

Galvanic Compatibility Assessment: New Methodology and Standardization

March 26th, 2019

Presented to: NACE Corrosion 2019

Presented by: Steven Kopitzke, on behalf of Victor Rodriguez-Santiago, Anna Safigan



Distribution Statement A - "Approved for public release; distribution is unlimited"

MIL-STD-889: Dissimilar Metals

- **Purpose:** This standard defines and classifies dissimilar metals and establishes requirements for protecting coupled dissimilar metals against corrosion with attention directed to the anodic member of the couple.
- Modernized Revision: Current version was modernized in 2016 to replace obsolete references to other standards (MIL-STD-889C).
- Last Technical Revision: The last technical revision was done in 1967, based on an AMCOM report (TR-67-11). Was not done in sea water.
- **Proposed Approach:** The proposed approach is to move to galvanic current, rather than potential, in order to determine galvanic compatibility.

Wrong Compatibility Decisions are Possible



Proposed Approach for Technical Revision

• Aim: Update MIL-STD-889C based on current density rather than ΔE , and to update the materials list.

Proposed Methods:

- <u>Method 0</u>: Replace galvanic series with a similar table based on current density for equal areas, but using alloys rather than the generic materials in the current standard. Include simple ways of adjusting for relative areas and finishes. Galvanic current would be obtained from polarization data, and curve crossing.
 - Task: Define methodology to acquire polarization data in bulk electrolyte using flat cell -- this methodology will be based on a Best Practices Document for generating polarization curves.
- <u>Method 1</u>: Define galvanic acceleration factors corrosion testing such as weight loss.
 - <u>Method 2</u>: Define computational method using curve crossing.
 - **Method 3**: Define methodology for full FEA approach.

Other Phases

What do we need to accomplish?

Development of a Methodology for Generating Standardized Electrochemical Data

Development of a Deconvolution Approach for Analyzing the Data

Determining Galvanic Currents and Establishing Compatibility Thresholds

Round Robin for Developing a Test Methodology

- A methodology was established in order to obtain potentiodynamic polarization data. This methodology provides a best-practices approach in order to generate data across laboratories that is consistent and valid.
- Round robin testing was established encompassing academia, industry, and NAVAIR:
 - UVA (Kelly)
 - OSU (Frankel)
 - Corrdesa (Keith, Siva)
 - MSU (Swain)
 - NAVAIR (Safigan, Rodriguez)
 - UTRC (Jaworowski)
 - Safran
- The round robin was conducted and analyzed per ASTM E691.

Best Practices Document

Best Practices for Polarization Data Acquisition: Data Collection Guide for MIL-STD-889C Technical Revision

Prepared by:

Naval Air Systems Command

For:

Collection of Electrochemical Data for MIL-STD-889C Technical Revision

Version 4: FINAL

POC: Victor Rodriguez-Santiago, Ph.D. Naval Air Systems Command - NAVAIR Corrosion and Wear Branch - Code 4.3.4.6 Ph: 301-342-8040 Fax: 301-995-0742 victor.rodriguezsant@navy.mil

Anna Safigan Naval Air Systems Command – NAVAIR Corrosion and Wear Branch – Code 4.3.4.6 Ph: 301-995-6549 anna.safigan@navy.mil

March 2018

NAVAIR Public Release 2018-289. Distribution Statement A – "Approved for public release; distribution is unlimited" $\,$

• Best Practices document has been finalized and it is Distribution A.

Item	Notes										
Equipment	Flat cell.										
Reference electrode	SCE, Ag/AgCl, or other suitable	e electrode.									
Electrolyte	Artificial sea water per ASTM metals, $25 \pm 3^{\circ}$ C, pH 8.2, vigor then quiescent condition (natu	D1141 (2013) without heavy ously aerated prior to testing, arally aerated; no bubbling)									
Working electrode	Specimen to be tested. Stationary. Abraded with appropriate P800 or ANSI 400 grinding paper, cleaned with acetone then ethanol, and surface treated appropriately (if required).										
OCP stabilization	The surface should be stabilized in the electrolyte, but not for a time that causes the surface condition to change significantly (e.g. crevice or pitting):										
	MORE Noble (OCP > -200 mV vs SCE):	LESS Noble (OCP < -200 mV vs SCE):									
	24 hours in electrolyte prior to polarization measurement	4 hours in electrolyte prior to polarization measurement									
Polarization curve	 Anodic polarization: OCP to +0.7 V vs OCP, or when the anodic current density reaches a maximum of 10 mA/cm² Cathodic polarization: OCP to -1.4 V vs REF, or when the cathodic current density reaches a maximum of 10 mA/cm² Note: Cathodic and anodic curves shall be obtained on separate specimens prepared according to section 3.1. 										
Sweep rate	0.2 mV/s for entire potential r	ange									
IR correction	The reference electrode should be placed >2x diameter of Luggin tip from the working electrode.										

What do we need to accomplish?

Development of a Methodology for Generating Standardized Electrochemical Data

Development of a Deconvolution Approach for Analyzing the Data

Determining Galvanic Currents and Establishing Compatibility Thresholds

Deconvolution Approach: Reactions

- Semi-automated approach published by Yeum and Devereux:
 - K.S. Yeum and O.F. Devereux, "An Iterative Method for Fitting Complex Electrode Polarization Curves", Corrosion, Vol. 45, pp. 478-487 (1989).
 - 1) Identify curve regions dominated by separate reactions
 - 2) Classify those reactions into one of six types
 - 3) Provide initial estimates for kinetic parameters
 - 4) Operate software to obtain the best fit

Reaction Type	Electron	Passivation	Diffusion	Ohmic-drop
1	Х			
2	Х	х		
3	Х		Х	
4	Х			Х
5	Х		Х	Х
6	X	Х		Х

Deconvolution Approach: Parameters

Reaction Type	<u>1</u>	<u>2</u>	<u>3</u>	4	<u>5</u>
1	V*	b	-	-	-
2	V*	b	Vp	ip	-
3	V*	b	m	is	-
4	V*	b	-	-	R
5	V*	b	m	is	R
6	V*	b	Vp	ip	R

Definition of parameters

Parameter	Definition		
b V*	2.303 * b is the Tafel slope. Positive for anodic as well a Combination of exchange current density (io) and equilibr $V_j^* = E_{0j} - s_j \cdot b_j \ln i_{0j}$	as cathodic react rium potential (Er	tion. o). Graphically, the intercept of the Tafel line to log (current) = 0.
is m s Vp ip	Limiting diffusion current. Reaction order for the diffusion (mostly 1.0). Sign of reaction (-1 = cathodic, +1 = anodic) Passivation peak potential Passivation current.	Ι Ι _ο Ε Ε β	is the current resulting from the reaction is a reaction-dependent constant called the exchange current is the electrode potential is the equilibrium potential (constant for a given reaction) also <i>Ecorr</i> is the reaction's Tafel constant (constant for a given reaction, with units of volts/decade
R	Cell resistance.		

Raw Data 13-8Mo PH



Distribution Statement A - "Approved for public release; distribution is unlimited"

Deconvoluted Components



Fully Deconvoluted Curve



Raw and Deconvoluted



Average Deconvoluted Curve for All Data Sets



A286 Raw and Deconvoluted



 Scattered data sets can be averaged and represented in one curve using individual fit parameters. What do we need to accomplish?

Development of a Methodology for Generating Standardized Electrochemical Data

Development of a Deconvolution Approach for Analyzing the Data

Determining Galvanic Currents and Establishing Compatibility Thresholds

Verifying Mixed Potential Approach



Distribution Statement A - "Approved for public release; distribution is unlimited"

Galvanic Current of Several Couples



*Conversion coatings and anodization treatments will be attacked in a localized manner. All galvanic current will be concentrated in a small area.

Galvanic Table – New Methodology (High)

				coat.		Coat.	cast A	I IOW	alloy		010	low a	alloy			MM20	124	116-4		CuBe 410		410 SS Inco			- 13-8			Passiva	ated	310 33	Grap	Pa	assivated
		1	2	3	_	4	5	<u> </u>	6	7	7	8		9	_	10		11		12	1	3	14		15	16		17		18	1	•	20
Mg WE43	1		1 4 An Ca	1 An C	1 Cal An	I Cal	1 An C	4 1 Sal An	I Ca	1 An	4 Cai	1 An	5 Cai	1 An	5 Cal /	1 An	4 1 Cal A		9 1 Cal An	I Ca	1 ai An	7 Cal	1 An (9 1 Cal An	9 Ca	1 An	9 Cali	1 An	9 Cati	1 An C	9 1 Cal An	13 1 Cai Ar	n I Cat
AA5083	2			4 An C	4 Cal An	3 Cai	4 An C	4 4 Sal An	I Ca	4 An	4 Cai	4 An	5 Cal	4 An	5 Cal /	4 An	44 Cal A		9 4 Cal An	I Ca	4 ai An	7 Cal	4 An 1	9 4 Cal An	9 	4 An	9 Cali	4 An	9 Cat i	4 An 1	9 4 Cal An	13 4 Cal Ar	l D Cat
ZnNiw/ conv. coat.	3				An	3 Cal	An C	4 Sal An	5 Ca	An	4 Cai	An	5 Cai	An	5 Cali	An I	4 Cal A		9 Cal An	I Ca	a An	7 Cali	An I	9 Cal An	9 	An I	9 Cali	An I	9 Cat /	An I C	9 Cal An	13 Cal An	9 Cat
Cdw/							3	4 3	5	3	4	3	5	3	5	3	4 3		9 3		3	7	3	9 3	9	3	9	3	9	3	9 3	13 3	9
conv.	4						An C	al An	Ca	An	Cat	An	Cal	An	Call	An	CallA		Cal An	Ca	a An	Cat	An C	Cal An	Ca	An C	Call	An I	Cat	An C	al An	Cal Ar	n Cat
 								4	5	4	4	4	5	4	5	4	4 4		9 4		4	7	4	9 4		4	9	4	.9	4	9 4	13 4	
cast Al	5							- An		An I	Cal	Αn	Cal	An I	Call	An I	CallA		a An					Cal An			т Сац		Cat			CalAr	
1020		The	a a h a l d	-10	w10	-7			00	5	4	5	5	5	5	5	4 5		9 5		5	7	5	9 5	9	5	9	5	9	5	9 5	13 5	9
low alloy	6	Inr	esnoia	= 1.0	XIU	'				An	Cai	An	Cal	An	Cal /	An I	Gal A		Cal An	l Ca	ai An	Cal	An I	Cal An	l Ca	An I	Cal /	An I	Cat	An C	al An	Cal Ar	n Cat
AA7075	7								-			4 An	5 Cai	4 An	5 Cali	4 An	44 Cal A		9 4 Cal An	I Ca	4 An	7 Cal	4 An (9 4 Cal An	l 9 Ca	4 An	9 Cali	4 An	9 Cati	4 An C	94 Xal An	13 4 Cal Ar	1 9 1 Cat
4340														5	5	5	4 5		9 5		5	7	5	9 5	9	5	9	5	9	5	9 5	13 5	9
low alloy	8													s	s,	An	Cal A	n ' 0	Cal An	Ca	al An	Cal	An (Cal An	Ca	An	Cali	An	Cat	An C	al An	Cal Ar	n Cat
HY80	9					Cat	: cath	odic (less	react	ive)	7			,	5 An	45 Cal A		9 5 Cal An	I Ca	5 4 An	7 Cali	5 An	9 5 Cal An	9 	5 An	9 Cali	5 An	9 Cat /	5 I An 0	9 5 Cai An	13 5 Cai An	9 N Cat
AA2024	10					An:	anod	ic (mo	ore r	eactiv	ve)						4	с	94 Cal An	I Ca	4 4	7 Calu	4 An	9 4 Cal An	1 9 1 Ca	4 An	9 Calu	4 An	9 Catu	4 Ap (9 4 Cal Ap	13 4 Cal Ar	9 Cat
Ti 6-4	11		a-1-1 a									_							9		9	7	9	9 9	9	9 C	9	9	9	9	9 9	13 9	9
CuBe	12	()	eft colum	n)		• ((Met (top)	al 2 row)				An	La		7	- C	9	9		9	- C	9		/a An 9	13	9 Lat
		d	Treatmer	nt -								<u>٦</u>		Reco	mme	nde					An	Cal	An (Cal An	Ca	An	Cali	An	Cat	An C	a An	Cal Ar	n Cat
410 SS	13				_			-(\vdash		-	_		arre	atme	ent							7 An C	9 7 Cal An	C 9 Ca	7 An C	9 Cali	7 An C	9 Cat /	7 C	9 7 Sal An	13 7 Cal Ar	C 9 Cat
Inconel	14	M	etal 1			*				(•		Meta	al 2									9	с 9 Са	9 00	9 Col	9 c	9	9 c	9 9 0	13 9 Cal Ar	с 9 С. С. 1
PH 13-8	15	mo	pre/less re) eactive				Ī						(top r more	ow) /less	react	ive							An	La	9	9 9	9	9	9	99	13 9	
																										An	Cal	An	Cat	An Č (al An	Cal Ar	n 🎽 Cat
Monel	16						<u>Co</u>	mpa	tibi ible	lity																		9 An	9 Cat /	9 C An C	9 9 0 Sal An	13 9 Cal Ar	C 9 Cat
PH 13-8						<u>ا</u>		mpat		coup	ne										+	++					F			9	9 9	13 9	9
Passivated	17						i : ine	comp	atibe	e cou	ple				_	_														An C	al An	Cal Ar	C Cat
							: di	screp	ancy	with	exis	sting	MIL	-STD	-889	C															9	13 9	9
316 SS	18						: in	agree	emer	nt wit	th ex	kistin	gМ	IL-ST	D-88	39C															An C	Cal Ar	n Cat
Graphite	19																							_								13 Ar	9 Cat
316 SS Passivated	20																																

Active

ОРС

Passive

Distribution Statement A - "Approved for public release; distribution is unlimited"

Galvanic Table – New Methodology (Low)

			Mg WE43	AA5083	ZnNiw/ conv. coat.	Cdw/ conv. coat.	A356 cast Al	1020 Iow alloy	AA7075	4340 low allo	y HY80	AA202	24 Ti 6	6-4 C	CuBe 41	IOSS	Inconel	PH 13-8	Monel	PH 13-8 Passivated	316 SS	Graph	ite 316 SS Passivated
			1	2	3	4	5	6	7	8	9	10	1	1	12	13	14	15	16	17	18	19	20
	Mg WE43	1		1 4		1 3	1 4	1 5	1 4		5 1 5		4 1	91	1	7	1 9	1 9	1 9	1 9	1 9	1	13 1 <u>9</u>
				An Ca	An Ca	An Ca	An Ca	a An Ca	An Ca	An (Cal An 🛛 Ca	An	Cal An	Cal An	Cal An	Cali	An Cal	An Ca	An Ca	An Ca	t An Ca	An	Cal An Cat
	AA5083	2			4	4 3	4 c 4	4 5	4 4	4	545	4	4 4	94	4	1 7	4 9	4 9	4 9	4 9	4 9	4	13 4 9
	ZoNiw/				An Cal	An Ca	An Ca	al An Ca	An Ca	i An U	Cal An Ca	An	Cal An	Cal An	Cal An	Cal A	An Cal	An Ca	An Ca	An Ca	tAn Ca	An	Cal An Cat
	conv.	3				3					5 5		4	9		1		• I 0	C S				
	coat. Cdw/					An <mark>u</mark> Ca		a An Ca	An Ca	An U	iai An Lia	An	Cal An	Cal An	Cal An	Ual A	An Cal	An Ca	An Ca	An Ca	t An L'a	An	Cal An Cat
	conv.	4																	3 C 3			3	
	Coat.						An Ca	a Ani Ca			S A S					7	An Ca	An Ca	An Ca	An La		An An	12 / 9
	cast Al	5																					
	1020		The	ochold	-10	10-6			5 4	5	5 5 5	5	4 5	9 5	5	7	5 9	5 9	5 9	5 9	5 9	5	13 5 9
	low alloy	6	Inre	esnoia	= 1.08	10			An Ca		Cal An Ca	An	Cal An	Cal An	L Cal An		An Cal	An Cal	Ap Ca				Cal Ap Cat
D										4	5 4 5	4	4 4	9 4	4	7	4 9	4 9	4 9	4 9	4 9	4	13 4 9
2	AA7075	7								An 0	Cal An Ca	An	Cal An	Cal An	T Cal An	Call	An Cal	An Ca	An Ca	An Ca	t An Ca	An	Cal An Cat
ۮ	4340	_									5 5	5	4 5	9 5	5	7	5 9	5 9	5 9	5 9	5 9	5	13 5 9
L	low alloy	8									s c s	An	Cal An	Cal An	Cal An	Call	An Cal	An Ca	An Ca	An Ca	t An Ca	An	Cal An Cat
		_								5		5	4 5	95	5	7	5 9	5 9	5 9	5 9	5 9	5	13 5 9
2	HY80	э				Ca	it: catho	dic (less	reactive)			An	Cal An	Cal An	Cal An	Call	An Cal	An Ca	An Ca	An Ca	t An Ca	An	Cal An Cat
5	A A 2024	10				Ar	n: anodio	c (more r	eactive)				4	94	. 4	. 7	4 9	4 9	4 9	4 9	4 9	4	13 4 9
	AA2024	10						•					An	Cal An	Cal An	Call	An Ca	An Ca	An Ca	An Ca	t An 🛛 Ca	An	Cal An 🛛 Cat
b	T: C 4	-1-1												9	9	7	9 9	9 9	9 9	9 9	9 9	9	13 9 9
S	110-4		N	/letal 1							Metal 2	2		An	Cal An	Cal	An Cal	An Ca	An Ca	An Ca	t An Ca	An	Cal An Cat
2	CuBe	12	(1	eft colum	in)						(top row	/)				c 7	6 9	9	9	9	9		13 9
ő			R	ecommer Treatmer	nde					•	Recomm	nende			An	Call	An ČCal	An Ca	An Ca	An Ca	t An 👅 Ca	An	Cal An 🛛 Cat
	410 SS	13	Ľ	meanner							d Treatn	nent					7 <mark>9</mark>	7 g	7 9	7 9	7 <u>9</u>	7	13 7 <u>9</u>
								$\overline{\mathbf{V}}$								/	An Ca	An Ca	An Ca	An Ca	t An ČCa	An	Cal An Cat
	Inconel	14	M	etal 1		(*	Metal 2							9 <mark>c</mark> 9	9 <mark>c</mark> 9	9 c 9	9 c 9	9 C	13 9 <u></u> 9
			(le	ft column)			1	- -		(top row)						An Ca	An Ca	An Ca	t An 🛛 Ca	An	Cal An Cat
	PH 13-8	15	ma	ore/less re	eactive						more/les	s reacti	ve						9 c 9	9 <u></u> 9	9 c 9	9 C	13 9 9 C
						F													An Ca	An Ca	tAn Ca	An	Cal An Cat
	Monel	16					Co	mpatibi	lity											9 C 9	9 C 9	9 . C	13 9 9
	PH 13-8						C : con	npatible	couple											An Ca	tAn Ca	An	Cal An Cat
L	Passivate	17					I : inc	ompatibo	e couple													9 C	
7	d						📕 : dis	crepancy	with exi	isting N	1IL-STD-88	9C									AN La		12 9 AN Lat
	316 SS	18					: in a	agreemei	nt with e	xisting	MIL-STD-8	389C											
																						An	13 9
	Graphite	19											1										
	316 55																						
	Passivate	20																					
	d																						

Distribution Statement A - "Approved for public release; distribution is unlimited"

Summary

- Galvanic current is a better assessment metric than galvanic potential for determining galvanic compatibility.
- A methodology was created to generate polarization data sets. The methodology was validated through a round robin test.
- A deconvolution approach was used to analyze the polarization data sets.
- The mixed potential approach to determine galvanic current is valid.
- A ranking for galvanic compatibility will be created.



Development and Validation of a Cyclic Humidity Corrosion Test

March 26th, 2019

Presented to NACE Corrosion 2019 Presented by Steven Kopitzke on behalf of Victor Rodriguez-Santiago, Alex Lilly



Distribution Statement A - "Approved for public release; distribution is unlimited"

Traditional ACT Fails to Replicate Representative Corrosion Severity

- What do we know?
 - Current accelerated corrosion tests (ACT) fail to replicate damage observed in field environments (e.g., ASTM B117, ASTM G85, MIL-STD-810, GMW14872, etc.).
 - In addition, current ACT is well known for chamber inconsistencies, which can be more pronounced during cyclic tests.
 - Recent studies indicate that controlling relative humidity is crucial to replicating damage, which is NOT accurately specified in current ACT.

• What can we do?

- Better understand the individual and combined effects of environmental factors and solution chemistry on the mechanisms and severity of corrosion.
- Better understand environment dynamic changes in order to quantify environmental severity.

Dynamic Monitoring of Corrosive Environments is Critical to Understand Corrosion Evolution

- Environmental exposure sites provide the closest correlation between corrosion degradation and damage experienced inservice, but:
 - Time-consuming
 - Not widely accessible
 - Provides cumulative data only
 - No dynamic monitoring



Outdoor Exposure of Samples by W.H. Abbott at Battelle Columbus Operations.¹

¹ W.H. Abbott, "A Decade of Corrosion Monitoring in the World's Military Operating Environments: A Summary of Results," DoD CorrDefense, 2008.

Dynamic Environmental Monitoring Devices Allow Correlation Between Environmental Conditions and Corrosion Severity

- Monitor environment through dynamic capture of temperature, relative humidity, and solution resistance across a gold interdigitated electrode
- No information of the sample's surface condition is necessary, i.e. salt concentration, surface contaminants, etc.
- Environmental data and statistical analysis can be used to develop an accelerated test better representative of exposure data



Gold interdigitated electrode

Multi-sensor device measuring temperature, relative humidity, and solution resistance across gold interdigitated electrode.

Traditional Environmental Severity Classification Methods Fail to Reliably Classify Corrosion Severity

- ISO 9223:2012²
 - Classification of the corrosion severity of atmospheres on the basis of three key factors:
 - TOW (time of wetness)
 - Temperature > 0 °C
 - Relative humidity > 80%
 - Deposition rate of chlorides
 - Sulfur dioxide concentration
 - Five corrosivity classes: C1 to C5

² ISO 9223, "Corrosion of Metals and Alloys – Corrosivity of Environments – Classification, Determination and Estimation" (Geneva, Switzerland: ISO, 2012).

Dynamic Environmental Monitoring Allows Correlation Between Environmental Conditions and Corrosion Severity



Variables of interest are plotted as a function of time showing the oscillatory surface temperature and relative humidity behavior expected due to day/night cycles. Changes in average temperature behave as expected due to changes in seasons. Solution resistance is measured across a broad range of values. Dashed lines represent data retrieval and therefore mass loss measurements.

Statistical Methodologies Allow Correlation of Environmental Variables to Corrosion Severity

- Data collected on-board USS Wasp over 9 months.³
- All data falling below 819 Ω will be considered 'wet' while data contained between 819 Ω and the 'dry' solution resistance limit are considered 'semi-wet'
- From these data, number of wetness and semi-wetness events can be determined, as well as their average duration



³ Cosima Boswell-Koller, Victor Rodriguez-Santiago, Statistical Analysis of Environmental Parameters: Correlations between Time of Wetness and Corrosion Severity, CORROSION.

Environmental Monitoring Allows the Development of Effective Accelerated Corrosion Methods



Distribution Statement A – "Approved for public	release; distribution is unlimited"
---	-------------------------------------

0.15 g

time

1020 CS

0.1457 g

Lessons Learned: Relative Humidity and Solution Chemistry Control Corrosion Severity and Mechanism

- The proposed methodology was developed through SERDP WP-1673.⁴
- <u>Main concept</u>: Relative humidity (RH) cycling is a major factor in controlling corrosion damage and mechanism.



⁴ James Dante, Accelerated Dynamic Corrosion Test Method Development, SERDP Project WP-1673.

Degradation Mechanisms are Dependent on Relative Humidity Cycling

Accelerated Test Cycle Conditions

- $T = 49^{\circ} C$
- TOW = 67% of total exposure time
- Salt deposition: 0.6M NaCl, pH = 3, salt dip = 15 min

	Cycle 1	Cycle 2	Cycle 3
Max RH	90%	90%	90%
Min RH	40%	65%	40%
Max RH Time (hr)	2	2	8
Min RH Time (hr)	1	1	4
Salt Dip Frequency (per wk)	1	1	1
	The	\checkmark	7
Effect of deg of drying	jree E c d	ffect of frequ ycles and hig well time	uency of gh RH

- •Cycle 1: Very shallow damage restricted to the uppermost surface layer.
- •Cycle 2: Exfoliation, extensive coating delamination and material volume loss.





• Cycle 3: Deep corrosion trenches along fastener and significant pitting.





Technical Approach: Specific Variables Allow for Tunable Environmental Corrosion Severity

- Main parameters affecting corrosion:
 - **<u>Relative Humidity</u>** defines periods when active electrolyte exists
 - **<u>Relative Humidity Duty Cycle</u>** determines attack morphology
 - **<u>Electrolyte chemistry and deposition rate</u>** determines degree of attack
- The innovative aspect of this methodology is the control of cyclic variation of relative humidity and the periodic salt deposition of salt solution within each cycle.
- Traditional cyclic tests do not include this degree of control, limiting their usefulness and introducing a high degree of variation in test results.
- The degree of detail in knowledge of the role of humidity cycling control has been gained only within the last 5 years.

Task 1: Optimization of Cycle Period



Proposed Chemistries*

performance and environmental severity will generated through g/L (Reagent) NE#1 g/L (Reagent) NE#2 Reagent image analysis of 3-D optical images. NaCl 24.53 22.26 MgCl₂.6H₂O 11.10 11.10 Na₂SO₄ 4.00 4 00 NaNO₃ Go/No-Go decision will be made at the HCI (1N) *Normalized to ionic stren end of this task.











hole

Ordinal rankings of coating





Border detected

Gravscale

Threshold applied Unconnected areas removed

Task 2: Round Robin Testing



Task 3: Standard Development & Acceptance

- The **objective** of this task is to **formalize** the test procedure into a NACE International laboratory accelerated corrosion **test standard**.
- A society standard offers several advantages over a MIL-STD:
 - OEMs can participate in development and drafting of the standard, thus reducing resistance to acceptance.
 - Society standards require revisions every three to five years. This means the standard can be updated as new technical developments are made.
 - If DoD components wanted a MIL-STD version, it is easier to convert a pre-vetted standard.
- The approach is to create a NACE Task Group (TG) within STG 41 (Electric Utility Generation, Transmission, and Distribution) to drive the development of the specification.
- Victor Rodriguez-Santiago (PI, NAVAIR), Sean Fowler (Q-Lab), James Dante (SwRI, PI from WP-1673) and Kris Williams (Boeing, Key personnel on WP-2521) will serve on the TG as representatives from this ESTCP effort.
- The front end of the specification will define the overall testing approach.
- Specific environmental test cycles will be included within the annex section of the specification.
- Because of the flexible nature of the specification, additional annexes can be created to include other types of environments

Summary

- Dynamic environmental monitoring devices and subsequent data analysis methodologies allow correlation between environmental conditions and corrosion severity.
- Dynamic environmental monitoring allows for development of effective accelerated corrosion test methodologies which replicate corrosion severity of outdoor field exposures.
- The combination of effects observed from varying solution chemistries, time of wetness, and drying to wetting time ratios may allow for full tunable corrosion severity.
- Corrosion severity and mechanisms will be quantified using 3-D image analysis.
- The present work aims to develop a more representative and repetitive accelerated corrosion test standard through inter-laboratory collaboration.

References

- 1. W.H. Abbott, "A Decade of Corrosion Monitoring in the World's Military Operating Environments: A Summary of Results," DoD CorrDefense, 2008.
- ISO 9223, "Corrosion of Metals and Alloys Corrosivity of Environments Classification, Determination and Estimation" (Geneva, Switzerland: ISO, 2012).
- 3. Cosima Boswell-Koller, Victor Rodriguez-Santiago, Statistical Analysis of Environmental Parameters: Correlations between Time of Wetness and Corrosion Severity, CORROSION.
- 4. James Dante, Accelerated Dynamic Corrosion Test Method Development, SERDP Project WP-1673.

Backup Slides

Round Robin: Combined Al 7075



Distribution Statement A – "Approved for public release; distribution is unlimited"

Round Robin Statistics: Al7075

Inter-lab statistics: indicator of how one laboratory's cell average, for a particular material, compares with the average of the other laboratories (n = 7).



Intra-lab statistics: an indicator of how one laboratory's withinlaboratory variability, under repeatability conditions (n = 3), on a particular material, compares with all of the laboratories combined (n = 7).



Round Robin: Combined Steel 1020



Round Robin Statistics: Steel 1020





Mixed Potentials with Data Variation



Mixed Potential Approach to Galvanic Current



Distribution Statement A – "Approved for public release; distribution is unlimited"

Validating Mixed Potential Approach



Effect of Conversion Coating



Conversion coatings do not offer a galvanic benefit but can cause severe localized damage when breached. The same applies to anodization.

Galvanic Table – New Methodology (Mid)

			Mg WE43	AA5083	ZnNiw/ conv. coat.	Cd con	w/ iv. it.	A356 cast Al	A356 1020 AA7075 4340 low alloy 6 7 8					нү	80	AA2	:024 1	i6-4	CuE	3e 4	10 55	Inco	nel	PH 13-8	Mo	nel	PH 13 Passiva	-8 ated	316:	ss	Graph	nite	316 Passi	SS vated
			1	2	3	4	_	5	6		- 7		8	1	,	1		<u>n</u>	12	2	13	14		15	1	6	17		18	\$	19	_	2	0
	Mg WE43	1		1 4 An Cai	1 An Ca	1 al An	3 Cal A	1 4 An Ca	1 An	5 Cali	1 An	4 1 Cal Ar	I Ca	1 An	5 Cai	1 An	4 1 Cal An	I Cal	1 An	1 Cal An	I Ca	1 I An	9 Cal A	1 9 In Ca	1 An	9 Cal	1 An	9 Cat	1 An	9 Cal	1 An	13 Cal	1 An C	9 Cat
	AA5083	2			4 An Ca	4 ai An	3 Cal A	4 4 An Ca	4 An	5 Cali	4 An	44 Cal Ar	I Ca	4 An	5 Cai	4 An	44 Cal An	I 9 Cal	4 An	4 Cal An	I 7 Ca	4 An	9 Cal A	4 9 Nn Ca	4 An	9 Cali	4 An	9 Cat	4 An	9 Cal	4 An	13 Cal	4 An	9 Cat
1	ZnNiw/	3					3	4		5	_	4	5		5	_	4	9	- 1		7		9	9		9	- 1	9	- 1	9		13	- 1	9
	Conv. coat.					An	Cal A	An Ca	a An	Cal	An	Cal Ar	n Ca	An	Cal	An	Cal An	Cal	An	Cal An	Ca	An	Cal A	in Ca	An	Cali	An	Cat	An	Cal	An	Cal	An	Cat
	CODU	a					:	3 4	3	5	3	43	5	3	5	3	43	9	3	3	7	3	9 :	3 9	3	9	3	9	3	9	3	13	3	9
	Coat.	-					Æ	An Ca	An	Cal	An	Cal An	Ca	An	Cal	An	Cal An	Cal	An	Cal An	Ca	An	Cal A	In Ca	An	Cal	An	Cat	An	Cal	An	Cal	An	Cat
	A356	_							4	5	4	44	5	4	5	4	44	9	4	4	7	4	9	4 9	4	9	4	9	4	9	4	13	4	9
	cast Al	5							An	Cal	An	Cal Ar	Ca	An	Cal	An	Cal An	Cal	An	Cal An	Ca	An	CallA	In Ca	An	Call	An	Cat	An	Cat	An	Cal	An	Cat
	1020		Thr	eshold	- 5 0	v10 ⁻⁷	· -				5	4 5	5	5	5	5	4 5	9	5	5	7	5	9 9	5 9	5	9	5	9	5	9	5	13	5	9
I	low alloy	6		Siloid	- 5.0	~ ~					An	Cal An	Ca	An	Cal	An	Cal An	Cal	An	Cal An	Ca	An	Cal A	In Ca	An	Cal	An	Cat	An	Cal	An	Cal	An	Cat
	447075	_										4	5	4	5	4	44	9	4	4	7	4	9	4 9	4	9	4	9	4	9	4	13	4	9
é	AA1015	1										An	Ca	An	Cal	An	Cal An	Cal	An	Cal An	Ca	An	Cal A	n Ca	An	Cal	An	Cat	An	Cal	An	Cal	An	Cat
€	4340	_												5	5	5	4 5	9	5	5	7	5	9 !	5 9	5	9	5	9	5	9	5	13	5	9
Ų A	low alloy	8												s	s	An	Cal An	C	An	Cal An	Ca	An	CallA	In Ca	An	Cat	An	Cat	An	Cat	An	Cat	An	Cat
4															-	5	4 5	9	5	5	7	5	9.1	5 9	5	9	5	9	5	9	5	13	5	9
	HY80	9							ю <i>п</i>			. F				0		C 🚽	<u> </u>	C-1 0-							÷ I		<u> </u>		<u> </u>	10 C	<u> </u>	Cat
C							Cat:	catho	dic (le	ss re	activ	ve)				AD		3	An		La			in ca		La	An	Cat	An	La	An	uan Ka	A	Lat
Ā	AA2024	10					An:	anodi	: (mor	e rea	activ	e)					4	c –	4	4	1	4	9	4 9 - 1 -	4	9	4	9	4	9	4	13	4	9
0						L											An	Cal	An	Cal An	Ca	An	Cal A	in Ca	An	Cal	An	Cat	An	Cal	An	Cal	An	Cat
	Ti 6-4	11																	9	9	7	9	9 :	3 9	9	9	9	9	9	9	9	13	9	9
Ð			N	letal 1										Met	tal 2				An	Cal An	Ca	An	Cal A	n Ca	An	Cal	An	Cat	An	Cal	An	Cal	An	Cat
<u>.</u>	CuBe	12	()	eft colum	in)	-								(top	row))					c 7		9	9		9	_	9		9		13		9
ŝ			R	ecommen T	nde	-	\neg							Reco	omme	ende				An	Ca	An	Cal A	In Ca	An	Cal	An 🎽	Cat	An	Cal	An	Cal	An	Cat
ä	410.55	13	la	Treatmen										d Tre	eatm	ent						7	9	7 9	7	9	7	9	7	9	7	13	7	9
0		15																				An	Cal A	In Ca	An	Cal	An 🎽	Cat	An	Cal	An	Cal	An	Cat
		14	M	etal 1					Ť		(Met	al 2								1	э э	9	9	9	9	9	9	9	13	9	9
	inconei	14	(le	ft column) -				4				\sim	(top)	row)								Æ	In Ca	An	Cal	An	Cat	An	Cal	An C	Cal	An C	Cat
	DU 40.0		ma	ore/less re	eactive									more	:/less	read	tive								9	9	9	9	9	9	9	13	9	9
	PH 13-8	15											4 1												An	Call	An	Cat	An C	Cat	An C	Cal	An C	Cat
								· (~	mnati	ihili	+.,																9	9	9	9	9	13	9	9
	Monel	16							npau		<u>LY</u> .																	Cat	- C	Cat	- C	Cat		Cat
	DU 12 0						Ľ	: cor	npatib	ole c	ouple	e														+ F		00.	9	9	9	13	9	9
	Passivated	17					- I I	: inc	ompat	tibe	coup	le																	÷ c	<u> </u>	÷ c		č c	
L								: dis	crepar	ncy \	with	existir	ng MI	L-STD)-889	ЭC													AD	La	An	Lai Ja	4n	Lat
•	316 SS	18					+	: in a	green	nent	t with	h exist	ting N	1IL-ST	D-8	89C			_												<u>9</u> c	13	⁹ c	9
							+																							╷╷┡	An	Cal	An	Cat
	Graphite	19																															13 C	9
	-																															Ŀŀ	An	Cat
	316 SS	20																																
	Passivated																																	

ISO Classification vs. SR Classification



The complete data set is shown in dark gray, while those data points consistent with ISO 9233 (T > 0 ° C and RH > 80%) are shown in black. The ISO data points are found to vary over a broad range of solution resistance values, while being expected to be found at low SR values, due to an increased conductivity.

Absolute Humidity Calculation

- Ideal gas law: *PV=nRT*
- Apply ideal gas law to a water vapor system:

 $e_{v}V=m_{v}R_{v}T,$

- e_v is the vapor pressure V is the unit volume of air m_v is the mass of water vapor R_v is the specific gas constant of water vapor T is the absolute temperature
- Define the relative (H_R) and absolute (H) humidity:

$$H_R = \frac{e_v}{e_s} \qquad \qquad H = \frac{m_v}{v},$$

 e_s is the saturation vapor pressure

• Rearranging:
$$H = \frac{1}{R_v} \cdot H_R \cdot \frac{e_s}{T}$$

 Goff-Gratch equation: temperature dependent saturation vapor pressure over liquid water (valid over temperature range of -50 to 100 °C) ⁵:

 $\log_{10} e_s = -7.90298 (373.16/T-1) + 5.02808 \log_{10}(373.16/T) - 1.3816 10^{-7}$

(10^{11.344}(1-7/373.16) -1) + 8.1328 10⁻³(10^{-3.49149}(373.16/7-1) -1) +

Log₁₀(1013.246)

⁴ O.O. Parish and T.W. Putnam, (1977), Equations for the Determination of Humidity from Dewpoint and Psychrometric Data, NASA Technical Note D-8401.

⁵ Goff, J. A., and S. Gratch (1946), Low-pressure properties of water from -160 to 212 ° F, Transactions of the Amer. Society of Heating and Ventilating Engineers, pp 95-122.

Data Analysis: Wet Data



Data Analysis

- All collected data were transformed to absolute humidity scale to simultaneously take into account both temperature and relative humidity
- Again, three distinct regimes are visible
- Further analysis will consider 'dry', 'semi-wet', and 'wet' solution resistance readings



Data Analysis



- Lowest RH readings: 20-25 %
- Initial value:

 ${H^{init}, SR^{init}} = {4.88224 \text{ g/m}^3, 24,497 \Omega}$

Fit data to exponential function:

 $SR(H) = c + a e^{-k H}$

Line of best fit:

SR(H) = 24,469 + 76,014.6 e^{-1.61963 H}

- 95% confidence interval band
- All data falling below the dashed line are now considered 'non-dry'

Mass Loss Prediction Calculations: 1020 Steel



Mass loss predictions of SAE-1020

	Retrieval #1	Retrieval #2
Actual	0.37 g	0.65 g
1. ISO 9223 (wet)	0.54 g (46%)	1.1 g (67%)
2. ISO 9223	0.19 g (-49%)	0.23 g (-65%)
(wet + semi-wet)		
3. This study	0.42 g (14%)	0.49 g (-25%)

CR_w = 12.7 *10⁻⁹ g/cm²s CR_{sw} = 3.29 * 10⁻⁹ g/cm²s

⁶ E.C. Rios, A.M. Zimer, E.C. Pereira, L.H. Mascaro, (2014), Analysis of AISI 1020 steel corrosion in seawater by coupling ..., Electrochimica Acta, 124, 211-217.

⁷ J.S. Lee, R.I. Ray, E.J. Lemieux, A.U. Falster and B.J. Little, (2004), An Evaluation of Carbon Steel Corrosion under Stagnant Seawater Conditions, Biofouling, 20 (4/5), 237-247.