

ENVIRONMENTAL MODIFICATION and ATMOSPHERIC CORROSION: CLEAR WATER RINSING, COVERING, and SEAWATER SPRAY

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ABSTRACT

The F-22 program office is seeking to better characterize the impacts of clear water rinsing and handwashing in different operational conditions. The Naval Research Laboratory's testing facility in Key West, FL was chosen to test multiple, modified conditions against the same ambient environment. The effect of select environmental parameters on the atmospheric corrosion of silver and steel was assessed. The effect of clear water rinsing (consistent with current preventative maintenance strategies) was evaluated by rinsing all samples with fresh water thrice/twice a week, once a week, or naught at all. The effect of covering was tested by sheltering a set of samples underneath a canvas shelter, consistent with aircraft covering currently used. The effect of natural seawater spray was tested on select samples by spraying them either once a day or twice a day. All conditions were compared against the ambient exposure condition of Key West. The steel mass loss was compared across all conditions. The accumulation of silver compounds was assessed with galvanostatic reduction. The role each parameter plays in the corrosion process is discussed. Specifically, findings will be used to quantify the short-term impacts from accelerated outdoor testing. This effort will serve to better inform aircraft maintenance.

Key words: atmospheric corrosion, environment, marine environments

INTRODUCTION

Aerospace assets are subjected to routine maintenance cycles to prevent, monitor, and repair corrosion damage. Currently, the maintenance cycles are determined according to its model and following its respective requirements document (eg: NA(1) 01-1A-509¹ or USAF(2) Technical Order 1-1-691).² 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

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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, is the desire to alter the effective environment to more favorably alter the requirements for maintenance. Strategies include clear water rinsing (CWR), sheltering/covering assets, wash practices, and maintenance “personalization” based on unique asset and environment combinations.

Briefly, corrosive attack is facilitated by the presence of salts on and in the aircraft.³⁻⁶ 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.⁷⁻¹⁰ The intent of rinsing the aircraft with clear water, or water that is relatively free of ions, is to reduce the concentration of salt on and in the aircraft.^{2, 11} 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.² The main vehicle for salt accumulation is the deposition of salt from the atmosphere from sea spray aerosols.^{4, 5, 12} Sea spray aerosols are small particles of either liquid sea water or solid sea salt suspended in air. According to maintenance documents (like Technical Order 1-1-691)², service conditions which have higher rates of salt deposition on the aircraft require a higher frequency of CWR. 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. Sea water can purposefully be sprayed onto a sample in a controlled testing environment to accelerate the rate of corrosion, to stress a system to its breaking point, to test the limits of CWR efficacy, or to simply determine the maintenance requirement for CWR as a function of salt deposition.

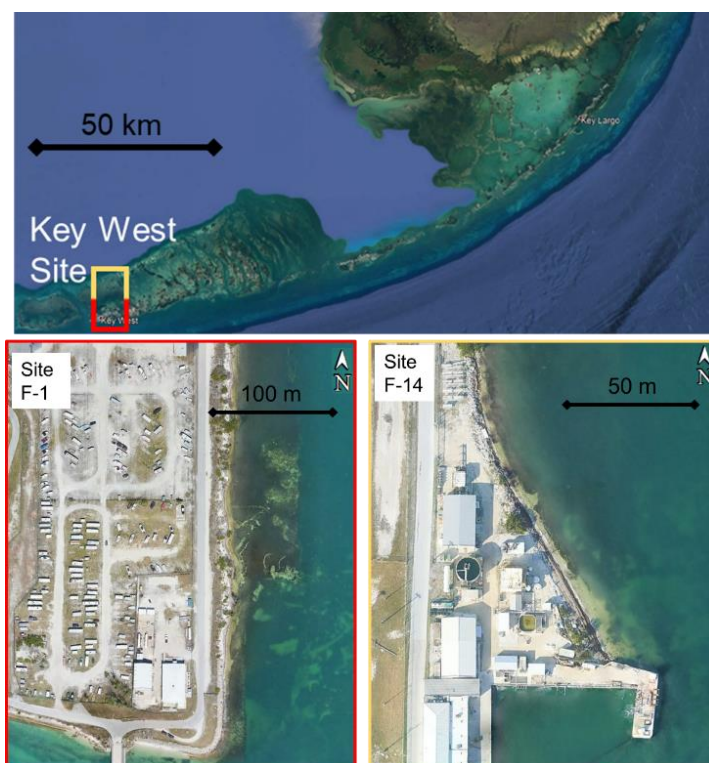


Figure 1: Overview of the Key West exposure site.

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.

Another maintenance strategy includes the application of an anti-corrosion coating on the surface of the aircraft.¹³⁻¹⁶ Aerospace coatings typically act to prevent corrosion in a passive manner by mitigating the accumulation of corrosive salts at the actual surface of the aluminum alloy (acting like a barrier) or in an active manner by actually preventing corrosion through some sophisticated mechanism. As the coating degrades, so too does its anti-corrosion capacity. Solar UV radiation is a primary culprit for coating degradation. The high energy rays from the sun promote undesirable organic reactions within the polymer matrix that alter the properties of the original formulation. Additionally, UV radiation commonly embrittles the coating, making it easier for it to crack and break down, which allows salt to reach the aluminum substrate. Sheltering the aircraft underneath a cover or within a hangar is the best preventative measure against UV degradation. It is unclear how an aircraft cover (shown in *Figure 2*) will affect the deposition of sea spray aerosols, since it is still an open-air structure. This investigation pursues a deeper understanding of how CWR, sea water spray, and covering impacts corrosion resistance.

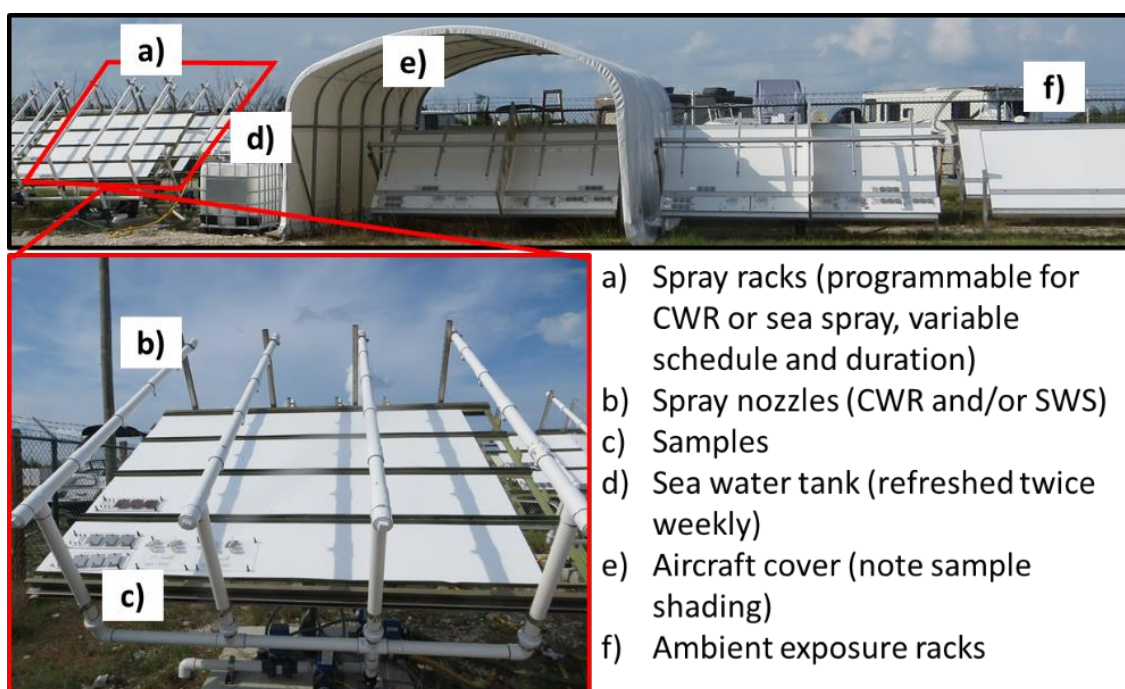


Figure 2: A selection of the exposure racks utilized for this environmental modification study. Included in this snapshot are spray racks which can be programmed to be completely ambient, CWR, or sea water spray. An aircraft cover which is the same as what is used on DoD assets (such as the F-22 fighter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

The potential time and cost savings of implementing CBM protocols in place of generic one-size-fits-all plans is substantial. Assets which are deployed in more benign environments should require less maintenance than those deployed in harsher environments. Thus, extra time and costs are avoided if unnecessary maintenance cycles can be reduced for those assets which need less frequent inspections. Similarly, an environmental condition can be modified with strategic CWR. Maintenance may be reduced if proper CWR routines are implemented. 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. *Table 1* summarizes all twelve of the different environmental conditions studied herein.

Table 1: Summary of the exposure conditions tested in this investigation.

Baseline Condition	No Rinse	Once Weekly Rinse	Multi-Weekly Rinse
Ambient (No Spray)	[A]	[A1]	[A2]
Covered (No Spray, No Rain, No Sun)	[C]	[C1]	[C2]
Daily NSW Spray	[S]	[S1]	[S3]
Twice Daily NSW Spray	[X]	[X1]	[X3]

EXPERIMENTAL PROCEDURE

Exposure

The Key West site is a state-of-the-art testing facility located on Fleming Key within the Naval Air Station. 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. An overview of the facility is shown in *Figure 1*. There are principally two sites at the Key West facility, F-1 and F-14. The F-1 test site was where this environmental modification testing was conducted. At this site, there are spray racks which have been designed to conduct clear water rinsing or sea water spray. 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 rinse was provided by the Florida Keys Aqueduct Authority via the fresh water supplied to NAS Key West.¹⁷ 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. *Figure 2* shows some of the details of the spray racks used in this investigation. Of special note is the configuration of the spray racks and the aircraft cover. The spray racks and nozzles shown in *Figure 2* were, in some instances, used for both the CWR and the sea water spray.

For this analysis, exposures were conducted from September 30th, 2020 through December 30th, 2020 at the F-1 test site described above (*Figure 1*). A combination of different exposure conditions were tested, as summarized by *Table 1*. There are essentially four base conditions, ambient [A], covered [C], daily spray [S], and twice daily 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*.

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	

Water Chemistry

Fresh water is provided to the facility by the Florida Keys Aqueduct Authority(3).¹⁷ An in-depth analysis of the water chemistry used in this investigation is reported in the NRL Letter Report entitled NRL-Key West Spray Rack Water Quality Report. The focus of that report was a) to determine if the sea water stored in the tank changed over time in between refills from the oceanic source, b) provide a relative comparison between the clear water, the rain water, and the sea water, and c) to determine if the current experimental setup (which utilizes the same water lines to spray freshwater and sea water) is valid or if a different design should be conceived. The result of the report showed that the sea water in the tank 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 the CWR source fresh water (the source water provided by the Aqueduct Authority¹⁷) 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.¹⁷

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^{8, 18} and was exposed as 0.5 x 3 x 0.011 inches in dimension. The silver was polished to 600 and then 1200 grit surface roughness. Both steel and silver were exposed in triplicate and mounted using nylon fasteners.



Figure 3: Representative image of the silver and steel coupons deployed in this investigation. These samples are shown after two months of the daily sea water spray with the weekly CWR.

Testing

Mass loss measurements were collected from the C1010 low carbon steel coupons. Accumulated corrosion product was removed via glass bead blasting to isolate the metallic substrate remaining after the exposure. The either the area normalized mass loss or the percent mass loss is reported.

Galvanostatic reduction was performed on the silver witness coupons to determine the relative oxidation power of the exposure condition and what atmospheric species were present during exposure.^{8, 18} Most

(3) Florida Keys Aqueduct Authority, 1100 Kennedy Drive, Key West, Florida 33040

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