

Timescale Correlation between Marine Atmospheric Exposure and Accelerated Corrosion Testing

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ABSTRACT

Evaluation of metal-based structures has long relied on atmospheric exposure test sites to determine corrosion resistance in marine environments. Traditional accelerated corrosion testing relies on mimicking the exposure conditions, often incorporating salt spray and ultraviolet (UV) radiation, and exposing the metal to continuous or cyclic conditions of the corrosive environment. Their success for correlation to atmospheric exposure is often a concern when determining the timescale to which the accelerated tests can be related. Accelerated laboratory testing, which often focuses on the electrochemical reactions that occur during corrosion conditions, has yet to be universally accepted as a useful tool in predicting the long term service life of a metal despite its ability to rapidly induce corrosion. Although visual and mass loss methods of evaluating corrosion are the standard and their use is imperative, a method that correlates timescales from atmospheric exposure to accelerated testing would be very valuable. This work uses surface chemistry to interpret the chemical changes occurring on low carbon steel during atmospheric and accelerated corrosion conditions with the objective of finding a correlation between its accelerated and long-term corrosion performance. The current results of correlating data from marine atmospheric exposure conditions at the Kennedy Space Center beachside corrosion test site, alternating seawater spray, and immersion in typical electrochemical laboratory conditions, will be presented.

Key words: atmospheric exposure, accelerated corrosion testing, alternating seawater spray, marine, correlation, seawater, carbon steel, long-term corrosion performance prediction, X-ray photoelectron spectroscopy.

INTRODUCTION

Lifetime prediction of metal-based structures has historically been based on performance at atmospheric exposure corrosion test sites. This real-time corrosion environment exposure requires a long time, often 3-5 years at a minimum, and usually relies on visual and weight loss methods to quantify the degree of corrosion of a particular metal in a specific environment. These methods are common and necessary. There is no question that the development of an accelerated method that successfully correlates results from accelerated corrosion tests to those obtained from atmospheric exposure would be very valuable.¹⁻⁴ It is also generally agreed that the development of degradation models, accelerated test methods, and other atmospheric correlations to real-time atmospheric exposure is a great challenge.¹⁻¹¹ To date, no accelerated method has been successful in correlating atmospheric exposure data to be considered satisfactory for universal use. In fact, at this time, a solution to that challenge is nearly inconceivable due to all the different parameters that must be considered.

The variables involved in predicting atmospheric corrosion in any specific environment, such as temperature, pollutants, and moisture, dictate that accelerated corrosion techniques must be tailored for each end-use environment.^{1,4,6,12-15} This paper provides a review of various challenges associated with correlating results obtained from accelerated corrosion techniques to those from atmospheric corrosion, primarily for steels in marine environments. A historical review of past work involving the most common accelerated corrosion test methods will be provided, along with past work in characterizing marine-induced iron corrosion products. This review was a necessary step in the development of an accelerated corrosion testing protocol for use in the unique environment at the Kennedy Space Center in Florida. Environmental variables within different corrosion environments have been studied by others^{12,14,16-18}; however, the unique natural environment at the Kennedy Space Center, which includes sea-salt, moisture, and intermittent rocket exhaust, has yet to be fully understood. The manner in which spaceport structures degrade is known to a degree, but degradation must be more completely understood in order to develop methods to predict them.

This objective of this paper is to determine correlations between accelerated and long-term corrosion at the Kennedy Space Center's Beachside Atmospheric Corrosion Test Site. The Kennedy Space Center is known to be one of the most corrosive places in North America¹⁹ and characterization of this site is imperative for accelerated corrosion correlations. Environmental factors including monthly chloride and sulfur dioxide concentration and wave height have been chosen to characterize this site. Corrosion rates for 1010 steel (UNS 10100) have been monitored for each corrosion environment to determine general correlations. The initial corrosion product formation is hypothesized to play a large part in determining correlation discrepancies. Both visual and surface chemistry (X-ray Photoelectron spectroscopy) methods were used to explain initial corrosion product formation.

BACKGROUND

Atmospheric challenges

Atmospheric corrosion of any metal should be studied in an environment that is the same as or as close as possible to the end-use environment.^{1,7,8,20,21} The authors in one study tried to predict the corrosion damage of metals in the atmosphere from meteorological and pollution parameters by establishing universal damage functions from 76 different references.⁶ The model was oversimplified and reinforced the fact that corrosion prediction is test-site specific. Measured corrosion rates are known to vary widely from location to location, and also vary based on the initial atmospheric exposure conditions.^{7,8,20-25} One challenge to understand atmospheric corrosion is that the initial environmental conditions, often seasonal, dictate the degree of initial corrosion product formation^{8,26} and thereby influence the specimen corrosion rate during the entire test time period. Lloyd et al.²⁴ planned to determine the seasonal influences of corrosion of steel by determining how the time of year chosen to start an exposure influenced the average corrosion rate. They could not make a satisfactory correlation, and

instead found that specific environmental events played a dominant role in the corrosion behavior of steel. Because the exposure site was inland, the events corresponded to large storms where pollutants, such as chloride, were more likely to be carried inland and deposited on the steel panels.

The review of studies throughout the past century has made it clear that many different variables affect the initial and subsequent atmospheric corrosion of a metal. These variables are primarily considered to be salt deposition, which can be affected by wind speed, wind duration, and distance from the salt source, sulfur dioxide and other pollutant deposition, time and type of wetness, environment temperature, sample temperature, and ultraviolet (UV) radiation exposure. Many studies have singled out one or only a few atmospheric environmental variables to understand how they impact corrosion. For example, Fitzgerald et al.¹⁷ reported the composition of marine air and its physico-chemical properties. Morcillo et al.¹⁸ studied the influence of winds on the salinity values of marine aerosols and found that salt deposition depends on velocity and time of winds. Morales et al.¹⁴ used thirty-five different atmospheric exposure corrosion test sites at the Canary Islands to correlate corrosion and found that salinity depends on the wind patterns at each site. They also concluded that corrosion prediction models cannot be transferred to different regions; meaning that corrosion studies must be established for each region rather than try to fit the corrosion behavior of one region into a model that was originally based on experimental data from a completely different region. Meira et al.¹⁶ tried to use previous data from seven different studies to model sea-salt transport and deposition; however, they concluded that the marine atmosphere was difficult to model and described it as "a complex phenomenon that conceals a significant number of influencing variables". Feliu et al.¹² modeled marine atmospheric corrosion based on the effect of sea distance on chloride deposition. They recognized that empirical models, based on experimental data, cannot be applied to other geographical locations, and that marine aerosol, influenced most by wave movement, is also influenced by wind speeds, surf action, averaged land and sea temperatures, latitude, coastline ruggedness, and undulations of the land surface, which in turn determine particle size and mass of salt and droplet. The model was ultimately deemed too simple to make generalizations about the effect of sea distance on sea-salt deposition.

A series of studies by Corvo et al.^{7,21-23} looked at water adsorption and salt content in atmospheric corrosion products of steel, how rainfall rates affect the corrosion rate of chloride-induced corrosion, and how to account for tropical climates when measuring time of wetness (TOW) according to ISO^a 9223²⁷. The first two studies revealed that chloride concentration in the atmosphere differed from chloride concentration on a test specimen. The specimen chloride concentration was directly related to the rain regime, such that more rain (rinsing) decreased the amount of chlorides available to take part in corrosion reactions. The last study used two atmospheric test stations located in Havana, Cuba and Medellin, Colombia to review the accuracy of using ISO 9223 to determine TOW. This is important when trying to use TOW as a correlation factor. Currently, ISO 9223 states that a surface is considered "wet" when the relative humidity (RH) is above 80% and the atmospheric temperature (T^a) is greater than 0°C.²⁷ In the climates studied, the RH is often over 80% and temperature is always greater than 0°C. When the dew point was lower than the temperature, the surfaces remained dry even at high humidity; therefore ISO standards would dictate that surfaces are considered wet when they are not.

Accelerated Corrosion Methods

Researchers have used accelerated corrosion techniques to simulate atmospheric corrosion environments for at least the past 60 years. A 1993 literature survey² reviewed the development of accelerated laboratory test methods for simulation of atmospheric corrosion. The author determined that developing a model to understand atmospheric corrosion was challenging in itself, since precise modeling of all the environmental variables was difficult. Correlations between the accelerated and atmospheric tests that they reviewed were considered poor due to the fact that, upon examination, less than 40 percent of variance was explained and errors could be estimated up to 50-70 percent of actual

^a Geneve, Switzerland

corrosion results.² Common problems they encountered when comparing their own results from accelerated corrosion testing to atmospheric testing centered around several key points: 1) simulated cycles produced heavy rusting on the cut edges, and this did not occur in the natural environment, 2) edge blistering followed by flaking occurred on the naturally exposed specimens and not the accelerated testing, and 3) the rank order of the accelerated tests was not always the same as for the atmospheric exposure tests. These discrepancies are common to many studies that try to correlate accelerated and atmospheric test results. The underlying problem is that the initial corrosion product formation differs between the techniques. If the manner in which the corrosion products form on the substrate is markedly different between the tests types, then trying to correlate parameters such as corrosion rate becomes subjective, and the ability to determine timescale correlations is subjective as well.

This paper focuses on the most common methods of accelerated testing used in practice, namely mimicking the atmospheric environment by using frequent cyclic wet-dry conditions, salt spray chamber, and laboratory electrochemical methods. Several studies are highlighted to give historical insight into the challenges of these techniques. In one study, the frequency and length of wet-dry cyclic conditions had a significant effect on the type of corrosion products formed on a substrate surface, specifically for low-alloyed and unalloyed steels.⁸ When wetting at more frequent cycles, the corrosion products formed evenly across the steel. When the wetting cycles occurred in longer wet-dry periods, the corrosion rate increased, and corrosion products formed unevenly across the steel surfaces to ultimately form localized corrosion and areas of high volume, and often cracked, corrosion. In another study²⁸ the authors tried to mimic marine atmospheric conditions at an atmospheric urban site by spraying a sodium chloride (NaCl) solution once a day onto exposure panels; however, the corrosion rate results for the sprayed panels were much higher than for the natural marine environment. In this same study, accelerated laboratory tests were performed to simulate cyclic wet-dry atmospheric marine conditions, in which electrochemical impedance and corrosion potential measurements were made during the wetting conditions. The authors were able to correlate, to their satisfaction, the atmospheric results to the corrosion rates calculated from the electrochemical methods, but timescale prediction modeling was not possible. A study by Corvo et al. exposed specimens to natural atmospheric conditions in Havana, Cuba in addition to specimens in the same conditions with an intermittent salt spray step (3 percent NaCl solution). The corrosion rates, in units of mass loss (g/m^2), were 9, 15, and 21 times higher for the salt spray specimens when measured sequentially for 1, 3, and 6 months.²¹ However, no timescale correlation was developed.

Another study²⁹ mimicked the atmospheric exposure of a marine environment in Japan in a test chamber by first measuring the relative humidity and temperature of the atmosphere and adjusting the chamber to similar conditions. The test chamber had a spray nozzle that deposited sea-salt at varying concentrations, and the RH and chamber temperature were constant. The study's results showed that the carbon steel panels exposed to the atmosphere had initially corroded more aggressively than the panels in the chamber. Further investigation found that the panels exposed to the natural atmosphere had additional moisture from condensation of dew because the temperature of the metal was lower than the dew point during the nighttime conditions. When this parameter was included in the chamber testing, the correlation greatly improved such that the corrosion rates for the two exposure conditions, atmospheric and chamber, were less than 10% different. This study showed that dew condensation highly influenced corrosion. Salt deposits were not rinsed away during these moisture events, but instead reactivated existing corrosion cells.

A well-known and often used salt spray method, ASTM^b B117,³¹ has been used to qualify many metals and paints, despite the fact that no satisfactory correlation to atmospheric timescales has been made. The ASTM B117 standard has been criticized as not representing or correlating with actual atmospheric environments.^{1,30} A recent review by Frankel¹ pointed out that even the introduction section of the B117 standard explains its shortcomings: "Prediction of performance in natural environments has seldom

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been correlated with salt spray results when used as standalone data. Correlation and extrapolation of corrosion performance based on exposure to the test environment provided by this practice are not always predictable. Correlation and extrapolation should be considered only in cases where appropriate corroborating long-term atmospheric exposures have been conducted." Nonetheless, the standard is widely used to qualify materials because it is a method that is fairly reproducible and constant when so many variables for natural atmospheric environments are not. A modified version of ASTM B117 was established to account for the shortcomings, ASTM G85-85 A2,³⁰ but this chamber environment only mimics a limited number of atmospheric conditions. Accelerated corrosion methods, such as ASTM B117³¹, ASTM D5894, ASTM G85-A5³⁰, SAE J2334, and GM 9540P, have been used in comparison to natural atmospheric marine environments in Hawaii(Sugamoto) and at the Kennedy Space Center(Matzorf and Miller). In these studies a qualitative prediction of corrosion performance as a function of accelerated test cycles was possible for some alloy types and not others. A five year study of coatings on aluminum alloys using ASTM B117, GM 9540P, and ASTM G85-A5 versus exposure at KSC's Beachside Atmospheric Corrosion Test Site concluded that no single accelerated method could be chosen to select the best performing coating for all four alloys tested; however the combination of accelerated methods did improve correlation factors.(Matzdorf)

Electrochemical methods have been used in conjunction with and as simulations for marine conditions. Azzeri³⁸ measured the polarization resistance and mass loss of plain carbon and low alloy steels in natural seawater during four years of immersion to mock the immersion of steel in shallow seawater. The corrosion rates calculated from polarization resistance matched those calculated from the mass loss method, thereby making the electrochemical method valid for predicting corrosion rates in un-accelerated conditions. McCafferty⁹ used Tafel extrapolation to show that laboratory tests and actual exposure rates are "reasonable"; however, he recognized the limitations that short-term laboratory experiments in simulated environments have in predicting atmospheric corrosion rates in natural environments. Tafel extrapolation was applied to various metals and environments, including comparing a 24-hour immersion of iron in 3.5-percent NaCl solution to the longer term behavior of plain carbon steel (AISI 1020 steel) in seawater. Tafel extrapolation, although hindered by a limiting diffusion current from oxygen reduction for the cathodic polarization curve, was possible for the author because both branches could be extrapolated back to the open circuit potential and could give the corrosion rate. The resulting corrosion rate for the laboratory experiments, 0.30 mm/y, could be compared to the atmospheric corrosion rate of 0.38 mm/y in the first year of exposure, but not compared to the corrosion rate of 0.13 mm/y after 1000 days. These logical attempts to experimentally determine corrosion rates in marine environments, did not obtain the anticipated correlation data to real world atmospheric corrosion.

A study by Drazic and Vascic¹⁵ aimed to correlate results from two accelerated corrosion conditions (laboratory immersion in aerated 3-percent NaCl solution and exposure in a salt spray chamber), to mass loss results of a five-year-long atmospheric exposure at the Adriatic coast in Yugoslavia. Both mass loss and electrochemical methods were used to measure the corrosion rate during the accelerated corrosion methods. For the accelerated corrosion conditions, corrosion rates determined by the two methods, electrochemical and mass loss, were similar to each other; showing that the electrochemical method, Tafel fitting via anodic polarization, was a precise predictor of the corrosion rate via mass loss in the same corrosion environment. When the corrosion rates for the three corrosion conditions (atmospheric, laboratory immersion, and salt-spray chamber) were compared to each other, their values were not at all comparable. The authors correlated the corrosion rates by using a factor, n , that represented how many times higher the salt spray and immersion conditions made the corrosion rate when compared to the atmospheric exposure conditions. The resulting correlation was too general and ineffective in relating the accelerated corrosion techniques to an atmospheric corrosion timescale.

In 2008 Frankel¹ gave an extensive review of the use and limitations of electrochemical techniques for assessing corrosion, including atmospheric exposure conditions. In this review, a statement was made of the fact that electrochemical methods provide an accurate measure of the instantaneous corrosion rate for the corrosion conditions while weight loss measurements generate an average corrosion rate of

a sample surface for the entire measurement period. Therefore, when using electrochemical methods for atmospheric corrosion, it is important to understand what the measurements can and cannot provide. Frankel reviewed the different electrochemical methods used to study atmospheric corrosion, as well as the Kelvin probe and coplanar reference electrodes, but ultimately concluded that "at present there is no good electrochemical technique for electrochemical testing of samples exposed in atmosphere. Electrochemical methods for samples in corrosive atmospheres are difficult due to the thin layer electrolyte...Furthermore, it is becoming evident that complex atmospheric chemistry can influence the local environment for a sample exposed outdoors in ways that are not simulated in lab exposure tests...The understanding of the atmospheric chemistry is still evolving and the influence of the environment on corrosion and the electrochemistry of this phenomenon are totally unknown."¹ Natural electrolytes formed on a metal during atmospheric corrosion are so thin and dynamic (they diminish continuously during evaporation) that the conditions are difficult to duplicate in the laboratory. The reactions occurring at the metal and electrolyte interface from time of initial wetting to evaporation change relative to other variables, such as oxygen supply, salt and pollutant deposition, and type of wetting (rain will rinse away pollutants, mist will deposit more pollutants, and dew will reactivate current surface pollutants).

Efforts to directly measure the electrical properties of corrosion test panels during atmospheric exposure have been developed for some time. In the 1970s and 1980s, Mansfeld³⁹⁻⁴¹ developed a method to electrochemically monitor atmospheric corrosion by measuring changes in current or potential as a function of exposure time. In one study,⁴¹ weight loss data was correlated to the electrochemical monitoring method; however, the electrochemical data did not correlate directly to mass loss information. Instead, the electrochemical data correlated to wetness events during atmospheric exposure, and was really the development of an accurate time of wetness sensor. More recently, electrical resistance sensors have been used²⁵ to study corrosion products formed during initial atmospheric exposure because of their ability to directly measure mass loss. This method relied on sensing changes in the resistivity of the metal as corrosion product formed on the metal surface. Due to the nature of their construction, the sensors would not be suitable for long-term exposure studies in aggressive marine environments.

Corrosion Product Formation during Atmospheric Exposure

Because many studies^{3,10,11,15,42} have noted differences between initial and longer-term atmospheric corrosion, in terms of both corrosion rates and corrosion product formation, researchers have used electrochemical and surface-specific analytical techniques to study the mechanisms of corrosion product formation. In the past, electrochemical methods were not commonly used for monitoring atmospheric corrosion, largely due to difficulties involving the thin film of electrolytes that form on the substrate surface. While iron corrosion is understood in laboratory simulations in the simplest of real environments, it is known that the chemical processes involved in the atmospheric corrosion of iron remain poorly understood.⁴³ Graedel compiled a list of twenty different iron-containing minerals relevant to the corrosion of iron⁴³ to illustrate the complexity of iron corrosion products formed in the atmosphere. A study by Cox and Lyon⁴⁴ reviewed early work, from the 1960s to 1990s, that used electrochemical and surface chemistry-based methods to determine corrosion mechanisms that occur during atmospheric exposure. In general, the studies focused on understanding what corrosion reactions occurred on the surface of iron and steel substrates through electrochemical methods,⁴⁵⁻⁴⁸ including scanning Kelvin probe methods,⁴⁹⁻⁵² and chemical analysis techniques such as X-ray diffraction (XRD)^{53,54} and Mossbauer spectroscopy.⁵⁵ More recently, it has become common to incorporate surface chemistry techniques into corrosion studies. Corrosion products formed by atmospheric corrosion, especially in marine environments, have been identified by many authors using surface-specific techniques, including XRD,^{4,11,56-58} SEM,^{11,42,58} Raman and Fourier-Transformed Infrared Spectroscopy (FT-IR)^{3,10,58-64}, XPS⁵², Mossbauer spectroscopy⁵⁷, Transmission Electron Microscopy (TEM),⁶³ and recently by soft X-ray transmission spectromicroscopy.²⁶ In general, the following observations have been made: 1) Chloride ions at marine areas are incorporated into initial corrosion products, but are not retained over time. This depletion occurs because the concentration of

ferrous or ferric chloride in the rust decreases unless a fresh supply of chloride ions to anodic sites is maintained. The thick layer of rust blocks the exposure to chloride ions over time, thus reducing the corrosion rate over long exposure periods, 2) hygroscopic magnesium chloride in sea-salt or mist enables corrosion to take place at a much lower relative humidity than if only NaCl is present, and 3) the initial corrosion products that form a layer between the metal and the environment greatly affect the subsequent longer term corrosion of the metal.

Challenges at NASA Kennedy Space Center

NASA Kennedy Space Center's (KSC) beachside corrosion test site has been documented as the most corrosive place known in the United States.¹⁹ Figure 1 displays the location of KSC and the beachside test site along Florida's Atlantic coast. The environmental challenges at KSC are both natural and man-made. The already higher-than-typical aggressive marine conditions are intermittently enhanced by the emission of 70 tons of hydrochloric acid into the atmosphere during launches using solid rocket fuel. Correlating corrosion rates from accelerated corrosion methods and real-time beachside atmospheric exposure at KSC is challenged largely by marine effects such as the type and time of wetness and chloride deposition. Despite the corrosive environment, launch structures are largely made using structural steel, namely AISI 1010 (UNS G1010), and different coatings, such as sacrificial coatings and paints, are used to slow corrosion. Current coating qualifications at KSC depend largely on a material's performance during atmospheric corrosion conditions for 18 months and ultimately a 5-year-period.⁶⁴ This testing, while necessary, is very time consuming when qualifying new materials. A testing protocol is needed to accelerate the material qualification time. Understanding correlations between accelerated corrosion and atmospheric corrosion timescales for KSC-specific environmental conditions is a logical step.

EXPERIMENTAL PROCEDURE

Test Plan Summary

Topics addressed in this study of corrosion conditions at KSC include:

- 1) Determining the degree of correlation between the corrosion test methods and, perhaps more importantly, the reasons why the different methods may not correlate.
- 2) Understanding the initial corrosion product conditions and composition thereof, especially for variations between the initial corrosion products formed during the different accelerated corrosion conditions.
- 3) Determining general seasonal-based changes in corrosion product formation for the methods exposed to atmospheric conditions.

This paper is based on work that is currently ongoing. Visual and surface analysis methods are being used to relate the different corrosion techniques by examining when similar corrosion products, and thereby mechanisms, are occurring on the metal surface. The predominant environmental factors, such as chloride and sulfur dioxide concentration and wave height, are also being monitored during atmospheric exposure.

Table 1 displays the techniques that are being used in the current test plan. The experimental techniques are described below.

**Table 1
Experimental Test Plan Summary**

Purpose	Corrosion Conditions	Analytical Techniques
Corrosion rate correlation	AE ¹ , ASST ² , B117 ³ ,	Corrosion rate by weight loss methods, chloride concentration

Initial corrosion product formation	AE ¹ , ASST ² , B117 ³ ,	XPS, photo-microscopy
Seasonal effects on corrosion rate	AE ¹ , ASST ²	XPS, microscopy, chloride and sulfur dioxide concentration, corrosion rate by weight loss method, wave height

¹ Atmospheric Exposure

² Alternating Seawater Spray Test

³ ASTM B117 method, used during accelerated salt spray method

Atmospheric Exposure

1010 steel (UNS 10100) panels were placed at 30-degree angles towards the Atlantic Ocean at KSC's beachside corrosion test site for varying exposure periods. The test racks are approximately 100 feet from the high tide line. Figure 1 shows the panel configuration at the test site. The panels were designated into categories corresponding to their method of evaluation: 1) corrosion rate via weight loss method ASTM G1 for a) panels for long-term exposure of one year, b) panels for monthly exposure, and c) panels for monthly successive exposure, and 2) panels that were exposed to initial corrosion conditions and removed for surface chemistry analysis. Time dependent photographs were taken during exposure.



Figure 1: Location of NASA Kennedy Space Center's Beachside Corrosion Test Site along the Atlantic Ocean (left) and panels exposed to the marine atmosphere at KSC (right).

Accelerated Seawater Spray

1010 steel (UNS 10100) panels were placed at 30-degree angles in a seawater spray apparatus, shown in Figure 2, and exposed to atmospheric conditions continuously and sea spray conditions in cycles for 10 minutes per hour. The panels were designated according to their evaluation process: 1) exposed at 180, 90, 60, and 30 day periods and removed for corrosion rate measurements using the weight loss method in ASTM G1 and 2) exposed to initial corrosion conditions and removed for surface chemistry analysis.

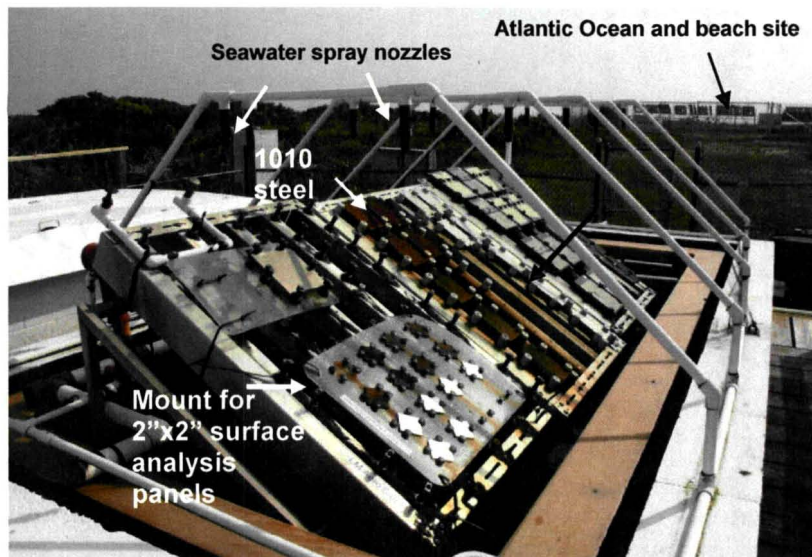


Figure 2: Alternating Seawater Spray apparatus with 1010 steel (UNS 10100) exposure panels, and modification for 1008 panels used in surface analysis.

Neutral Salt Fog Chamber (ASTM B117)

1010 steel (UNS 10100) panels were placed in a neutral salt fog chamber in 5% NaCl, using the ASTM B117³¹ method. The panels were designated according to their evaluation process: 1) exposed at 100, 250, 470, 750, 1000, and 1500 hours and removed for corrosion rate measurements using the weight loss method in ASTM G1 and 2) exposed to initial corrosion conditions and removed for surface chemistry analysis.

Surface Analysis

X-ray photoelectron spectroscopy (XPS), using an Al K-alpha X-ray source (Thermo Scientific^b), was used to determine the types of corrosion products formed on the surface of the panels for the different corrosion conditions. In some cases, depth profiles were measured for typical iron, carbon, oxygen, and chloride peak ranges with an ion energy of 3000eV at rate of 0.37nm/s for 15 seconds per etch.

Optical microscopy was used to evaluate the different topographies of the corrosion products formed on the panels that were exposed to different corrosion conditions.

Atmospheric Conditions

The temperature, relative humidity, and total precipitation values are recorded at the beachside atmospheric test site continuously. The precipitation values are measured as a total amount collected every 20 minutes and the temperature and relative humidity are measured every twenty minutes.

Chloride deposition at the atmospheric test site is being monitored continuously during the exposure period using the wet candle method.⁶⁵ Two replicates of each set are exposed for a one-month period before replacement. The two different sets are exposed in staggered time periods that are two weeks apart. Chloride concentration is measured using a chloride ion probe. Figure 3 shows the wet candle exposure alongside the beachside panel exposure.

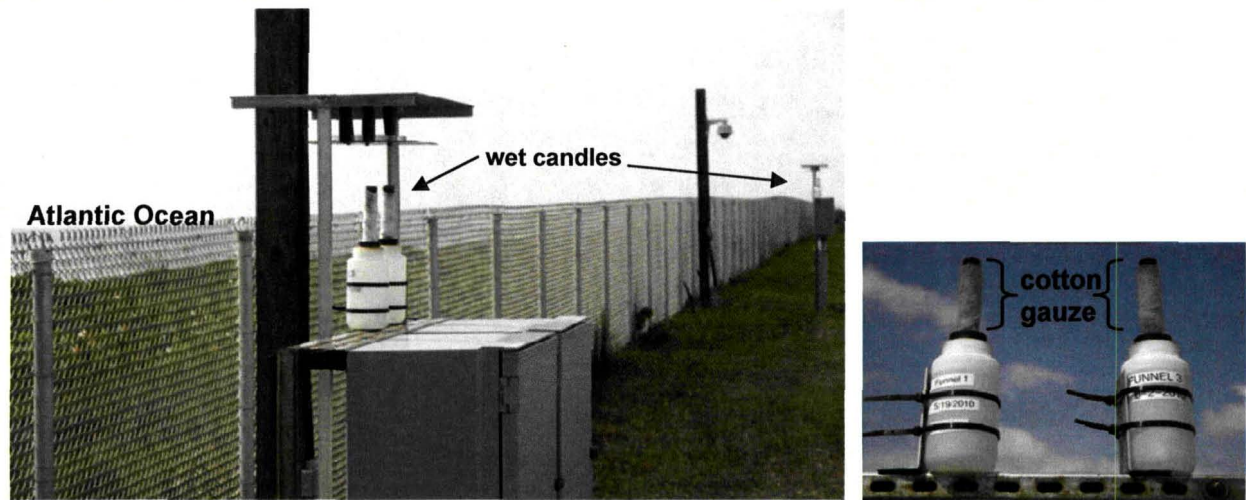


Figure 3: Wet candles exposed to KSC beach site atmospheric conditions and used to measure chloride concentration per month.

Sulfur dioxide concentration was measured through the National Atmospheric Deposition Program (NADP) monitoring location FL99, which is located at the Kennedy Space Center and operated by NASA. The sulfur dioxide deposition data, in kg s/ha-yr, is taken from the NADP database website⁶⁶ and translated into mg/m²-day values.

Wave height measurements were collected from a weather buoy, buoy #41009, off the coast of Cape Canaveral that is funded by NASA and operated by the National Oceanic and Atmospheric Administration's (NOAA) National Data Buoy Center. The wave height data was extracted from the database website.⁶⁷ Figure 4 shows the physical location where the sulfur dioxide concentration, chloride concentration, and wave height values are measured.

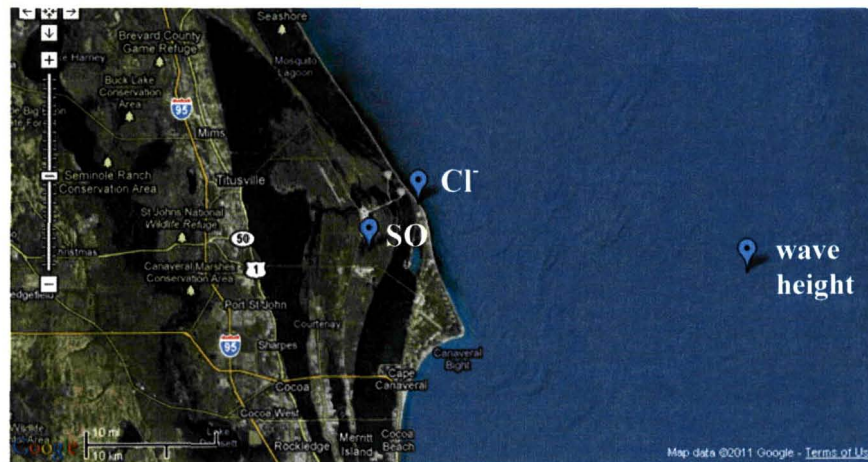


Figure 4: Map of physical locations where the chloride concentration, sulfur dioxide concentration, and wave height values are obtained.

RESULTS AND DISCUSSION

When determining correlations between the different corrosion conditions, atmospheric corrosion, ASST, and salt fog, the long-term atmospheric corrosion environment was first characterized. The

corrosion behavior of the 1010 steel panels in the long term and accelerated environments were then measured using corrosion rate, visual, and XPS methods.

Characterization of Beachside Atmospheric Exposure Site

In order to understand the corrosion conditions of the natural environment at the Kennedy Space Center, various environmental factors such as temperature, relative humidity, precipitation, chloride and sulfur dioxide concentration, and wave height were measured. The average monthly temperature, relative humidity, and precipitation values for April 2010 through April 2011 are shown in Figure 5.

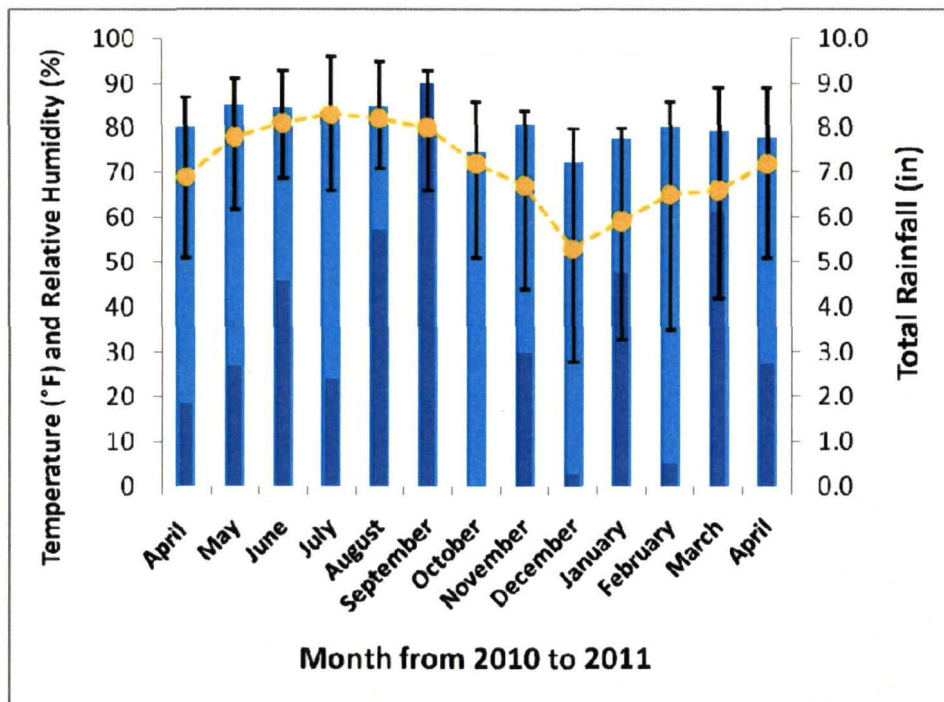


Figure 5. Average temperature (line) with maximum and minimum values, relative humidity (top bar), and precipitation (bottom bar) values from April 2010 to April 2011 recorded at the KSC Beachside Atmospheric Corrosion Test Site.

The chloride concentration, shown in Figure 6, was measured during an exposure period from May 19, 2010 through May 19, 2011. The measurements taken from Funnels 1 and 2, and then from Funnels 3 and 4, show that the salt deposition was consistent between replicates despite that fact that the two funnels were about 500 feet different in latitude from one another. Overall, the chloride deposition at the KSC site is high when rated using criteria from the ISO 9223 standard²³, where the highest level of chloride deposition is related to a deposition rate of between 300 and 1500mg/m²d. The chloride deposition rate at KSC's beachside test site recorded ranges between 150 and 1900mg/m²d, with a mean value of 640mg/m²d.

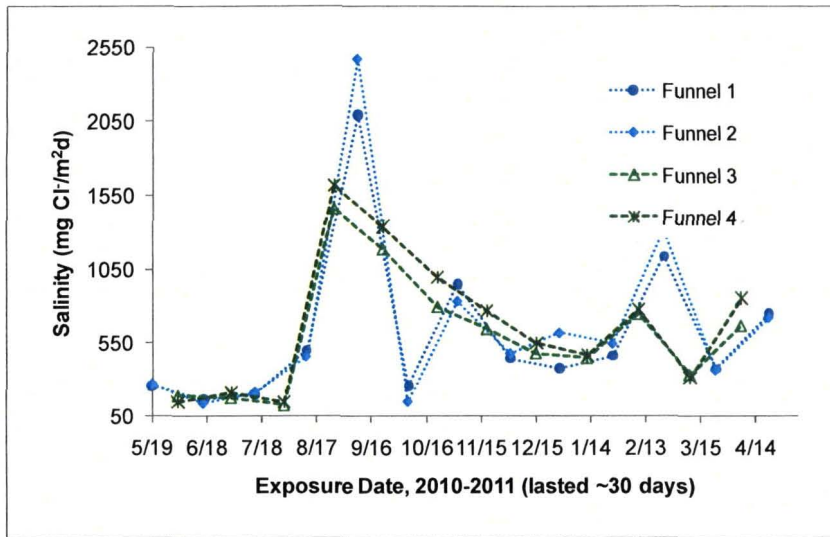


Figure 6: Chloride concentration as a function of exposure period, obtained using wet candles exposed at NASA Kennedy Space Center's Beachside Corrosion Test Site.

The wave height was monitored because of the relationship between wave height and concentration of marine aerosols, where increased wave height is generally related to an increase in chlorides in the air.⁶⁸ Bubbles created from increased wave action are the main generator of marine aerosols^{69,70} and are generally directly related to wave height. The monthly average wave height for ocean water off the coast of Cape Canaveral and approximately twenty-five miles from the wet candle location was compared to the monthly average chloride concentration values to verify the general relationship, shown in Figure 7. The comparison shows that higher wave heights do generally directly relate to increase chloride concentration values, assuming that major weather events or ignored.

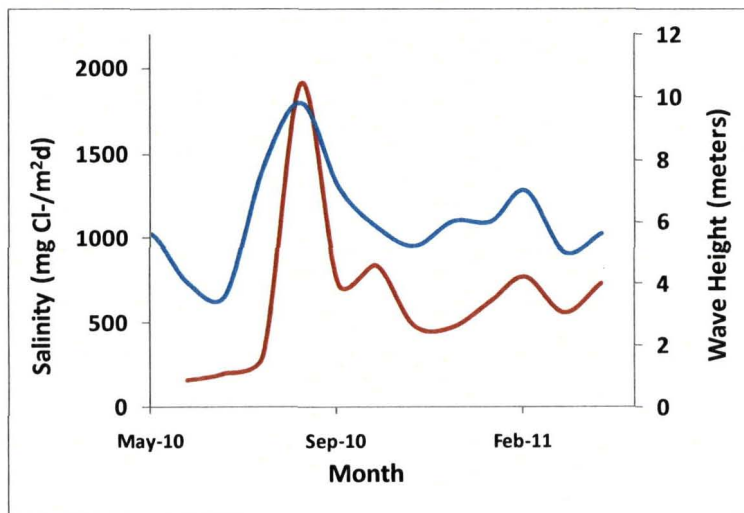


Figure 7: Average monthly chloride concentration (bottom line) and wave height (top line) values.

Sulfur dioxide concentration was found to be very low within the Kennedy Space Center, with yearly totals ranging from 0.92 to 1.81mg/m²-d from 2002 to 2010. A value of less than 4mg/m²-d is ranked as the lowest level in the ISO 9223 standard for pollution by sulfur-containing substances represented by sulfur dioxide.

Obviously characterization of atmospheric conditions also includes other factors such as wind, time of wetness, weather events, and ultraviolet exposure. The paper does not aim to include all the atmospheric factors and uncertainties that exist, but instead to acknowledge them and report on selected atmospheric conditions.

Corrosion Behavior of 1010 Steel at the Beachside Atmospheric Exposure Site

The corrosion rate of 1010 steel panels exposed at KSC's beach site is variable and dependent on seasonal conditions, as shown in Figure 8. From April 1975 through February 1977 panels were exposed each month for one year, and seasonal changes that influence corrosion rate are evident. An average corrosion rate for 1010 steel panels at KSC is thus difficult to define by one value without considering other seasonal characteristics of the exposure site. Although corrosion rates have been monitored yearly since 2004, they are now being monitored again seasonally starting in 2010.

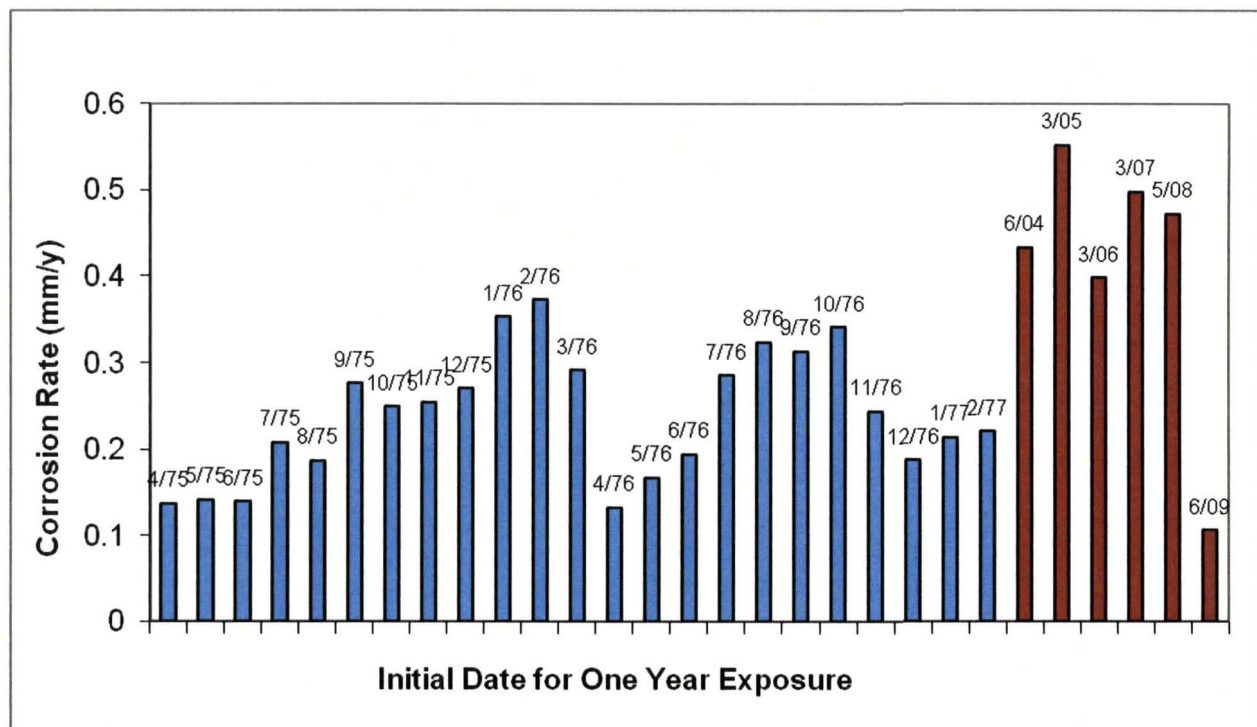


Figure 8: Corrosion rate of 1010 steel panels exposed at the KSC Beachside Atmospheric Test Site for one year. Initial exposure dates are from 4/1975 through 2/1977 and 6/2004 through 6/2009.

Corrosion rates of the 1010 steel panels was measured as a function of both monthly and successive monthly exposure times to understand the seasonal characteristics of corrosion rate at KSC. Thus far the corrosion rates, in mm/y, have remained statistically similar throughout the exposure time period from November 2010 to April 2011. Figure 9 shows the corrosion rate and total mass loss of the 1010 steel panels as a function of exposure time. The panels that were newly exposed each month had a higher overall corrosion rate, but that was not unexpected since corrosion rates tend, in general, to be highest when corrosion products are not blocking corrosion sites (all areas of the metal surface are available for corrosion). Once corrosion formed on the surface the corrosion rate generally decreases, as verified for the successively exposed panels in Figure 9. The amount of mass loss decreased initially after corrosion product formed across the entire panel surface; however, the mass loss did not continue to decrease directly as a function of time. The changes in mass loss as a function of exposure time were likely influenced by seasonal factors as well. At this time it is not possible to fully separate out seasonal and corrosion product influences. The successive corrosion rate monitoring is ongoing and will continue up to one year.

Corrosion rates based on seasonal influences are more prominent for the monthly panels and can be compared to the chloride concentration values recorded monthly, Figure 10. While a longer data set in the future will provide a more definitive comparison, there is a definite direct correlation between the salinity and corrosion rate values thus far. Comparisons were made to monthly corrosion rates and other seasonal characteristics such as temperature and relative humidity. Figure 11 shows that there are direct correlations to relative humidity, corrosion rate, and temperature, where increased moisture (humidity) should provide more time for active corrosion on the steel panel surface. As the temperature increases seasonally and the values of temperature and relative humidity grow closer there are less opportunities for moisture to form on the panel surface due to humidity alone. Time of wetness will not be discussed in this paper, but is a factor currently being addressed.

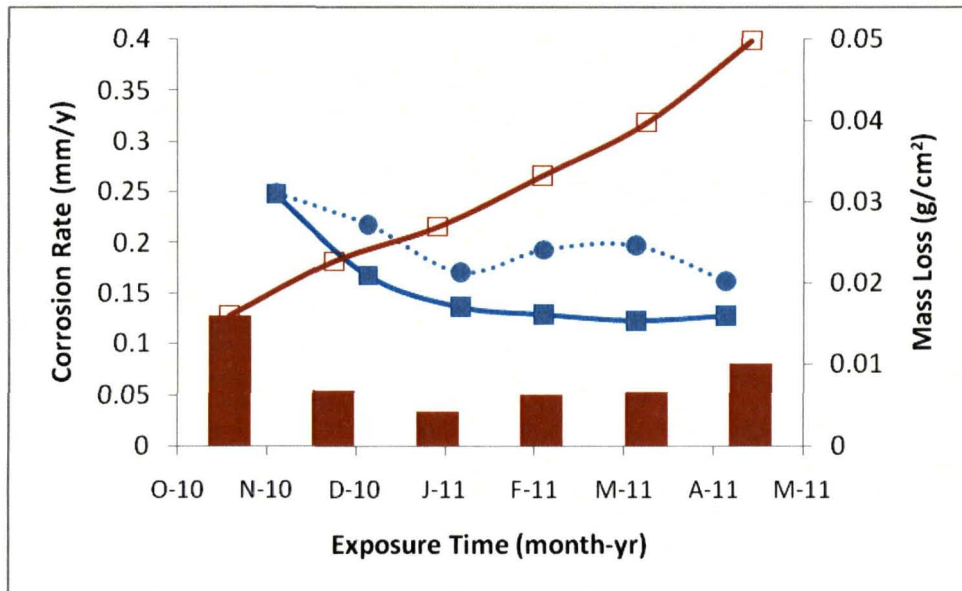


Figure 9: Corrosion rate (solid marker) and mass loss (open marker and bar) values of 1010 steel panels exposed at the KSC Beachside Atmospheric Test Site and exposed and collected monthly (dotted line) and successive monthly (solid line).

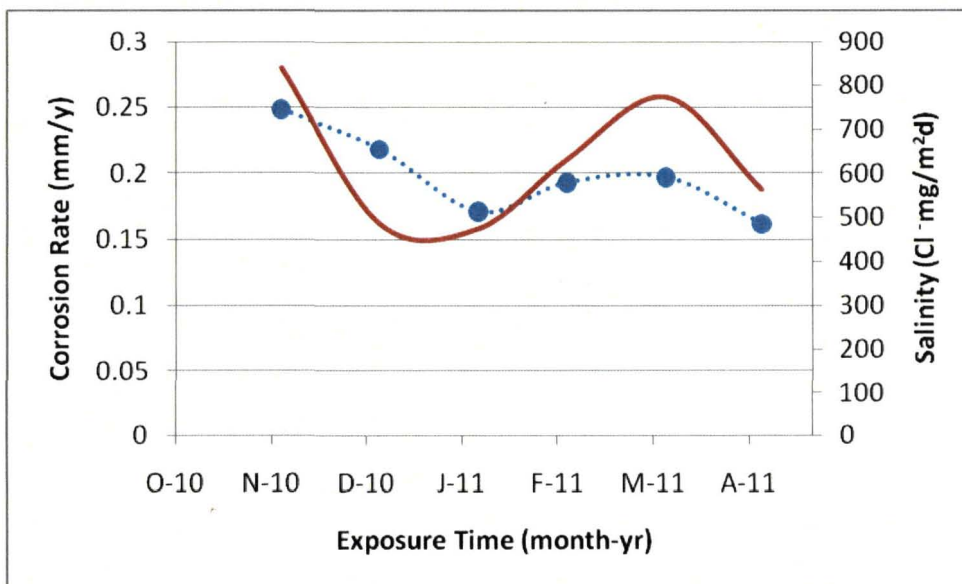


Figure 10: Comparison of corrosion rate (dotted line) and salinity (solid line) values for 1010 steel panels and wet candles exposed at the KSC Beachside Atmospheric Test Site from November 2010 through April 2011.

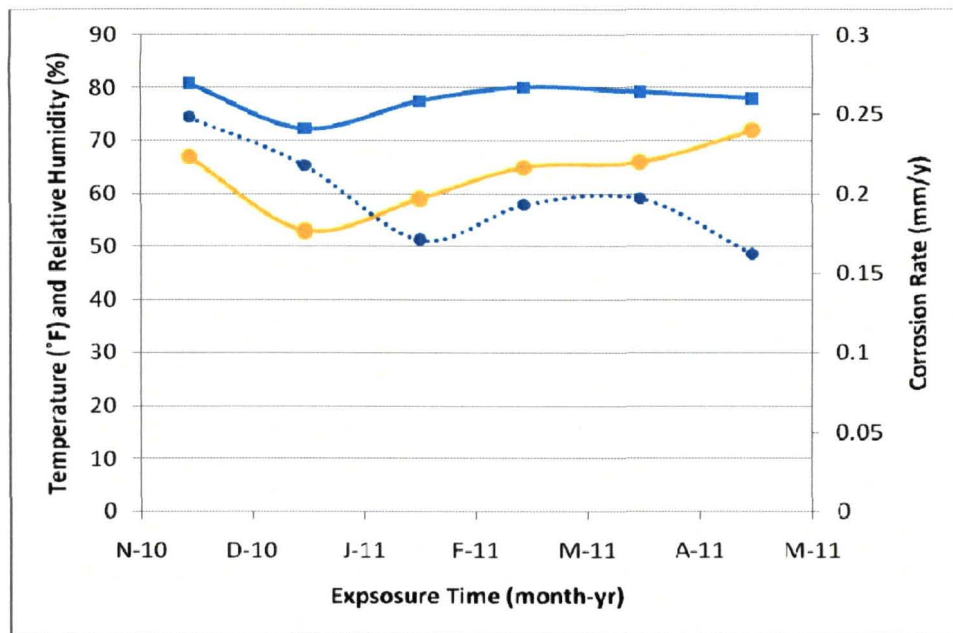


Figure 11: Comparison of monthly averages for temperature (circle marker), relative humidity (square marker), and corrosion rate values for 1010 steel panels (dotted line) recorded at the KSC Beachside Atmospheric Test Site from November 2010 through April 2011.

Correlation of Long-term and Accelerated Corrosion of 1010 Steel

The corrosion rates and behaviors of panels exposed to long-term corrosion and accelerated conditions, neutral salt fog and ASST, were compared to determine possible timescale correlations. Corrosion rates for long-term exposure and accelerated corrosion methods, shown in Figure 12 as a function of exposure time, did not correlate because the accelerated conditions tested thus far were too aggressive compared to the long-term exposure. Since one primary aim of this work is to find timescale correlations of these accelerated test results to corrosion rates measured after long-term exposure, the corrosion rate values measured in the accelerated tests must be within a reasonable range to match corrosion rates of long-term exposure. For the corrosion rate data measured in the accelerated timescales thus far, the corrosion rates are higher, at 0.71mm/y and above, than even the highest value of 0.55mm/y recorded for long-term exposure. Work is currently being completed to scale down the accelerated timescales so that they all within a reasonable range for corrosion rates based on KSC's historical corrosion rate data and data currently being collected at the beachside exposure site.

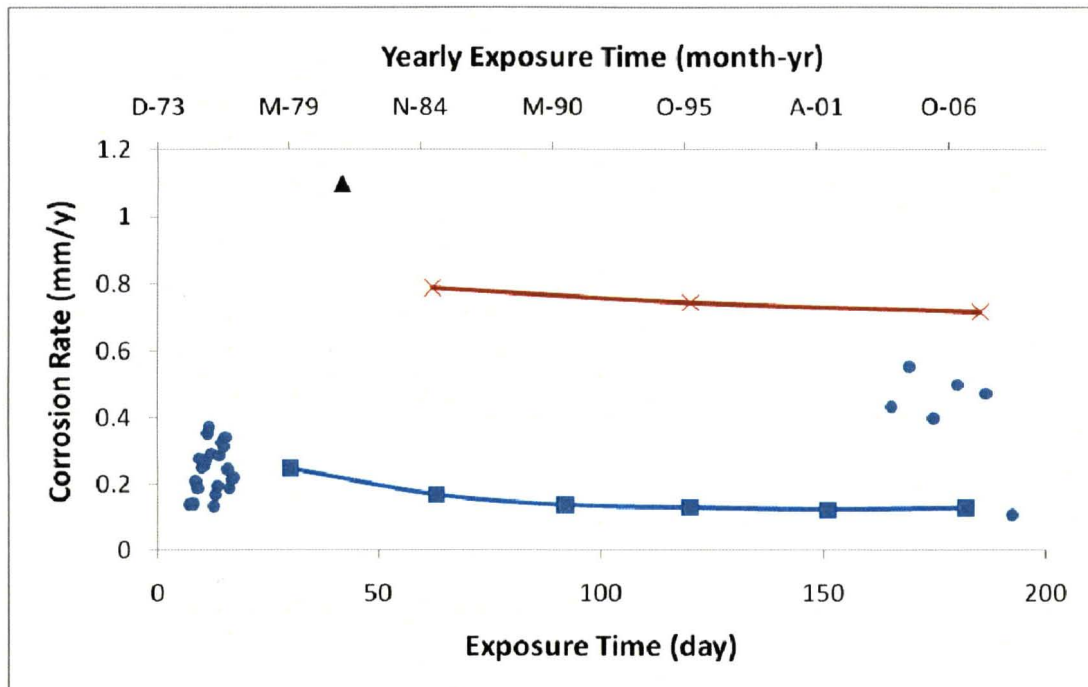


Figure 12: Comparison of corrosion rates as a function of exposure time for 1010 steel panels under long-term atmospheric exposure (square marker) and accelerated corrosion methods, including neutral salt fog (triangle marker) and ASST (X marker). Historical yearly corrosion rates (circle marker) have been included for comparison on the secondary (month-yr) axis.

Further analysis of the ASST and long-term exposure results showed that the mass loss versus timescale behaviors of the two corrosion methods could be compared, Figure 13. The mass loss of panels exposed to ASST conditions seemed to corrode at a consist rate as a function of exposure time, and more data points are currently being generated over a wider variety of timescales to confirm this initial conclusion. Interestingly the ASST mass loss values all fall within the range of yearly mass loss values for the long-term atmospheric exposure panels. Current work is analyzing whether mass loss rates for new long-term exposures can be extrapolated to predict yearly corrosion rates and if ASST mass loss values can be correlated to these predictions as well. Simple mass loss correlations cannot, however, be the only factor for correlation. The manner in which the carbon steel panels corrode are markedly different during the long-term and accelerated corrosion conditions.

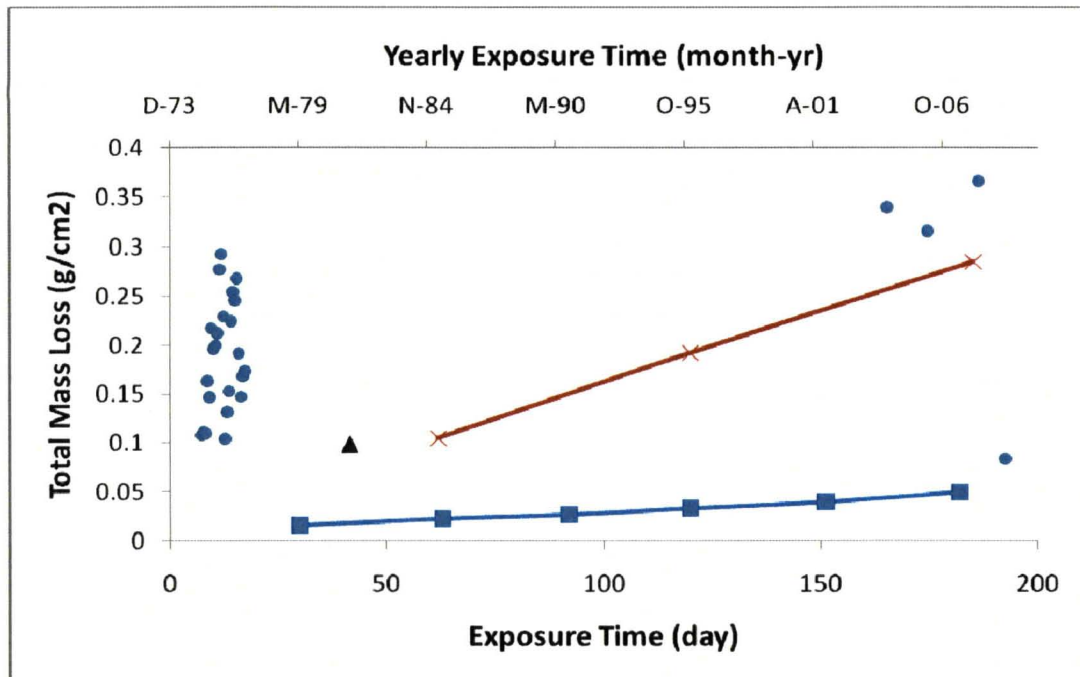


Figure 13: Comparison of mass loss as a function of exposure time for 1010 steel panels under long-term atmospheric exposure (square marker) and the ASST accelerated corrosion method (X marker). Historical yearly mass loss (circle marker) has been included for comparison on.

During observations of corrosion product formation, distinct differences about the manner in which corrosion formed on the carbon steel surfaces were obvious. Panels exposed to atmospheric corrosion have corrosion products that form evenly across the substrate surface as general corrosion. Regardless of the amount of moisture that the panels were exposed to each month, the corrosion product still formed evenly across the surface, as shown in Figure 14 for 5 and 55 days of exposure for the same panel. The manner in which the corrosion product formed on the surface directly related to the manner in which moisture was introduced onto the surface of the panel. In the case of atmospheric exposure, the moisture in the form of fog, rain, or dew formed evenly across the surface and the evaporation rate across the surface also occurred evenly. The panels exposed to the ASST had seawater sprayed directly onto the surface so that the moisture ran across the panels in a continuous vertical stream for 10 minutes of each hour, after which large droplets of seawater remained. The corrosion products formed more heavily in the regions where the seawater remained the longest on the panel surface. Because corrosion rates are known to reach a maximum value during the last stages of moisture film evaporation where oxygen concentration is highest^{28,39-41}, the repeated hourly spray caused the corrosion product to form aggressively especially where the largest droplets formed. Figure 14 shows where corrosion product formed selectively across the surface after one seawater rinse and after 24 rinses. By the 13th day of seawater rinsing, the corrosion product had formed more evenly across the same panel surface; however, the corrosion products were formed as prominent surface scales. A distinct vertical build-up of corrosion products formed on the panels in an exaggerated manner as the ASST exposure time increased. During the neutral salt fog exposure the continuous fog caused smaller droplets to collect and eventually stream down the surface of the panels, where the corrosion products then formed most distinctly in the same streaming pattern as the path of the stream of 5-percent sodium chloride solution. Figure 14 shows examples of this corrosion product formation for the neutral salt fog progressively after 30 minutes, 2 hours, and 100 hours.

1008 Steel (UNS 10080)

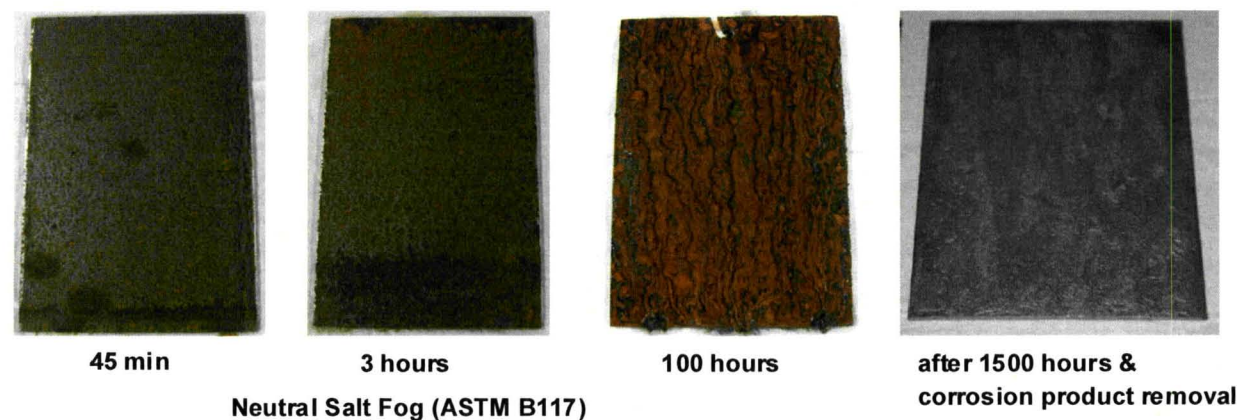
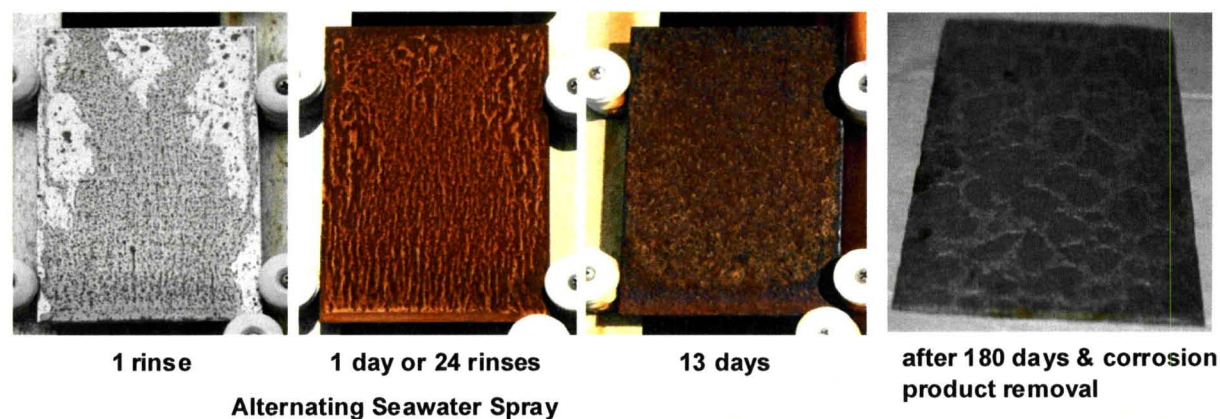
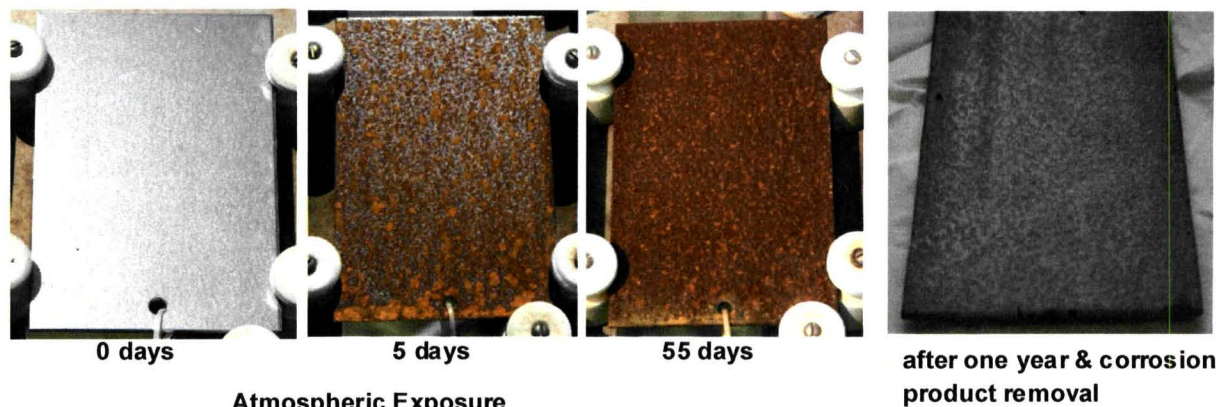
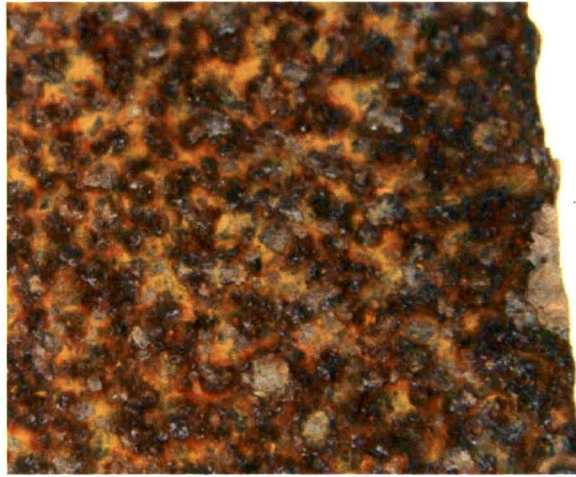
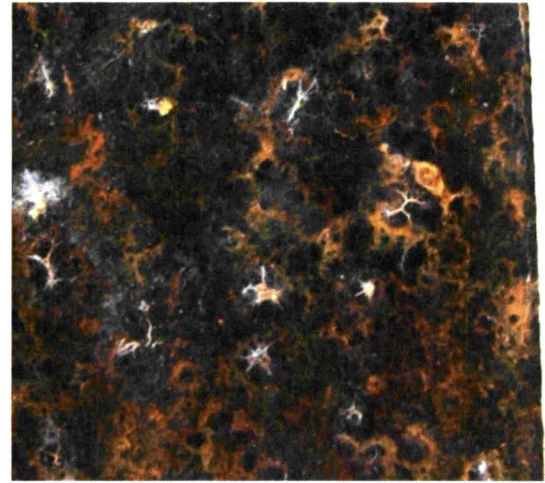


Figure 14: Examples of 1010 steel (UNS 10100) panels after exposure to atmospheric (top row), alternating seawater spray (middle row), and neutral salt fog (bottom row) corrosion.

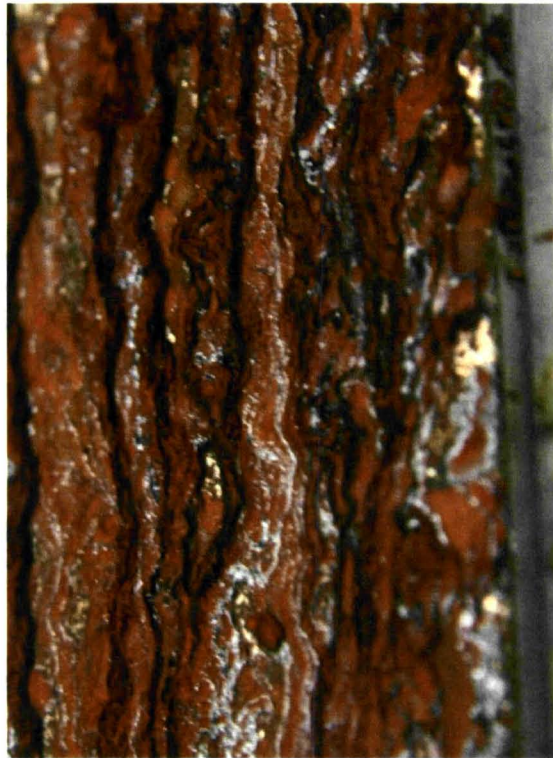
The metal surface after prolonged exposure and removal of corrosion products is markedly different for the different corrosion environments. Figure 14 shows examples of the cleaned 1010 steel surfaces, where the interfacial pattern between the corrosion products and metal directly relate to the exposure type as described above. A closer picture of the corrosion products formed after progressive corrosion for long-term atmospheric exposure and compared to neutral salt fog and ASST accelerated methods is shown in Figure 15. The progressive corrosion product formation follows the same pattern as during initial corrosion, as described in the preceding paragraph for each corrosion exposure type. Correlations of corrosion rates and mass losses are evidently more complex when considering these visual comparisons of corrosion product formation.



atmospheric exposure



alternating seawater spray



neutral salt fog

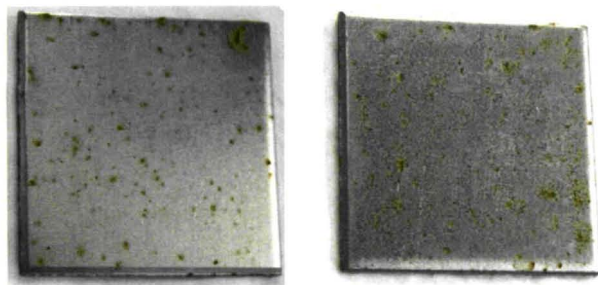
Figure 15: Examples of 1010 steel (UNS 10100) panels after prolonged exposure to atmospheric (top left), alternating seawater spray (right), and neutral salt fog (bottom left) environments.

Unknown is whether the visual differences relate to purely physical differences in corrosion product formation or if chemical differences also exist. Although a myriad of iron oxides are known to form during corrosion of carbon steel^{43,59}, a question arose as whether different kinds of initial iron oxide corrosion products formed for each corrosion condition since the aggressiveness of each condition varied greatly. Because initial and progressive corrosion products form in generally the same way for each of the corrosion environments, initial corrosion product formation was chosen as a factor related to corrosion method correlation. XPS and microscopy were used to monitor the initial corrosion product formation for each corrosion condition.

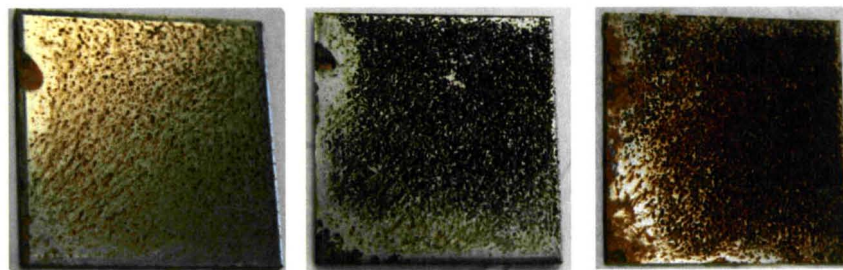
The progression of initial corrosion as a function of exposure time was markedly different between the panels exposed to beachside atmospheric and each type of accelerated corrosion. Again the corrosion products formed in the same pattern as the way that moisture (electrolyte) was introduced onto the panel surface. The initial corrosion product was monitored each month during atmospheric exposure to monitor seasonal differences and include a large range of atmospherically-induced corrosion product types. The atmospherically exposed panels had corrosion that formed initially by local anodic and cathodic reactions that most likely occurred where hygroscopic salts or moisture had collected. More humid initial conditions meant that the corrosion products formed at a faster rate, but the physical progression, shown in Figure 16, was the same regardless of rate. The panels exposed to neutral salt fog were introduced to a continuous moisture-saturated environment, therefore the corrosion products first formed at local droplet locations and often at the site where a NaCl crystal had formed, shown in Figure 16. The panels used for ASST had initial corrosion product formation in the same pattern as the seawater spray stream that ran down the panel mixed with smaller local corrosion sites, shown in Figure 16.

Microscopy of the same panels subject to atmospheric exposure from March and April 2011, shown in Figure 16, is shown in Figure 17 for the first two days of exposure. The panels from March were initially more corroded due to more humidity during the initial exposure stages than for the panels from April. Both photographs and microscopy represent the range of initial corrosion types that are common for the 1010 steel panels exposed to atmospheric corrosion at KSC's beachside test site. All the panels in Figure 17 were evaluated using XPS to determine the kinds of corrosion products typical for atmospheric corrosion. Microscopy was used to help determine what points to target for further XPS study since the optical resolution of the XPS is poor compared to microscopy techniques. Currently XPS data analysis is in progress, but an example of the data analysis process is provided for the atmospheric corrosion panels shown in Figures 16 and 17.

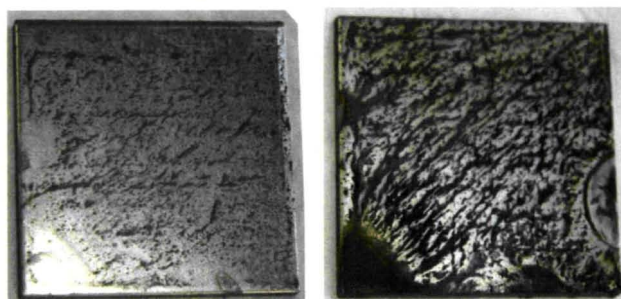
Analysis of corrosion products on 1010 steel panels exposed to marine atmospheric corrosion, shown in Figures 16 and 17, revealed common features for the iron, carbon, oxygen, and chloride-containing corrosion products. The general composition of the 1010 steel surface after initial corrosion was comprised of varying amounts of iron, oxygen, carbon, chloride, sodium, magnesium, manganese, silicon, sulfur, and calcium, depending on the degree of corrosion or the amount of sea salts deposited on the exposed panel. All the components, except for iron, oxygen, and carbon, could be accounted for by the elements in the exposure environment, while the iron, oxygen, and carbon elements were from the base metal. Depth profiling of various points on the panels showed that several shifts resulted during the through-the-thickness transition from corrosion product to iron metal. Figure 18 shows the most general results for a thin layer of initial corrosion product. The iron peaks shift from a surface layer mix of iron(II) chlorides (FeCl_2) and iron oxy-hydroxides (FeOOH) to a thicker layer of bulk iron(III) oxide (Fe_2O_3) and eventually to the metal surface. This transition always occurred for the iron components regardless of degree of corrosion. However, the profiling did not always reach the metal surface for thicker corrosion products. The oxygen-based peaks indicated the initial presence of FeOOH , as well as the shift to Fe_2O_3 during depth profiling. The carbon-based peaks were consistently present, but at varying degrees of intensity through the thickness of the corrosion layer. Different points scanned revealed that chloride-containing carbons, known to naturally occur during degradation of marine aerosol⁷¹⁻⁷³, existed on the surface along with elemental carbon. This constituent was confirmed for the chloride peaks, where chlorinated hydrocarbons (R-Cl) were notably present along with iron(III) and iron(II) chlorides.



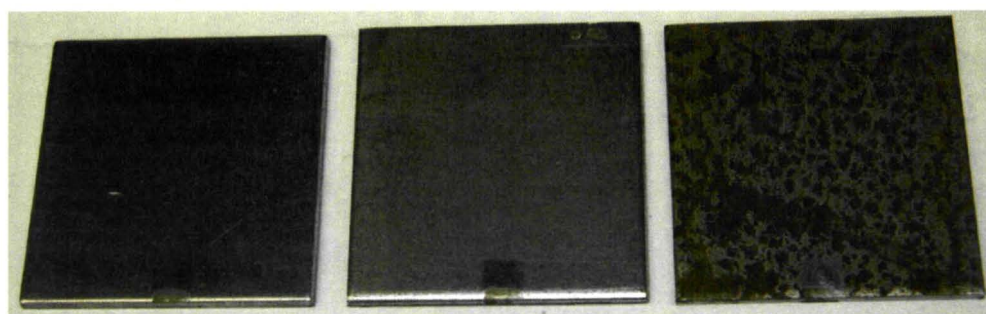
1 day 2 days
Atmospheric Exposure (April 2011)



1 day 2 days 3 days
Atmospheric Exposure (March 2011)

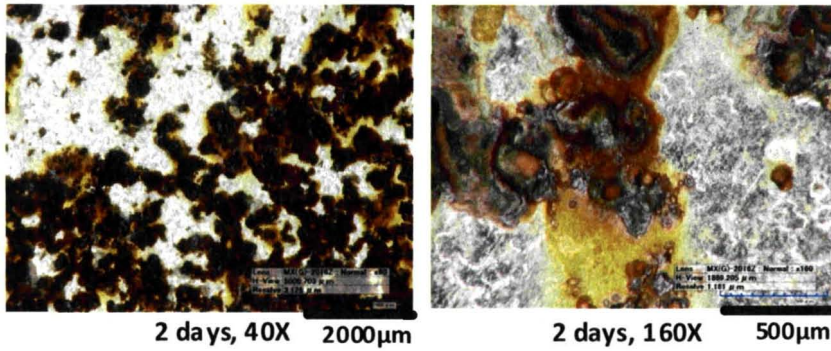
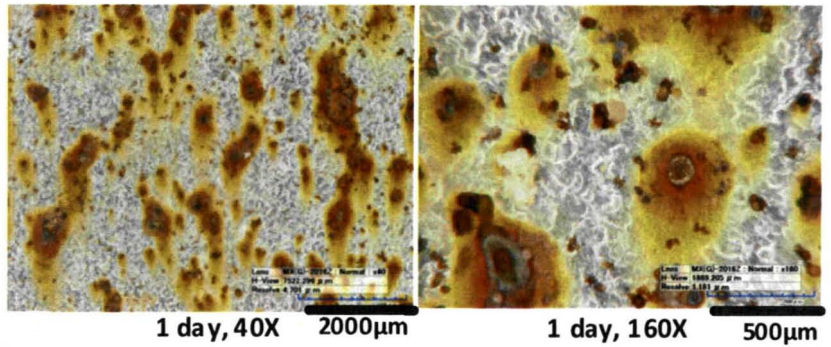


1 rinse 3 rinses
Alternating Seawater Submersion

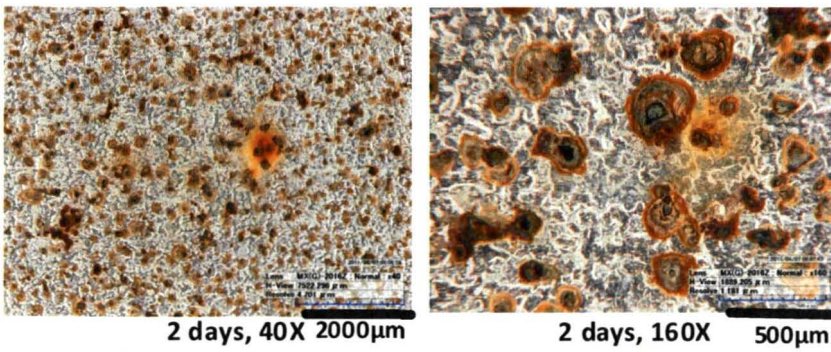
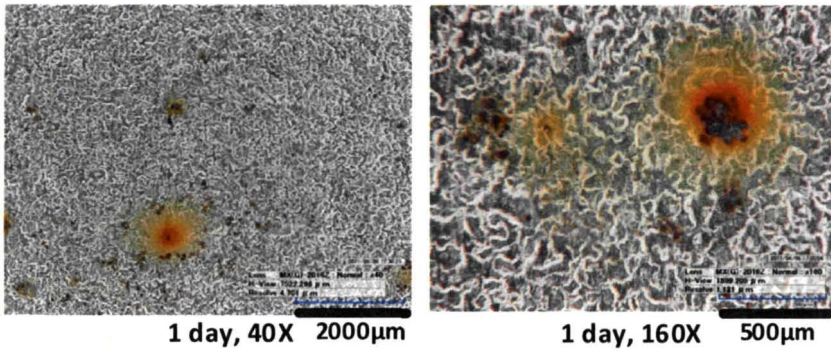


5 min. 15 min. 30 min.
Neutral Salt Fog (ASTM B117)

Figure 16: Examples of 1010 steel (UNS 10100) panels after initial exposure to atmospheric (top), alternating seawater spray (middle), and neutral salt fog (bottom) environments.



Atmospheric Exposure March 2011



Atmospheric Exposure April 2011

Figure 17: Microscopy of 1010 steel (UNS 10100) panels after initial exposure to atmospheric corrosion for one and two days during March 2011 (top group) and April 2011 (bottom group).

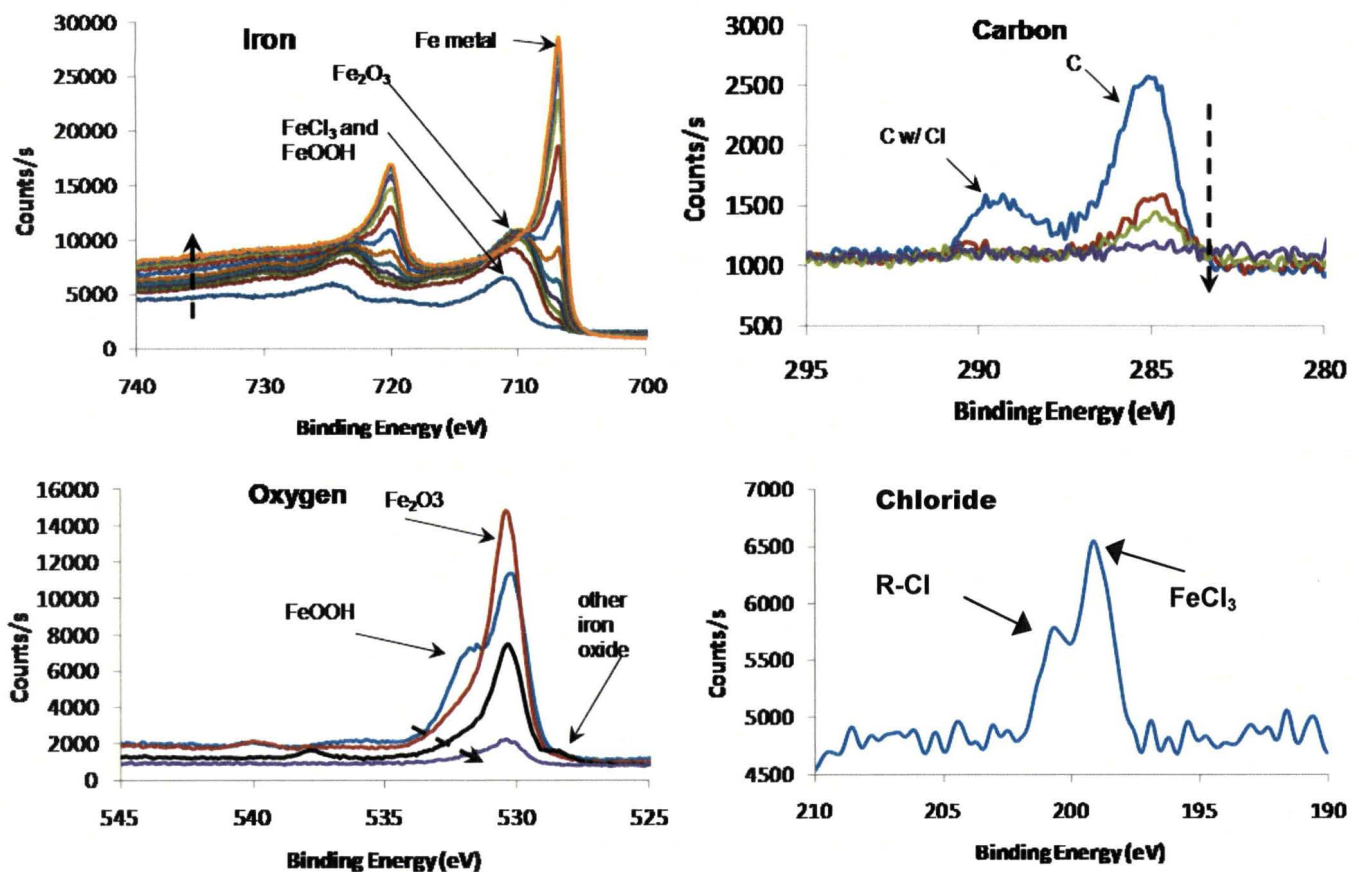


Figure 18: Depth profile results from XPS analysis of 1010 steel (UNS 10100) panels after initial exposure to atmospheric corrosion. The arrows indicate the direction of peak shifting as the depth profiling progressed.

SUMMARY

Although this work is still in progress, a summary of current results and analysis can be made.

- The Kennedy Space Center's Beachside Atmospheric Corrosion Test Site can be characterized as having high chloride levels between 150 and 1900mg/m²d, with a mean value of 640mg/m²d, which can be directly related to wave height. The chloride concentration varies seasonally along with other weather conditions such as temperature, humidity, and precipitation. Overall the sulfur dioxide concentrations are very low year-round, estimated to have yearly totals of about 1.0mg/m²-d based on 2003 through 2010 data.
- Corrosion rates and mass loss values for the three different 1010 steel exposure techniques, long-term atmospheric, alternating seawater spray, and neutral salt fog, are difficult to compare directly since they form corrosion products in different manners. Mass loss as a function of exposure time will be the most reliable way to make correlations between the long-term exposure and accelerated techniques. At this time, the exposure times for the accelerated corrosion methods need to be decreased to correlate mass loss rates to long-term atmospheric corrosion.

- There are distinct physical differences between corrosion products formed with the different exposure techniques. 1010 steel panels exposed to natural atmospheric conditions at the Kennedy Space Center's Beachside Atmospheric Corrosion Test Site formed slowly and evenly across the panel surfaces. On the panels exposed at the test site and subjected to the Alternating Seawater Spray Test, the initial corrosion products formed aggressively only where the seawater spray settle on the panels. Atmospheric-induced corrosion formed on the rest of the panel, such that the overall corrosion products formed in exaggerated scales across the panel surface. Panels exposed to the neutral salt fog had initial corrosion products that initially formed where the droplets collected and later along the streams of moisture that collected down the vertically-oriented panel.
- Despite the physical differences between the corrosion products formed with the different exposure methods, it is unknown at this time if there are chemistry differences between the types of iron-based corrosion products formed during initial corrosion of the 1010 steel. This work is in progress.

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REFERENCES

1. G.S. Frankel, "Electrochemical Techniques in Corrosion: Status, Limitations, and Needs", 2008, Vol. 5, 2.
2. B. Boelen, B. Schmitz, J. Defourny, F. Blekkenhorst, "A Literature Survey on the Development of an Accelerated Laboratory Test Method for Atmospheric Corrosion of Precoated Steel Products", 1993, Vol. 34, 11, p. 1923.
3. Y. Ma, Y. Li, F. Wang, "The Atmospheric Corrosion Kinetics of Low Carbon Steel in a Tropical Marine Environment", *Corrosion Science*, 2010, Vol. 52, p. 1796.
4. E. M. Oliveira, J. R. G. Carneiro, V. F. Cunha Lins, "Evaluation of the Atmospheric Corrosion Resistance of AISI A-36 Steel Painted with Coatings Based on Epoxy and Poly(urethane) Resins Using Semi-accelerated Testing", *Journal of Coating Technology*, 2009, Vol. 6, 2, p. 213.
5. S. Feliu, M. Morcillo and S. Feliu, Jr, "The Prediction of Atmospheric Corrosion from Meteorological and Pollution Parameters- II: Long-Term Forecasts", 1993, Vol. 34, 3, p. 415.
6. S. Feliu, M. Morcillo, S. Feliu, Jr., "The Prediction of Atmospheric Corrosion from Meteorological and Pollution Parameters - I: Annual Corrosion", *Corrosion Science*, 1993, Vol. 34, 3, p. 403.
7. F. Corvo, A.R. Mendoza, M. Autie and N. Betancourt, "Role of Water Adsorption and Salt Content in Atmospheric Corrosion Products of Steel", 1997, Vol. 39, 4, p. 815.
8. H. Schwitter, H. Bohni, "Influence of Accelerated Weathering on the Corrosion of Low-Alloy Steels", 1980, Vol. 127, 1, p. 15.
9. E., McCafferty, "Validation of Corrosion Rates Measured by the Tafel Extrapolation Method", *Corrosion Science*, 2005, Vol. 47, 12, p. 3202.
10. Y. Ma, Y. Li, F. Wang, "Corrosion of Low Carbon Steel in Atmospheric Environments of Different Chloride Content", *Corrosion Science*, 2009, Vol. 51, p. 997.
11. J.G. Castaño, C.A. Botero, A.H. Restrepo, E.A. Agudelo, E. Correa, F. Echeverría, "Atmospheric Corrosion of Carbon Steel in Colombia", 2010, Vol. 52, p. 216.
12. S. Feliu, M. Morcillo, B. Chico, "Effect of Distance from Sea on Atmospheric Corrosion Rate", *Corrosion*, 1999, Vol. 55, 9, p. 883.
13. J.A. Jaen, M.S. de Villalaz, L. de Araque, A. de Bosquez, "Kinetics and Structural Studies of the Atmospheric Corrosion of Carbon Steels in Panama", *Hyperfine Interaction*, 1997, Vol. 110, p. 93.

14. J. Morales, S. Marti'n-Krijer, F. Di'az, "Atmospheric Corrosion in Subtropical Areas: Influences of Time of Wetness and Deficiency of the ISO 9223 Norm", *Corrosion Science*, 2005, Vol. 47, p.2005.
15. D.M. Drazic, V. Vascic, "The Correlation Between Accelerated Laboratory Corrosion Tests and Atmospheric Corrosion Station Tests on Steel", *Corrosion Science*, 1989, Vol. 29, 10, p. 1197.
16. G.R. Meira, C. Andrade, C. Alonso, I.J. Padaratz, J.C. Borba, "Modelling Sea-salt Transport and Deposition in Marine Atmosphere Zone – A Tool for Corrosion Studies", *Corrosion Science*, 2008, Vol. 50, p. 2724.
17. J. W. Fitzgerald, "Marine Aerosols: A Review", *Atmospheric Environment*, 1991, Vol. 25A, 3/4, p. 533.
18. M. Morcillo, B. Chico, L. Mariaca, E. Otero, "Salinity in Marine Atmospheric Corrosion: Its Dependence on the Wind Regime Existing in the Site", *Corrosion Science*, 2000, Vol. 42, p. 91.
19. S. Coburn, "Atmospheric Corrosion Properties and Selection, Carbon Steels", *Metals Handbook*, Metals Park, American Society for Metals, 1978, p. 720.
20. J.J., Santana Rodriguez, F.J. Santana Hernandez, J.E. Gonzalez Gonzalez, "XRD and SEM Studies of the Layer of Corrosion Products for Carbon Steel in Various Different Environments in the Province of Las Palmas (The Canary Islands, Spain)", *Corrosion Science*, 2002, Vol. 44, p. 2425.
21. F. Corvo, J. Minotas, J. Delgado, C. Arroyave, "Changes in Atmospheric Corrosion Rate Caused by Chloride Ions Depending on Rain Regime", *Corrosion Science*, 2005, Vol. 47, p. 883.
22. R.T. Vashi, H.G. Patel. *Bull. Electroche*, 1997, Vol. 13, 8-9, p. 345.
23. F. Corvo, T. Pe'rez, Y. Martin, J. Reyes, L.R. Dzib, "Time of Wetness in Tropical Climate: Considerations on the Estimation of TOW According to ISO 9223 Standard", *Corrosion Science*, 2008, Vol. 50, p. 206.
24. B. Lloyd, M.I. Manning, "The Episodic Nature of the Atmospheric Rusting of Steel", *Corrosion Science*, 1990, Vol. 30, 1, p. 77.
25. J.-P. Cai, S.B. Lyon, "A Mechanistic Study of Initial Atmospheric Corrosion Kinetics Using Electrical Resistance Sensors", *Corrosion Science*, 2005, Vol. 47, p. 2956.
26. J. Forsberg, J. Hedberg, C. Leygraf, J. Nordgren, L.-C. Duda, "The Initial Stages of Atmospheric Corrosion of Iron in a Saline Environment Studied with Time-Resolved In Situ X-Ray Transmission Microscopy", *Journal of the Electrochemical Society*, 2010, Vol. 157, 3, p. C110.
27. ISO-9223 (latest revision), "Corrosion of Metal and Alloys, Corrosivity of Atmospheres – Classification", (*Geneve, Switzerland ISO*).
28. A. Nishikata, Y. Yamashita, H. Katayama, T. Tsuru, A. Usami, K. Tanabe, H. Mabuchi, "An Electrochemical Impedance Study on Atmospheric Corrosion of Steels in a Cyclic Wet-Dry Condition", *Corrosion Science*, 1995, Vol. 37, 12, p. 2059.
29. H. Katayama, K. Noda, H. Masuda, M. Nagasawa, M. Itagaki, K. Watanabe, "Corrosion Simulation of Carbon Steels in Atmospheric Environment", *Corrosion Science*, 2005, Vol. 47, p. 2599.
30. ASTM G85-85 A2, STP 866 (latest revision), "Modified Salt Spray (Fog) Testing, Laboratory Corrosion Tests and Standards", (*West Conshohocken, PA: ASTM*).
31. ASTM B117 (latest revision), "Standard Practice for Operating Salt Spray (Fog) Apparatus", *West Conshohocken, PA (ASTM)*.
32. ASTM D5894 (latest revision), "Standard Practice for Cyclic Salt Fog/UV Exposure of Painted Metal," American Society for Testing and Materials, (*West Conshohocken, PA*).
33. SAE J 2334 (latest revision), "Cosmetic Corrosion Lab Test," Society for Automotive Engineers, (*Warrendale, PA*).
34. General Motors Engineering. *Accelerated Corrosion Test; GM 9540P*. GM 9540P, Detroit, MI, 1997.
35. R. Sugamoto, G.A.Hawthorn,L.H. Hihara, "Comparison of Accelerated Corrosion Tests to Corrosion Performance in Natural Atmospheric Environments", 2009 DoD Corrosion Conference, NACE International, 2009.
36. C.A. Matzdorf and W.C.Nickerson, "Assessment of Accelerated Tests Compared to Beachfront Test and Proposed Evaluation Method", 2009 DoD Corrosion Conference, NACE International, 2009.
37. C.E. Miller, E.A Chareton, T.A Considine, "Comparison of Electrochemical Impedance Spectroscopy (EIS) Results for Four Accelerated Exposures Versus Outdoor", 2009 DoD Corrosion Conference, NACE International, 2009.

38. N. Azzetti, R. Bruno, L. Splendorini, "Assessment of Corrosion Rate of Steel in Sea Water by Polarization Resistance Technique", *Corrosion Science*, 1981, Vol. 21, 11, p. 781.
39. F. Mansfeld, "Monitoring of Atmospheric Corrosion Phenomena with Electrochemical Sensors", *Journal of the Electrochemical Society*, 1988, Vol. 135, p. 1354.
40. F. Mansfeld, J.V. Kenkel, "Electrochemical Monitoring of Atmospheric Corrosion Phenomena", *Corrosion Science*, 1976, Vol. 16, p. 111.
41. F. Mansfeld, S. Tsai, "Laboratory Studies of Atmospheric Corrosion - I. Weight Loss and Electrochemical Measurements", *Corrosion Science*, 1980, Vol. 20, p. 853.
42. W. Han, G. Yu, Z. Wang, J. Wang, "Characterisation of Initial Atmospheric Corrosion of Carbon Steels by Field Exposure and Laboratory Simulation", *Corrosion Science*, 2007, Vol. 49, p. 2920.
43. T.E. Graedel, R.P. Frankenthal, "Corrosion Mechanisms for Iron and Low Alloy Steels Exposed to the Atmosphere", *Journal of the Electrochemical Society*, 1990, Vol. 137, 8, p. 2385.
44. A. Cox, S. B. Lyon, "An Electrochemical Study of the Atmospheric Corrosion of Iron - II. Cathodic and Anodic Processes on Uncorroded and Pre-Corroded Iron", *Corrosion Science*, 1994, Vol. 36, 7, p. 1177.
45. I.L. Rozenfeld, "Proceedings of the 1st International Congress on Metallic corrosion", 1976, p. 243.
46. S.G. Fishmann, C.R. Crowe. *Corrosion Science*, 1977, Vol. 17, p. 27.
47. C. Faiud, H. Maurin, Proceedings for the 8th International Congress on Metallic Corrosion, Toronto. NACE. 1981, p. 18.
48. M. Stratmann, K. Bohnenkamp, H.J. Engell, "An Electrochemical Study of Phase-transitions in Rust Layers", *Corrosion Science*, 1983, Vol. 23, p. 969.
49. M. Stratmann, "The Investigation of the Corrosion Properties of Metals, Covered with Adsorbed Electrolyte Layers—A New Experimental Technique", *Corrosion Science*, 1987, Vol. 27, p. 869.
50. M. Stratmann, H. Streckel, "On the Atmospheric Corrosion of Metals Which are Covered with Thin Electrolyte Layers—I. Verification of the Experimental Technique", *Corrosion Science*, 1990, Vol. 30, p. 681.
51. M. Stratmann, H. Streckel, "On the Atmospheric Corrosion of Metals Which are Covered with Thin Electrolyte Layers—II. Experimental Results", *Corrosion Science*, 1990, Vol. 30, p. 697.
52. M. Stratmann, H. Streckel, K.T. Kim, S. Crockett, "On the Atmospheric Corrosion of Metals Which are Covered with Thin Electrolyte Layers-III. The Measurement of Polarisation Curves on Metal Surfaces Which are Covered by Thin Electrolyte Layers", *Corrosion Science*, 199, Vol. 30, p. 715.
53. I. Suzuki, N. Masuko, Y. Hisamatsu, "Electrochemical Properties of Iron Rust", *Corrosion Science*, 1976, Vol. 19, p. 521.
54. I. Suzuki, N. Masuko, Y. Hisamatsu, "Nature of Atmospheric Rust on Iron", *Journal of the Electrochemical Society*, 1980, Vol. 127, p. 2210.
55. M. Stratmann, K. Hoffman, "In Situ Mößbauer Spectroscopic Study of Reactions Within Rust Layers", *Corrosion Science*, 1989, Vol. 29, p. 1329.
56. J. Guo, S. Yang, C. Shang, Y. Wang, X. He, "Influence of Carbon Content and Microstructure on Corrosion Behaviour of Low Alloy Steels in a Cl₂ Containing Environment", *Corrosion Science*, 2008, Vol. 51, p. 242.
57. A.K. Singh, T. Ericsson, L. Haggstrom, "Mossbauer and X-Ray Diffraction Phase Analysis of Rusts from Atmospheric Test Sites with Different Environments in Sweden", *Corrosion Science*, 1985, Vol. 25, 10, p. 931.
58. I. M. Allam, J. S. Arlow, H. Sacricimen, "Initial Stages of Atmospheric Corrosion of Steel in the Arabian Gulf", *Corrosion Science*, 1991, Vol. 32, 4, p. 417.
59. J.T. Keiser, C.W. Brown, "Characterization of the Passive Film Formed on Weathering Steels", *Corrosion Science*, 1983, Vol. 23, 3, p. 251.
60. K. Inoue, K. Shinoda, M. Saita, S. Suzuki, Y. Waseda, "Atomic-scale Structure and Morphology of Gamma-FeOOH Particles Formed during Corrosion of Fe-based Alloys in Aqueous Solution", *e-Journal of Surface Science and Nanotechnology*, 2008, Vol. 6, p. 49.
61. A. V. Ramesh Kumar, N. Singh, "Conversion Electron Mössbauer Spectroscopy Study of Growth and Nature of Corrosion Products on Mild Steel Exposed to Different Environments", *Hyperfine Interactions*, 2009, Vol. 188, p. 51.

62. A. Raman, B. Kuban, A. Razvan, "The Application of Infrared Spectroscopy to the Study of Atmospheric Rust Systems - I. Standard Spectra and Illustrative Applications to Identify Rust Phases in Natural Atmospheric Corrosion Products", *Corrosion Science*, 1991, Vol. 32, 12, p. 1295.
63. K. Asami, M. Kikuchi, "In-depth Distribution of Rusts on a Plain Carbon Steel and Weathering Steels Exposed to Coastal-Industrial Atmosphere for 17 years", *Corrosion Science*, 2003, Vol. 45, p. 2671.
64. NASA-STD-5008A, "Protective Coating of Carbon Steel, Stainless Steel, and Aluminum on Launch Structures, Facilities, and Ground Support Equipment", 2004.
65. ISO-9225 (latest revision), "Corrosion of Metals and Alloys - Corrosivity of Atmospheres - Measurement of Pollution", (*Geneve, Switzerland ISO*).
66. Environmental Protection Agency, <http://java.epa.gov/castnet/viewsiteinfo.do?siteId=IRL141>
67. National Oceanic and Atmospheric Administration, http://www.ndbc.noaa.gov/view_climplot.php?station=41009&meas=wh
68. A. Clarke, V. Kapustin, S. Howell, K. Moore, B. Lienert, S. masonis, T. Anderson, D. Covert, "Sea-Salt Size Distributions from Breaking Waves: Implications for Marine Aerosol Production and Optical Extinction Measurements during SEAS", *Journal of Atmospheric and Oceanic Technology*, 2003, 20, p1362-1374.
69. M.E.R. Gustafsson and L.G. Franzen, "Inland Transport of Marine Aerosols in Southern Sweden," *Atmospheric Environments*, 2000, 34, 313-325.
70. S.R. Massel, "Ocean Waves Breaking and Marine Aerosol Fluxes," *Atmospheric and Oceanographic Sciences Library*, 2007, Volume 38, p207-228.
71. G.W.Gribble, "Naturally Occurring Organohalogen Compounds - A Comprehensive Survey". *Progress in the Chemistry of Organic Natural Products*, 1996, **68**: 1-423.
72. E.J. Ledet and J.L.Laseter, "Alkanes at the Air-Sea Interface from Offshore Louisiana and Florida," *Science*, 1974, 186, 4, pg 305-314.
73. M. Barbier, D. Joly, A. Saliot, D. Tourres, "Hydrocarbons from Sea Water," *Deep Sea Research Oceanographic*, 1973, 20, 4, pg 305-314.