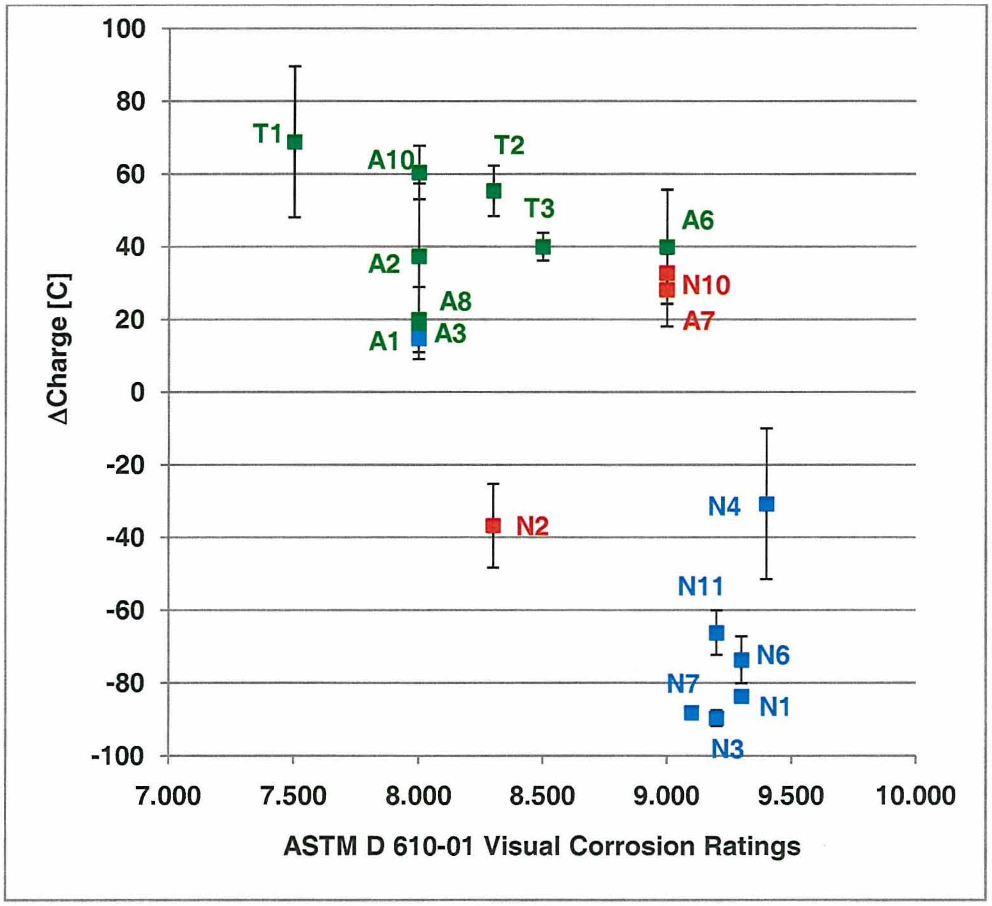


Figure 11. Correlation between the ASTM D 610-01 corrosion ranking at 18 months and difference between the charge observed after 1 hours of anodic potentiostatic polarization and 7 hours.

SUMMARY AND CONCLUSIONS

This study reinforces the importance of the interfacial stability in determining the corrosion protection properties of a coating system. 19 different coating systems on steel substrates were investigated through both electrochemical testing methods and conventional beachside atmospheric exposure tests. In a blind study, short-term (4-7 days) electrochemical characteristics of coatings with a through-film defect showed a high correlation (79%) to 18-month beachside exposure results. It was determined that:

1) 79 % correlation existed between the ASTM 610-01 visual corrosion ranking after 18 months of beachside exposure and the change in OCP observed over 4 days of immersion time in 0.5 M NaCl following the introduction of a through-film defect.
2) 78% correlation existed between the ASTM 610-01 visual corrosion ranking and the change in charge measured during 7 hours of anodic potentiostatic polarization.
3) 68% correlation existed between the ASTM 610-01 visual corrosion ranking and the steady state OCP observed after a total anodic potentiostatic polarization time of 7 hours.
4) 67% correlation existed between the ASTM 610-01 visual corrosion ranking and a negative or close to zero percentage capacitance increase observed after a total anodic potentiostatic polarization time of 7 hours.

In this study, the corrosion protection mechanism of the Zn-filled coating systems on steel substrates required modification of the original DTT testing scheme developed for inhibited coating systems on aerospace aluminum alloys.

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