Effect of Chromate Containing Primers on Corrosion Fatigue in Legacy Al-Zn-Mg-Cu Alloys

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ABSTRACT

Corrosion fatigue is an area of concern for the USAF and other DoD organizations. Often the DoD corrosion prevention systems include chromate containing coatings, typically in the form of chromate conversion coatings and primers. Chromate has been used successfully for many years within the DoD to prevent corrosion damage. However the environmental and personnel risks associated with chromate coatings have caused the USAF to pursue non-chromate containing corrosion prevention coatings [1]. To fully quantify chromate replacement coatings, an understanding of the effects that chromate has on corrosion fatigue must be fully documented and understood. Some researchers have shown that high levels of chromate added to 0.6 M NaCl full immersion corrosion fatigue tests on 7xxx series aluminum alloys slow the fatigue crack growth rate substantially [2]. The limitation of that research was that the amount of chromate present in the environment was not connected to expected leach rates of chromate from polymeric coatings and a high solubility salt was used.

The majority of DoD assets are protected from corrosion by polymer coatings loaded with corrosion inhibitors. For these inhibitors to slow fatigue crack propagation the corrosion inhibitors must become mobile as a consequence of hydration of the polymer coating matrix. Based on this mechanism of corrosion inhibitor release, the examination of atmospheric corrosion fatigue becomes important to help understand how inhibitors work in real world situations with hydrated salt layers rather than only fully immersed solutions.

The development of the database for the effect of chromate on corrosion fatigue in aluminum alloys has been slowed by the presence of bacteria, *Ralstonia pickettii*, which slows fatigue crack growth rates in 7xxx series aluminum alloys to near the crack growth rate with 0.5 M sodium chromate (Na_2CrO_4). The mechanism by which the bacteria are lowering fatigue crack growth rates in sodium chloride solutions is not currently understood, but is being investigated. The current hypotheses are the development of a

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protective film, whether oxide or some other material (biofilm), on the crack surface or effects on the overall corrosive environment such as desalination of the test solution.

Future work will continue to investigate the effect of chromate and other corrosion inhibitors on environmentally assisted fatigue. This dataset will allow for a baseline comparison for chromate replacement corrosion inhibitors

Key words: chromate, corrosion fatigue, AA7075-T651, *Ralstonia pickettii*, environmentally induced cracking, microbial induced corrosion (MIC), microbial inhibited corrosion

INTRODUCTION

As the USAF and DoD extend the life of current assets, corrosion damage becomes a larger concern. At the same time the DoD has moved to phase out the use of chromates as a corrosion inhibitor due to the environmental and personnel risks [1]. Chromates are used in a variety of corrosion prevention coatings including conversion coatings and primers. Corrosion damage is of concern to the aircraft sustainment community for many different structural integrity reasons, including situations in which corrosion damage may act as a stress raiser and initiate fatigue cracks. While it has been documented that high levels of chromate and a chromate replacement inhibitor, molybdate, added to a bulk solution can inhibit fatigue crack propagation, it has not been shown that these inhibitors leaching from a coating can do the same [2-6]. However, if chromate does provide protection that slows corrosion fatigue crack propagation the removal of chromate from coating systems would mean that current systems have protection that is currently unaccounted for, that will be lost in chromate-free systems. At the same time, chromate is considered the benchmark for all other corrosion inhibitors to meet, so an understanding of the protection chromate provides to corrosion fatigue is needed.

EXPERIMENTAL PROCEDURE

To determine the effect chromate has on corrosion fatigue damage in DoD-relevant materials, a single edge notch specimen, shown in Figure 1, was used for all fatigue testing. The samples were made from a peak-aged, legacy age-hardenable Al-Zn-Mg-Cu aluminum alloy and temper (7075-T651). The sample was loaded into a computer-controlled servohydraulic test frame and crack growth was measured using a direct current potential drop (dcPD) system. The test load was controlled to provide a constant ΔK=6 MPa$\sqrt{m}$ with a stress ratio (R) of 0.65. The loading frequency was varied from 0.02 to 20 Hz in a bulk 0.06 M NaCl environment.

All of the prior corrosion fatigue work with aluminum alloys was completed using inhibitors added to a bulk NaCl solution or deliquesced onto the surface of a sample rather than the migration of inhibitors from polymer matrix coatings [2-6]. The inhibitors used for most of these fatigue studies were high rather than low solubility inhibitors, the latter of which are typically used in corrosion prevention military aviation coatings [2-8]. This difference may be of importance as the leaching of inhibitors is purposely controlled in organic coatings via salt solubility in order to make the life of the coating acceptable. That said, this inhibitor leaching would be the source of any inhibitor that could affect fatigue crack propagation. All of these variables make understanding the leaching rate of known coatings and inhibitors critical to designing appropriate fatigue test criteria. An understanding of the chromate leaching rate from coatings and how chloride concentration and pH and could change the amount of chromate present in a solution was needed. To answer these questions a literature review of chromate leaching rates, inhibitor pigment solubility effects and leaching studies was performed.

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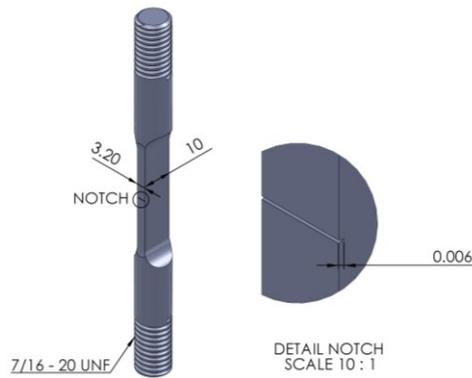
Figure 1: Single edge notch (SEN) specimens were made of 7xxx series aluminum alloy. All dimensions in millimeters.

INHIBITOR LEACHING

The leaching of inhibitors from coatings is affected by many things: nature of the polymer matrix, inhibitor loading, inhibitor pigment and inhibitor solubility, and chemical composition of the leaching solution including the pH [7-9]. The polymer matrices typically used with chromate and molybdate pigments include epoxies, polyurethanes, and acrylics. In the studies reviewed, the epoxy primers leached at higher rates than the polyurethane but lower than acrylic coatings, which are typically used with a topcoat [7-9].

For commercial coatings the loading amounts of inhibitors can vary, but are designed such that the coating is not depleted of inhibitor during a maintenance cycle, typically 6 to 8 years [8,9,12]. Organic coatings with inhibitors are understood to readily absorb water or other liquid environments through inherent defects in the coating resulting in interconnected pores which allows inhibitor pigments within the coating to dissolve and dissociate in electrolyte within the coating itself [7-11].

Table I gives the properties desired for inhibitor pigments for loading into a polymer coating [8,9]. Typically, pigments with low water solubility are selected for use in coatings so that (a) osmotic pressure-induced blisters are avoided, and (b) the inhibitor remains in the coating over long times rather than rapidly dissolving out when first in contact with corrosive environments [8,9]. Because of the low solubility, inhibitor leaching would be expected to only allow low concentrations of inhibitors to be reached in the surrounding solution before precipitation occurs. For the bulk solution fatigue testing previously completed, Na_2CrO_4 and Na_2MoO_4 were typically used, which are salts with much higher water solubility than typical in an inhibitor pigment loaded into a coating [8,9]. Table II shows the solubility of typical coating pigment, $SrCrO_4$ and $CaMoO_4$, pigments in water compared to those of Na_2CrO_4 and Na_2MoO_4. It should be noted that all other physical properties of Na_2CrO_4 and Na_2MoO_4 are within the acceptable limits for coating use other than solubility [8]. The high water solubility can cause blistering of the polymer and cause the inhibitor to leach from the polymer too quickly which also make them undesirable for use in coatings [8,9]. However, these salts have advantages in studies of corrosion fatigue inhibition in that the high solubility prevents precipitates that cause crack closure, allowing for a better understanding of the crack tip passivation mechanism.

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Table I: Property requirements of inhibitor pigments [8].

Inhibitor Pigment Parameter	Desired Value
Solubility in Water	< 2g/100mL
pH of Saturated Solution	7-9.5
Specific Gravity	1.5-5
Particle Size Distribution	2-6 μm
Solubility in Organic Medium	Practically Insoluble
Vapor Pressure at 20 C	<1/10,000 mmHg
Melting Point	>100 C

Table II: Solubility in water for typical chromate and molybdate pigments compared to Na_2CrO_4 and Na_2MoO_4 [13]. It should be noted sodium chromate is within acceptable ranges for all of the other parameters in Table I.

Inhibitor Pigment	Solubility in Water
$SrCrO_4$	0.096 g/100mL
Na_2CrO_4	87.6 g/100mL
$CaMoO_4$	0.0011 g/100mL
Na_2MoO_4	65.0 g/100mL

For our previous leaching studies, Luna Innovations developed four coatings containing different loading amounts of $SrCrO_4$ (either 12 or 17 weight percent) and epoxy bases. The leaching studies were completed by exposing the free-standing films in 100 mL of DI water for 2 and 4 days. The surface area in contact with water for each film was 29 cm^2. The leached liquid samples were then examined using UV-Vis Spectroscopy using 0.001299 M and 0.00033 M CrO_4^{2-} standards serially diluted from a 1000 ppm CrO_4^{2-} (0.0065 M) purchased standard solution (K_2CrO_4 was used for the standards) to determine the amount of CrO_4^{2-} present. The leaching data from the free films were extrapolated from the standards by the WinUV software on the Varian Cary Series spectroscope.

The results of the leaching from the $SrCrO_4$ films appear in Table III in terms of mg CrO_4^{2-}/cm^2 of coating. Table IV gives the leaching data converted into mol/L of CrO_4^{2-} to allow comparison with published results. Based on the leaching results, Film 1 was selected for fatigue crack growth testing given the high leaching amount and relatively high remaining CrO_4^{2-} remaining in the film, both desired for fatigue testing.

Table III: Leaching results for $SrCrO_4$ primer films with 29 cm^2 surface area leached into 100 mL DI water. Original leaching data obtained by UV-Vis Spectroscopy.

Film Number	Concentration (mg/cm^2) 2 Days	Concentration (mg/cm^2) 4 Days
1	0.310	0.414
2	0.241	0.310
3	0.483	0.552
4	0.310	0.379

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Table IV: Leaching results for SrCrO₄ primer films with 29 cm² surface area leached into 100 mL DI water converted into millimol/L (mM) CrO₄²⁻. Original leaching data obtained by UV-Vis Spectroscopy.

Film Number	Concentration (mM) 2 Days	Concentration (mM) 4 Days
1	0.4	0.6
2	0.3	0.4
3	0.7	0.8
4	0.4	0.5

Table V shows the expected leaching concentrations of CrO_4^{2-} based on the film leaching results for the different testing geometries used in the program. Figure 2 shows the single edge notch (SEN) sample and three different test configurations. The Bulk Testing label refers to a standard test cell filled with 500 mL of solution with a SEN sample primed on all four sides (Coating Surface Area: 7.92 cm²). The Restricted Volume refers to a very small cell containing approximately 0.1 mL of solution covering a 2 cm high portion of the flat on the SEN sample (Coating Surface Area: 5.28 cm²) which seeks to mimic areas such as lap joints and other occluded regions of aircraft. The Coating Surface Area to Volume ratio for the reduced volume cell was determined using aircraft components at USAFA. Thin Film refers to salt deliquesced to form a 100 µm thickness film (8×10^{-5} L) onto the four flat surfaces of the SEN sample (Coating Surface Area: 7.92 cm²).   The Thin Film environment is used to mimic how atmospheric corrosion is understood to occur on aircraft structure rather than a large pool of liquid around the sample.

Table V: Expected leaching results for SrCrO₄ primer films converted to the test three geometries. All concentrations are in terms of mol/L (M) CrO₄²⁻. Original leaching data obtained by UV-Vis spectroscopy.
***above the SrCrO₄ solubility limit of 0.0047 M CrO₄²⁻ [13]**

Film Number	Expected Concentration (M) Bulk Solution (500mL) 4 Days	Expected Concentration (M) Restricted Volume (0.1 mL) 4 Days	Expected Concentration (M) Thin Film (0.1 mL) 4 Days
1	3.21×10^{-5}	0.021*	0.201*
2	2.41×10^{-5}	0.016*	0.151*
3	4.28×10^{-5}	0.029*	0.268*
4	2.95×10^{-5}	0.020*	0.184*

Bulk Solution Test Cell (500 mL)   Reduced Volume Test Cell (0.1 mL)   Atmospheric (Thin Film) Exposure [4]

Figure 2: Sample Volumes used for Concentration Calculations

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The leach rates from the model films were compared to that expected from published CrO_4^{-2} leaching in Table VI and Table VII [8-10]. To make the comparison, the published leaching data were converted to molarity using the geometries and volumes of the Luna film leaching experiments and the testing geometries reviewed above. The Luna films were able to leach about 6-20 times more chromate into solution than the commercial epoxy primer. This result suggests that the Luna film is likely more porous than the commercial primer as the loaded salt was the same ($SrCrO_4$). Also a 12-17% loading amount is on the low end for chromate, so that is unlikely to be the cause of the leaching differences [8,9]. Porosity and how the pores are connected in a polymer greatly affects leaching of inhibitors, so porosity differences could account for the observations [8,9]. The porosity is related to the pigment volume concentration present in a coating and the resin used in the polymer [9]. Often these parameters are not reported. However pore size, crosslink density binders and other polymer matrix information that would be helpful to understanding the mechanism behind the porosity effect were not provided [8,9].

Table VI: Chromate leaching data from a commercial epoxy primer in different chloride solutions [9]. Original leaching data obtained by capillary ion analysis spectroscopy. *above the SrCrO$_4$ solubility limit of 0.0047 M CrO$_4^{2-}$ [13]

Chloride Concentration	Expected Concentration (M) per Film Dimensions (0.1L) 225 Hours	Expected Concentration (M) Bulk Solution (500mL) 225 Hours	Expected Concentration (M) Restricted Volume (0.1 mL) 225 Hours	Expected Concentration (M) Thin Film (0.1 mL) 225 Hours
0.1 M	8.5×10^{-5}	4.7×10^{-6}	0.003	0.029*
0.01 M	7.0×10^{-5}	3.8×10^{-6}	0.003	0.024*
0.001 M	8.5×10^{-5}	4.7×10^{-6}	0.003	0.029*
0.0001 M	10.0×10^{-5}	5.4×10^{-6}	0.004	0.034*

Table VII: Leaching data from a SrCrO$_4$ commercial epoxy primer. Original data obtained by atomic absorption spectroscopy [8]. *above the SrCrO$_4$ solubility limit of 0.0047 M CrO$_4^{2-}$ [13]

Solution	Expected Concentration (M) per Luna Film Dimensions (0.1L) 50 Days	Expected Concentration (M) Bulk Solution (500mL) 50 Days	Expected Concentration (M) Restricted Volume (0.1 mL) 50 Days	Expected Concentration (M) Thin Film (0.1 mL) 50 Days
H$_2$O	5.1×10^{-5}	2.8×10^{-6}	0.002	0.012*
0.85 M NaCl	8.7×10^{-5}	4.8×10^{-6}	0.003	0.020*

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Table VIII: Chromate leaching data from a commercial epoxy primer in 0.85 M NaCl adjusted to different pH levels [10]. Original leaching data obtained by inductively coupled plasma atomic emission spectroscopy (ICP-AES).
*above the SrCrO$_4$ solubility limit of 0.0047 M CrO$_4^{2-}$[13]

pH adjusted 0.85 M NaCl	Expected Concentration (M) per Luna Film Dimensions (0.1L) 60 Days	Expected Concentration (M) Bulk Solution (500mL) 60 Days	Expected Concentration (M) Restricted Volume (0.1 mL) 60 Days	Expected Concentration (M) Thin Film (0.1 mL) 60 Days
1	3.6×10^{-4}	1.9×10^{-5}	0.013*	0.121*
3	3.6×10^{-4}	1.9×10^{-5}	0.013*	0.121*
5	3.6×10^{-4}	1.9×10^{-5}	0.013*	0.121*
7	3.6×10^{-4}	1.9×10^{-5}	0.013*	0.121*

Table IX: Chromate leaching data from a commercial epoxy primer in 0.85 M NaCl adjusted to different pH levels [10]. Original leaching data obtained by inductively coupled plasma atomic emission spectroscopy (ICP-AES).
*above the SrCrO$_4$ solubility limit of 0.0047 M CrO$_4^{2-}$ [13]

pH adjusted 0.85 M NaCl	Expected Concentration (M) per Luna Film Dimensions (0.1L) 60 Days	Expected Concentration (M) Bulk Solution (500mL) 60 Days	Expected Concentration (M) Restricted Volume (0.1 mL) 60 Days	Expected Concentration (M) Thin Film (0.1 mL) 60 Days
1	8.5×10^{-4}	4.7×10^{-5}	0.031*	0.291*
3	4.1×10^{-4}	2.3×10^{-5}	0.015*	0.141*
5	3.1×10^{-4}	1.7×10^{-5}	0.011*	0.107*
7	3.6×10^{-4}	1.9×10^{-5}	0.013*	0.121*

Interestingly, in the published data on the leaching of four commercial epoxy primers in Tables VI-IX studied varied by about 16 times between the high and low leaching coatings [8-10]. The loading amount of chromate for all of the coatings can vary, however as the porosity of the film can also greatly affect the leaching rates there may be some difference in the polymer filler between the two primers [8,9]. More research is needed into how the polymer matrix changes the leaching rates.

From the data in Table VI, there is no significant difference in leaching rates with the variation of chloride content, which are all relatively low concentrations (0.1 M or less NaCl). In Table VII however the higher chloride content (0.85 M) makes a large difference, nearly doubling the amount of CrO$_4^{2-}$ leached from the coating. This result suggests there could be a threshold of chloride content over which the chloride is detrimental to the polymer matrix allowing for more inhibitor release. Because the baseline leaching rates for the two commercial primers are different it is difficult say what the overall effect of chloride has, but some publications state that chloride content affects leaching because chloride is detrimental to the polymer matrix [8,9].

In the primers shown in Table VIII and Table IX, the change in pH does not cause large changes in the amount of chromate leached. There is some suggestion in Table IX that more acidic environments cause more leaching for that coating, but the change in the amount of chromate leached is about the same as the scatter with NaCl concentration changes, which is less that the leaching amount changes from one epoxy primer to the next.

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The University of Southern Mississippi (USM) developed three $CaMoO_4$ containing primers. Each primer had a different loading amount of MoO_4^{2-} (20.8%, 28.7%, 36.9% weight percent). USM coated and scribed AA 7075 panels (Surface Area: 6.45 cm^2) prior to completing leaching experiments in 100 mL DI water. The leaching results appear in Table X along with the concentrations expected for the three test conditions. Table X shows that the higher the loading amount of MoO_4^{2-}, the lower the leaching amount. This result is highly unexpected, and the mechanism behind this result is currently not understood. USM originally thought they might be exceeding the solubility limit between the $CaMoO_4$ and solution, but that is not the case as the leaching values are always below the solubility limit of 0.05mM [13]. Also, as the inductively coupled plasma mass spectrometry (ICP-MS) is capable of detecting 1 part per billion, it is unlikely they are having trouble measuring the molybdate leaching from the coating. The explanation for these results remains to be determined.

Table X: Leaching results for the CaMoO₄ coatings developed by USM. Original leaching data produced by inductively coupled plasma mass spectrometry (ICP-MS).
*above solubility CaMoO₄ limit of 0.055mM [13]

Loading Amount	Leaching Concentration (100mL) 4 Days	Expected Concentration (M) Bulk Solution (500mL) 4 Days	Expected Concentration (M) Restricted Volume (0.5 mL) 4 Days	Expected Concentration (M) Thin Film (0.1 mL) 4 Days
20.8% MolyWhite	1.8×10^{-6}	4.3×10^{-7}	2.9×10^{-4}*	0.003*
28.7% MolyWhite	4.1×10^{-7}	1.0×10^{-7}	6.7×10^{-5}*	6.0×10^{-4}*
36.9% MolyWhite	4.7×10^{-7}	1.1×10^{-7}	7.7×10^{-5}	7.0×10^{-4}*

Based on the leaching results presented, the plan was to move forward with the test matrix in Table XI for all corrosion fatigue inhibition testing. This testing was to determine the effect of the corrosion inhibitors chromate and molybdate in amounts that could be leached from at a coating on fatigue crack growth rates. Another theory to be tested was the low solubility inhibitors could inhibit fatigue crack propagation by forming solids within the crack and causing crack closure.

Table XI: Proposed test matrix to determine the effect of chromate and molybdate in leached concentrations.

Inhibitor	Inhibitor Form	Environment	Amount (concentration in solution or wt % in coating)
Na_2CrO_4 /Na_2MoO_4	Salt	Bulk Solution NaCl	<0.5/0.002mM
$SrCrO_4$ /$CaMoO_4$	Salt	Bulk Solution NaCl	<0.5/0.002mM
$SrCrO_4$ /$CaMoO_4$	Salt	Bulk Solution NaCl	>4.7/0.05mM
$SrCrO_4$ /$CaMoO_4$	Primer	Reduced Volume NaCl (< 0.1 mL)	17%/20.8%
$SrCrO_4$ /$CaMoO_4$	Primer	Atmospheric NaCl	17%/20.8%
$SrCrO_4$ /$CaMoO_4$	Primer	Bulk Solution NaCl	17%/20.8%

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RESULTS

Testing was completed using inhibitor pigments that would be found in commercial molybdate coatings, calcium molybdate ($CaMoO_4$). All testing was completed at a constant $\Delta K=6$ MPa√m, $R=0.65$ in a bulk (500 mL) 0.06 M NaCl solution. The results for this test are shown in Figure 3. The starting concentration of $CaMoO_4$ was 0.002 mM (yellow star) which is below the solubility limit, the concentration was then increased to 0.01 mM $CaMoO_4$ (orange star), for these concentrations the solubility limit would be expected to have been exceeded in the crack. The crack growth rates for the two concentrations of $CaMoO_4$ are in line with the pure 0.06 M NaCl showing no inhibition with the low concentrations of calcium molybdate added to a bulk solution and no inhibition due to crack closure. All other data in Figure 3 are from [3].
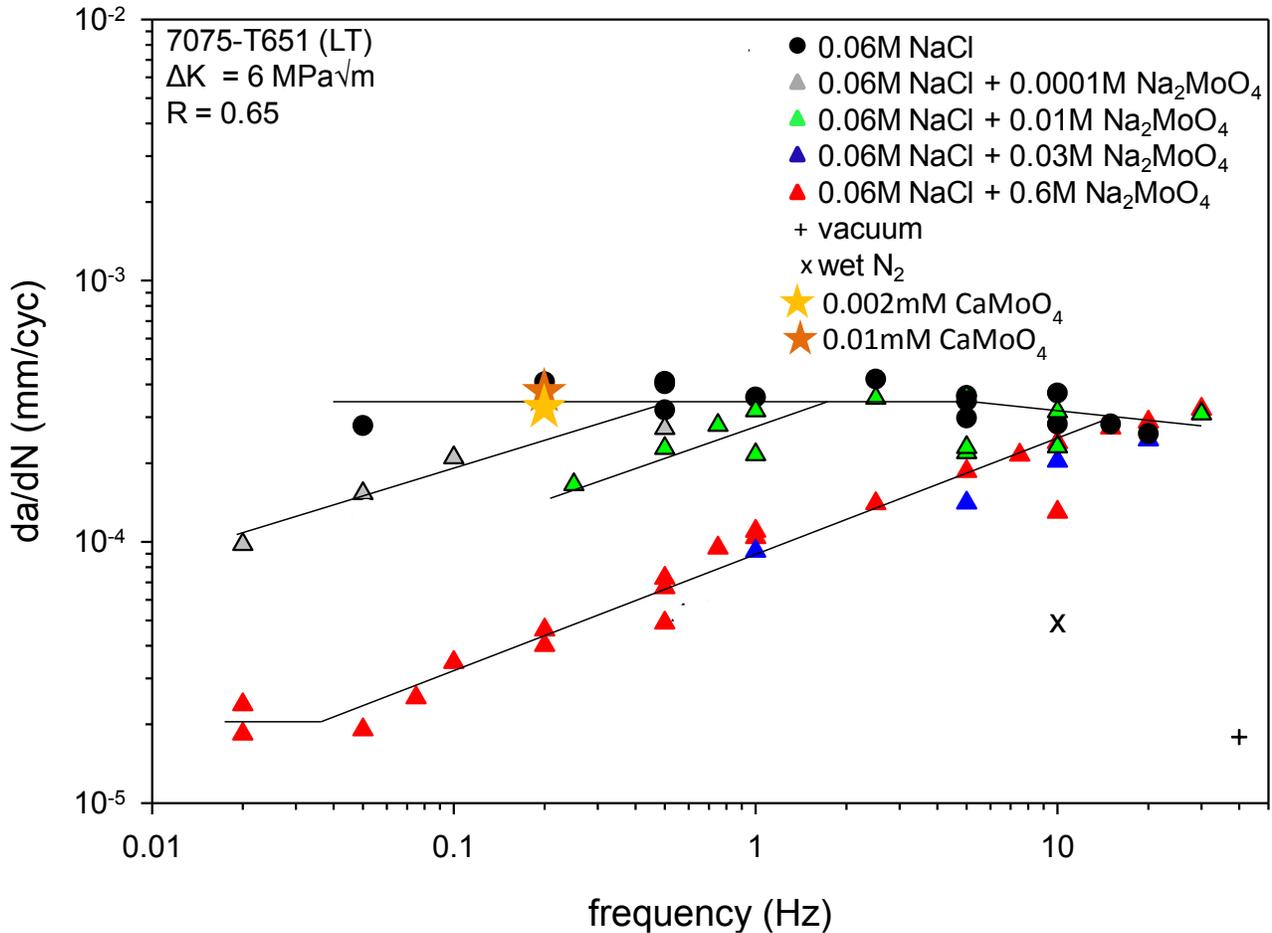
Figure 3: Corrosion fatigue testing with low concentrations of low solubility corrosion fatigue inhibitor calcium molybdate (CaMoO4) [3].

A secondary issue greatly slowed progress on the fatigue testing in Table XI, which is a consistent bacterial growth in the full immersion and atmospheric test cells. The bacteria are *Ralstonia pickettii*, a gram-negative, biofilm forming, bacillus which grows in environments in which there is limited competition [13-17]. The original infection is thought to have come from a deionized (DI) water source in the building, which would be in line with other documented *R. pickettii* infections in water purification systems including the International Space Station [14]. Figure 4 shows the growth of *R. pickettii* after 12 hours on an AA7075-T651 SEN sample in 0.06 M NaCl. The white coating on the wires is a protective epoxy, but the "fuzzy" matter at the bottom of the sample is the bacteria and its associated biofilm. The "fuzz" continues up the sample on all sides. The infection has proved extraordinarily

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difficult to eradicate, even with the introduction of rigorous sterilization procedures. Table XII shows all of the disinfection techniques that have been tried to remove the bacteria. Some of these techniques have been shown to work on free-living, (e.g., not in a biofilm) bacteria, however the disinfection is less effective when the biofilm is present. The items in blue in Table XII are the remaining items to be tested for disinfection success.

Figure 5 shows the effect of the biofilm formation over time on the crack growth rate of an AA7075-T651 alloy. There are two tests completed in 0.06 M NaCl with no inhibitor added. The test started at 20 Hz (yellow triangle) and ended at 0.05 Hz shows a great reduction in the fatigue crack growth rate from 3.1×10^{-4} mm/cycle to 9×10^{-5} mm/cycle. It should be noted that the higher frequency tests (20, 10, 2 Hz) take only minutes to run to achieve sufficient crack growth for reliable *da/dN* measurement, whereas the lower frequency tests (0.2, 0.05, 0.02 Hz) take days to complete, allowing for the growth of the bacteria and slowing of the fatigue crack growth rates. The second test was completed from low frequency (0.02 Hz) to high (20 Hz). By the time of the 20 Hz test, the bacteria have slowed the crack growth rate from 2.4×10^{-4} mm/cycle to 1.4×10^{-4} mm/cycle.
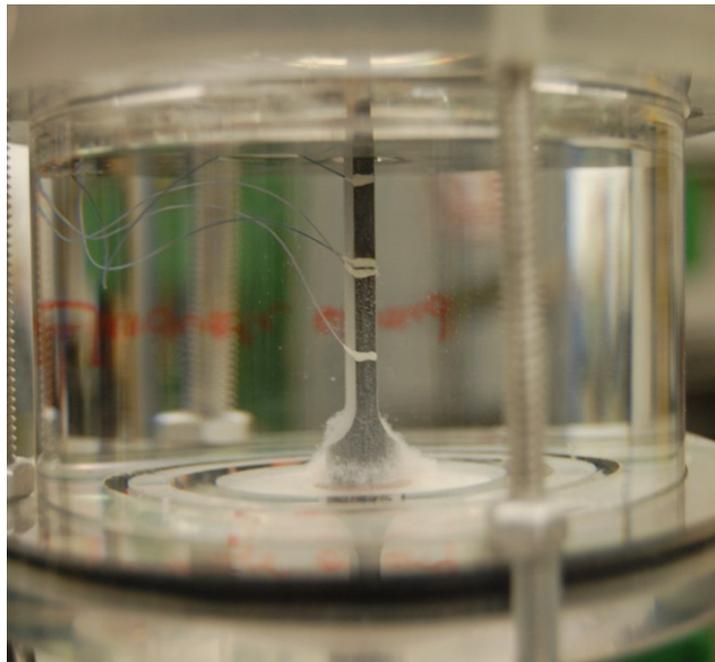
Figure 4: *Ralstonia pickettii* on SEN sample in 0.06 M NaCl.

As can be seen from Figure 5 the effect of the bacteria can completely overwhelm the inhibition by low concentration inhibitors. This bacteria issue needs to be resolved to move inhibitor research forward. Work is underway to better isolate the test frames from the general laboratory environment and testing will be completed using various filtration levels and hydrogen peroxide. Literature reviews have shown that the use of 6% hydrogen peroxide was effective at removing *R. pickettii* biofilms [18]. The documentation of the removal of a *R. pickettii* biofilm is particularly noteworthy as most other research has documented effects on free-living bacteria. It has also be documented that *R. pickettii* can pass through some water purification filters from 0.2 to 0.1 μm [13, 14]. Testing will be competed using a bacteria filter (0.1 micron) with a 99.99999% removal rate; following that test fatigue testing will be completed using a virus filter (0.02 micron) with 99.9997% removal rate [19]. The 0.02 micron filter should be able to completely remove any bacterial contamination without affecting the crack growth rate data.

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Table XII: Disinfection techniques attempted to remove the bacterial infection.

Sanitation Method	On Agar (Free-living)	On Metal (Biofilm)
Antibiotic Testing	Susceptible-Tetracycline	Slight Effect
UV Light	Susceptible	No Effect
Heat	N/A	No Effect
Cold (Liquid Nitrogen)	Slightly Susceptible	Slight Effect
Bleach/EtOH Solution	Susceptible	No Effect
Autoclave	Susceptible	Slight Effect
Sonication	N/A	Slight Effect
Acidified Bleach (pH 7)	Susceptible	Slight Effect
Hydrogen peroxide (3%)	N/A	No Effect
0.1 Micron Filtration	Susceptible	????
0.02 Micron Filtration	Susceptible	????
Hydrogen peroxide (6%)	Susceptible	????
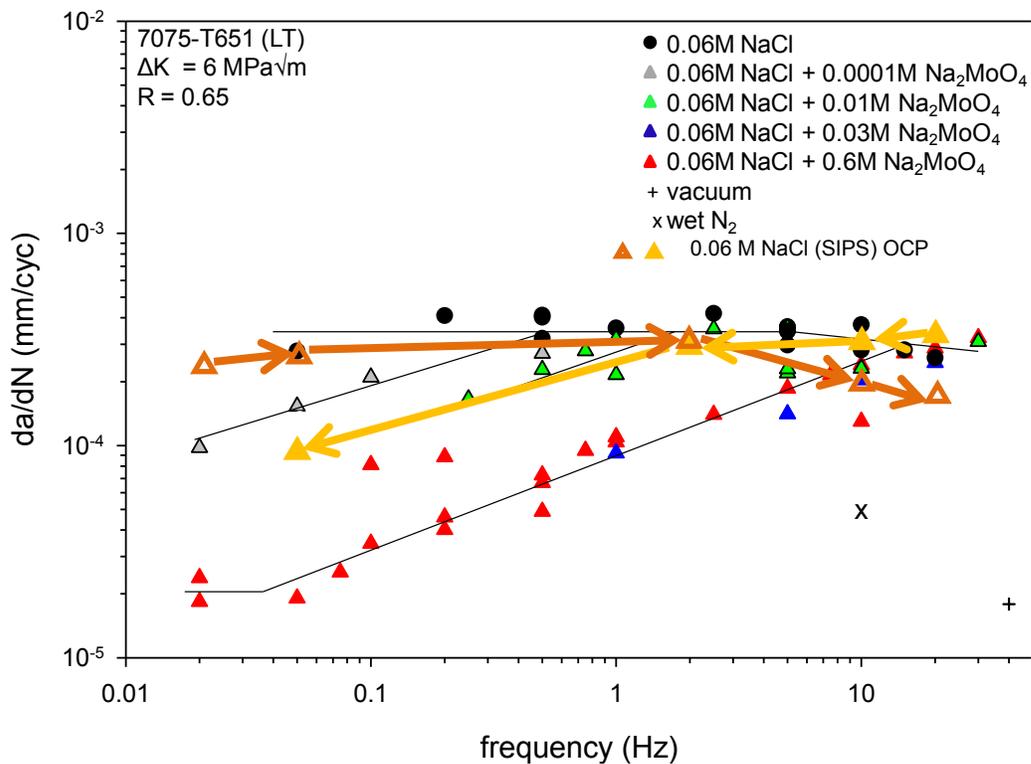
Figure 5: Effect of *R. pickettii* on fatigue crack growth rates over time, as denoted by arrows [3].

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CONCLUSIONS

Low solubility corrosion inhibition pigments ($CaMoO_4$) have not shown the ability to reduced fatigue crack growth rates in bulk 0.06 M NaCl solutions whether through passive film formation or crack closure. The corrosion fatigue inhibitor testing has otherwise been limited by the presence of bacteria forming a biofilm on the aluminum alloy surface. New disinfection steps are being taken to remove the bacteria from testing so that the inhibition testing can continue. That said, the results do point to possible future inhibition strategies using naturally occurring species. The effect of chromate on small scale fatigue damage can be characterized for the different primer types. The analysis of surface area-to-volume for leaching suggests that a thin salt film may be more applicable than full immersion testing for aircraft applications, particularly lap joints.

ACKNOWLEDGEMENTS

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