The Effect of Bacteria on Corrosion Fatigue in AA7075

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ABSTRACT

As more industries and nations focus on environmental protection, the desire to develop non-toxic, sustainable coatings to protect against corrosion becomes a primary focus. One of the areas on the cutting edge of new coating development is the use of bacteria in corrosion prevention coatings. For many years the focus in the corrosion community was on microbial influenced corrosion with the assumption that all bacteria had negative consequences for corrosion and corrosion fatigue. More recently it has been documented that a variety of bacteria can protect against general surface corrosion. None of the work to date on bacteria preventing general corrosion has shown that the inhibitive effects could also be applied to corrosion fatigue. Researchers at the United States Air Force Academy discovered that a bacteria, *Ralstonia pickettii*, is capable of reducing the fatigue crack growth rate of AA7075-T651 and AA7475-T7351 in 0.06M NaCl to near that of chromate.

Key words: Corrosion fatigue, corrosion fatigue inhibition, *Ralstonia pickettii*, microbial induced corrosion, environmentally assisted cracking

INTRODUCTION

Historically researchers have observed that microbial induced corrosion was detrimental to the metal and accelerated the corrosion process. More recent research has started to look at the ability of microbe to protect aluminum against corrosive effects [1]. Given that bacteria are diverse living organisms with many reactions and processes available depending on the genus and species, it is likely that the reason for corrosion protection or acceleration can be material, bacteria and/or environment dependent.

While there is some research looking at the effect of bacteria on pitting and general corrosion very little work has been completed looking at the effect of bacteria on corrosion fatigue inhibition [1-3]. The Center for Aircraft Structural Life Extension (CAStLE) at the United States Air Force Academy (USAFA) has discovered that a bacteria *Ralstonia pickettii* slows the fatigue crack growth rates in 7xxx series aluminum alloys [4].

EXPERIMENTAL PROCEDURE

In 2011, stress life corrosion fatigue tests were being completed at varying stress levels and stress ratios (*R*) of either 0.1 or 0.65 to examine the effect of a modern alloy and temper (AA7475-T7351) on the initiation of a crack from corrosion damage (pit) compared to a legacy alloy and temper (AA7075-T651) at a frequency (*f*) of 1 Hz. Figure 1 shows the sample and test chamber used for this testing. Bacteria grew on some of the samples changing the fatigue life.

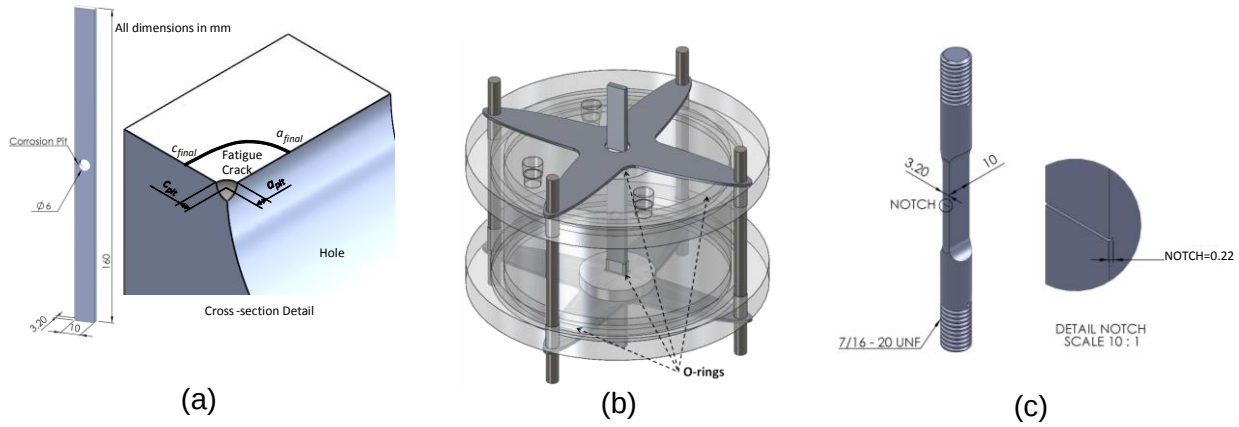


Figure 1: (a) Fatigue sample with a preferential pit for crack initiation used in stress life corrosion fatigue testing. (b) Environmental test chamber used for corrosion fatigue testing. (c) Single edge notch (SEN) specimens were made of 7xxx series aluminum alloy. All dimensions are in millimeters (mm).

After the stress life testing was completed, the bacterial effect was examined using the direct current potential drop (dcPD) method to measure the effect on the crack growth rate. All fatigue crack growth rate testing was completed using a single edge notch specimen, shown in Figure 1. The fatigue test was completed at a constant stress intensity ΔK (6 MPa$\sqrt{m}$) at a frequency of 1 Hz and at a stress ratio (*R*) of 0.10. The test parameters were selected to compare the crack growth rates to published inhibited corrosion fatigue crack growth rates using chromate [5]. The corrosive environment was 0.6 M NaCl. The bacteria were allowed to grow naturally or intentionally added to solution to quantify the effect. To add bacteria to solution, colonies of *R. pickettii* were grown on R2A agar and single colonies were added to the 0.06 M NaCl solution. Figure 2 shows the growth of the bacteria on the aluminum sample. *R. pickettii* is known to build biofilms and the growth is thought to be a biofilm [4,6-8].

As the original stress life testing was completed using samples that initiated a fatigue crack from a corrosion pit meaning the cycles to failure includes crack nucleation time. The stress-life tests were repeated using precracked single edge notch (SEN) samples to make a better determination on the effect of the bacteria. For this testing the samples were precracked to 1 mm in air, then placed into 0.06 M NaCl either with or without bacteria. The samples were left in solution for 3 days to allow the bacteria to grow. Then the stress life tests were repeated with a maximum stress (σ_{max}) of 55 MPa, 94 MPa and 125 MPa with a stress ratio (*R*) of 0.1 at a frequency of 1 Hz. For this testing there was also a concern about bacterial misidentification so testing was also completed on *Sphingomonas paucimobilis* which has been misidentified as *R. pickettii* using standard laboratory identification methodologies. All testing was completed at open circuit potential, which was not measured. It should also be noted that the use of the dcPD system has shown no effect on bacteria growth.

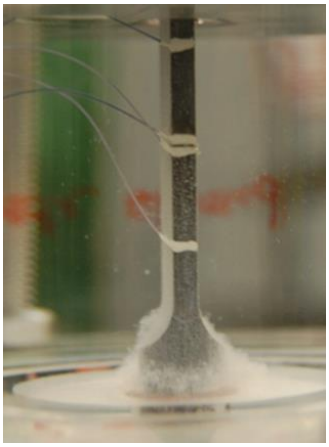


Figure 2: Bacterial growth ("fuzz" at bottom of samples) on the 7xxx series aluminum alloy in 0.06M NaCl solution. The white on the dcPD wires is a protective coating. The fuzz continues up the entire length of the sample.

RESULTS AND DISCUSSION

The results from the stress life fatigue testing showed that the presence of the bacteria during the tests completed with an *R*=0.1 saw approximately 5-fold increase in fatigue life,
Figure **3**. The samples tested with an *R*=0.65 saw a 6-fold increase in fatigue life. Figure 4 shows the comparison of high and low amounts of *R. pickettii* when added to a 0.6 M NaCl solution to a known corrosion fatigue inhibitor chromate (Na_2CrO_4) at *f* = 1 Hz at a ΔK of 6 MPa$\sqrt{m}$ [(5)]. The addition of 0.03 M of chromate lowers the fatigue crack growth rate for frequencies just below 1 Hz; when 0.5 M chromate is added, the inhibition occurs over the entire frequency range (0.1-70 Hz) [5]. The amount of bacteria was quantified visually, based on the amount of “fuzz” seen. For crack lengths of 2-4 mm both the high and low bacteria concentrations slow the crack growth rates to near that of high amounts of inhibiting pigments and better than the lower levels of chromate [(5)]. At higher ΔK levels (12 MPa$\sqrt{m}$) the inhibition provided by the bacteria is better or equal to the higher levels of added chromate, shown in Figure 5 [(5)].

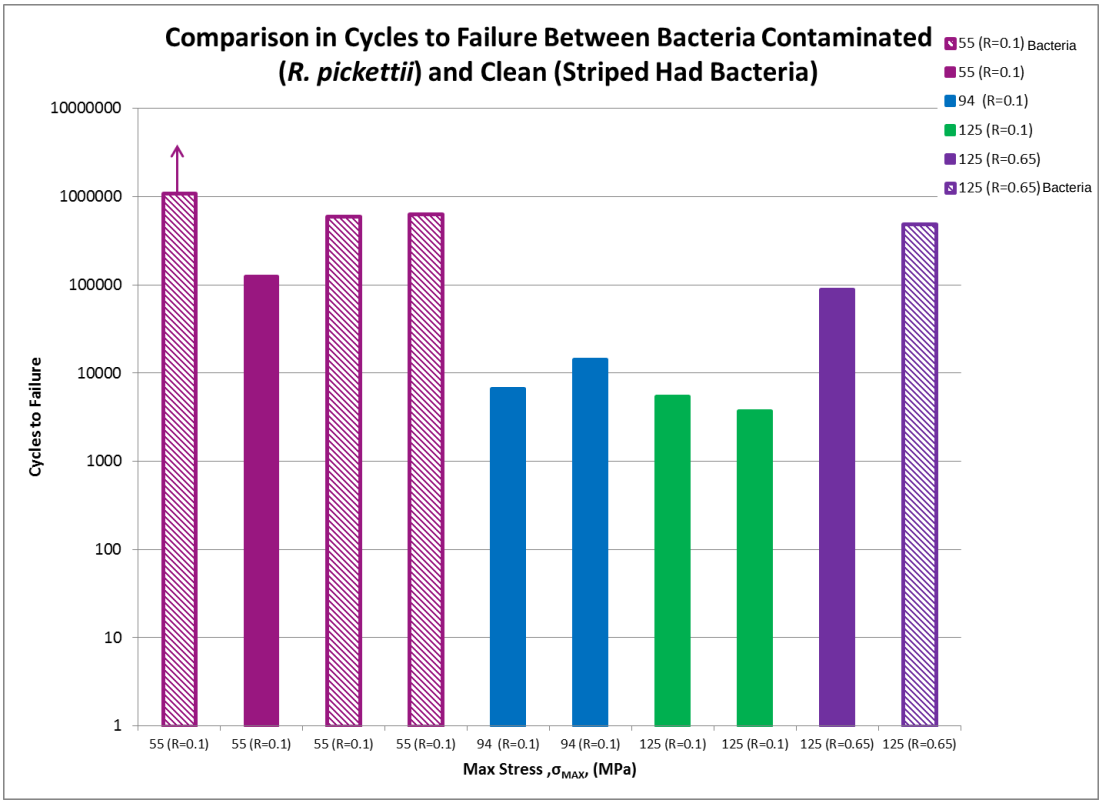


Figure 3: Stress-life testing of *R. pickettii* compared to clean samples in 0.06M NaCl. The bacteria growth occurred randomly during testing, accounting for the fatigue tests completed without bacterial growth.

R. pickettii consistently shows inhibition on the order of known corrosion inhibitors as shown in Figures 3 and 4 [5]. The reason for this inhibition is currently unclear however there are three leading theories being investigated: (1) *R. pickettii* is sequestering metal (copper) into its cell wall which is stabilizing the passive film at the crack tip [3,8,9], (2) the bacteria creating an environment which promotes oxide formation protecting the crack tip, (3) the polymeric biofilm the bacteria produces allows for protection of the crack through an inhibitive species or coating [12]. *R. pickettii* has been shown to uptake certain metals into its cell wall to protect itself from hazardous environments [10,11]. Based on aluminum corrosion fatigue inhibition research and *R. pickettii* metal uptake literature, copper and silicon were loaded into R2A agar and *R. pickettii* colonies grown on the agar were analyzed by scanning electron microscopy and electron dispersive spectroscopy (EDS) [10, 11]. The results did not show evidence of metal uptake. The ability of bacteria to help repair the oxide layer is supported by the literature and could possibly be occurring in this case [1]. When the aluminum samples with bacterial growth were analyzed using EDS, the areas with biofilm have large amounts of oxygen present, suggesting a heavy oxide layer.

During the corrosion fatigue testing it has been shown that *R. pickettii* can desalinate the sodium chloride test solution. The salinity is expected to drop by approximately half in 48 hours when the bacteria is present. For aluminum alloys the presence of chloride can be detrimental to corrosion fatigue but is not a primary driving force as the presence of water vapor is sufficient to raise crack growth rates over that of dry air or inert environments [13]. This suggests that the desalination of the test solution is not the primary cause of the corrosion fatigue inhibition. Fatigue testing was also completed using 0.03 M NaCl solution without bacteria, and no reduction in the crack growth rate was noted as compared to 0.6M and 0.06 M NaCl solutions.

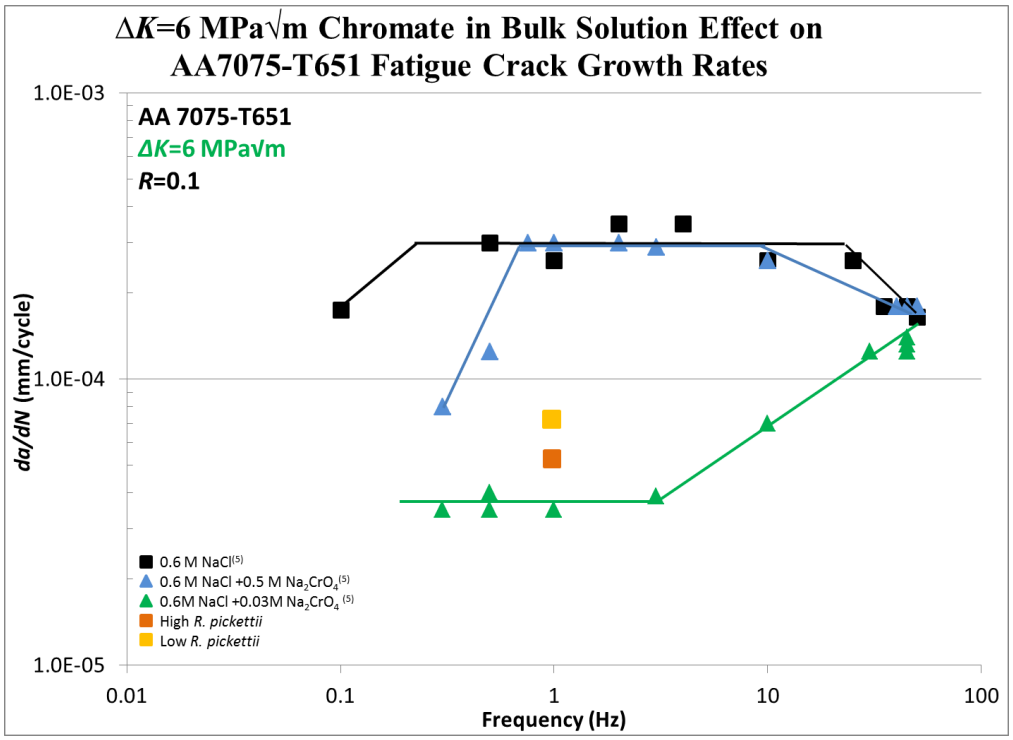


Figure 4: Comparison of the effect of *R. pickettii* on fatigue crack growth rates on AA7075-T651 to a known corrosion fatigue inhibitor chromate at ΔK=6 MPa$\sqrt{m}$; R=0.1, f=1 Hz in 0.6 M NaCl [5].

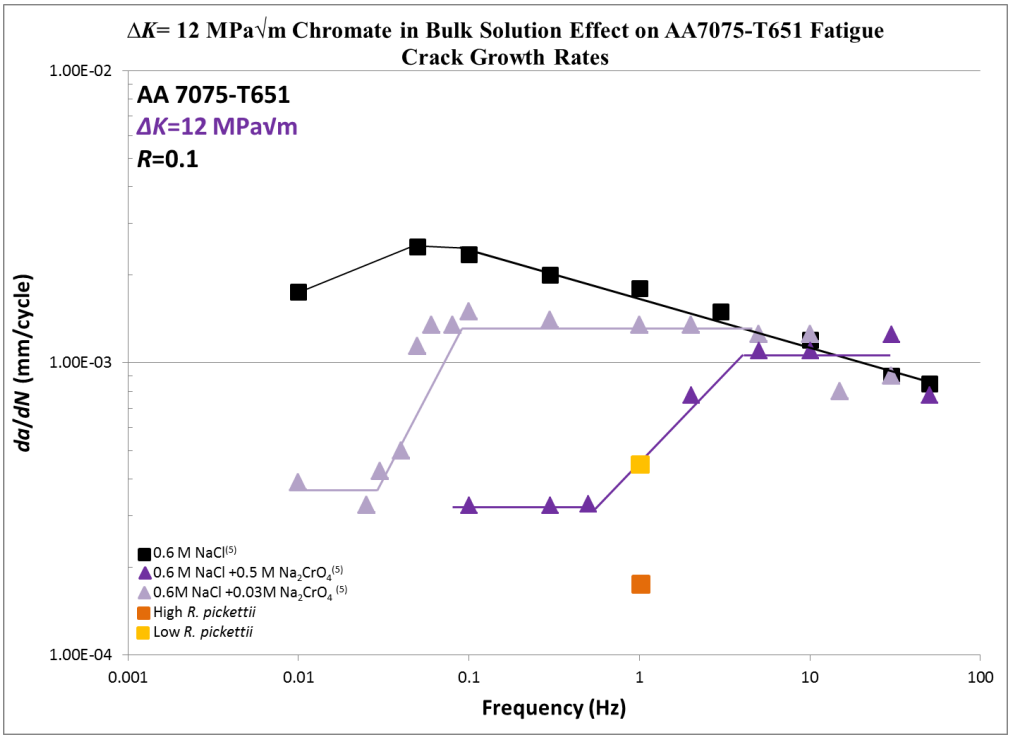
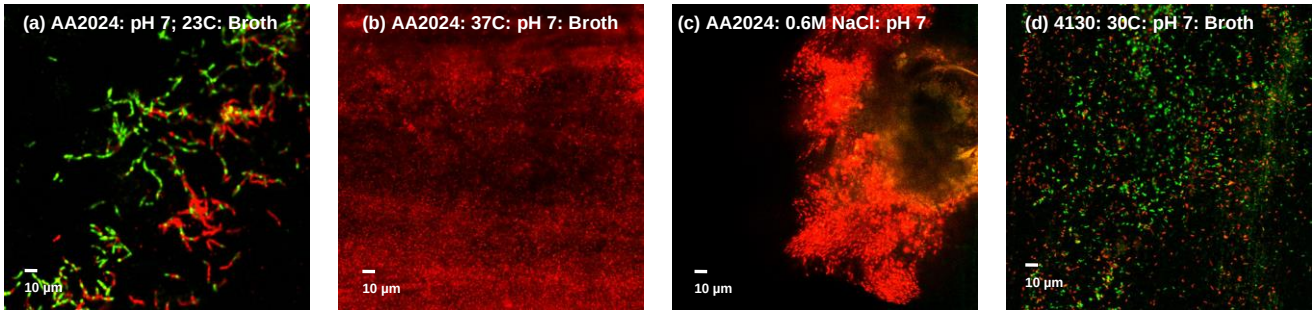


Figure 5: Comparison of the effect of *R. pickettii* on fatigue crack growth rates on AA7075-T651 to a known corrosion fatigue inhibitor chromate at ΔK=12 MPa$\sqrt{m}$; R=0.1, f=1 Hz in 0.6 M NaCl [5].

Work is underway to analyze the structure of the biofilm. The early research has looked at how the biofilm develops under varying conditions in an effort to understand why the biofilm sometimes appears

to be produced faster and thicker than at other times [14]. Figure 6 shows the development of the *R. pickettii* biofilm using a live/dead stain with confocal microscopy under varying temperatures, pH, and salinities and with various alloys. The amount of growth and living bacteria is rated from no growth/living (-) to heavy biofilm/all living (++++). It appears that a neutral to slightly basic pH (7-8) allows for string-like bacteria formations (5a). Higher temperatures (30 and 37 °C) (5b) and low salt content (0.06 to 0.6 M NaCl) (5c), or neutral to slightly basic pH (7-8) cause thick biofilm formation. Formation on 4130 steel is scattered but not stringy (5d). Interestingly these are conditions very close to what exist in the corrosion fatigue test cell.



24 Hr Biofilm Development

Alloy	Exposure Parameters	Growth Amount	Amount Living	Morphology
AA2024	10C	+	++	Scattered
AA2024	30C	+++	-	Fuzzy
AA2024	37C	++	+	Fuzzy
AA2024	Broth	++++	+	Fuzzy
AA2024	0.03 M NaCl	++++	+	Fuzzy
AA2024	0.06M NaCl	++++	+	Fuzzy
AA2024	0.6M NaCl	++++	+	Fuzzy
AA2024	pH 6	+	++	Scattered
AA2024	pH 7	++	+++	Stringy
AA2024	pH 8	++++	++++	Fuzzy
4130	30C	+++	++	Scattered
4130	37C	++	+	Scattered
AA7075	37C	+++	+	Scattered
AA2024	Mn	+++	-	Stringy
AA2024	Fe	+++	-	Fuzzy
AA2024	Cu	++	++	Scattered
AA2024	Ni	+	-	Fuzzy

48 Hr Biofilm Development

Alloy	Exposure Parameters	Growth Amount	Amount Living	Morphology
AA2024*	10C	-	-	N/A
AA2024	30C	+++	-	Fuzzy
AA2024	37C	++++	-	Fuzzy
AA2024	Broth	+++	+	Fuzzy
AA2024	0.03 M NaCl	+++	+	Fuzzy
AA2024*	0.06M NaCl	-	-	N/A
AA2024	0.6M NaCl	++++	-	Fuzzy
AA2024	pH 6	+	+	Scattered
AA2024	pH 7	+++	++	Stringy
AA2024	pH 8	++++	++	Fuzzy
AA2024	30C	+	+	Scattered
AA7075	30C	+	+	Scattered
AA2024	Ni	-	-	N/A
AA2024	Mn	++	-	Stringy
AA2024	Fe	+++	-	Fuzzy
AA2024	Cu	++++	-	Fuzzy

Figure 6: Development of a *R. pickettii* biofilm under varying conditions; pictures and charts [14]. The amount of growth and living bacteria is rated from no growth/living (-) to heavy biofilm/all living (++++).

At the same time some work has suggested that *R. pickettii* is difficult to identify when sampled from the wild. Sampling of the CAStLE laboratory area, as well as intentionally inoculated tests, have consistently not been identified as *R. pickettii* when analyzed using the VITEK II system. This system completes a series of tests to determine what reactions a bacteria is capable of completing and based on the results identifies the bacteria. *R. pickettii* and *S. paucimobilis* share many of these reactions leading to questions about mistaken identity.

Based on the questions of which bacteria was present, testing was completed using *S. paucimobilis* added to solution, Figure 7. For the test completed at a maximum stress of 55 MPa the presence of the

bacteria did greatly increase the fatigue life. The test was stopped at 1,000,000 cycles without noted crack growth. For the 94 MPa and 125 MPa test the presence of the bacteria did not increase the fatigue life. The 55 MPa test takes about 12 hours to complete in pure 0.06 M NaCl, while the 95 MPa (3 hours) and 125 MPa (2 hours) tests are substantially shorter suggesting that the bacteria may not have time to slow the mechanical damage. It should be noted that there has been no research to date into the ability of *S. paucimobilis* to desalinate the test solution.

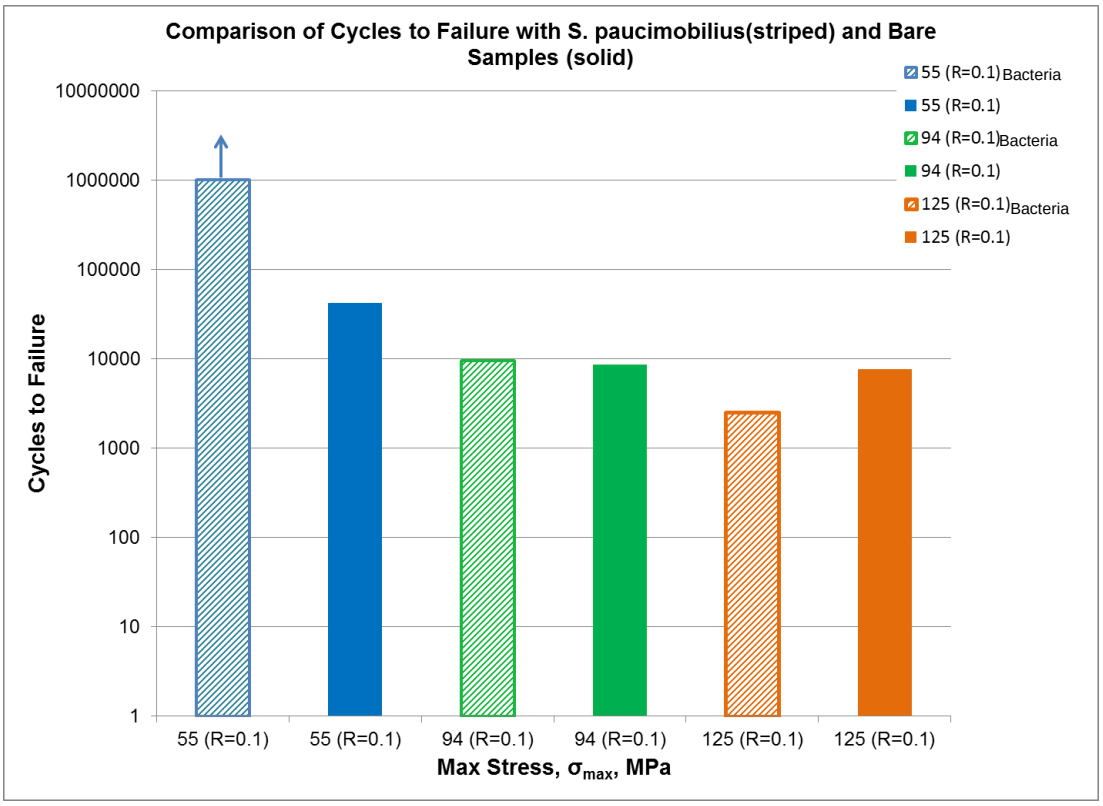


Figure 7: Stress-life testing of *S. paucimobilius* compared to clean tests. Arrow denotes test did not fail after 1,000,000 cycles.

CONCLUSIONS

Based on the current results it appears that both *R. pickettii* and *S. paucimobilis* can inhibit corrosion fatigue particularly at lower stress levels where the mechanical damage takes longer to occur allowing the bacteria time to protect against the environment. As most microbial growth is viewed as causing corrosion and understanding that some bacteria could be beneficial would allow for less aggressive mitigation methods in areas where corrosion damage does not seem to be an issue for the DoD.

Over the course of this project, research has also been conducted into how difficult *R. pickettii* is to kill. This is particularly important because if bacteria were to be developed into a natural protective coating for any sort of military or commercial application it needs to be able to withstand a variety of environmental conditions. To date the bacteria has proven to be extremely resistant to most forms of disinfection including, heat, freezing, bleach solutions, heavy metal exposure, hydrogen peroxide and UV light exposure. The ability of these bacteria to resist disinfection suggests that the processes of living bacteria could be placed into a coating to make a non-toxic, environmentally friendly coating with corrosion fatigue protection on the order of chromate.

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REFERENCES

1. Busalmen, J.P. et al, "New evidences on the catalase mechanism of microbial corrosion*"* *Electrochimica Acta* 47 (2002) pp.1857–1865.
2. Zou, R. et al, "The importance of live biofilms in corrosion protection," *Corrosion Science* 47 (2005) pp. 279-287.
3. Stadler, R. et al, "First evaluation of the applicability of microbial extracellular polymeric substances for corrosion protection of metal substrates," *Electrochimica Acta* 54(2008) 91-99.
4. Kulakov, L.A., McAlister M.B., et al., "Analysis of bacteria contaminating ultrapure water in industrial systems," *Applied Environmental Microbiology*, 2002; **68** pp. 1548-1555.
5. Gasem, Z. and R.P. Gangloff, R.P., "Rate-Limiting Processes in Environmental Fatigue Crack Propagation in 7000-series Aluminum Alloys*"*, in *Chemistry and Electrochemistry of Corrosion and Stress Corrosion Cracking*, R.H. Jones, Editor. 2001, TMS-AIME: Warrendale, PA. pp. 501-521.
6. http://mathbio.colorado.edu/mediawiki/index.php/MBW:Role_of_Biofilm_Matrix_in_ Structural_Development
7. Koenig, D.W. and Pierson, DL., " Microbiology of the space shuttle water system," *Water Science Technology* 1997; **35**: pp.59-64.
8. Wong, W.C. et al, "Efficacy of Various Chemical Disinfectants on Biofilms formed in Spacecraft Potable Water System Components," *Biofouling*, 2010 **26**(5) pp. 583-586
9. Hartt, W.H., J.S. Tennant, and W.C. Hooper, *Solution Chemistry Modification within Corrosion-Fatigue Cracks*, in *Corrosion-Fatigue Technology, ASTM STP 642*, H.L. Craig Jr., T.W. Crooker, and D.W. Hooper, Editors. 1978, ASTM: West Conshohocken, PA. p. 5-18.
10. March, T. "Genomic Plasticity" in *Ralstonia eutropha* and *Ralstonia pickettii*: Evidence for Rapid Genomic Change and Adaptation," Final Report Grant #DE-FG02-01ER63141.
11. Konstantinidis, K.T., et al, "Microbial Diversity and Resistance to Copper in Metal-Contaminated Lake Sediment," *Journal of Microbial Ecology*, 2003, **45**: pp. 191-202.
12. Ornek, D. et al, "Pitting corrosion control using regenerative biofilms on aluminum 2024 in artificial seawater" *Corrosion Science*, 2001 43(11): pp. 2121-2133.
13. Gangloff, R.P., "Corrosion fatigue crack propagation in metals," *Environmental-Induced Cracking of Metals; NACE-10*, R.P. Gangloff and M.B. Ives, Editor. 1990 NACE: Houston, TX pp., 55-105.
14. Collins, S.E. et al, "The effect of environment on the growth of *R. pickettii*," *Technical Corrosion Collaboration*, Columbus, OH, August 14, 2013.