ELECTROCHEMICAL “STRESS” –

COMBINED LOADING IN THE NAVAL ENVIRONMENT

PERSPECTIVES ON TREATING ENVIRONMENTAL LOADING AT MACRO AND MICRO SCALES

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Introduction

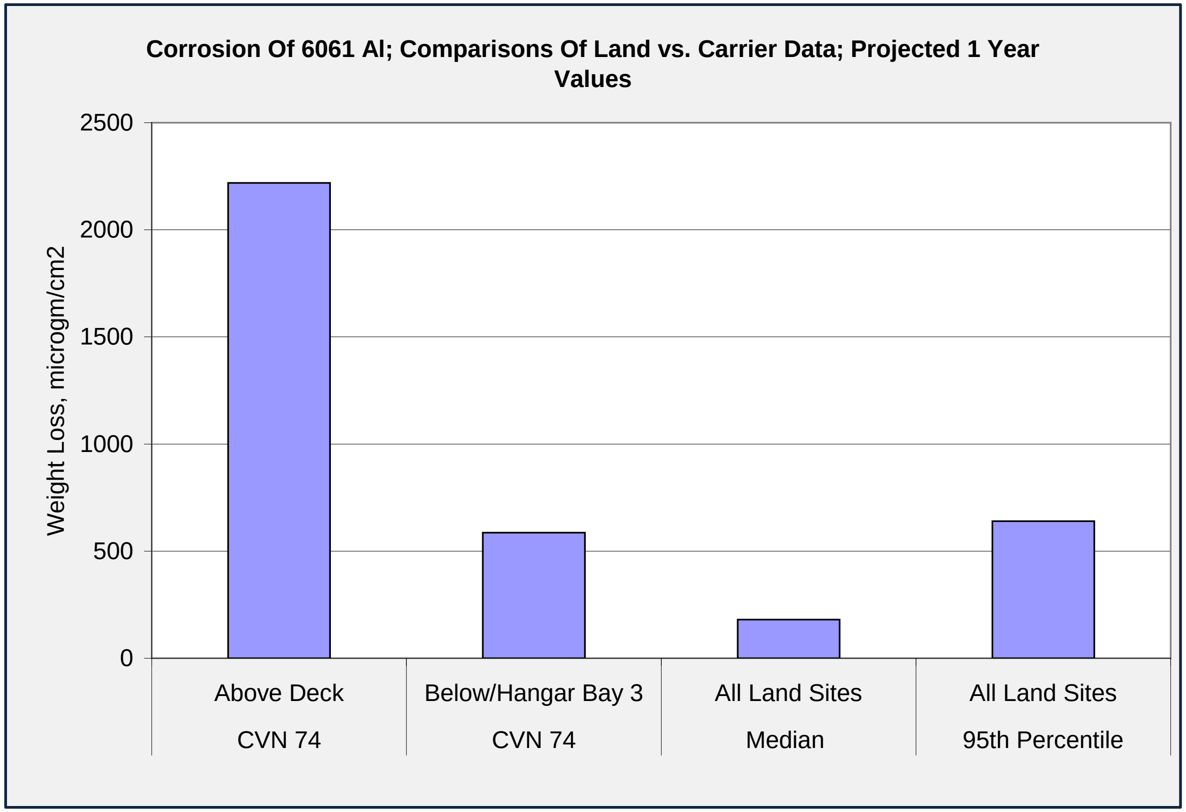
- Stress-free and stress-assisted corrosion
  - Significant in Naval aircraft structures
- Environmental effects increase the complexity of life prediction models
- Engineering and lifing models needed
  - Account for both mechanical and environmental crack driving forces
  - AND their interactions
    - i.e. covariance / codependence

Experience

- Metallic Structure Durability
  - Joint service, fixed wing tear down analysis
    - Approximately 80% of structural cracks initiated from a corrosion pit
  - Navy FRC structural engineering assessment of tear-down / rework
    - 60/40 split of stress-corrosion cracking / fatigue (mechanical & corrosion)
    - **75-90% of structural damage initiated at galvanic interfaces**
  - OSD Geographic Corrosivity Study
    - Average ship deck environment 4-8X more aggressive than worst land site
  - **Materials selection – primarily mechanical function / ease of purchase**
    - Cannot assess structural risk – location or relative severity of galvanic stress
    - Cannot conduct material alternative analysis for galvanic mitigation
  - **Coatings, Sealants & Polymers – performance varies – T, RH, application**
    - Application, cure & repair – environment and space constraints aboard ship
    - Moisture permeation and galvanic interactions

Geographic Assessment

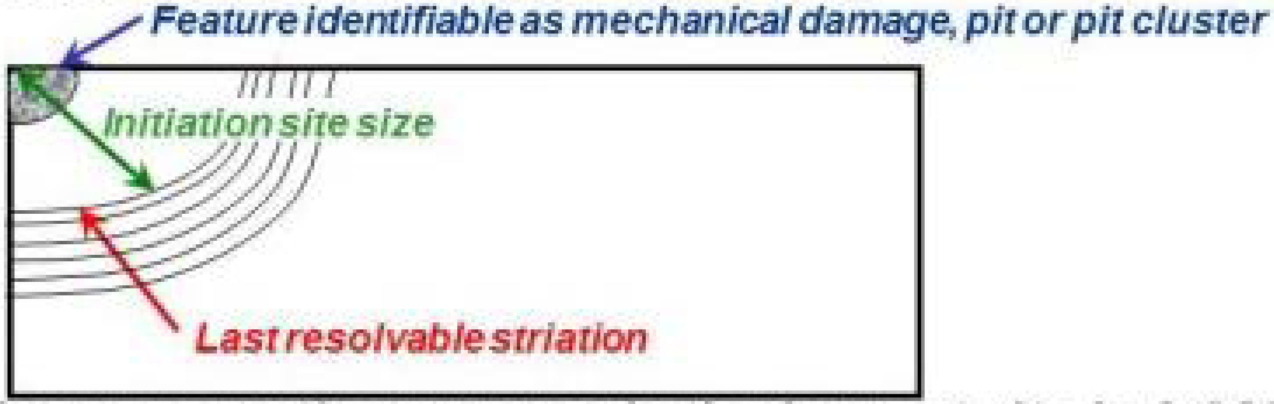

Carrier Exposure Rack on CVN 74



(Abbott and Kinzie, 2004)

Environmental Structural Damage

- What is "initiation feature" type and size?



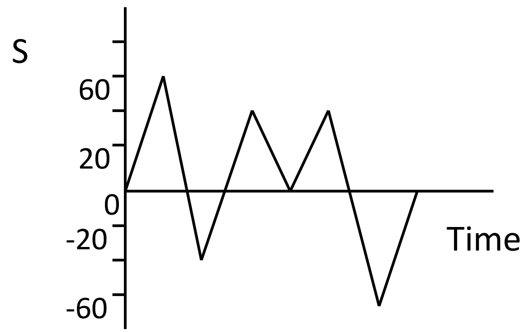
- Even with conservative approach, the largest site is 0.025 in
  - 90% are less than 0.010 in
  - 48% are less than 0.005 in

Initiation Feature	%	Dimensions (in)		
		Minimum	Maximum	Average
Corrosion Pit	80%	0.001	0.025	0.005
Mechanical Damage	20%	0.002	0.013	0.006
Percentage of Initiation Sites on Faying Surface				31%

- Most damage initiated from corrosion pits

Fawaz, S., "Technical Corrosion Collaboration Program Overview" 2012 NAVAIR

SAFE-Life Approach to Structural Integrity

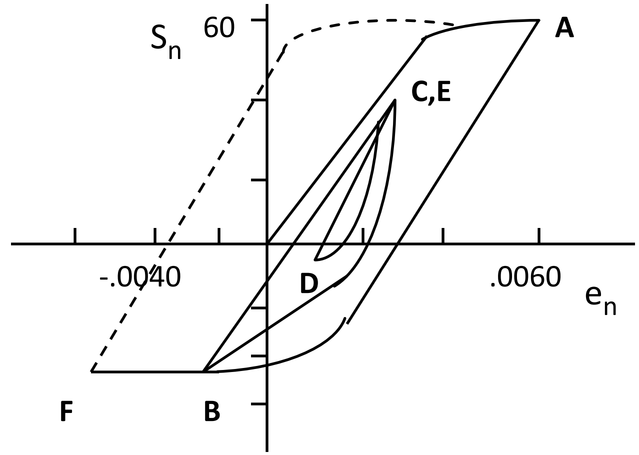


Component Stress History

Neuber's Rule

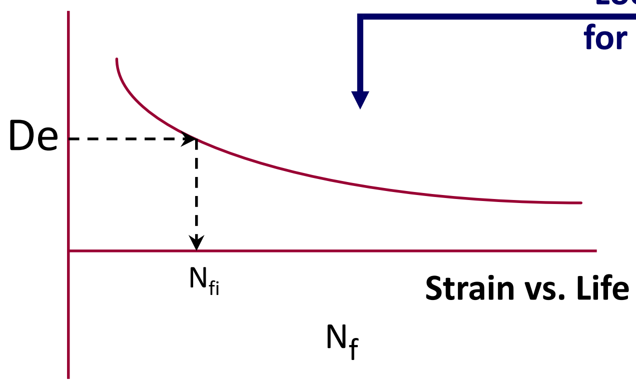
$$K_t = \sqrt{K_\sigma K_\varepsilon}$$

Rainflow Cycle Count



Notch Stress-Strain Response

Look up Crack Initiation Life for each strain amplitude, De



Compute

$$\text{Damage} = \sum \frac{n_i}{N_{fi}}$$

FLE = 2 * Damage * 100%

Loads Only Analysis – No Accounting for Environmental Effects

Damage Index Calibrated to FSFT Results (Life to 0.010 in. crack)

Hoffman, P., Rusk, D., Roerden, A., Modarres, M. and Rabiei, M., "A Hybrid Two-Phase Assessment Approach," NATO/RTO Symposium, Sept. 2008.

What Makes Corrosion Management of Airframe Designs a Challenge?

Influence of multiple parameters

- Stress/Strain Level – Plastic Straining
- Strain Rate and Hold Time
- Degree of Electrochemical Activity -Electrolyte, pH, Dissolved O_2
- Temperature
- Microstructure
- Surface Conditions
- History of environmental loading
- …

Corrosion effects cannot be separated from structural life predictions
How to include corrosion considerations during design stage?

Challenges in Modeling

- Environmental driving forces at a critical location
  - may be significantly more aggressive than those of bulk environments
- Experimental characterization of electrochemistry
  - [potential, pH, concentration, activity] at critical location such as at a crack or defect is difficult
- Surface effects largely ignored
  - diffusion, electrical resistivity, thermal conductivity, magnetic permeability, etc.
- Analytical models are specific to individual mechanisms
  - no model fits all forms of corrosion

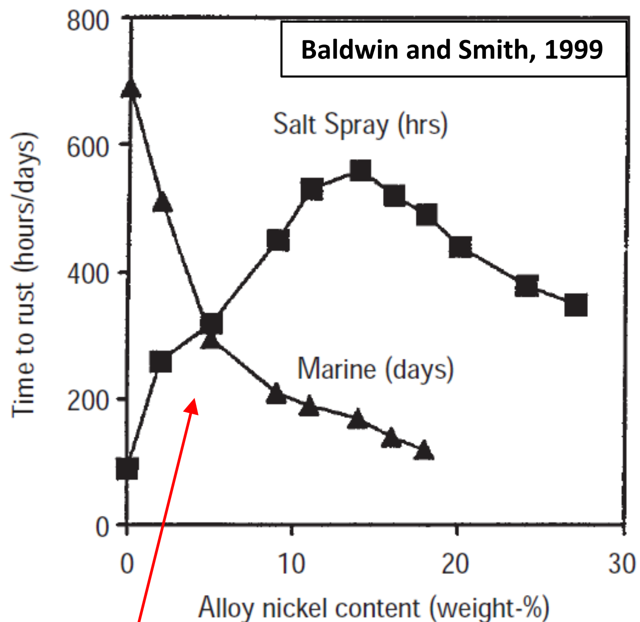
Challenges in Modeling

- Working Hypotheses
  1. Environmental loading analogous to mechanical loading
     - driving Force – electro-chemical, chemical, thermal
     - history / accumulation Effects
  2. “TYPE” of corrosion
     - galvanic coupling is a type of applied stress
     - pitting, anodic dissolution, etc. are types of response, i.e. corrosion/local damage
  3. Galvanic coupling analogous to stress intensity
     - current density distribution – stress intensity
     - reaction/response – strain, dislocation, ionization, dissolution, etc.
  4. Localized damage initiation linked to crack nucleation
     - D_{local} controlled by surface chemistry and morphology – influenced by mechanical surface energy
     - D_{nuc} controlled by microstructure and strain response – influenced by surface chemistry
- Note the importance of electrochemical galvanic activity, both at macro and micro scale

Issue of Corrosion for Naval Aircraft

Accelerated tests Vs. **Marine exposure**

- The drawbacks with some current accelerated corrosion tests are poor correlation to real-world exposure and the inconsistency of test results.



In the salt spray test, the corrosion resistance of the zinc-nickel alloy coatings on steel initially increases with increasing nickel content while marine exposure shows opposite trend.

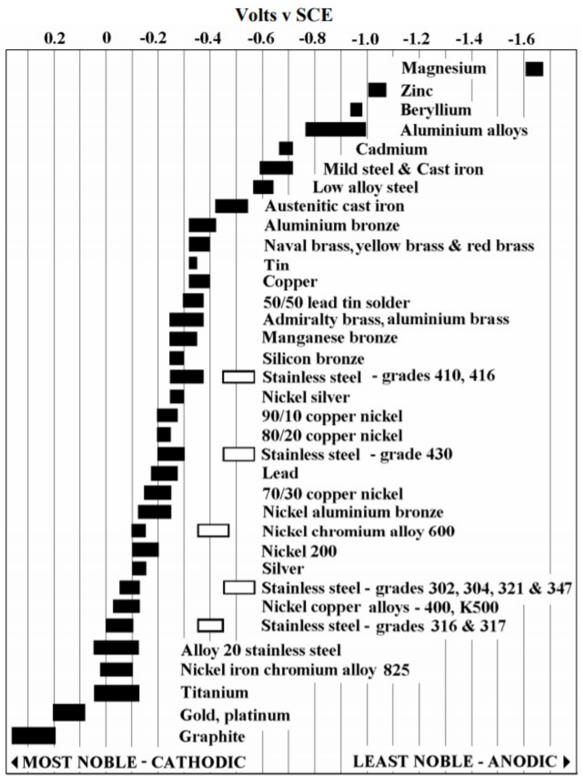
Table I Corrosion rankings for some aerospace aluminium alloys

Marine exposure	Neutral salt spray	Alternate immersion
Clad 7075-T6	Clad 2024-T3	Clad 7075-T6
Clad 2024-T3	Clad 7075-T6	Clad 2024-T3
7075-T6	2024-T3	7075-T6
2014-T3	7075-T6	2024-T3
2014-T6	2014-T3	2014-T3
2024-T3	2014-T6	2014-T6

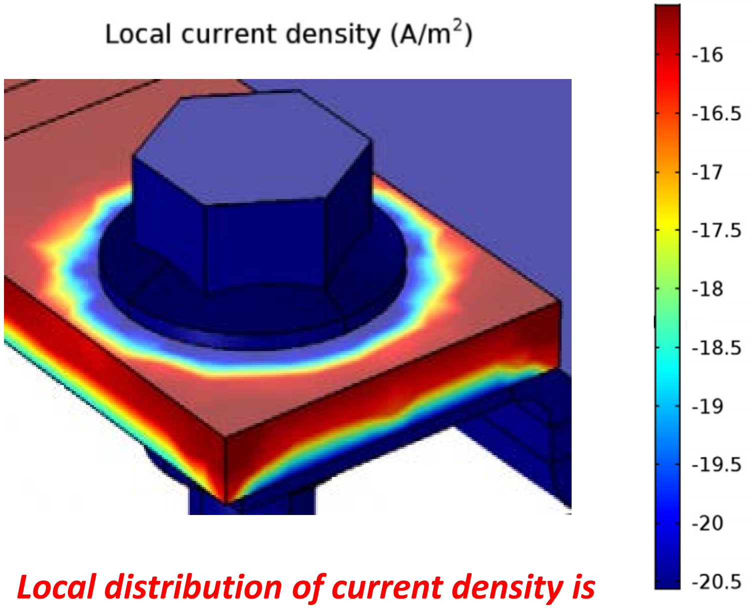
Neutral salt spray test fails to reproduce the ranking orders obtained for any of the materials (above) when compared with marine exposure.

Issue of Corrosion for Naval Aircraft

Galvanic series Vs. Current Density



Atlas Steels Technical Note No.7



Local distribution of current density is critical for damage assessment.

- MIL-STD-889 currently bases the analysis on galvanic potential.
- There is a need to shift from potential-based analysis to current-based galvanic analysis.

Materials Selection / Corrosion

- ***Traditional galvanic compatibility theory – |ΔE|***
  - Ignores rate and severity control of current density
  - Ignores location effects of distribution
  - Potential only analysis leads to less durable materials selection
    - ignores conductivity / resistivity effects of cathode surface chemistry
    - exchange current density at cathode surface dominates localization
  - Does not account well for thin-film, high O_2 transport conditions
  - Equilibrium vs. actual reaction conditions
    - scalability, extrapolation from OCP often inaccurate
    - geometry and contact area / electrolyte-coverage area effects missing
  - **$\Delta E \geq \Delta E_{th}$ is a more accurate view of galvanic susceptibility**

Galvanic Series

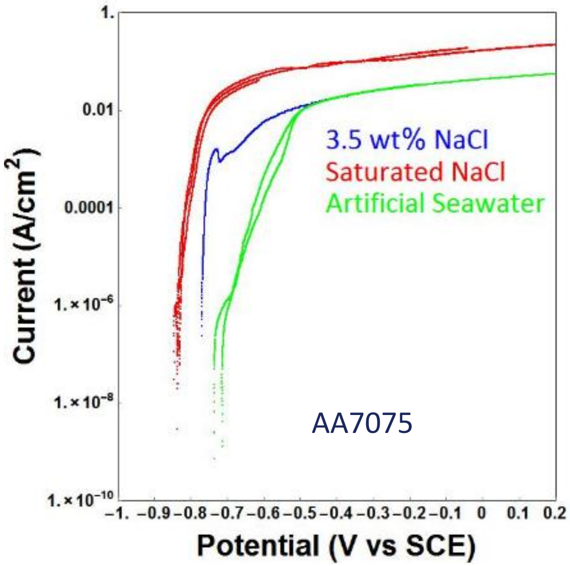
- **Galvanic Series in Seawater**: This well known series indicates the relative nobility of different metals and alloys in seawater, based on the measurement of corrosion potentials. In a galvanic cell, the more noble material in this series will become the cathode (no metal dissolution), while the less noble material will corrode as the anode. **A greater separation of the materials in the galvanic series indicates a bigger potential difference between the materials; *generally indicating a greater degree of galvanic incompatibility when coupled.***

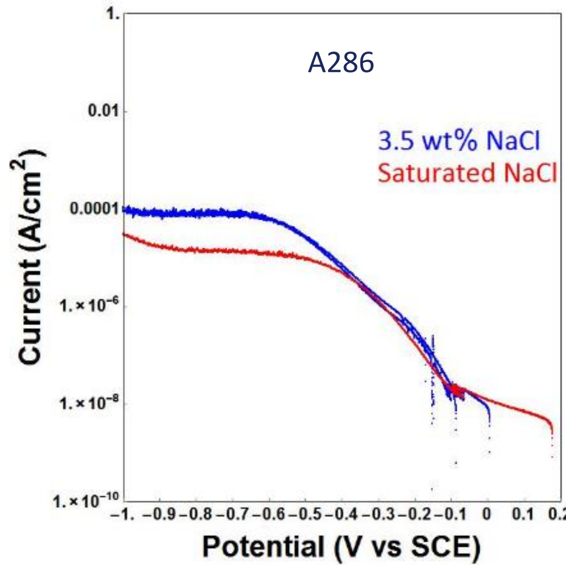
- Note that this galvanic series was derived for **one specific electro**lyte (seawater) only. **The materials can have a different nobility ranking in different environments and at different temperatures. The series is based on (averaged) corrosion potential data and therefore does not give a direct indication of the rate of galvanic corrosion.**

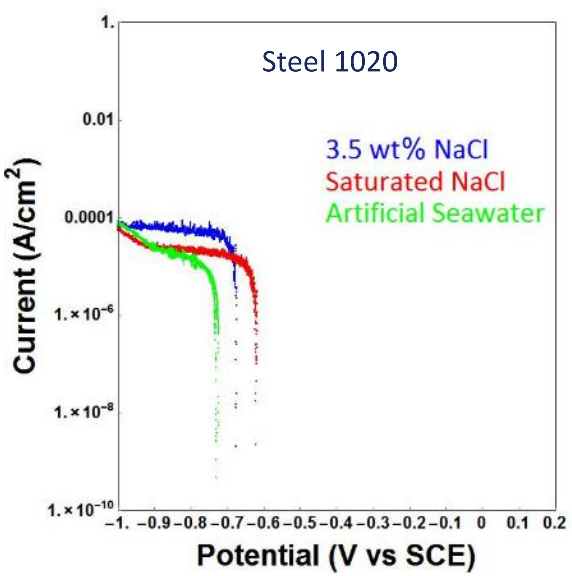
Validation: Laboratory Data

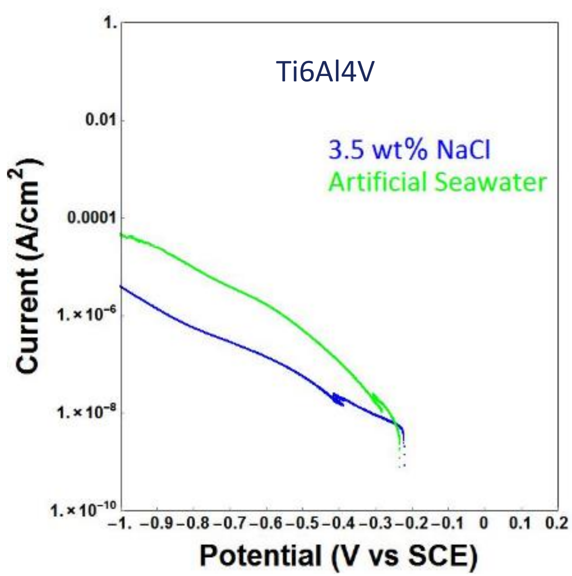
Polarization Data

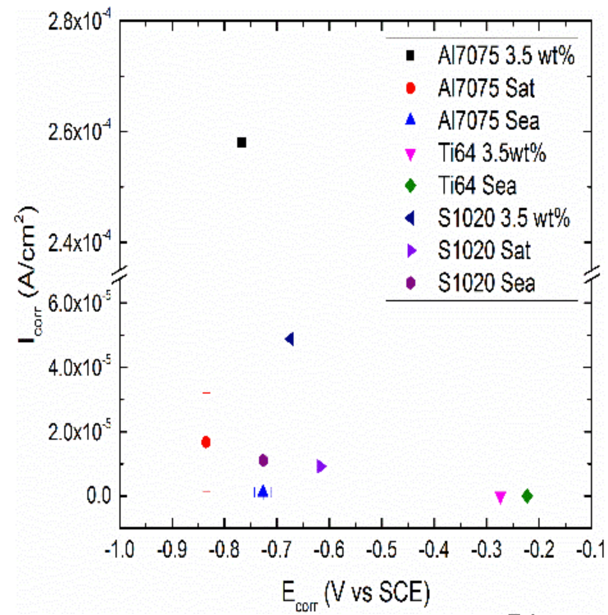
- **Noticeable differences as a function of electrolyte composition are observed.**
- Careful consideration at the time of choosing electrolyte to ensure consistency for both E_{corr} and I_{corr}





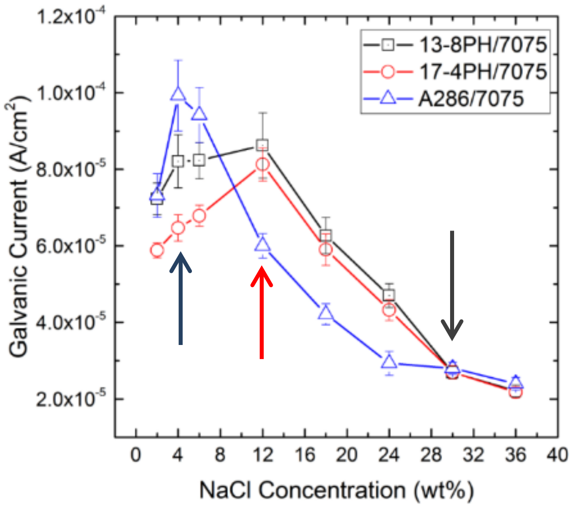


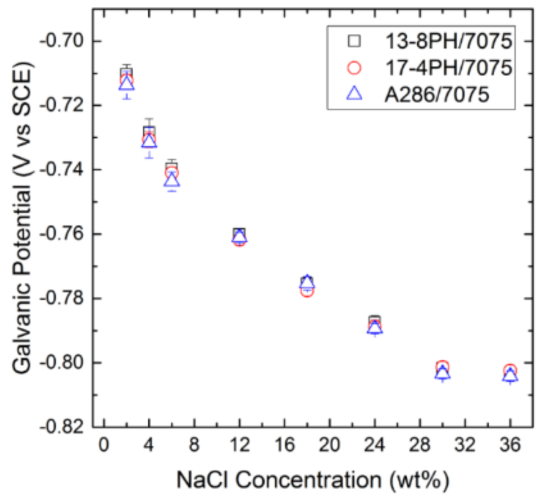




Validation: Laboratory Data

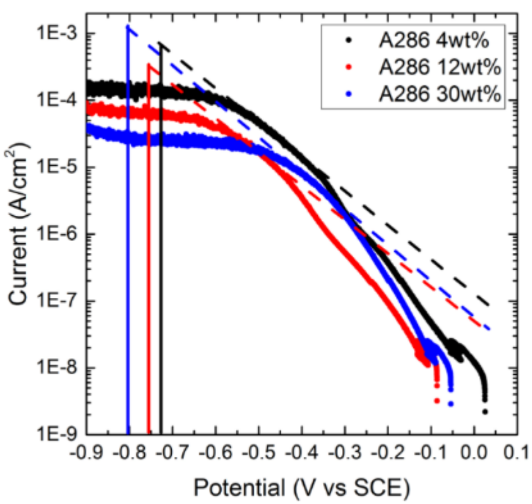
- For all couples studied, galvanic potential is controlled by Al and current by the cathode material.
- **Galvanic current for the different cathode materials peaks at a different concentration.**

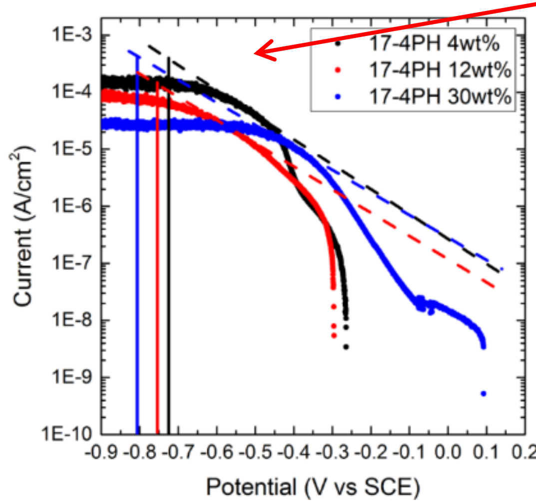


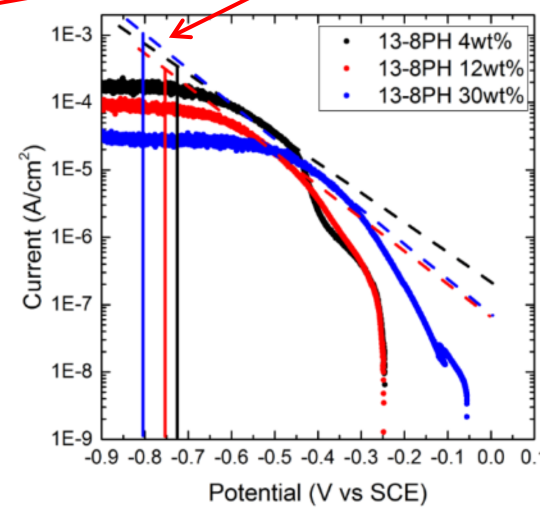


O_2 diffusion limitations exacerbated at higher salt concentrations.

Extrapolation of O_2 reduction reaction gives max galvanic current at thin film conditions.

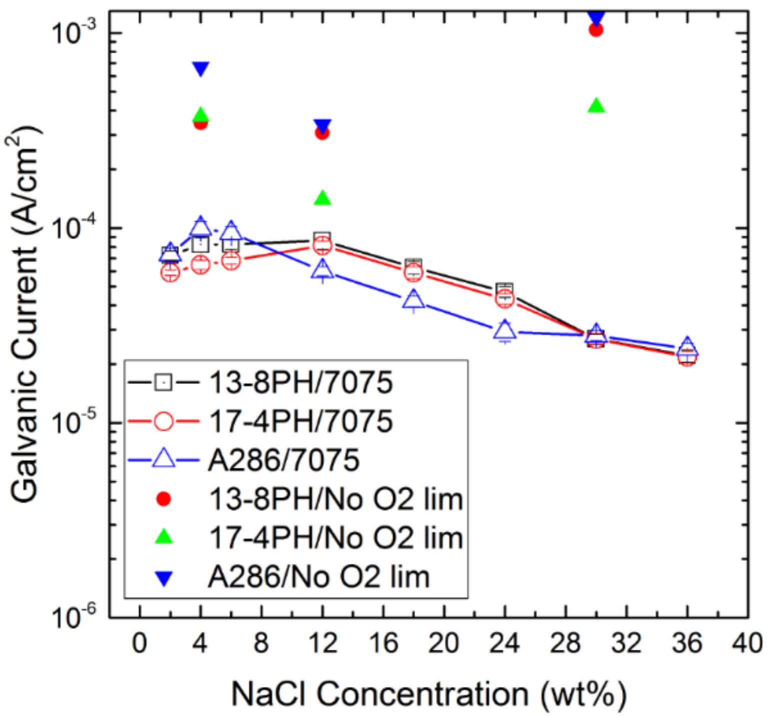


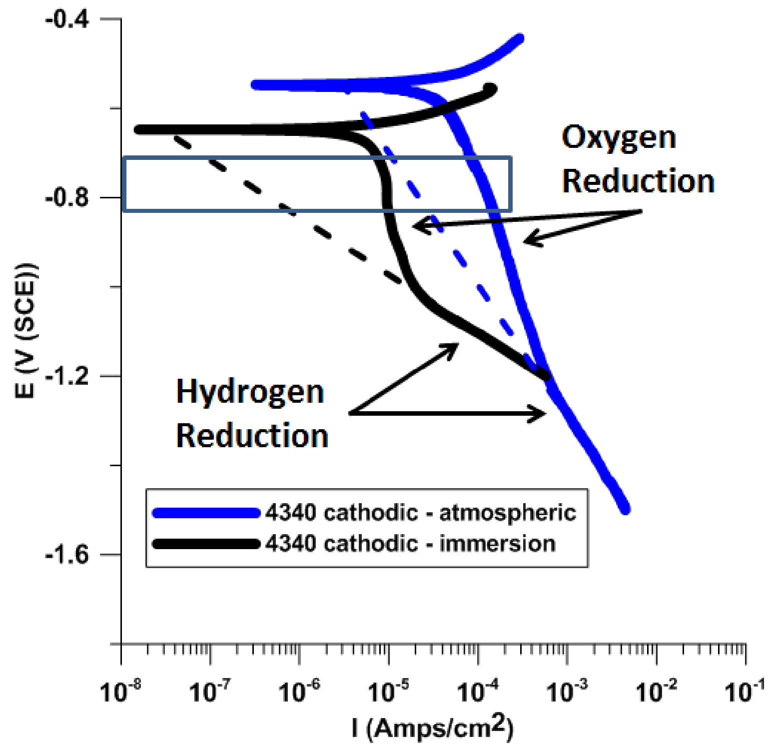




Validation: Laboratory Data

- Extrapolation to the non-limiting region is confirmed by non-immersion measurements on steel 4340.





SwRI

Kinetics of O_2 reduction reaction (cathode) control galvanic current!

Galvanic Activity, at Macro and Micro Scales

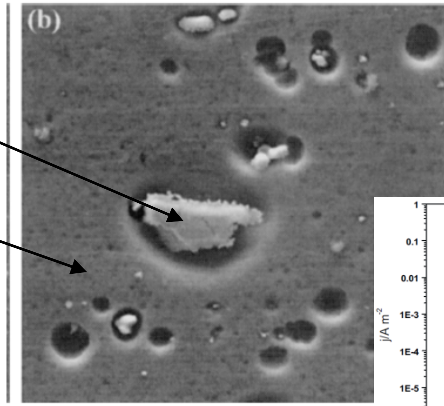
- Macroscopic galvanic corrosion is a major factor in Naval structures
- Stress assisted microscopic galvanic corrosion is significant in aircraft aluminum alloys (2xxx and 7xxx series aluminum)

Galvanic Activity at Macro and Micro Scales

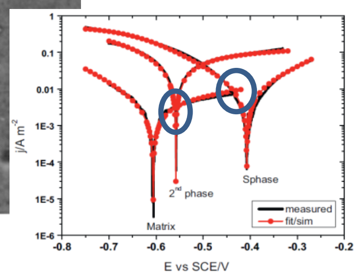
Micro-galvanic corrosion

Constituent particle

Matrix

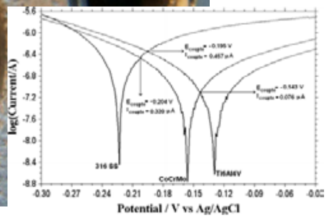


Micro polarization curves



Al2024-T3 immersion in 0.5M NaCl
Source: R.P. Wei, et al., *Metall. Mater. Trans A.* 39, 486-492, 2002.

Macro-galvanic corrosion



Macro polarization curves

Micro-galvanic cell between constituent particles

- Provide local corrosion activity
- Provide microscale interaction between stress and corrosion
- Develop a multi-physics program for environmentally assisted crack modeling
- Provide guidance for microstructural optimization

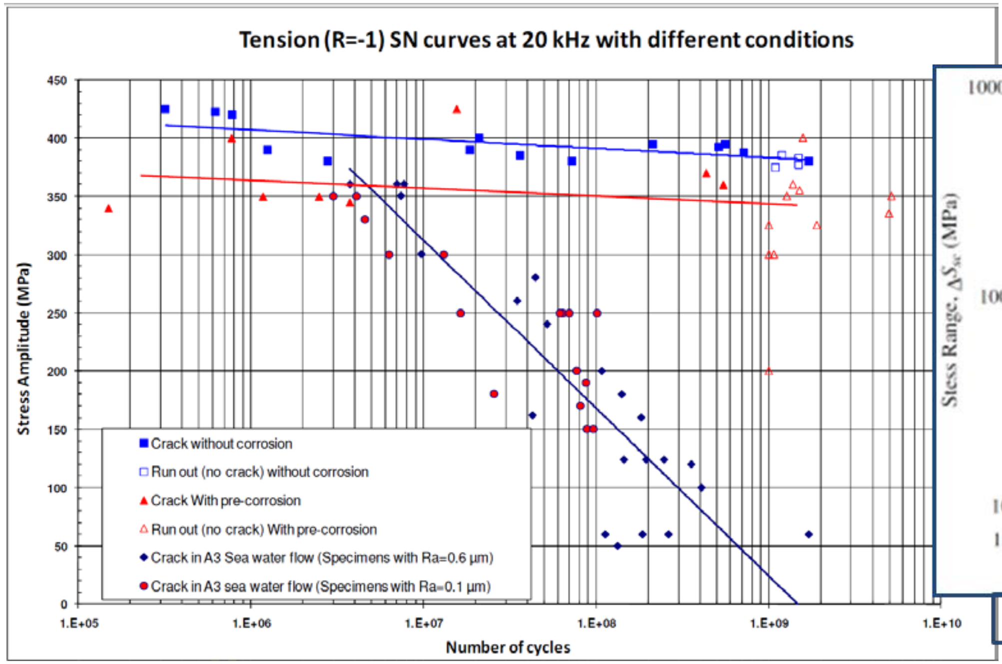
Macro-galvanic cell between dissimilar metals

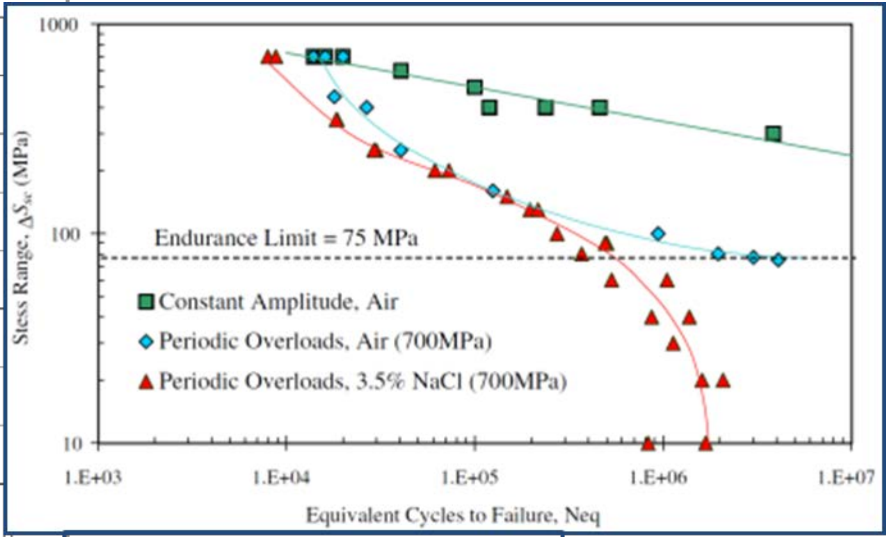
- Provide corrosion hot spot
- Provide macro galvanic corrosion current
- Provide driving force for corrosion damage
- Develop a numerical tool to predict galvanic corrosion rate
- Provide design specifications

Issue of Corrosion for Naval Aircraft

Pre-corrosion fatigue | Vs. | Corrosion fatigue

- Evidence of synergistic effect between fatigue and corrosion.
- The resulting damage is higher compared to when each is active individually.





Chlistovsky, et al., *Int J Fatigue* 2007.

The fatigue strength at 10^8 cycles is significantly reduced by a factor of 74% compared to the virgin specimens and of 71% compared to the pre-corroded ones. **Dramatic reduction in strength** is observed due to simultaneous corrosion-fatigue in the UHCF regime.

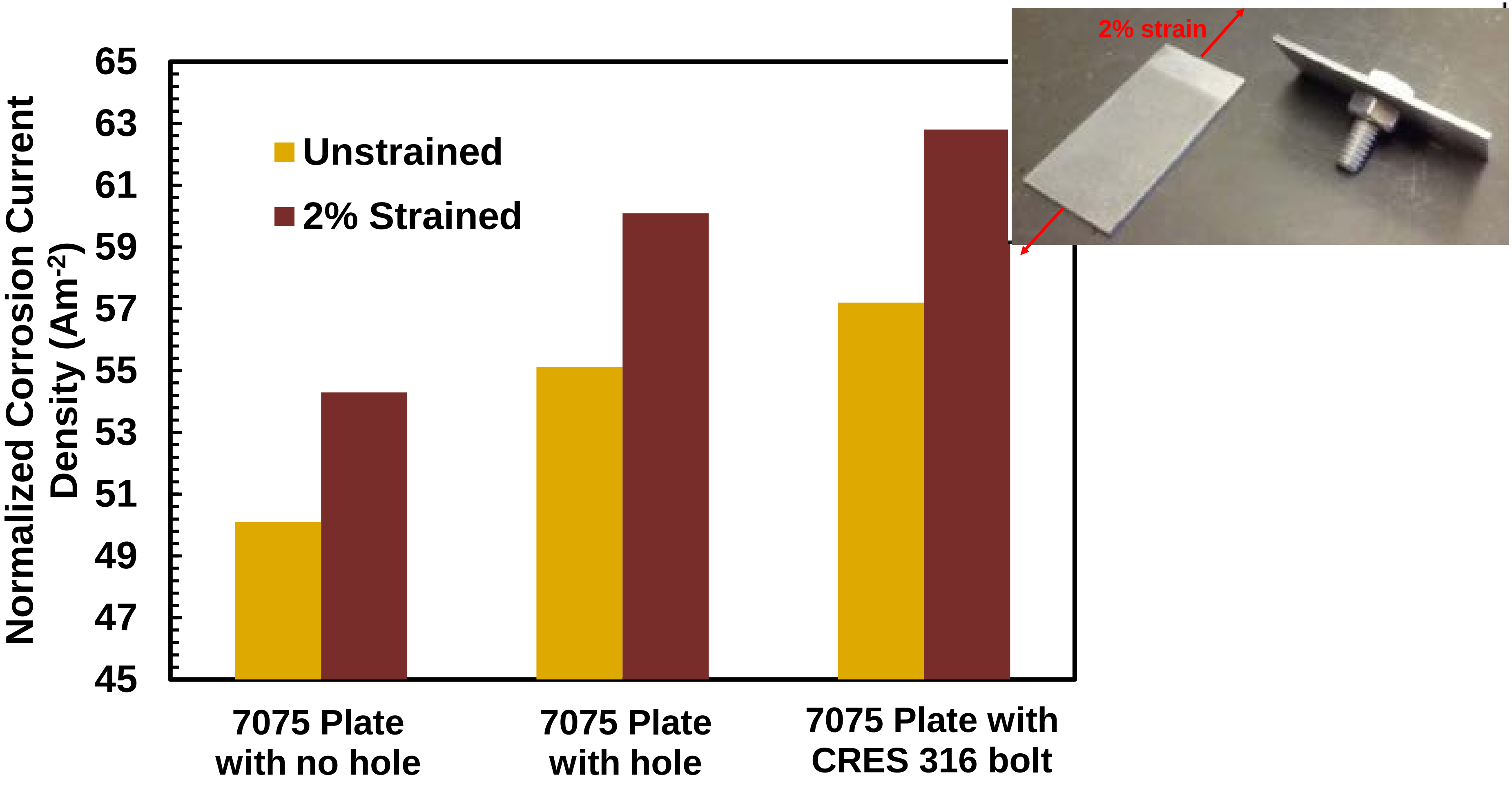
Bathias, C., Palin-Luc, T. "Exploration of the corrosion fatigue of steel in the gigacycle regime for oil industry," AFA WORKSHOP, 25 - 27 Nov 2012

Effect of Mechanical Load/Stress

- Increased electrochemical activity
  - Mechanical disruption of an otherwise protective or metastable corrosion oxide film
  - Inhibition of surface oxide formation due to hydrolytic acidification of the crack tip electrolyte
  - Extrusion of high index slip planes that dissolve at a larger rate than the original low index planes at a metal surface
  - Increased anodic dissolution current density due to cathodic shift of the corrosion potential

Reliable quantification of effects is an on-going process with continuous model verification and validation

Effect of Load on Corrosion Current



K. Solanki, ASU [ONR Grant] Experimentally obtained corrosion current for Al 7075 plate for strained and unstrained sample.

Corrosion stress equivalence

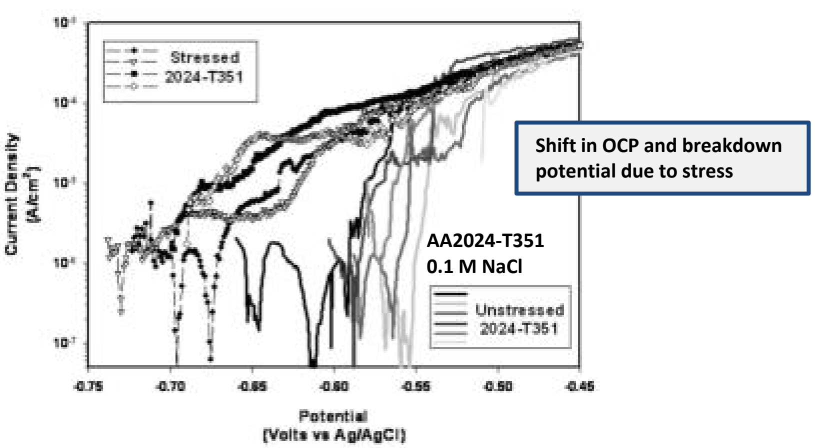
Damage (Pit) initiation	Damage (Pit) progression		Crack initiation	Crack growth
Localized Damage	Localized Propagation		Fracture, Crack Transition	Crack Growth
Pitting, Exfoliation, Anodic Dissolution	Pit growth, Multi-site, Chemo-thermo-mechanical effect	Pit to crack transition (nucleation) →	Continuum mechanics, Crystal plasticity, Surface Energy / Chemistry	E'chemical crack driving force, Chemical energy, H-E, Film rupture

Stress Corrosion Equivalence

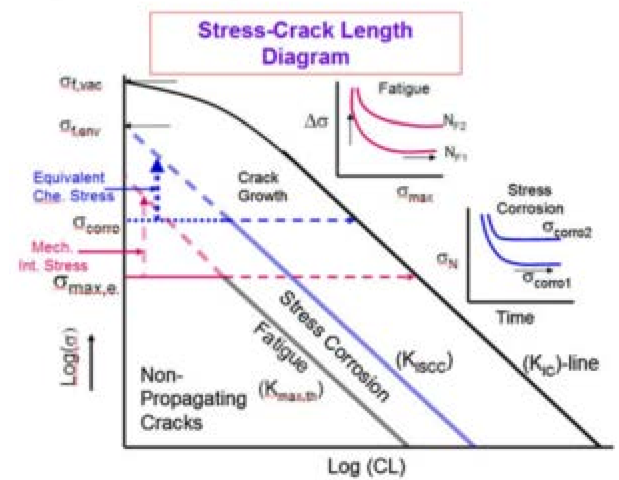
$$[^I/_A]\; J_{corr} \propto \sigma\; [^F/_A]$$

Corrosion Stress Equivalence

$$\left[^{I^2 x}/_{position}\right] K_{corr} \propto K_{(\Delta K, K_{max}, K_\perp)}$$



Connolly, in: *Local Probe Techniques in Corrosion Research*, Cambridge, UK, p. 155-166, 2007.



Sadananda, *Metall and Mat Trans A*, 2013.

Corrosion Crack Initiation and Growth

Environmental Crack Driving Force (ECDF)

Objective

Develop analytical expressions relating electrochemical crack driving force (ECDF) to solution conductivity, pH, anion and cation concentrations, aqueous hydrogen concentration and temperature.

Mechanical Crack Driving Force:

$$G(\text{joules}/\text{m}^2) = -\left(\frac{dU_e}{dA}\right)_\Delta = -\frac{1}{B}\left(\frac{dU_e}{da}\right)_\Delta$$

Electrochemical Crack Driving Force:

1: Hydrogen Embrittlement:

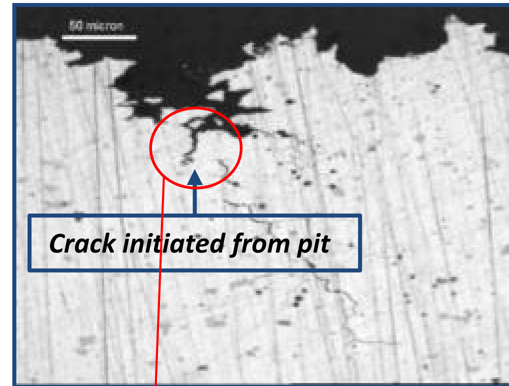
$$\tilde{G}_c(\text{joules}/\text{m}^2) = -\left(\frac{d\Delta\bar{G}_H}{dA}\right)_{T,P} = \left(\delta_{int}\bar{\theta}_{int}/2\bar{V}_M\right)\times\left[zF\eta_c - \frac{RT}{2}\ln\left(f_{H_2(a)}\right)\right]$$

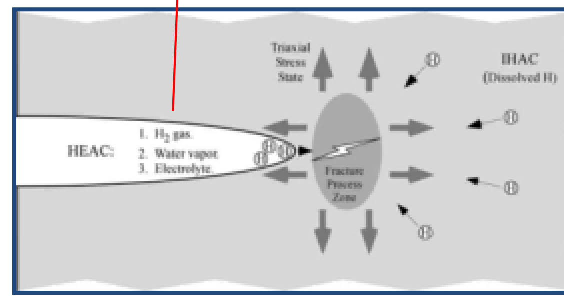
2: Active Path Dissolution :

$$\tilde{G}_a(\text{joules}/\text{m}^2) = -\frac{d\Delta G_a}{dA} = (\delta_{cor}/2\bar{V}_m)zF\eta_a$$

$$\left(\frac{da}{dN}\right)_{CF} = \Phi\left(\frac{da}{dN}\right)_{inert} + \left(\frac{da}{dN}\right)_{EAC}$$

Environmentally Assisted Crack Growth





F/A-18 lever arm collapse due to corrosion+sustained stress

Issue of Corrosion for Naval Aircraft

Global Env. Vs. **Local Env.**

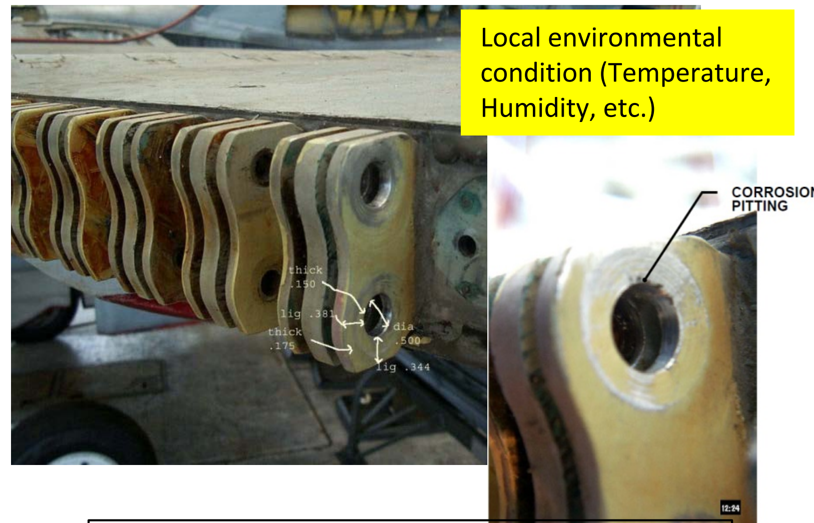
- Local environment (part scale) can be significantly different from global environment (system scale)

Global environmental condition (Temperature, Humidity, etc.)

Mendoza, 2012

- Global weather conditions
- Squadron location
- Shelter condition
- Flight requirement
- Wash cycle
- Ground activity

Local environmental condition (Temperature, Humidity, etc.)



- Local environment
- Dissimilar materials
- Part geometry, lap joints, fasteners
- Capillary action
- Occluded areas
- Accumulation of dirt and debris
- Coatings
- Mechanical loads

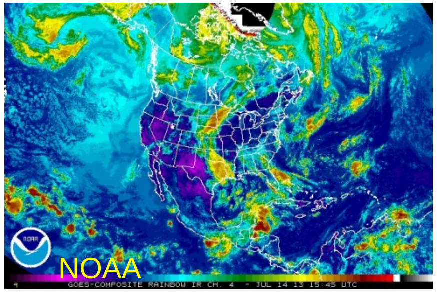
The Need for an Environmental Builder

- **Incorporate available sensor data**
  - Sampled or continuous information at sensor location(s) on aircraft
- **Link the ground station and sensor information to predict local/part environment**
  - Need a transfer function
- **Extract damaging events from assembling the dynamic environment - environment history**
  - Identify type of corrosion type and extent at different locations
- **Invoke suitable prediction models by combining ‘electrochemical stress’ with mechanical stresses**
  - Sensor informed degradation prediction and prognosis
  - Use advanced machine learning techniques to gap fill sparse service data

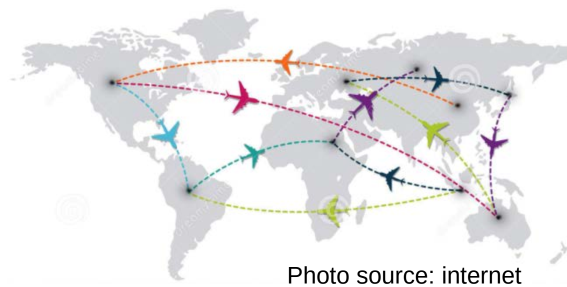
Overview of the Environmental Builder

Weather database

Global climate



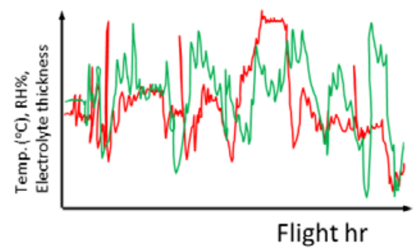
Flight pattern

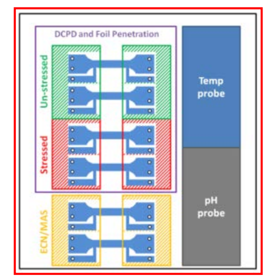


Flight database

Simulations

Part-specific micro-climate



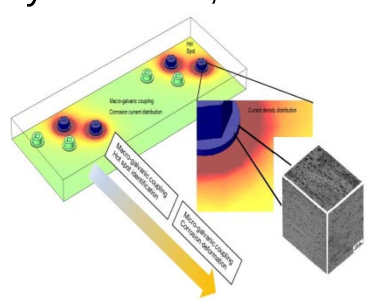


Sensor data

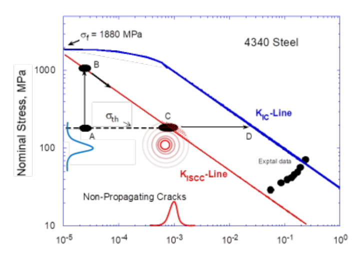
ISO 9223

Corrosivity	Category
Very low	C_1
Low	C_2
Medium	C_3
High	C_4
Very high	C_5

Cyclic stress, corrosion



Life prediction



Prospects for Future Work

- Include the environmental builder as well as life prediction models
- Integrate corrosion modules with structural modules for *incubation life and initiation*
- Combine synergistic actions at micro, meso, and macro levels at occluded regions
- Provide guidance for design data extrapolation
- Make a connection between material design and structural application (Corrosion MMPDS)