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Local Corrosivity Classification and Enhancement of Corrosion Rate via Environmental Modification

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ABSTRACT

United States Naval Research Laboratory, Key West is a state-of-the-art testing facility for atmospheric and marine corrosion. Recently, the testing capabilities were expanded to mitigate baseline corrosivity by mimicking preventative maintenance strategies such as programable clear water rinsing and sheltering within a protective aircraft cover, and to increase baseline corrosivity via natural sea water spray. These capabilities will serve to better inform aircraft maintenance policies. For example, several programs want to explore the impacts of clear water rinsing and handwashing in different operational conditions. Additionally, by adjusting the corrosivity of Key West, it can be tuned to mimic the exposure conditions of other sites of relevance to Navy operations. To facilitate comparisons of Key West to other sites, two site severity campaigns were conducted to compare 16 sites to Key West in the first and 3 sites in the second. Data presented will include steel mass loss, galvanostatic reduction of silver, and profilometry of base plate aluminium. Meteorological data was also recorded and will be presented as needed. An understanding of how different local environments affects site-specific corrosion is developed and although many of the alternate test site environments are very different from the ambient conditions in Key West, there is an opportunity to simulate the environments of various bases at this one location through environmental modification.

Keywords: AVT Symposium, atmospheric corrosion, environmental modification, environmental severity index, clear water rinsing.

1.0 INTRODUCTION

The exposure environment of an engineering material quite often has a large impact on how that material behaves over time. Environments are distinguished by differences in meteorological patterns, geography, salinity, UV radiation, etc[1-3]. Thus, the degradation of various materials scales proportionately to the characteristics of the exposure site, with more severe sites leading to worse degradation. Briefly, corrosive attack is facilitated by the presence of salts on and in the aircraft[4-7]. In humid conditions, salts will absorb moisture to form a thin, liquid salt solution. This salt solution allows for corrosion to occur. Even the salt itself (particularly the anion chloride component) works to enhance corrosive action[8-11].

Developing an understanding of how the local environment impacts the corrosion rates of metals is critical for informing asset maintenance schedules and lifetime predictions[12]. For example, aerospace assets are subjected to routine maintenance cycles to prevent, monitor, and repair corrosion damage. Sheltering the aircraft underneath a cover or within a hangar is meant to limit exposure to the elements, especially solar (UV in particular) radiation. Rinsing the aircraft with clear water, or water that is relatively free of ions, is intended to reduce the concentration

of salt on and in the aircraft[12, 13]. This in turn should reduce the risk of corrosion. Typically, any water that is as pure as or purer than fresh/tap/drinking/potable water is considered clear water. The frequency of this clear water rinsing (CWR) depends on the rate at which the salts accumulate on or in the aircraft, with environments having a higher rate of salt deposition requiring a higher frequency of CWR, as prescribed by its governing requirements document (e.g.: United States Air Force Technical Order 1-1-691[12] or United States Naval Air Systems Command 01-1A-509[14]). Typically, marine service environments (i.e., shipboard environments, port environments, or coastal air station environments such as at NAS Key West shown in Figure 1) are among the most severe environments in the DoD sphere of operations.

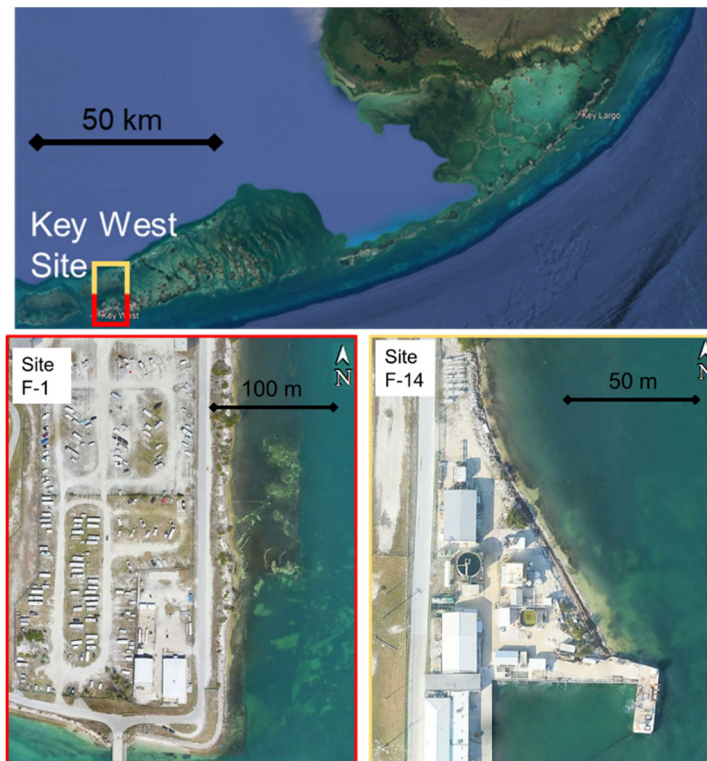


Figure 1: Overview of the Key West exposure site.

A new paradigm of condition-based maintenance (CBM) is highly desired, as a given asset will require different prevention, monitoring, and repair maintenance cycles depending on where it is deployed. As corrosion is the degradation of a material in response to its environment, CBM takes into consideration the variability of the environment (the conditions to which an asset is exposed) when determining appropriate maintenance intervals and what should be done at each interval. Implicit in this endeavour is the possibility of optimizing maintenance requirements in response to actual observed material in accurately replicated corrosive environments. Strategies include clear water rinsing (CWR), sheltering/covering assets, wash practices, and maintenance “personalization” based on unique asset and environment combinations. A deeper understanding of the effects of environmental modification on corrosion maintenance is needed before the CBM paradigm can be optimized.

This investigation pursues a deeper understanding of how CWR, sea water spray, and covering impact corrosion behaviour. With a proper understanding of the effect CWR has on atmospheric corrosion, the rinsing routine can

be optimized. The results of this analysis inform this optimization process. Additionally, deeper mechanistic understanding of the atmospheric corrosion process is gleaned by the selective removal of certain parameters to determine their respective role in the whole process.

The NRL Key West facility is a rigorously characterized atmospheric corrosion test site. It offers a platform for elucidating the effects of the environment on the atmospheric corrosion of engineering materials. Furthermore, it is possible that the local Key West environment can be “tuned” in order to replicate a variety of service conditions. This is accomplished by the combination of sea water spray, clear water rinsing, static or dynamic loading, covering/sheltering, etc. (Figure 2). However, to be able to fine tune the Key West environment, the relationship between environmental parameters, corrosion rates, and coating degradation must be known. This understanding is developed through comparison of the Key West test site with other exposure test sites via witness coupon corrosion. A first campaign of 17 different sites (including Key West) was followed by a second campaign of 4 different sites, as listed in Table 1. Sites were spread across DoD installations in the United States and Japan, as shown in Figure 3. This offered practical utility to the DoD since operationally relevant sites were being examined. It also provided a large parameter space for testing a range of variables.

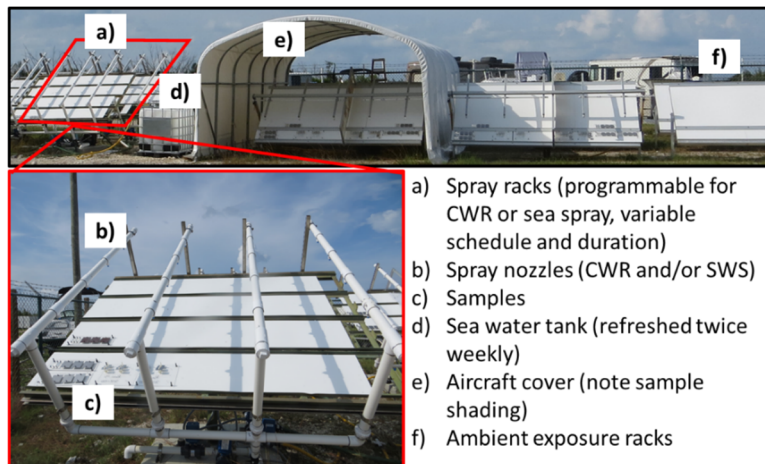


Figure 2: A selection of the exposure racks utilized for this environmental modification study. Included in this snapshot are spray racks which can be programmed to be completely ambient, CWR, or sea water spray. An aircraft cover which is the same as what is used on DoD assets (such as the F-22 fighter jet) is also shown.

<i>Site (Alphabetical)</i>	<i>Site ID</i>	<i>Köppen Code</i>	<i>Exposure Start</i>
<i>NAS Corpus Christi</i>	<i>CC</i>	<i>Cfa</i>	<i>21DEC2020</i>
<i>NAS Ft. Worth</i>	<i>FW</i>	<i>Cfa</i>	<i>17DEC2020</i>
<i>MCAS Iwakuni</i>	<i>Iw</i>	<i>Cfa</i>	<i>01DEC2020</i>
<i>NAS Jacksonville</i>	<i>Ja</i>	<i>Cfa</i>	<i>17DEC2020</i>
<i>MCAS Kaneohe Bay</i>	<i>KB</i>	<i>Aw</i>	<i>30NOV2020</i>
<i>NRL Key West</i>	<i>KW</i>	<i>Aw</i>	<i>14DEC2020</i>
<i>NAS Lemoore</i>	<i>Le</i>	<i>BSk</i>	<i>23DEC2020</i>
<i>NS Mayport</i>	<i>Ma</i>	<i>Cfa</i>	<i>14DEC2020</i>
<i>NAS New Orleans</i>	<i>NO</i>	<i>Cfa</i>	<i>15DEC2020</i>
<i>NAS North Island</i>	<i>NI</i>	<i>Csa / BSk</i>	<i>04FEB2021</i>
<i>NAS Oceana</i>	<i>Oc</i>	<i>Cfa</i>	<i>17DEC2020</i>
<i>MCAS Futenma, Okinawa</i>	<i>Ok</i>	<i>Cfa</i>	<i>31DEC2020</i>
<i>NAS/NAVAIR Patuxent River</i>	<i>PAX</i>	<i>Cfa</i>	<i>16DEC2020</i>
<i>NAS Pensacola</i>	<i>Pe</i>	<i>Cfa</i>	<i>14JAN2021</i>
<i>Boeing, St. Louis</i>	<i>SL</i>	<i>Cfa</i>	<i>13JAN2021</i>
<i>JB San Antonio</i>	<i>SA</i>	<i>Cfa</i>	<i>17DEC2020</i>
<i>NAS Whidbey Island</i>	<i>WI</i>	<i>Csb</i>	<i>14DEC2020</i>
<i>Elmendorf AFB</i>	<i>Elmo</i>	<i>Dsc</i>	<i>23FEB2021</i>
<i>Hickam AFB</i>	<i>Hick</i>	<i>Aw</i>	<i>26FEB2021</i>
<i>NAS Key West</i>	<i>KW</i>	<i>Aw</i>	<i>17FEB2021</i>
<i>Langley AFB</i>	<i>Lang</i>	<i>Cfa</i>	<i>17MAR2021</i>

Table 1. List of the sites compared in this paper.

If the NRL Key West site can be successfully modified to mimic the conditions of other sites, then it will confirm that a proper understanding of the effect of environmental conditions on atmospheric corrosion has been achieved. This understanding can be used to inform engineering modification for testing in the future. Furthermore, with this understanding, the NRL Key West site can be modified to mimic other service conditions of interest, greatly increasing the applicability and versatility of Key West. A detailed mechanistic understanding of environmental parameters allows the Key West exposure site corrosivity to become tunable according to test specifications. Finally, the wide variety of sites assessed in this phase of the program offers a chance to improve our current understanding of how the local environment influences atmospheric corrosion. The environmental character of all the sites is diverse, as shown in Figure 3. Locations, Köppen code, and exposure start date for each site is listed in Table 1.

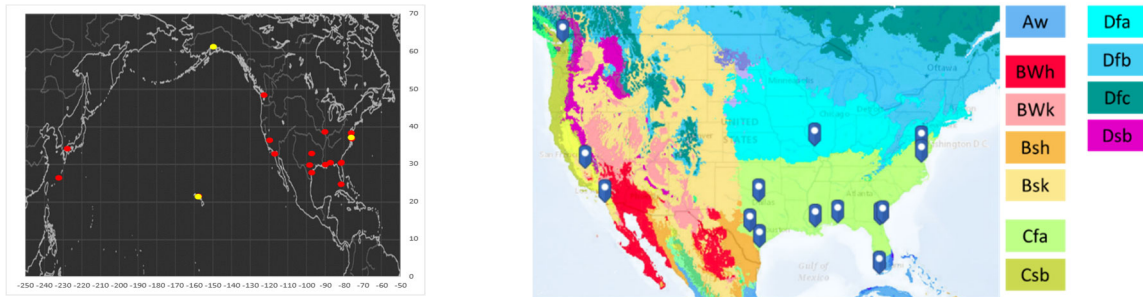


Figure 3. Global overview (left) of the NAESC Phase II sites. Location of the continental US (right) sites overlaid on a Köppen Climate Map (ArcGIS). The climate zones are color coded to highlight the diversity of sites analyzed in this study. A=Tropical, B=Arid, C=Temperate, D=Cold, a=Hot Summer, b=Warm Summer, c=Cold Summer, f=No Dry Season, h=Hot, k=Cold, s=Dry Summer, w=Desert

2.0 EXPERIMENTAL PROCEDURE

Exposure

NRL Key West is a state-of-the-art testing facility located on Fleming Key within the Naval Air Station in Key West, Florida, USA. The facility is equipped for structural testing, coating application, and outdoor exposure (both marine submersed and marine atmospheric). Its location at the end of the Florida Keys makes it an ideal test site for isolating atmospheric effects in the absence of influences from industrial or continental containments. Weather and water data is continuously collected to supplement a rich database of environmental parameters measured at the site with the goal of correlating the environment to material performance. There are principally two sites at the NRL Key West facility, F-1 and F-14, Figure 1. The F-1 test site was where testing for this effort was conducted. At this site, there are spray racks which have been designed to conduct clear water rinsing or natural sea water spray, Figure 2. Collocated at this site is an aircraft cover, such as is used to cover DoD aircraft. There is also a freshwater spray rack located underneath the cover. The clear water was provided by the Florida Keys Aqueduct Authority via the tap water supplied to NAS Key West[15]. The sea water was collected from the ocean and stored in a tank located at the spray racks. The tank was resupplied on a twice weekly basis.

An in-depth assessment of various environmental modifications was conducted in 2 campaigns. The first campaign was conducted from September 30th, 2020 through December 30th, 2020 at the F-1 test site. A combination of different exposure conditions was tested, as summarized by Table 1. There are essentially four base conditions, ambient [A], covered [C], daily seawater spray [S], and twice daily seawater spray [X]. For each base condition there is either no CWR, weekly CWR, or a multi-weekly CWR. All CWR was conducted for 600 s at each occurrence. For [A] and [C] the multi-weekly CWR occurred twice weekly on Tuesdays and Fridays. For [S] and [X] the multi-weekly CWR occurred thrice weekly on Mondays, Wednesday, and Fridays. All NSW spray was conducted for 45 s at each occurrence, which was either once daily or twice daily. The rinse/spray schedule is reported in Table 2. The second campaign was conducted from February 17th, 2021 through February 17th, 2022. The conditions tested in the second campaign were similar to those use in the first campaign except all multi-weekly CWR became thrice weekly.

Table 2: Reported schedule of the rinse and spray durations used.

Rinse and Spray Schedule with Durations (s)												
Time	[A]	[A1]	[A2]	[C]	[C1]	[C2]	[S]	[S1]	[S3]	[X]	[X1]	[X3]
0700										45 D		
0800											45 D	
0900							45 D					45 D
1000								45 D				
1100									45 D			
1200											600 M	
1230		600 M	600 T,F		600 M	600 T,F						
1300												600 M,W,F
1400								600 M		45 D		
1500									600 M,W,F		45 D	
1600												45 D
1700												
	CW Rinse	NSW Spray					D = Daily	M = Monday	T = Tuesday	W = Wednesday	F = Friday	

Baseline Condition	No Rinse	Once Weekly Rinse	Multi-Weekly Rinse
	Ambient (No Spray)	[A]	[A1]
Covered (No Spray, No Rain, No Sun)	[C]	[C1]	[C2]
Daily NSW Spray	[S]	[S1]	[S3]
2x Daily NSW Spray	[X]	[X1]	[X3]

The Key West facility served as the ground-base or headquarters against which to compare all other sites for this investigation. Sites consisted of Navy/Marine/Air Force installations around the United States and Japan (15 continental US sites shown in Figure 3). The Köppen climate code of Cfa was by far the most common climate type sampled in this investigation. The complete list of sites is given in Table 2. For the first campaign of the environmental severity correlation, exposures began over the course of 65 days around December 2020. Due to the dispersion of sites around the globe and travel restrictions associated with the COVID-19 pandemic, exact start times were staggered. In each instance, samples were exposed at the best possible available location, as described by the joint NRL-Naval Air Systems Command (NAVAIR) Technical Action Guide for Atmospheric Exposure Testing (NRL internal Letter Report). At Key West, samples were exposed on a fence line to mimic the conditions used at the other sixteen sites. The samples are attached to a chain-link fence in proximity to where aircraft are stored at a height of 4 ft off the ground and facing South (toward the equator for maximum solar impingement). Exposures were conducted in a cumulative fashion in which samples were deployed all at once and selectively retrieved at intervals of 1, 3, 6, 9, and 12 months. The second environmental severity correlation campaign began over the course of 30 days around late February 2021. Samples were exposed in the same fashion as the first campaign except retrievals were executed at 6- and 12-month intervals and were affixed to exposure racks instead of on fencing, but the angle of exposure was similar.

Samples

Witness coupons consisted of C1010 low carbon steel and pure (99.99%) silver. The C1010 is a common proxy sample for steels in general (although it is starkly different from other classes of steel like stainless, cast iron, or high strength steels). The steel coupons were 3 x 3 x 1/16 inches in dimension and surface-finished via glass bead

blasting. Silver is also a commonly used proxy for monitoring the corrosivity and chemistry of an exposure site[9, 16] and was exposed as 0.5 x 3 x 0.011 inch samples. The silver was polished to 600 and then 1200 grit surface roughness. Both steel and silver were exposed in triplicate and were used in all campaigns for environmental modification and environmental severity correlation testing.

Corrosion sensors purchased from Luna Labs, Inc. from the Acuity suite (both CR and LS models) were exposed in several of the exposure conditions at Key West and the F-22 AFB locations, Table 2. These sensors measure temperature, relative humidity, solution conductance (related to time of wetness), galvanic (dual alloy) and free (single alloy) corrosion in 30-minute intervals. The usage of these sensors is becoming more and more prominent within the atmospheric corrosion and environmental severity classification communities. Careful consideration must be taken when analysing and reporting this data so that it can be fully leveraged and interpreted correctly.

Water Chemistry

It has been determined that the sea water in the tank used for spraying retained the original chemistry of fresh sea water after 4 days. It also showed that a CWR following a previous sea water spray was able to purge the spray line of sea water after 1 minute of rinsing. For a sea water spray following a previous CWR, it is suspected that the sea water may not return fully to its undiluted composition after 45 seconds of spray. However, the final composition will be close to that of undiluted seawater. This sequence of CWR preceding a sea water spray occurs 1/7 times a week for [S1], 3/7 times a week for [S3], 1/14 times a week for [X1], and 3/14 times a week for [X3]. It should also be noted that fresh water is provided to the facility by the Florida Keys Aqueduct Authority[15], which reports that the fresh water contains chloramine disinfectant, which can change the oxidation power of the fresh water. However, the fresh water measured exiting the spray rack hose after 1 minute of flushing does not contain chloramine, but only free chlorine at a concentration of 0.94 mg/l. Free chlorine also increases the oxidizing power of the fresh water, but this amount of free chlorine is much lower than the level of chloramine present in the source water upstream, cited by the Aqueduct Authority as being 3.35 mg/l[15].

Testing

Mass loss measurements were collected from the C1010 low carbon steel coupons, consistent with previous testing at NRL-KW. Accumulated corrosion product was removed via glass bead blasting in order to isolate the metallic substrate remaining after the exposure. Then, the area normalized mass loss, the percent mass loss, or the area normalized mass loss rate is reported. This steel mass loss information will provide an understanding of the total corrosion rate associated with the different locations and/or different conditions at each location.

Galvanostatic reduction was performed on the silver witness coupons in order to determine the type and quantity of corrosion products. This information provides insight into the identity of the atmospheric species present and the oxidation power of the local environment during exposure[9, 16]. Most silver compounds are insoluble and remain on the surface of the coupons. In this way, silver acts as a chemical trap to preserve species of interest for analysis. The silver products were reduced back to metallic silver in a 0.1 M Na₂SO₄ (pH 10) electrolyte by applying a constant cathodic current of either -0.0266 or -0.1125 mA to a 1 cm diameter exposure window. The potential transient was measured to determine which species were present on the surface and how much of each species was present. Results are commonly plotted in terms of total charge and in terms of speciated charge. The silver reduction analysis will provide information on the characteristics of the local environment.

3.0 RESULTS

Environmental Modification Testing

The first campaign of the environmental modification testing was a three-month assessment. The steel mass loss increased throughout the course of the campaign, but the steel mass loss rate decreased as the exposure progressed. This is attributed to the formation and thickening of an iron scale which somewhat mitigates the corrosion rate of iron. For the ambient exposure, the effect of CWR is readily seen in the mass loss results. As the frequency of CWR increases, the steel mass loss decreases (Figure 4). This is true at every step of the exposure (1, 2, & 3 months). The benefits of CWR can also be observed for the covered condition. Again, as CWR frequency increases the mass loss decreases, consistent for each time stamp. Interestingly, the overall amount of mass loss was noticeably higher for the covered condition than for the ambient condition. The higher mass loss for the covered condition is consistent across all time stamps and for all CWR frequencies in this first campaign. The addition of sea water spray drastically increases the observed steel mass loss, so much so that the scale has been increased by a factor of 25. The results for the daily and the twice-daily sea water spray are essentially the same, despite the difference in spray frequency. Furthermore, there seems to be little effect of CWR on the mass loss for these NSW sprayed specimens. There is very little difference between the samples which were not rinsed at all and the samples that were rinsed weekly or thrice weekly. This indicates that in a severe marine environment, where the seawater spray dominates the surface chemistry, CWR may be of no substantial benefit.

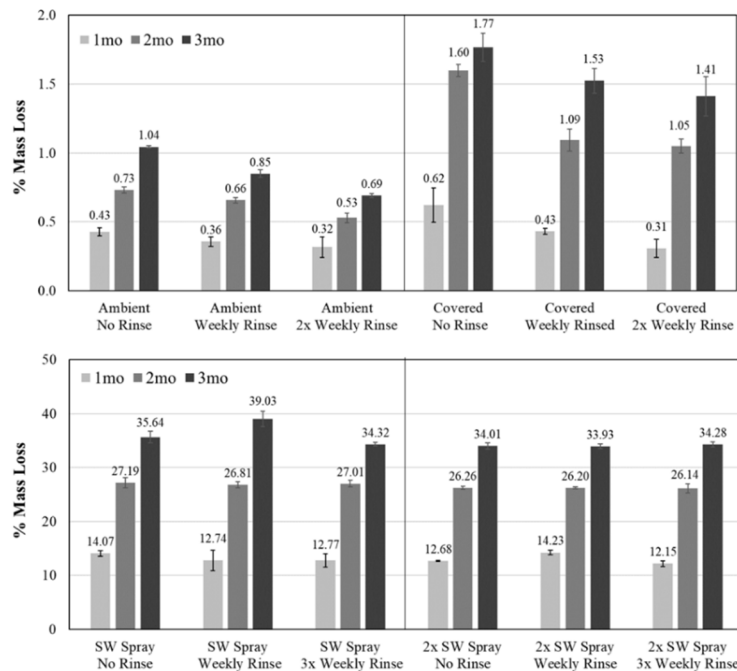


Figure 4: Steel mass loss as a function of exposure condition and duration for campaign 1.

The results of the silver reduction analysis are shown in Figure 5, which reports the contribution of each species towards the overall reduction charge. Results are again grouped by exposures without sea water spray and those with sea water spray. The ambient exposure consistently formed and/or retained the most silver corrosion product on the surface of the samples. Both the ambient and covered exposures had a higher fraction of AgCl on the surface than did the sea water spray conditions, which were much richer in Ag₂S. This difference in the AgCl vs Ag₂S content also manifested itself in the colour of the samples. The covered samples had much less silver corrosion product on the surface than the ambient samples. Furthermore, the sea water spray reduced the total amount of corrosion product on the surface compared to the ambient control, regardless of how frequently the samples were sprayed with seawater.

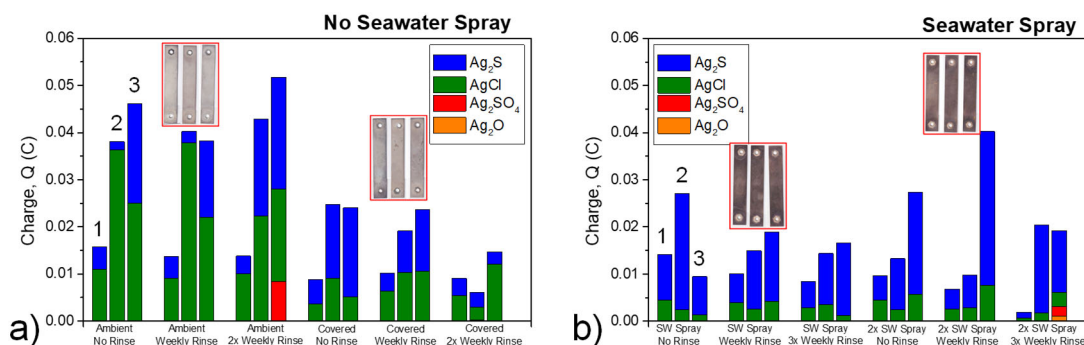


Figure 5: Stacked column plots of reduction charge distributed according to the contribution of each species present on the silver surface. The ambient and covered conditions, which contained no sea water spray, are shown in a). The daily and twice daily sea water spray conditions are shown in b).

Overall, there appears not to have been a significant effect of CWR on the formation/retention of silver products on the surface. For almost every condition tested, there was essentially no impact of CWR; the non-rinsed specimens were about equivalent to the weekly and multi-weekly rinsed specimens. The one exception was the covered condition, for which the amount of silver products on the surface decreased with increase rinse frequency.

The second campaign of environmental modification testing was a one-year assessment, with second and third years of testing still left to finish. The mass loss data are shown in Figure 6 and Figure 7 for Key West and the F-22 AFB locations, respectively. (The y-axis is different between the graphs due to the differences between the spray conditions in Key West versus all other conditions.) A summary of the mass loss results from Elmendorf, Hickam, and Langley is shown in Figure 8. The twelve-month mass loss data from the F-22 AFB locations is overlaid with a curve of Key West ambient corrosion rate over time. The filled in data markers represent the ambient condition and the open data markers are the modified conditions (SW spritz/hangar).

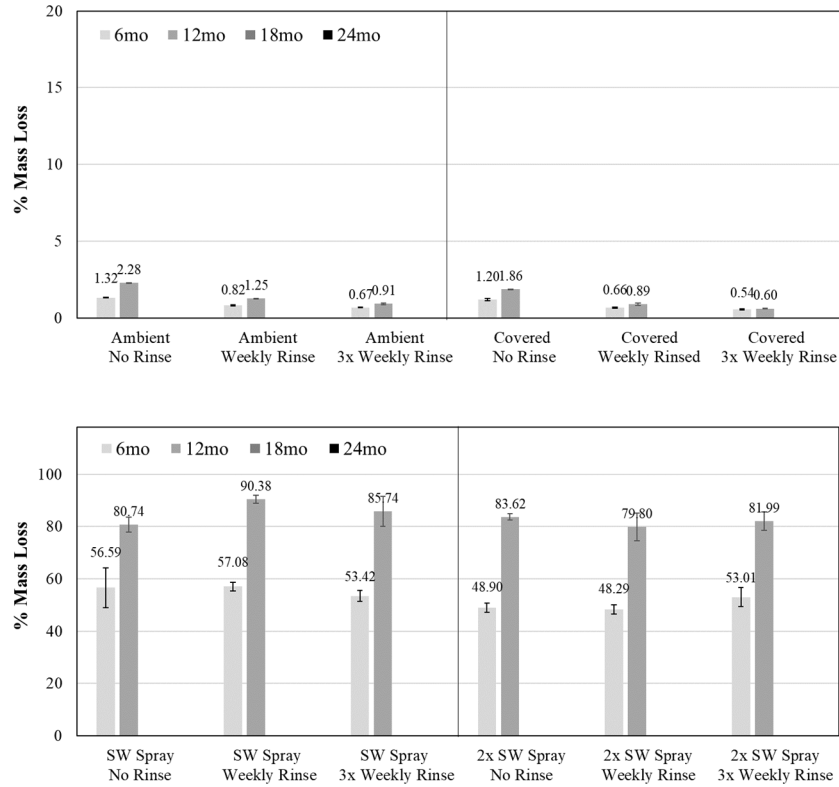


Figure 6. Steel mass loss as a function of NRL-KW exposure condition and duration for campaign 2.

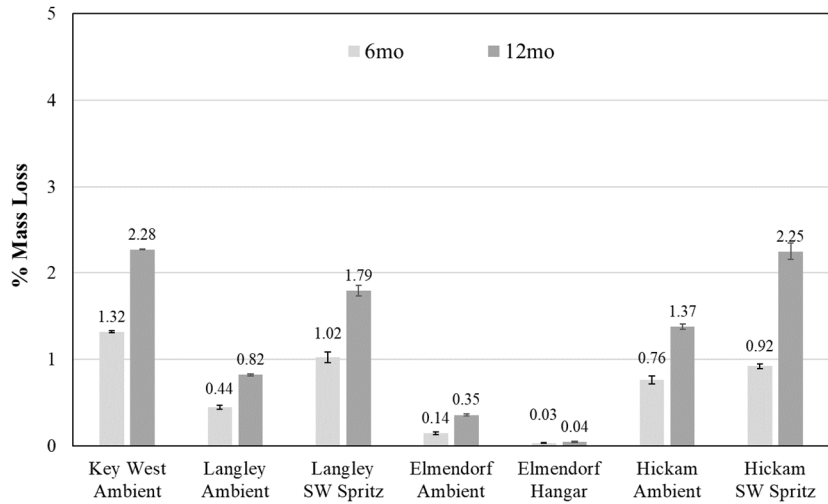


Figure 7. Mass loss for the second environmental modification campaign.

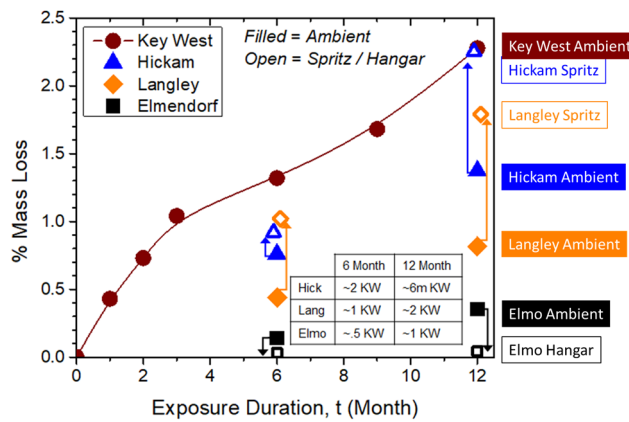


Figure 8. Mass loss of the twelve month F-22 AFB locations compared to a curve of Key West samples. The open data markers are the modified conditions of the corresponding filled data markers (Hickam/Langley Spritz and Elmo Hangar).

Analysis of the steel mass loss data shows that although the F-22 AFB locations are less severe than Key West, they become more similar with the addition of a once-per-week spritzing of the surface with local seawater. The amount of salt that this would deposit is not unreasonable for aircraft operating around the local area of the respective bases. Furthermore, at twelve months of exposure, the steel samples in the hangar at Elmendorf have very minimal amounts of corrosion which is consistent with the expected results. Comparing the amount of corrosion from the F-22 AFB locations and KW ambient and covered versus the much more heavily corroded samples under accelerated salt spray in Key West is significant. The amount of corrosion on the steel samples is between 40-90 times greater with the addition of seawater spray. Once samples are experiencing this level of

corrosion, the frequency of freshwater rinsing is inconsequential. However, the less severe conditions in Key West (ambient and covered) indicate that more frequent CWR does decrease the amount of corrosion. Of all conditions for steel in Key West, the least corrosive condition was covered with a 3x/week CWR interval. Since the amount of steel corrosion at the F-22 AFB locations is consistent with KW ambient, it is presumed that the benefits from covering and CWR would be consistent as well.

Another useful assessment is to rank properties measured by corrosion sensors (T, RH, conductivity, corrosion) at various exposure conditions is by using the Empirical Cumulative Distribution Function (ECDF) plot. This plot constructs a cumulative distribution curve using real data - in other words, there is no assumption regarding the underlying distribution of the data set with this visualization. An ECDF plot for Relative Humidity is shown in Figure 9, which shows how if one considered only the median relative humidity across all sites, they would all be between 70 – 80%. However, there is separation in the ECDF curves at lower relative humidity, which suggests some of those sites fluctuated to lower relative humidity than others. Relative humidity fluctuation plays an important role in corrosion damage morphology and development, so understanding when data sets have significantly different relative humidity fluctuation is important and made possible using the ECDF plot.

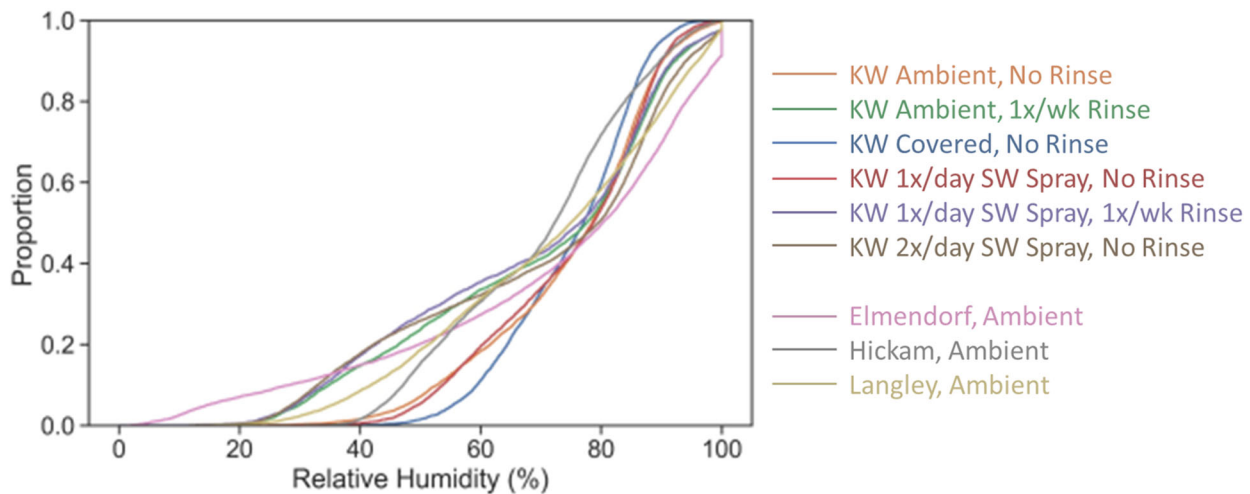


Figure 9. ECDF plot for relative humidity spanning all exposure conditions and locations.

While the differences in temperature and relative humidity ECDF plots are more nuanced, the ECDF plots for conductivity is more obvious. When considering the conductivity, Figure 10, the covered condition and the sea water spray conditions all showed high values. It is interesting to observe that the added conductivity intensity in the covered condition did not manifest additional mass loss corrosion like it did with the semi-frequent seawater rinses.

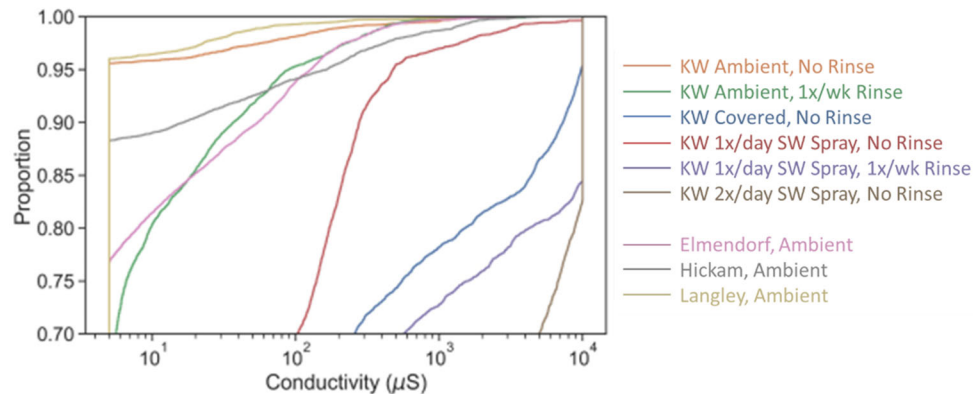


Figure 10. Conductivity for each exposure condition and location.

Environmental Severity Correlation Testing

A bar chart of the percent mass loss over the course of the first environmental severity correlation campaign is given in Figure 11. There is a wide distribution of mass loss values over the 17 sites, with WI exhibiting a 5 % reduction in sample mass after a year of exposure, while sites like FW and PAX did not see half a percentage point mass reduction in the same period. The mass loss tends to steadily increase over time. Due to natural scatter associated with any measurement recording process, there are a few instances where a later time step exhibited less mass loss than a previous time step, but the general trend still holds. The mass loss density rate is highest at the 1-month mark for all sites and steadily declines as time elapses. It seems that the mass loss rate reaches a steady state at the 6-month mark for most exposures (Figure 11b). It should be noted that some sites have a significant knock-down in the mass loss rate over tie, while other sites exhibit very mild differences between the 1-month and 12-month corrosion rates.

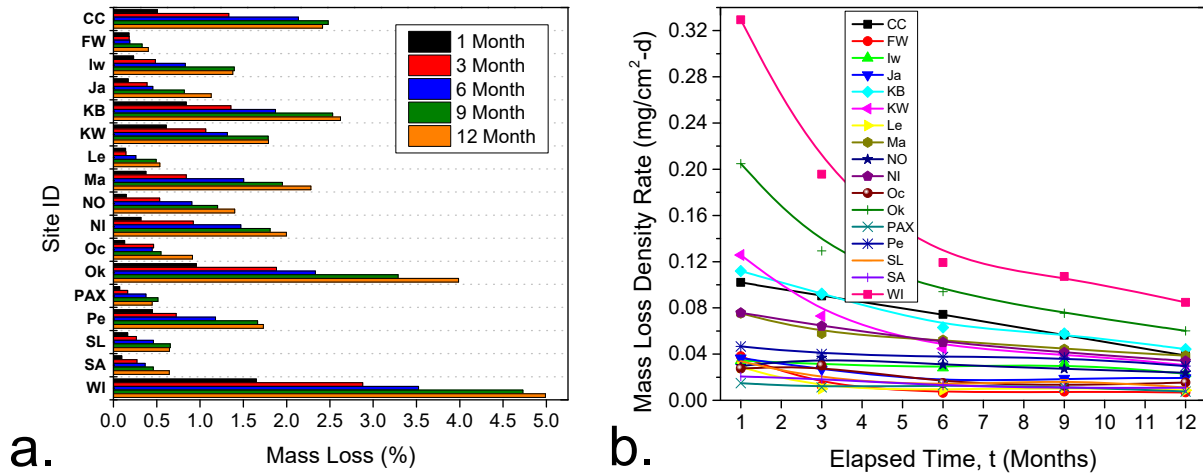


Figure 11. Steel mass loss reported as percent mass loss (a.) and mass loss density rate (b.).

The first campaign steel mass loss results for the 17 sites are presented in decreasing order in Figure 12a along with proposed severity categories. The proposed bins are: Very Severe (red), Severe (Orange), Moderate (Yellow), and Mild (Green). A scaling factor for the 17 sites based on the number of equivalent Key West months is presented in Figure 12b. As an example, this would mean a sample exposed for 1 year in Key West would equate to the same mass loss observed for 4 months at Whidbey Island or 55 months at Ft. Worth. This information is useful when comparing field exposure of systems in Key West to predict performance at the various other sites. Furthermore, the steel mass loss values are reported in Figure 13 in the form of heat maps. A time series of discrete mass loss ratings for each assessment period shows the variability between the sites over the year. The final image in Figure 13 is a corrosion rate map of the U.S. generated by extrapolating values between the various sites. The corrosion rate is taken as the mean average corrosion rate recorded for the 6, 9, and 12-month assessment intervals.

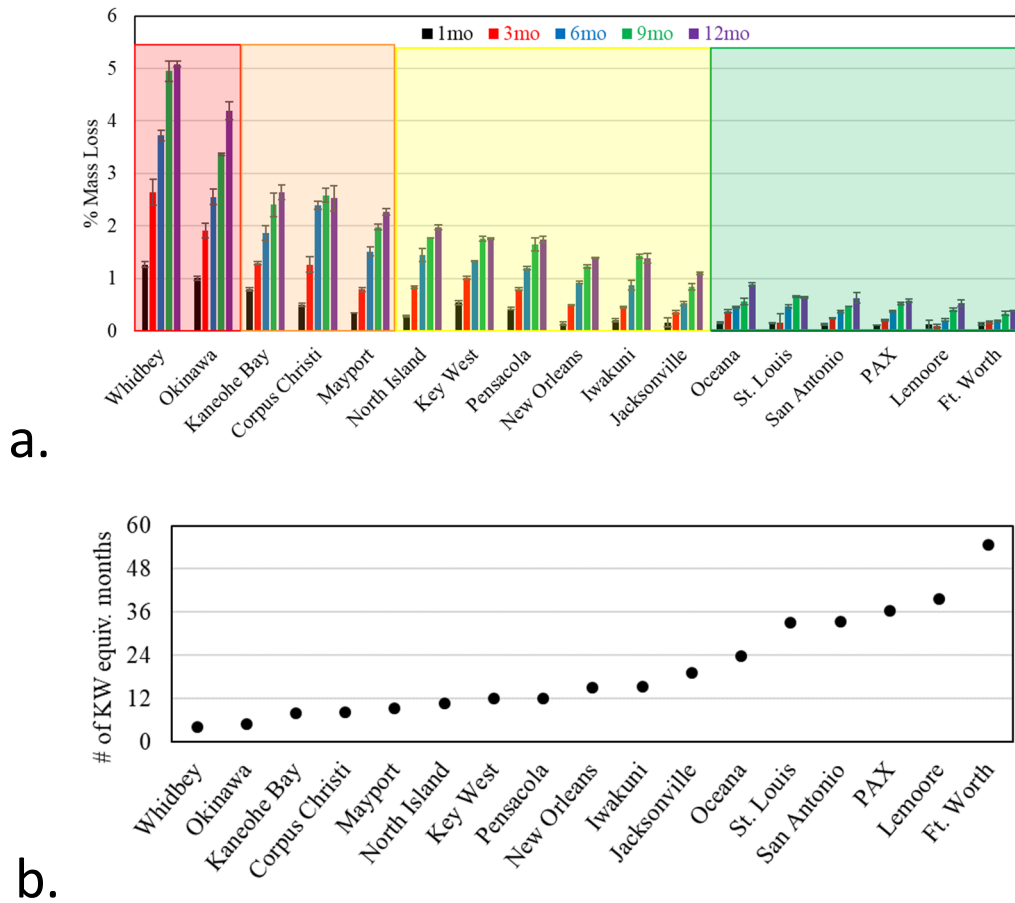


Figure 12. Steel mass loss reported by decreasing order and binned into severity categories (a.) and scaling factor for steel at the 17 sites in terms of Key West corrosion rate (b.).

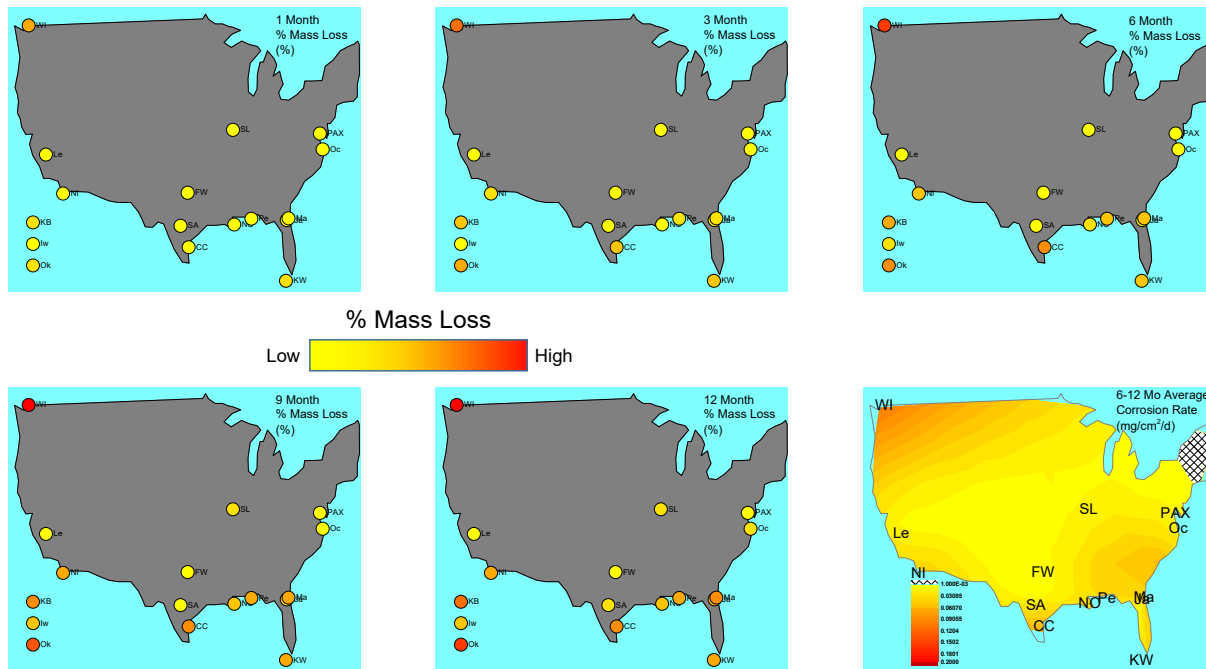


Figure 13. Select examples of steel samples after 1 month of exposure at the included sites. The effect of site location on steel corrosion is evident. The underlying map (left) indicates the NADP estimate for yearly dry chloride deposition and includes optical images of some samples. The continental US outline (right) depicts the mass loss data as a coloured scatter plot, where marker colour corresponds to percent mass loss.

Silver reduction results for Phase II are shown in Figure 14. Figure 14a shows a coloured bubble chart of select sites overlaid on a map of the continental US (left). The size of each bubble corresponds to the total reduction charge measured during galvanostatic reduction analysis (which in turn correlates to the amount of silver products on the surface). The colour of each bubble corresponds to the fraction of AgCl vs Ag₂S on the silver surface. The bar chart includes the speciated charge measured between AgCl reduction and Ag₂S reduction and the total charge. Most sites contain a mix of AgCl and Ag₂S, however a few sites were almost entirely composed of Ag₂S (Lemoore, Mayport, & New Orleans). Ag₂S is the most stable of the silver compounds, though AgCl is also very stable. There is a trend that the total charge increases over time, but the trend is not nearly as strong as it is for the steel mass loss. More importantly, silver acts to distinguish important chemical differences between the various sites.

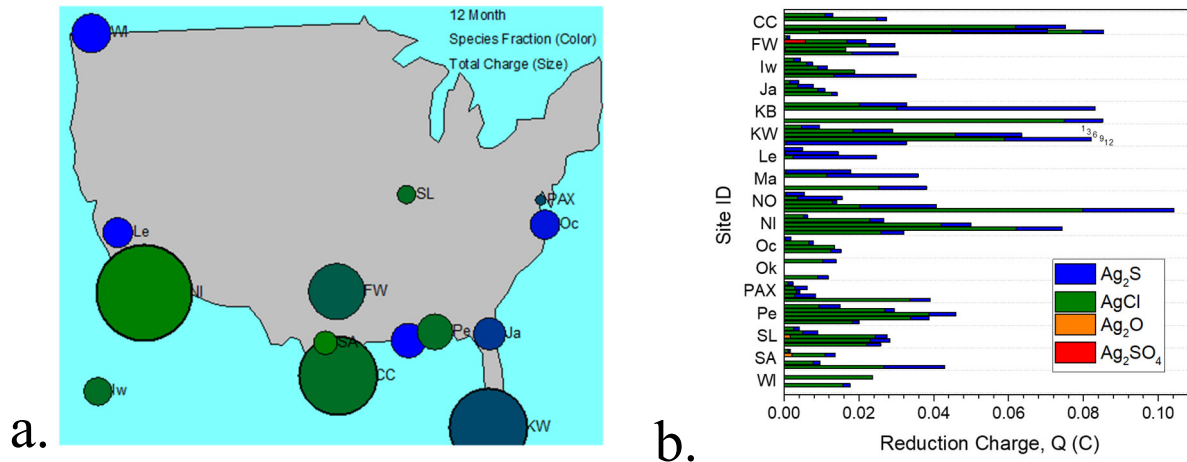


Figure 14. Available results from the silver reduction analysis highlighting the effect of site location on silver corrosion. The continental US outline (a.) depicts the galvanostatic reduction data as a bubble chart, where size corresponds to total reduction charge and color to AgCl/Ag₂S fraction. A bar chart of the speciated charge for each site for the five sampling intervals is included (b.).

The sites can be characterized both by the total charge and by the relative distribution of charge between various silver species. Figure 15 highlights these two aspects of silver reduction analysis. The total charge as a function of time is shown in Figure 15a. Within this period, sites fall into one of three categories based on total charge. Some sites like PAX and SA have relatively low charge for most of the exposure until later intervals when there is an uptick in the recorded charge. Next, sites like Pe exhibit moderate increases in the total charge at shorter times but plateau to a certain level at longer times. Finally, some sites like NI and KW have high charges over the entire course of the exposure with no real indication of diminishing accumulation. In terms of the relative chloride fraction (Figure 15b), sites again fall into one of three categories. Sites like Le and NI maintain a relatively constant chloride ration over time. Most of the other sites, like KW and Pe tend to have increasing content of AgCl over time. A few sites, like WI and Ja have a drop in the chloride content at the later sampling intervals (even if the chloride content had been steadily increasing in earlier intervals).

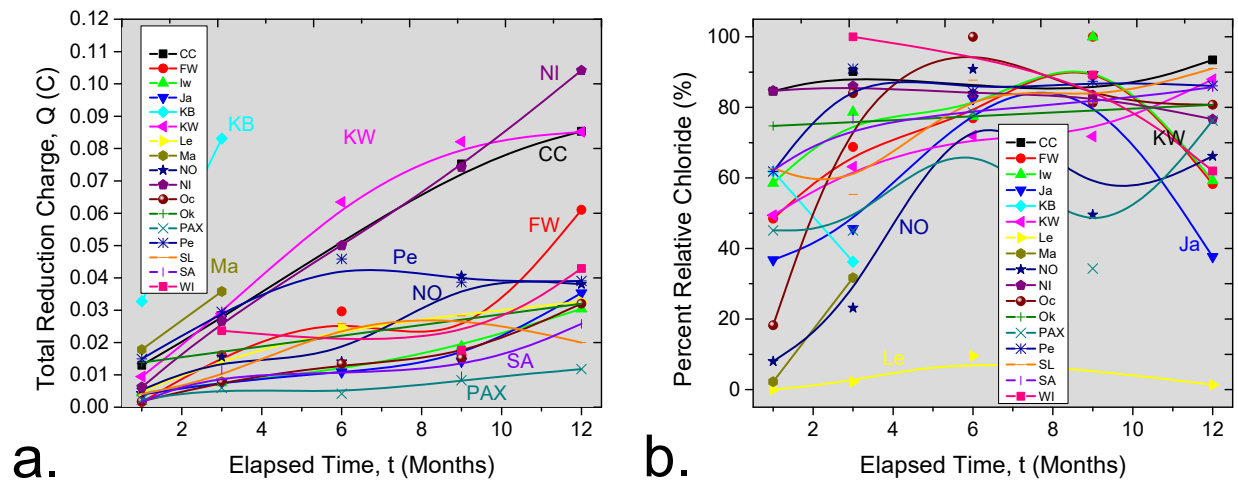


Figure 15. Silver corrosion product results from galvanostatic reduction. The total reduction charge is shown over the course of the year for each site (a.). The percent of the charge as AgCl relative to Ag₂S is shown as well (b.).

4.0 DISCUSSION

Steel mass loss is a common metric for assessing corrosion severity. As a preliminary analysis, higher mass loss values were typically observed for coastal sites. This is not a deterministic factor however, as some coastal sites had moderately low mass loss, such as Oc and Iw (Figure 12). More importantly, the mass loss is likely a function of sea spray produced by coastal wave breaking that contributes to salt deposition on the surface. Chloride deposition is strongly correlated to C1010 mass loss. Initially, the spread in the mass loss rate is quite high. Over time, the mass loss rate decreases for each site, and the spread becomes tighter between the sites. This reduction in the mass loss rate over time has been observed in other programs. In general, this decrease in the mass loss rate is attributed to the development of a corrosion product scale on the surface that inhibits the corrosion process over time. The corrosion scale is dependent upon the nature of the material in question. It may be that at short times, the corrosion rate is highly dependent on the exposure environment, while at longer times the corrosion rate becomes increasingly more dependent on the material in question (C1010 in this case).

The higher year-over-year mass loss for Phase II compared to Phase I may be due to the differences in the exposure start dates. If the earliest portion of the exposure were dominated by the environment, then the seasonal difference between starting Phase I in the late spring and Phase II in the early winter would affect the cumulative comparison of the mass loss between the two phases. If the post-6-month steady state mass loss rate is material dependent (all samples are C1010), then differences in the environment at earlier times will affect the cumulative comparison. The effect of climate may be important as well, as climates with high seasonal variability are likely to see a great effect of exposure start time on early rates of corrosion. Furthermore, another program is currently underway which directly assesses the effect of different exposure start times (spring, summer, fall, winter) on observed corrosion performance.

Alternatively, the possibility that the differences between Phase I and Phase II are due purely to statistical variations inherent in atmospheric exposure testing cannot be ruled out at this moment. Such a statistical analysis has not been conducted to our knowledge. A statistical spread would also explain why there are some cases where

longer term mass loss values are lesser than shorter term mass loss values (Figure 12, Ok 9 and 12 month values, for example). Perhaps this anomaly is indicative of the variability of the atmospheric corrosion mass loss assessment.

Low levels of silver products retained on the surface of the sample can be indicative of either low amounts of oxidation of silver (Ag) to silver cation (Ag⁺), washing of the surface so that atmospheric species do not have the chance to react with oxidized silver cations, or potentially photo-reduction of the oxidized species. Given the rather insoluble nature of common silver compounds and the rather high Nernst potential for silver oxidation, it is more likely that low reduction charge is a result of correspondingly lower levels of silver oxidation. Typically, UV radiation is needed to produce oxidizing species with high enough Nernst potentials to oxidize silver[9]. This explains why the KW and KB sites (which are high in UV radiation) have more silver compounds on the surface than the WI site (which is lower in UV radiation). Conversely, it is also possible that higher UV radiation could lead to photo-reduction of the silver compounds[9] but it is likely that this would quickly re-oxidize in a corrosive environment. Availability of corrosive species also plays a role in the corrosion film thickness on silver samples. It is theorized here that the lower levels of silver corrosion products at WI is consistent with a combination of lower UV loading and local concentrations of oxidizing species.

In terms of the speed at which corrosive attack occurs, as with all chemical processes, the overall rate of the corrosion process is limited by whatever step is rate-limiting. If a modification in the environment produces a faster corrosion rate, then it must facilitate (speed up) the rate limiting step (RLS). Conversely, if an environmental modification makes the corrosion rate slower, then it must have impeded (slowed down) the RLS or impeded some other step in the process to the point where it becomes the new, more impeded RLS. It should be noted that different materials corrode differently and have different RLS involved in the overall corrosion process. This concept helps explain why natural sea water spray accelerates corrosion and clear water rinsing impedes corrosion.

The conceptual diagram of Figure 16 provides a layout of the processes which control steel corrosion. First, salt is deposited on the surface of the steel via sea spray aerosol dry deposition as a function of the deposition velocity, V_d . This provides chloride, which is an accelerant for steel corrosion. The salt itself can also respond to the relative humidity at the sample surface (RH_{Surf}) by either absorbing water in higher humidity (deliquescence) or drying out back to crystalline solid in lower humidity (efflorescence)[17]. When the thin film salt solution is present at higher humidity, then the steel can oxidize via aqueous corrosion. Oxidized iron can dissolve into solution and be lost to the system during wetting events (rinse, spray, rain, etc.). The oxidized iron can also form iron scales that precipitate or dissolve as a function of the solubility product (K_{SP}) of the individual products. The scale can sometimes influence the further dissolution of iron by acting as a barrier. The glass bead blasting removes these iron scales so that only the non-oxidized iron remains. In this way, the iron oxidation is assessed via iron mass loss measurement.

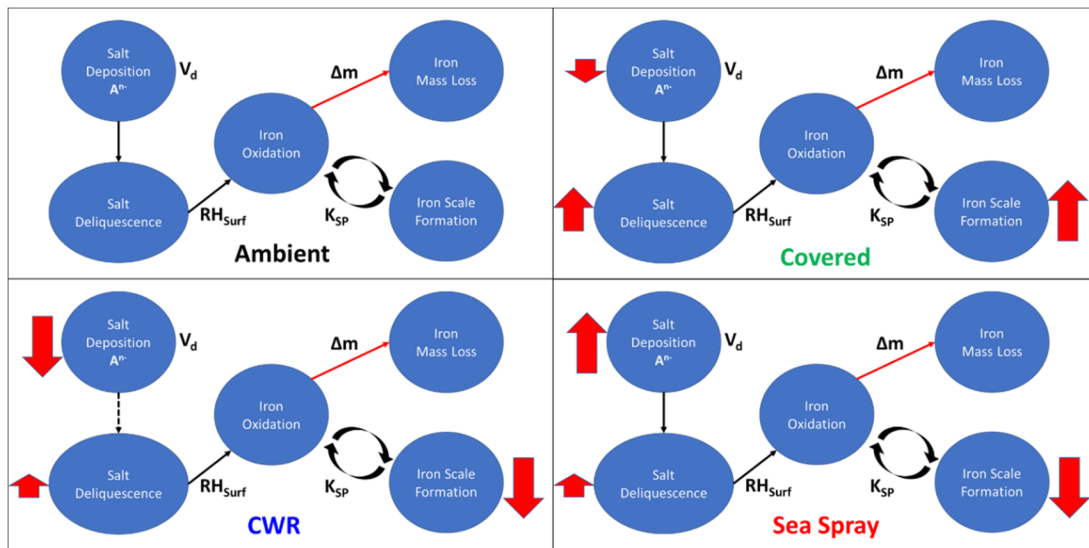


Figure 16: Conceptual diagram highlighting the processes controlling steel corrosion. The effect each test condition has relative to the ambient control condition is depicted with arrows for each portion of the process.

In the absence of sea water spray, the effect of CWR on reducing steel mass loss was readily seen (Figure 6). CWR is intended, by design, to remove salts from the surface which is why the salt deposition step is greatly impeded [12, 13]. The addition of periodic CWR may increase the overall humidity levels the samples experience, but this facilitation of salt deliquescence is expected to be small. Furthermore, frequent CWR of relatively pure water likely leads to iron scale dissolution, thereby limiting a potential avenue for iron oxidation impediment.

The effect of covering on increasing the steel mass loss was also clear (Figure 6). In this case, salt deposition is not expected to be largely impacted, since the aircraft cover is an open-air structure. While the orientation of the structure with respect to wind patterns at the sites and direction to nearest salt bodies influence salt deposition, the effect of covering is anticipated to slightly reduce the salt deposition. The cover is designed to protect the samples from solar impingement and precipitation. Solar radiation tends to heat up the surface of the sample and drive down the relative humidity at the surface, thereby reducing the time in the semi-wet phase or the time of wetness (TOW) [18, 19]. Additionally, the covered condition will experience less overall rinsing from precipitation effects, outside of the scheduled CWR routine, and therefore relatively less salt removal [20]. Both effects work to facilitate salt deliquescence on the samples. Less frequent rinsing from precipitation would have the effect of retaining iron oxide scales relative to the ambient condition, though this effect seems to have been negligible given the larger mass loss measured for the covered case.

The effect of sea water spray on increasing the steel mass loss was dramatic (Figure 5). The sea water spray is intended to, by design, increase the severity of the exposure. The sea water spray readily supplies salt to the sample surface and the frequent wetting is expected to increase the overall humidity experienced by the sample. Further, frequent spraying also likely leads to dissolution of iron scales. All these effects lead to an increase in the steel mass loss. The trade-off between the beneficial effect of CWR and the detrimental effect of sea water spray seems to depend largely on the salt deposition on the steel surface, since other factors are influenced similarly between the two conditions. Given that the CWR seemed to have no large effect on the sea water sprayed samples (Figure 5), the accumulation of salt on the surface from spraying must have significantly outpaced the removal of salt from

rinsing. This makes sense given that the spray interval was daily or twice daily (7 or 14 times a week, respectively) while the rinse interval was once or thrice weekly. Some beneficial effect of CWR was anticipated, however for this rinse and spray schedule the effect of rinsing was drowned out by the effect of spraying. It would be interesting to determine a what point would the effect of rinsing start to contribute to the overall process.

Finally, it is important to note that there was no large difference in steel mass loss between the once daily and the twice daily sea water spray. At first glance this seems odd given the accelerating effect the sea water spray has on steel corrosion. However, referring to the conceptual diagram of Figure 16 and the previous discussion on RLS, it is likely that the salt deposition step of the iron oxidation process was the RLS under ambient conditions. This being the case, the sea water spray readily facilitated salt deposition and made the whole process faster. It appears that with the daily sea water spray a new RLS is established since the salt deposition step is facilitated to such a large extent. In this case, facilitating further salt deposition with a twice daily spray has no impact on the overall iron oxidation process. Based on the conceptual diagram posited here, it is likely that the steel mass loss is limited by the deliquescence of the salt on the surface, which is governed by relative humidity. While the twice daily spray is likely to exhibit a longer overall time of wetness than the daily spray, it appears that the gain is negligible compared to the difference between the ambient control condition and either of the spray conditions.

The conceptual diagram of Figure 17 provides a layout of the processes which control silver corrosion, this time the focus is on silver product (Ag_nA) formation. To form Ag_nA products, Ag^+ ions must be supplied from silver oxidation and anions (A^-) must be supplied from atmospheric salt deposition. The deposition of species like chloride, sulphate, and sulphide has been discussed above regarding sea spray aerosols. The oxidation of silver is unique from that of iron due to the difference in their respective Nernst potentials. Silver is a more noble metal than iron and requires more potent cathodic reactions for metallic silver to oxidize to form silver cation. The predominant factor that governs silver corrosion has been shown to be UV radiation.[8] The highly energetic UV radiation can form highly oxidizing species like ozone and other atmospheric radicals. These UV-dependent species can oxidize silver to produce Ag^+ cations. The silver cations and atmospheric anions can form silver products based on the solubility product (KSP) of the silver compounds. For most silver compounds the KSP is quite low, meaning that the solid phases are much more stable than the dissolved aqueous phases. For this reason, it is generally stated that all the oxidized silver remains on the surface of the silver because formation of solid silver products is so favourable. These products can then be assessed via galvanostatic reduction.

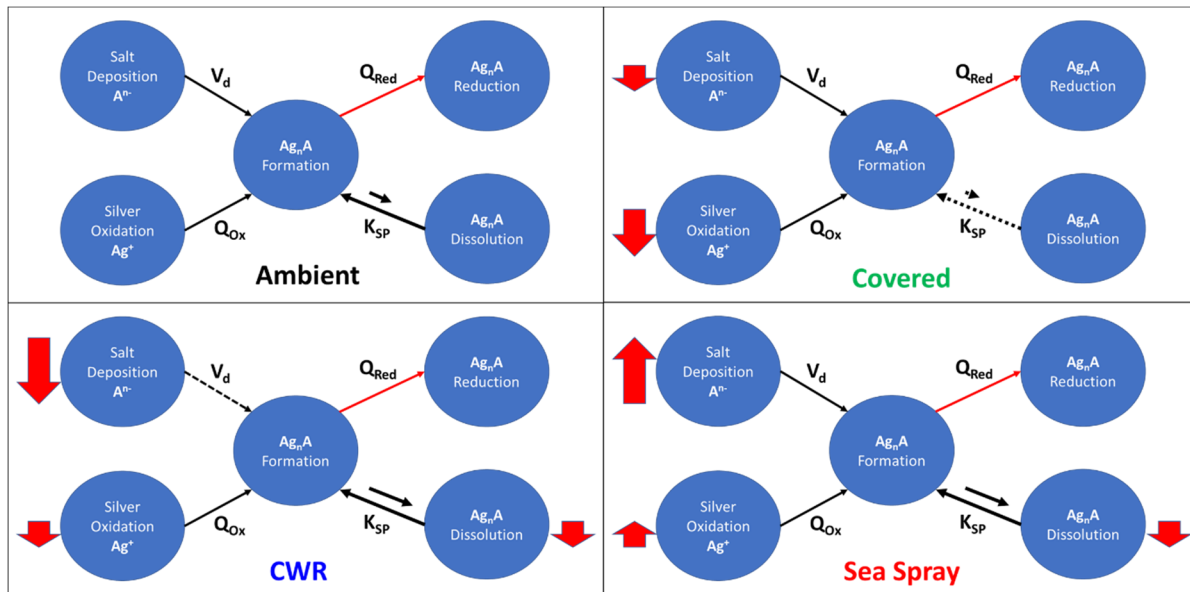


Figure 17: Conceptual diagram highlighting the processes controlling silver corrosion. The effect each test condition has relative to the ambient control condition is depicted with arrows for each portion of the process.

The ambient and covered conditions did not include sea water spray and exhibited a silver product distribution that was much richer in chloride than the sea water spray conditions. The source of chloride in marine environments is predominately from inorganic chloride salts present in the ocean water (NaCl, MgCl₂, CaCl₂, etc.). The source of sulfur (to include sulfur, sulfate, sulfide, sulfite, etc.) in marine environments includes inorganic sea salt sulfur but also non-sea-salt (nss) organosulfur[16, 21-23]. Non-sea-salt sulfur most commonly includes dimethyl sulfide (DMS), dimethyl sulfoxide (DMSO), and methanesulfonic acid (MSA), for example. Briefly, at the sea-air interface, agitation produced sea spray aerosols. These small particles have an airborne lifetime inversely proportional to their deposition velocity and a high surface area to volume ratio. Due to the high proportion of reactive surface and the airborne lifetime, these particles tend to lose volatile components normally present in sea water. Gaseous sulfur can volatilize from the aerosols, reducing the overall amount of elemental sulfur. These organosulfur compounds can also oxidize to form higher oxidation states of sulfur, like sulfate. Silver sulfate is less stable than silver chloride and will react to form silver chloride if conditions are favorable for the transformation to occur. The higher chloride content of the ambient and covered condition likely reflects this sulfur oxidation process, since the delivery mechanism is through sea spray aerosol deposition. For the sea water spray the situation is quite different. This water remains relatively fresh compared to that of the sea spray aerosols. In this case, there may be larger fractions of sulfur and more specifically sulfide with which to form silver sulfide species. Once formed, silver sulfide is unlikely to react to form silver chloride.

The only discernible trend for the effect of CWR on silver product formation/retention was observed for the covered condition, where increased frequency of rinsing resulted in decreased amount of silver products on the surface. One possible explanation is that the CWR tended to dissolve away some of the silver products. However, given the low solubility product of silver compounds and that this trend was not observed for other conditions, silver product dissolution may not be a sufficient rationalization of the observed behavior. Currently, it is unclear what the effect of CWR is on silver product formation/retention. The observed trend is weak and may be artificial

Environmental Modification

based on the possibility of scatter in the data. The effect will be probed in depth during the next phase of the F-22 CWR program, which spans a longer exposure duration.

Finally, there was less silver product on the sea sprayed samples than the ambient control case. The amount of silver on the surface of the sprayed samples was in a similar range to that observed for the covered case, but in the sprayed condition there was no covering so solar radiation should not be directly limited. The frequent spraying with sea water also rules out limitations from salt deposition. Given the very low solubility product of silver compounds, it is also unlikely that silver product dissolution was more prevalent for the more frequent wetting condition, although this explanation cannot be ruled out at this time. Furthermore, while the solubility product of silver compounds precludes chemical loss due to dissolution, there still may be physical loss due to silver product spalling from the silver coupon. This could arise uniquely for NSW spray if the silver products adhere less securely to the silver than in other conditions, or if the products are more aggressively disturbed by this condition during the spraying phase. Currently, the exact reason why there are fewer silver products retained on the surface of the sprayed samples is unknown.

5.0 CONCLUSIONS

- In Phase I, the steel mass loss measurements followed a linear pattern over time and were more similar between the three sites than initially expected. This indicates that historical assumptions of WI being less severe than KB are not entirely accurate (consistent with anecdotal evidence from WI). This finding supports on-going efforts to re-evaluate current maintenance intervals based on updated Environmental Severity Index (ESI) data. The results of Phase II were consistent in ranking WI as a very aggressive site, despite any clear or obvious reason.
- Mass loss rates initially began high but decayed to a steady state value after approximately 6 months. This highlights the importance of long-term atmospheric corrosion testing. Short term testing may indicate corrosion rates which are larger than what is actually experienced in the long-term and may incorrectly rank site severity from transient short-term corrosion rate values.
- Silver reduction analysis differentiates the ambient environment between the seventeen sites in terms of quantity and type of deposited species. The data is indicative of the total oxidizing power of a site and the atmospheric composition of species like chloride and sulfide. This data will be used to tune the KW accelerated test conditions used to mimic conditions at other sites.
- The corrosion behavior between seventeen sites was successfully differentiated on the basis of steel mass loss and silver reduction. The data generated under this program will be used to adapt the NRL-Key West test site to mimic different local conditions (with salt spray, length of exposure, or freshwater rinsing).
- The steel mass loss results were utilized to bin site severity into four categories: mild, moderate, severe, and very severe. Additional work will incorporate the results from the silver sample analysis to provide a more holistic corrosion risk factor for the 17 sites.
- Finally, a scaling factor was reported to estimate the amount of corrosion at the sites based on performance at NRL Key West. As this site is used more frequently, it is important to understand how to interpret future results in terms of operational locations for the Fleet.
- The Key West C-CoAST spray rack capabilities were successfully tested and assessed in this investigation. The combination of clear water rinsing (CWR), sea water spraying, and covering produced very different local exposure conditions. These environmental modifications definitively altered the steel mass loss and silver compound accumulation of the tested samples.

- The effect of covering the samples was to increase the steel mass loss and decrease the accumulation of silver products. The increased mass loss was attributed to higher time of wetness under the cover (or longer amounts of time at higher relative humidity). The decrease in silver product accumulation was attributed to less oxidizing power of the condition due to the removal of UV radiation impingement on the sample.
- The effect of CWR was to reduce the steel mass loss by removal of accumulated salt deposited on the surface via sea spray aerosol deposition. However, for the sea spray intervals assessed here, CWR made no beneficial impact in reducing the corrosion of steel. No correlation was observed for CWR and silver corrosion.
- The effect of sea water spray was to dramatically increase to steel mass loss. Sea water spray provided ample amounts of salt on the surface to facilitate corrosion. There was no large difference between daily and twice daily sea water spray on steel mass loss. Sea water spray also reduced the amount of silver products formed/retained on the surface, though for unknown reasons.
- Addition of seawater spray in Key West accelerates the corrosion by ~40-90x on corrosion witness coupons.
- The least amount of steel corrosion in KW was observed on covered, 3x/week CWR condition. (Bare materials would do well to be protected and rinsed off frequently.)
- Ambient KW condition is similar to both Hickam and Langley with the addition of once-per-week seawater spritzing. (Therefore, observed trends in Key West should also apply to the other locations in this study.)
- Silver corrosion film indicates that acceleration of the KW environment with seawater spray does not change the relative ratios of S/Cl on the surface. (Providing an acceleration of the condition but maintaining the correct chemistry.)
- Silver corrosion amounts show that composition of the silver corrosion products is consistent between Key West and Hickam, but Langley and Elmendorf have lower ratios of Ag₂S/AgCl.
- Information from the corrosion sensors can be relied upon for temperature, relative humidity, and solution conductance to provide continuous data about the local environment.
- Data from the bare and coated sensors for free and galvanic corrosion are a bit more complicated for interpretation.

7.0 ACKNOWLEDGMENTS

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