This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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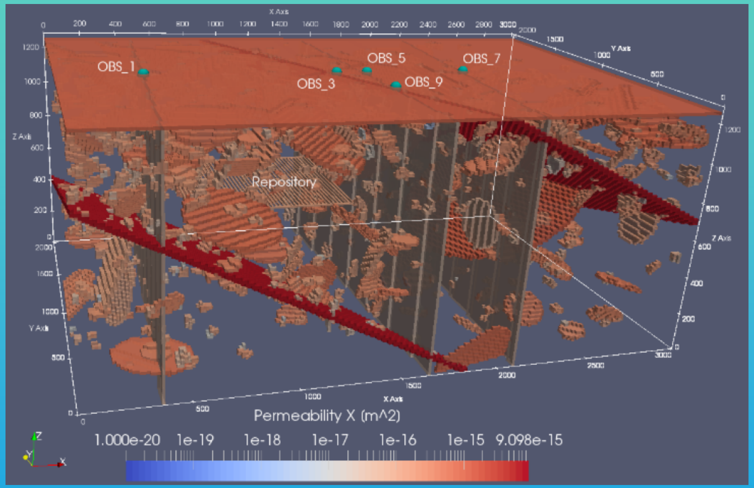
U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY

Spent Fuel and Waste Science and Technology (SFWST)

Clean. Reliable. Nuclear.



Evaluation of Coatings and Cold Spray as Potential Mitigation and Repair Strategies

Andrew Knight, Rebecca Schaller, Brendan Nation, and Charles Bryan

Sandia National Laboratories

EPRI ESCP 2022

November 9, 2022

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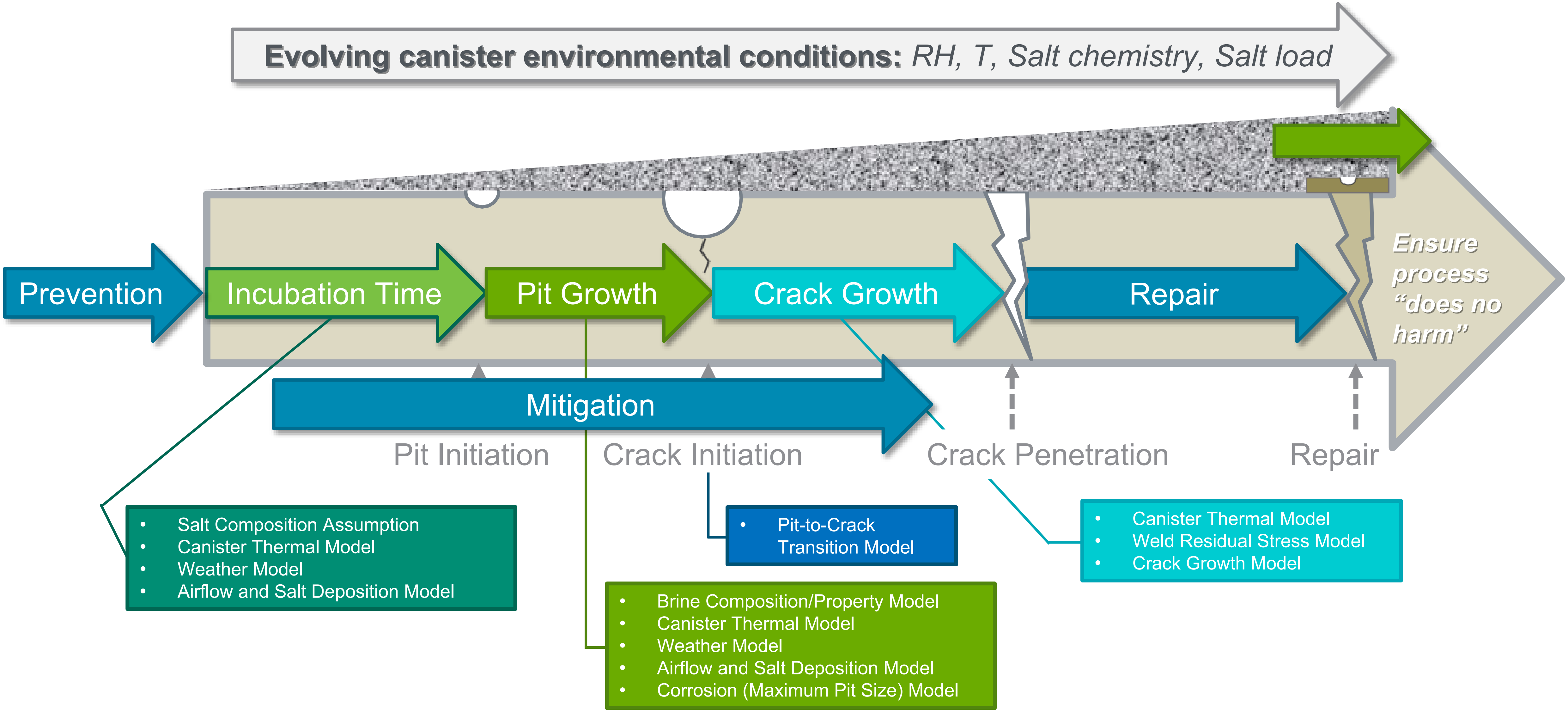
Mitigation and Repair

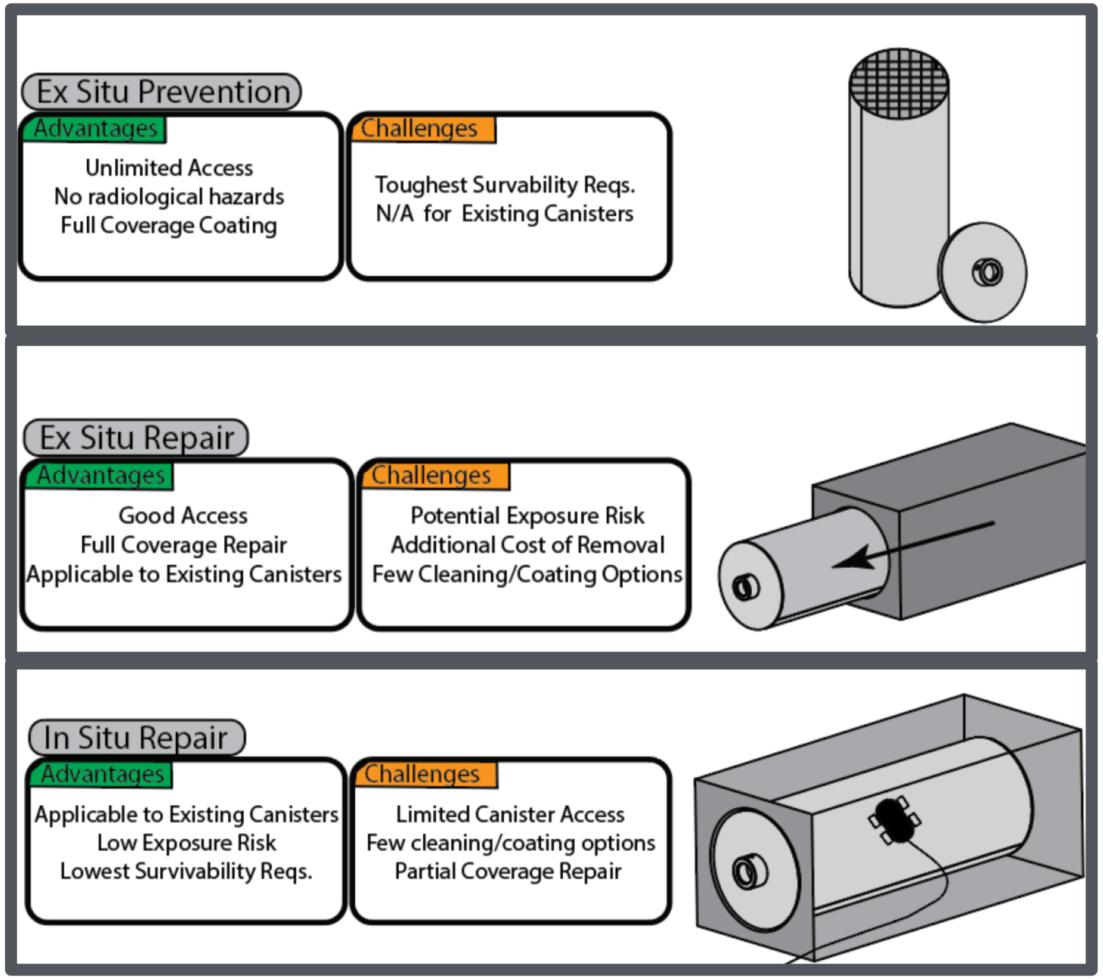


What Makes an Effective Mitigation and Repair Technology?

- Primary goal of any mitigation and repair technology is to "**Do No Harm**"
- Environment experienced by the coating depends on when it is applied
  - **Acceptance criteria** dependent on **application scenario**
- ***What are the acceptance criteria for a particular mitigation and repair technology?***

Initial Scoping studies on:

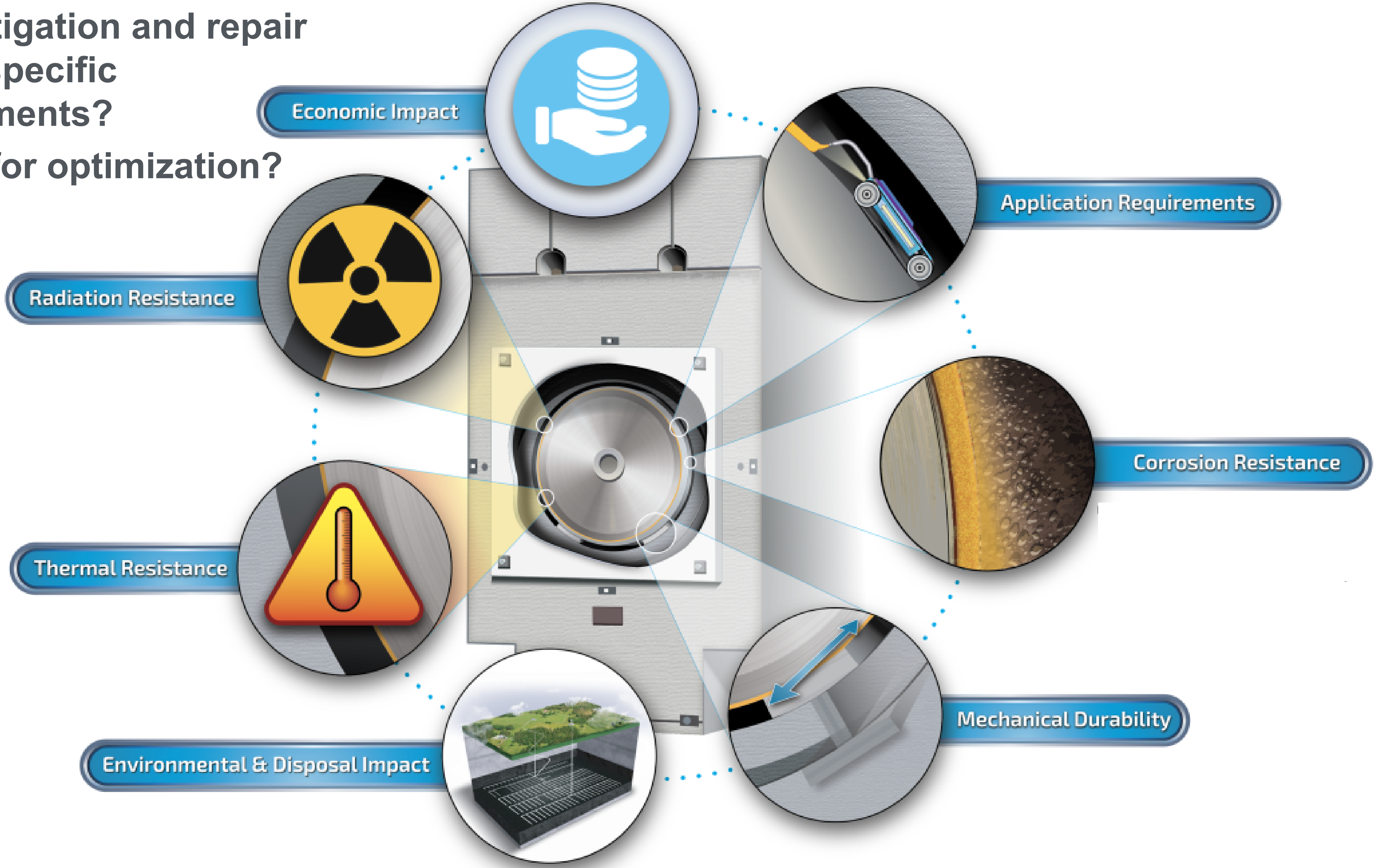
1) *Cold Spray*
2) *Coatings technologies*



Knight, A. W. et al., FY21 Status Report: SNF Canister Coatings for Corrosion Prevention and Mitigation. 2021 M3SF-21SNN010207062

Mitigation and Repair Strategies – How to evaluate?

- **How to evaluate mitigation and repair strategies without specific guidelines/ requirements?**
- **What is necessary for optimization?**

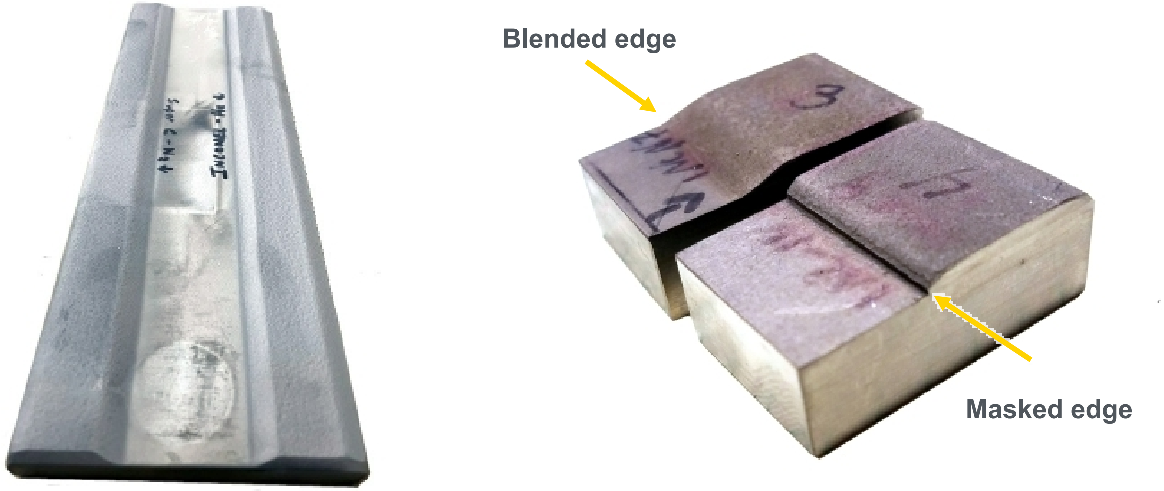


Cold Spray – Potential Mitigation/Repair Strategy

“Requirements”:

- Withstand T ~ 300 °F
- Remote Application (6 in. annulus at best)
- Radiation resistance
- Wear resistance
- Corrosion resistance
- “Do no harm”

Cold Spray is a promising mitigation candidate



Cold Spray Samples with Edge Processing

Cold Spray Testing of Samples Provided by PNNL in FY22

Cold Spray	Edge	Process Gas	Potentiodynamic Polarization		Accelerated Pitting Exposure	Atmospheric Exposure			Boiling $MgCl_2$ Exposure
			NaCl	$FeCl_3$		40 % RH, 35 °C	75 % RH, 35 °C	Cyclic	
Inc	Tapered	He	x	x	x	x	-	x	x
Inc	Tapered	N	x	x	x	-	-	x	x
Inc	Masked	N	-	-	x	x	x	x	x
Ni	Tapered	N	x	x	x	x	-	x	x
Ni	Masked	N	-	-	x	x	x	x	x
Ni	Tapered	He	-	-	x	-	-	-	-
Ni	Masked	He	-	-	x	-	-	-	-
SC	Tapered	N	x	x	x	x	x	x	-
SC	Tapered	He	-	-	x	-	-	-	-
SC	Masked	He	-	-	x	-	-	-	-
SS316 + 25% CrC 410	Tapered	N	-	-	x	-	-	-	-
SS316 + 25% CrC 410	Tapered	N	-	-	x	-	-	-	-
SS316 + 25% CrC 410	Tapered	N	-	-	x	-	-	-	-

Cold Spray – Potential Mitigation/Repair Strategy

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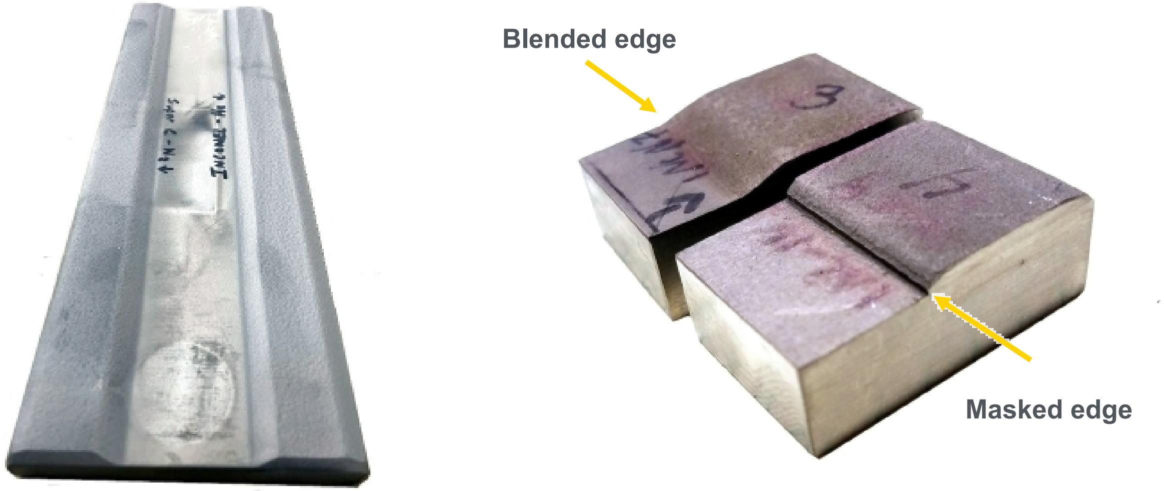
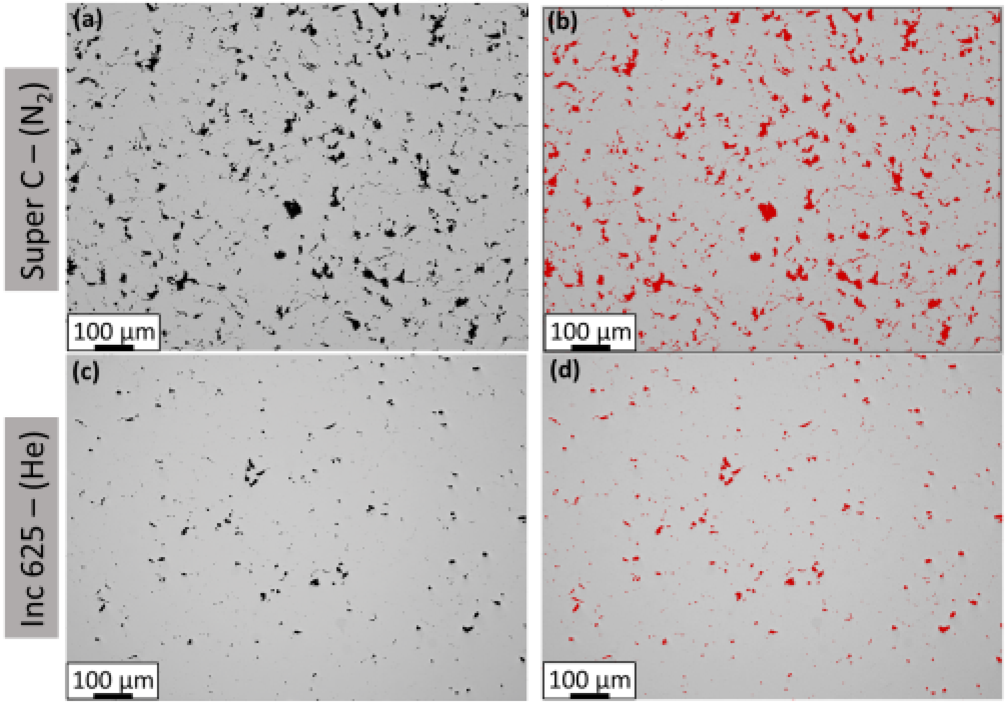


Cold Spray Samples with Edge Processing

Example polished surfaces



** Note: surface finished to <u>mirror polish</u> for measurements*

Porosity Measurements:

- *Calculated from image processing of bright field optical measurements*
- *Influenced by carrier gas type*

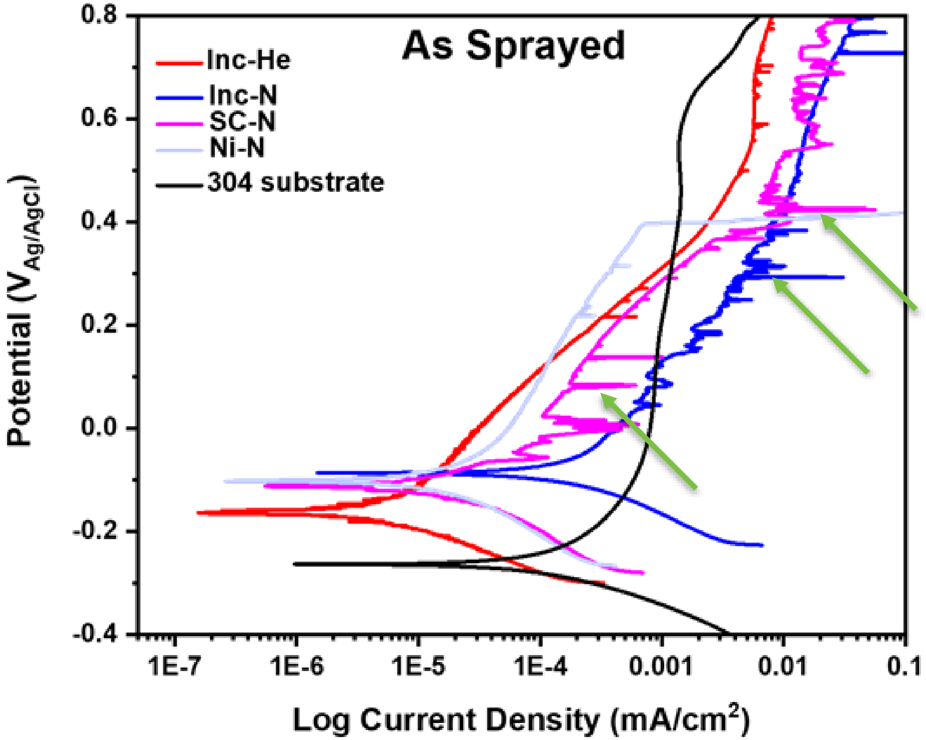
PNNL M3 Report 2021

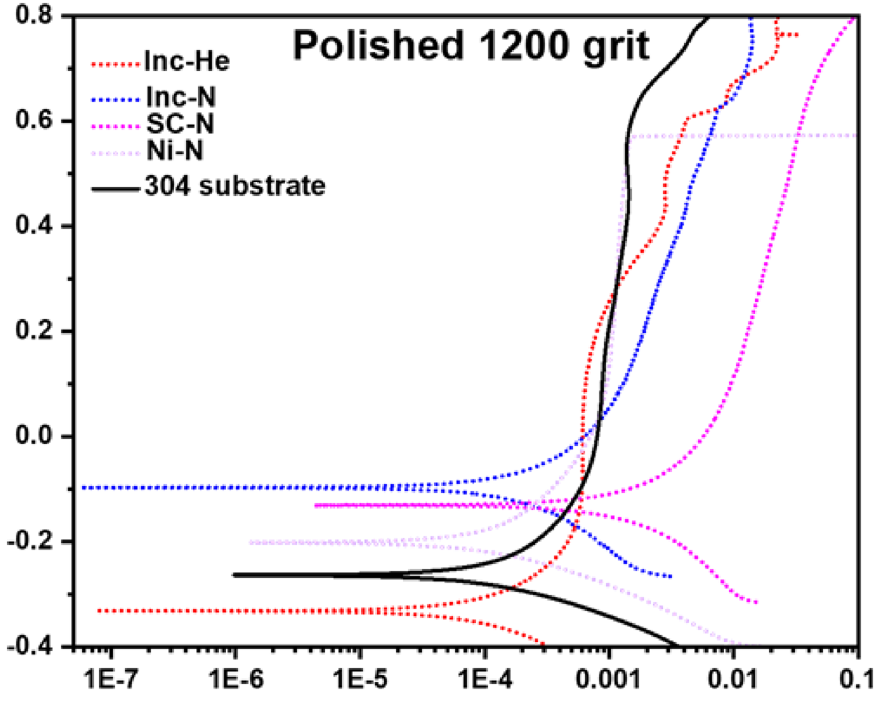
CS	Super C (N_2)	Inc-625 (He)	Inc-625 (N_2)	Ni (N_2)
Porosity (%)	5.51 ± 0.44	1.21 ± 0.20	5.79 ± 0.18	3.78 ± 0.59

Cold Spray – Accelerated testing for optimization

Electrochemical Characterization:

- *0.6 M NaCl*
- *1 h Open circuit potential followed by anodic polarization, 0.1667 mV/s*
- *CS or base material examined*
  - *As-sprayed, 600, and 1200 grit*



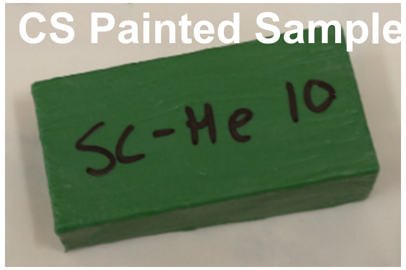


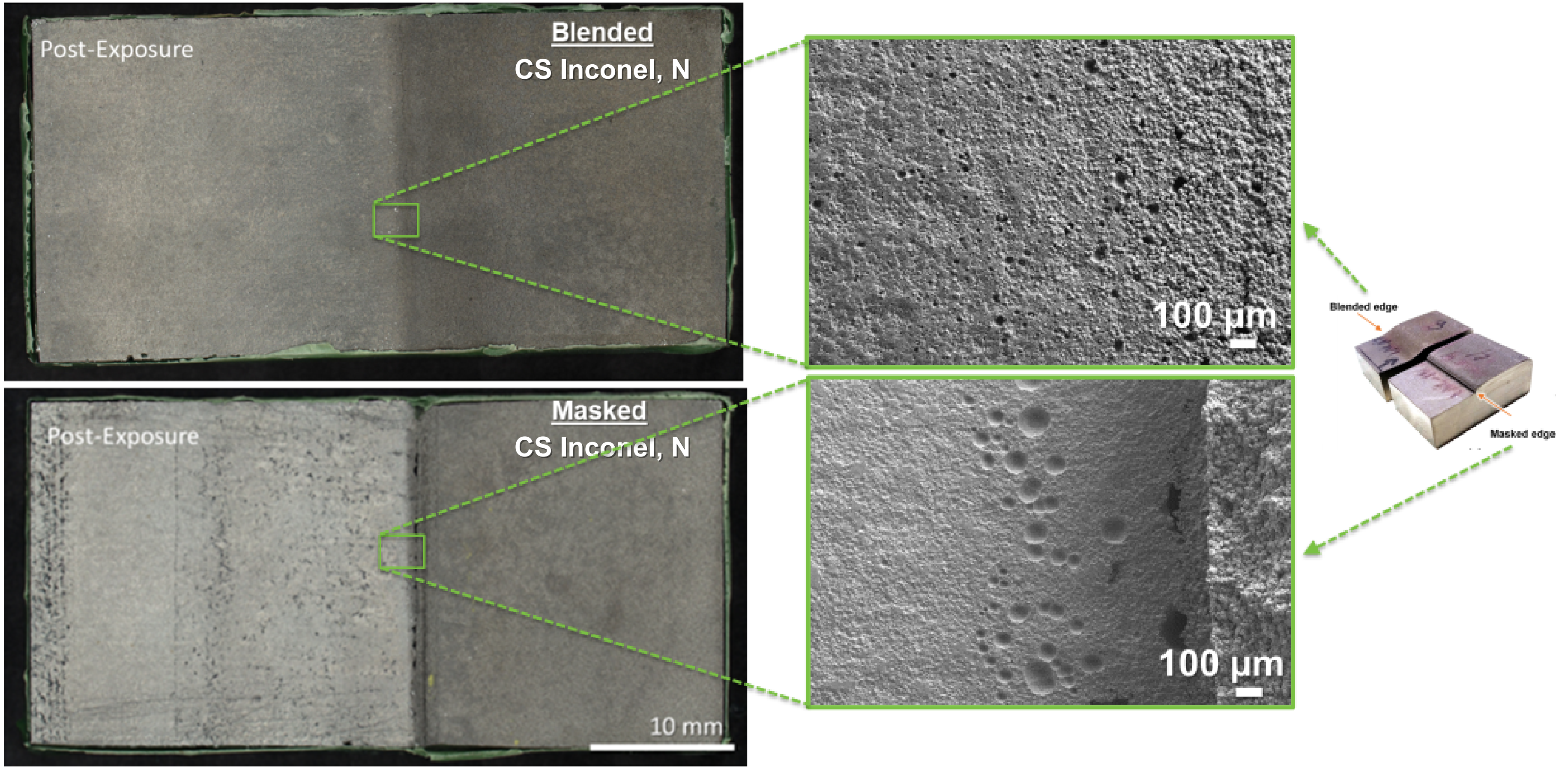
Metastable pitting reduced when polished

Cold Spray – Accelerated testing for optimization

Pitting Characterization:

- *6% by mass Ferric Chloride*
- *Full Immersion 72 h, 22 °C*
- *Entire top surface tested*
    - *Other surfaces painted*





Edge morphology influences corrosion morphology

Cold Spray – Accelerated testing for optimization

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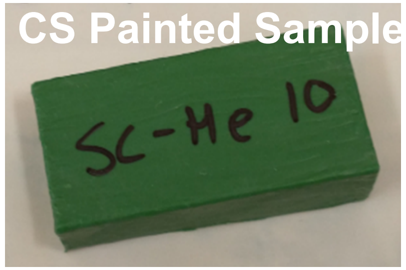
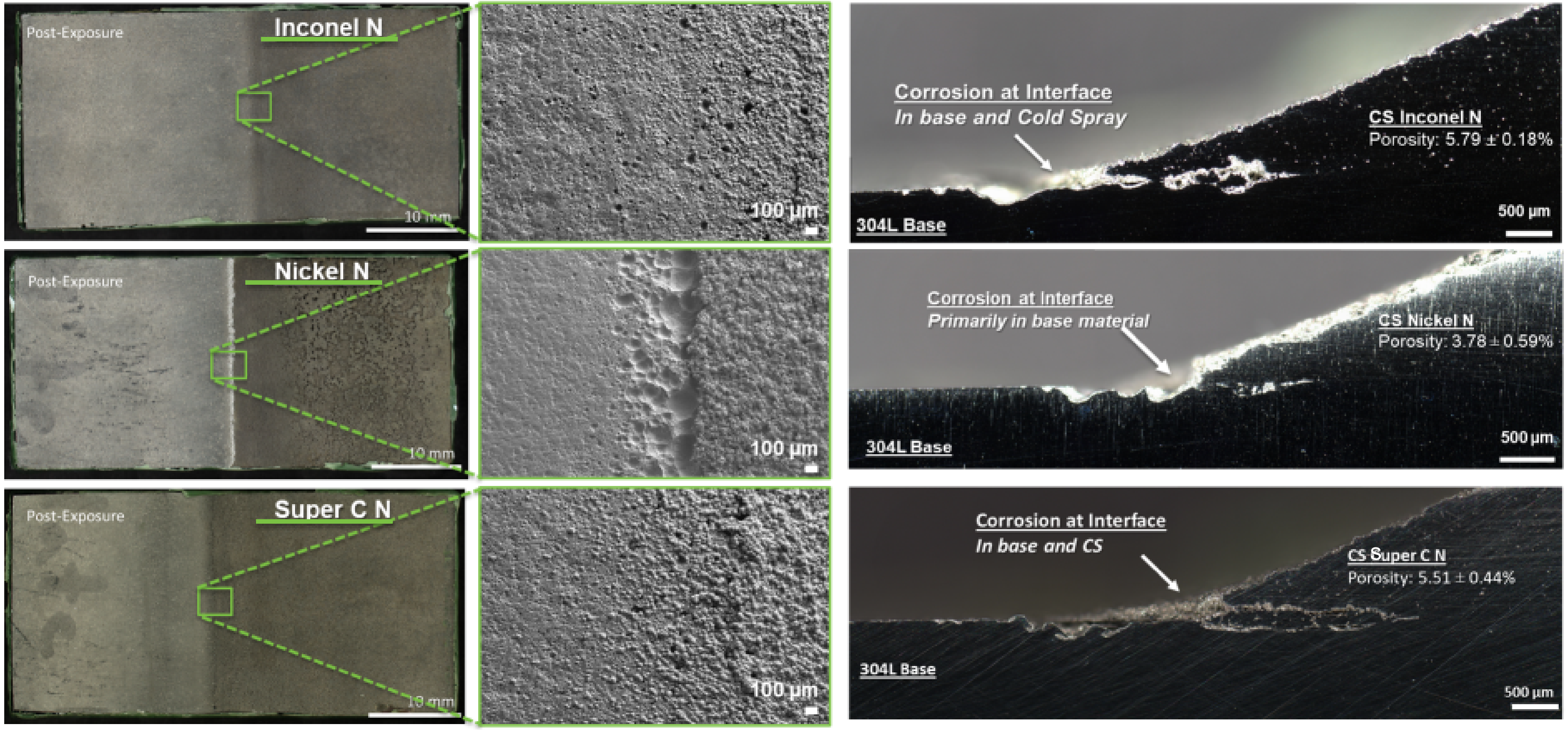


CS Painted Sample

Post ASTM G-48 Exposure | **Cross section Post Exposure**



Attack at interface influenced by cold spray material

Cold Spray – Accelerated testing for optimization

Pitting Characterization:

- *6% by mass Ferric Chloride*
- *Full Immersion 72 h, 22 °C*
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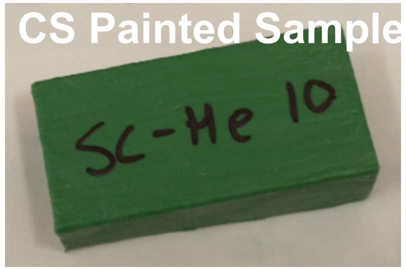
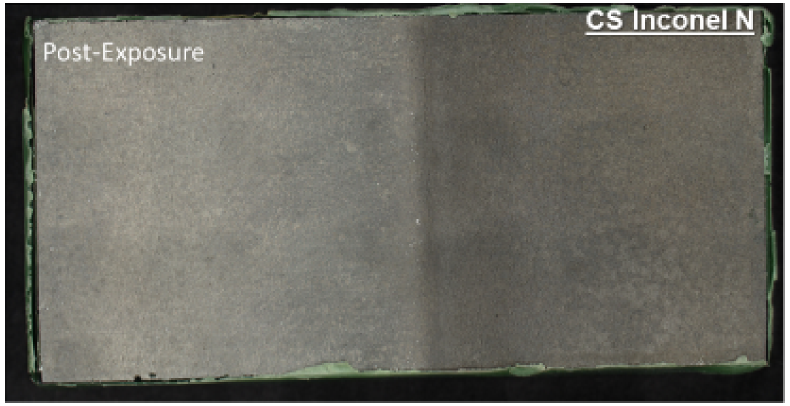
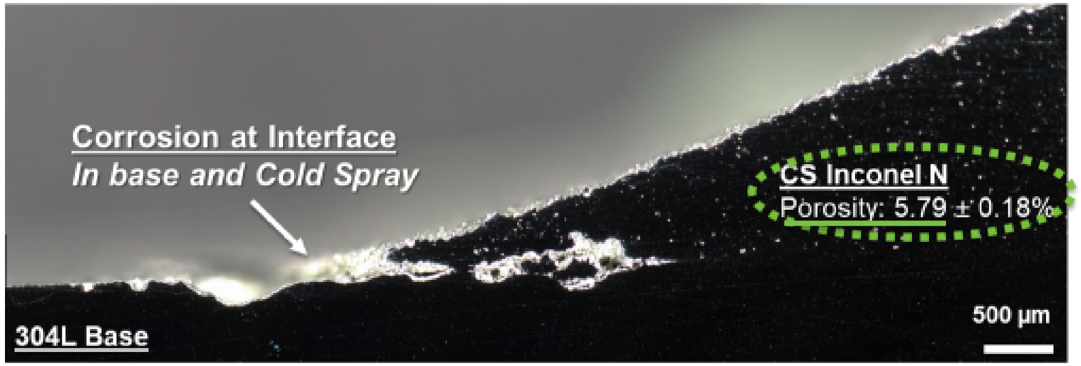
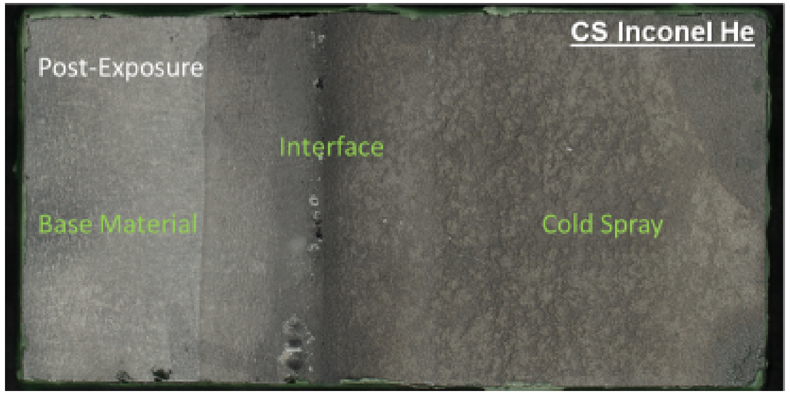
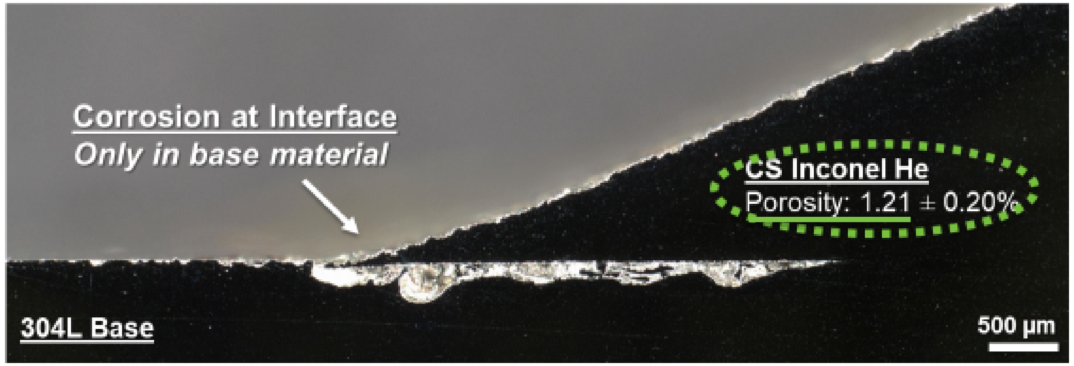










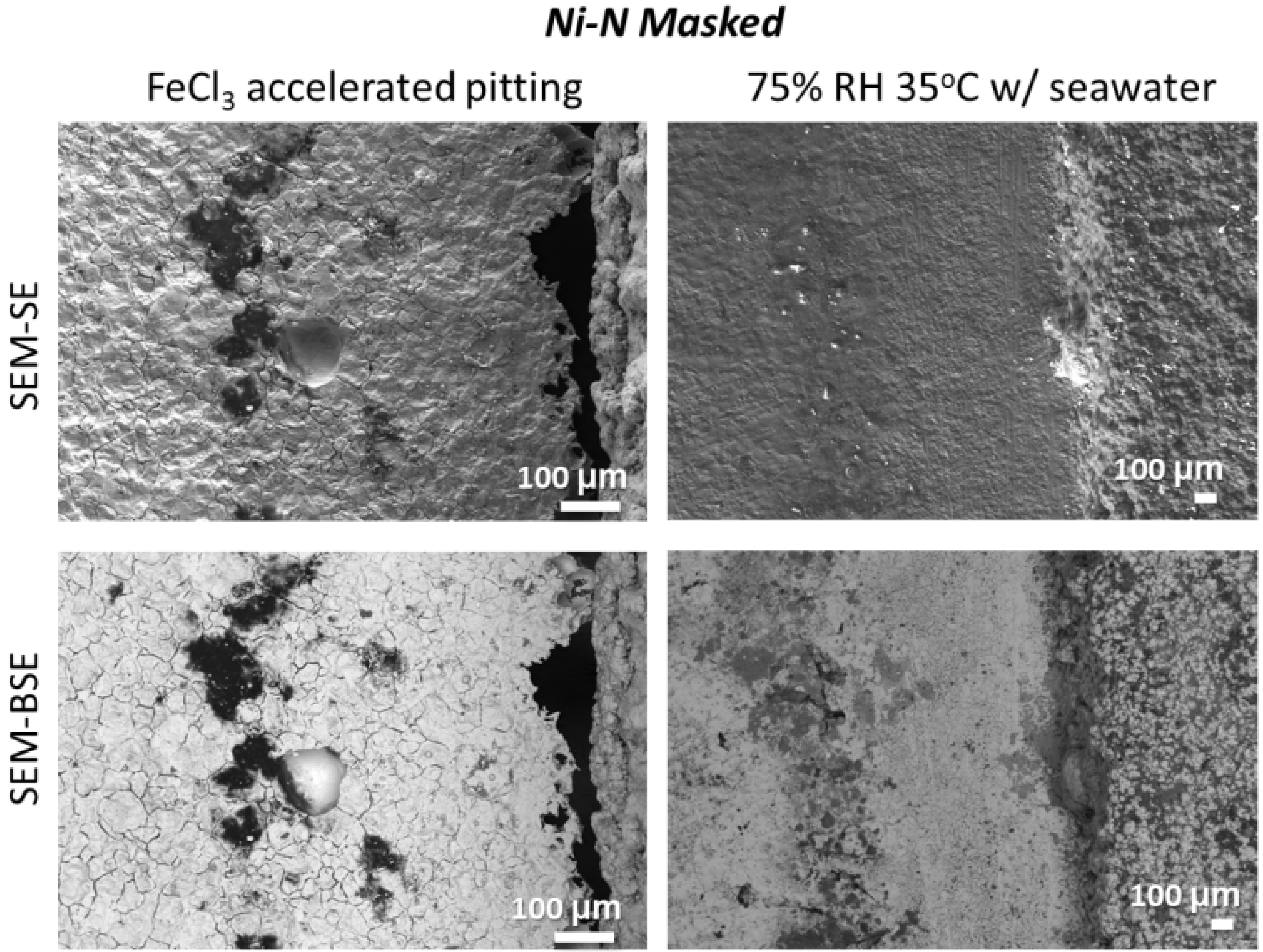
Process gas can influence porosity and thus corrosion at the interface

Cold Spray – Comparison to Atmospheric Exposures

Pitting Characterization:

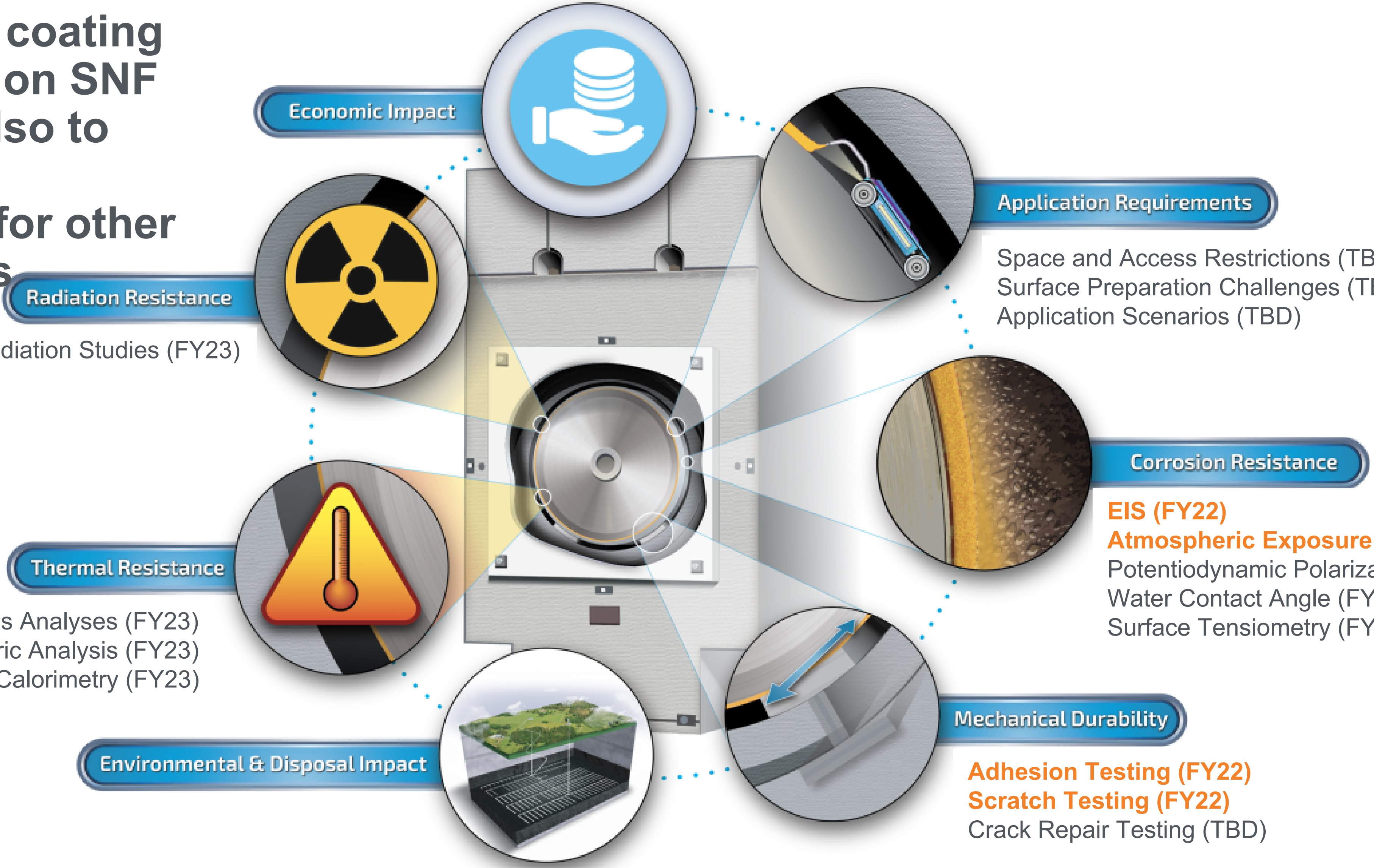
- *Ferric chloride test compared to atmospheric exposure:*
    - *1 month exposure at 75% RH and 35°C with 300 μg/cm² Artificial seawater*

Corrosion morphology is similar for accelerated full immersion exposures and atmospheric exposures



Evaluating Coating Performance

Aim to evaluate coating viability for use on SNF canisters, but also to develop test methodologies for other coating systems



Radiation Resistance
- Gamma Irradiation Studies (FY23)

Thermal Resistance
- Outgasses Analyses (FY23)
- Thermogravimetric Analysis (FY23)
- Dynamic Scanning Calorimetry (FY23)

Application Requirements
- Space and Access Restrictions (TBD)
- Surface Preparation Challenges (TBD)
- Application Scenarios (TBD)

Corrosion Resistance
- **EIS (FY22)**
- **Atmospheric Exposure (FY22)**
- Potentiodynamic Polarization (FY23)
- Water Contact Angle (FY22)
- Surface Tensiometry (FY22)

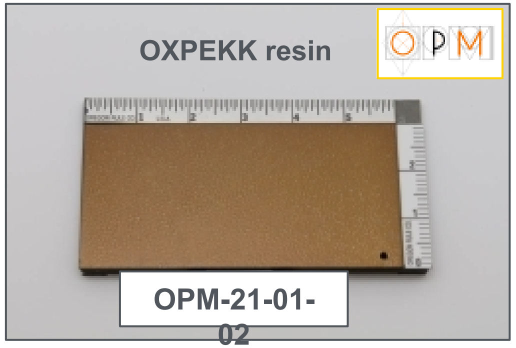
Mechanical Durability
- **Adhesion Testing (FY22)**
- **Scratch Testing (FY22)**
- Crack Repair Testing (TBD)

Corrosion Resistant Coatings

Naming Convention
VENDOR-YEAR-VARIANT#-COUPON#

4 collaborating companies, 11 total coating variants (*adding 2 Coatings from TDA, Research in FY23)

Polymeric (5)



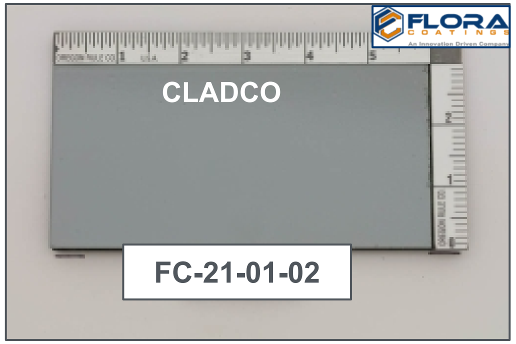
2 variants of Polyetherketoneketone. High temperature thermoplastic with high radiation resistance

3 variants of modified polyimide, polyurea, phenolic resins. Durable, chemically inert and can be loaded with desired additives to increase corrosion and radiation resistance

Ceramic/Organic

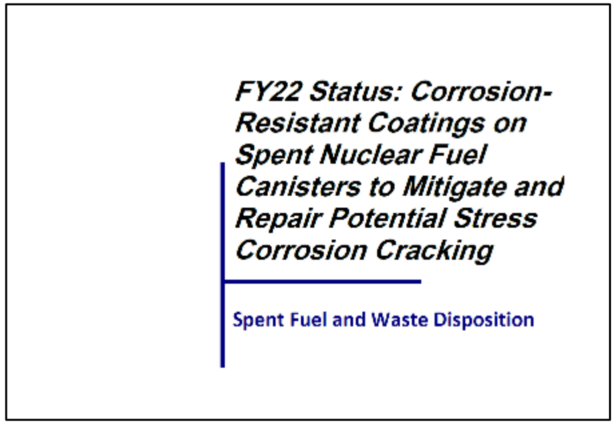
With Zn-Rich

2 variants of GENTOO with and without Zn-rich primer to provide a durable ceramic hybrid inorganic/polymer coating with/without galvanic protection



Single component hybrid inorganic/modified polyurethane coating resulting in a quasi-ceramic structure.

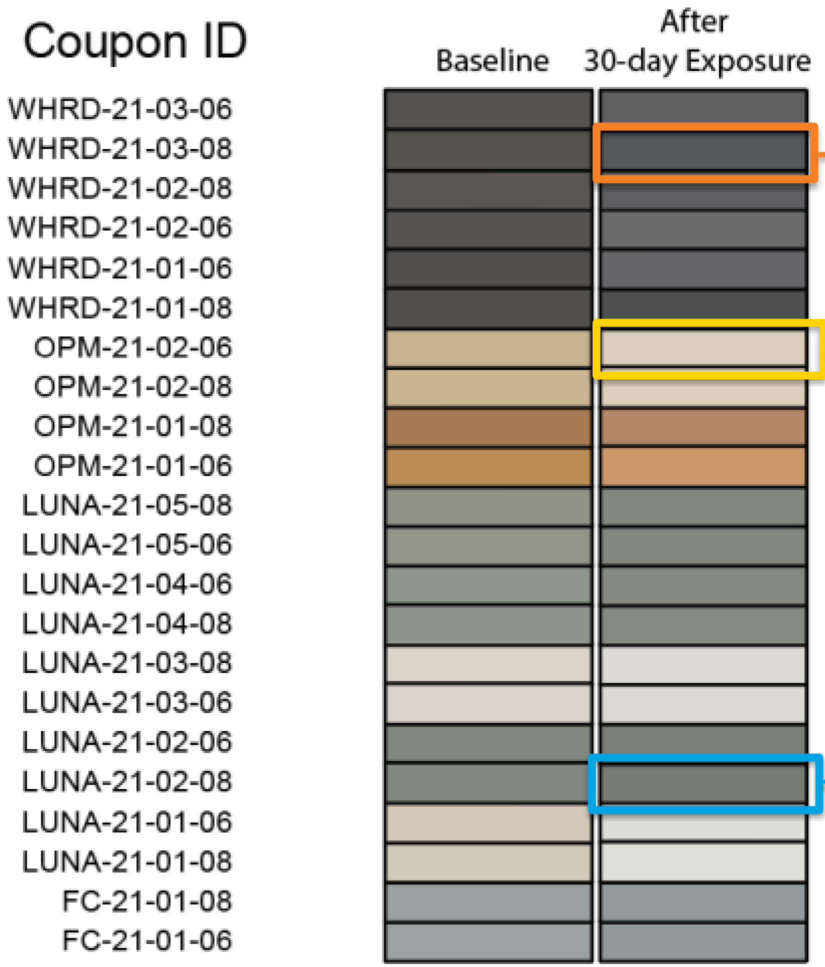
More detail can be found in our recent report

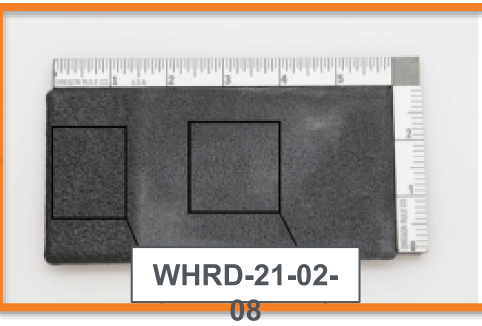

FY22 Status: Corrosion-Resistant Coatings on Spent Nuclear Fuel Canisters to Mitigate and Repair Potential Stress Corrosion Cracking

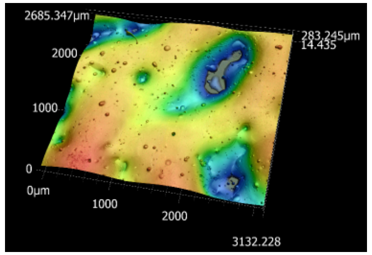
Spent Fuel and Waste Disposition

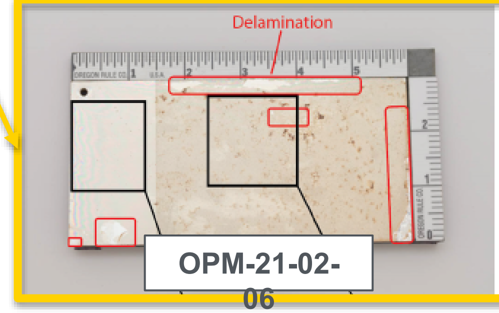
Atmospheric Exposures

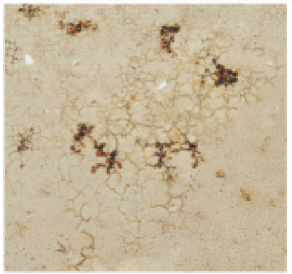
Colorimetric Assessment and visible inspection to track possible coating degradation

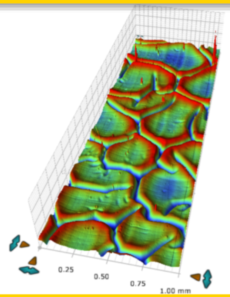




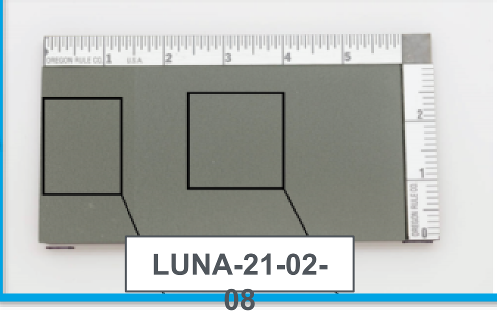


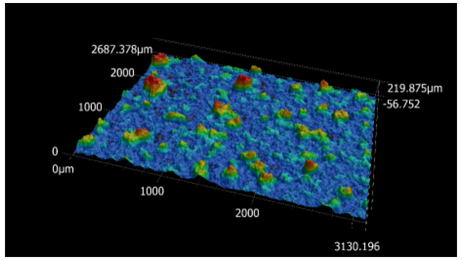




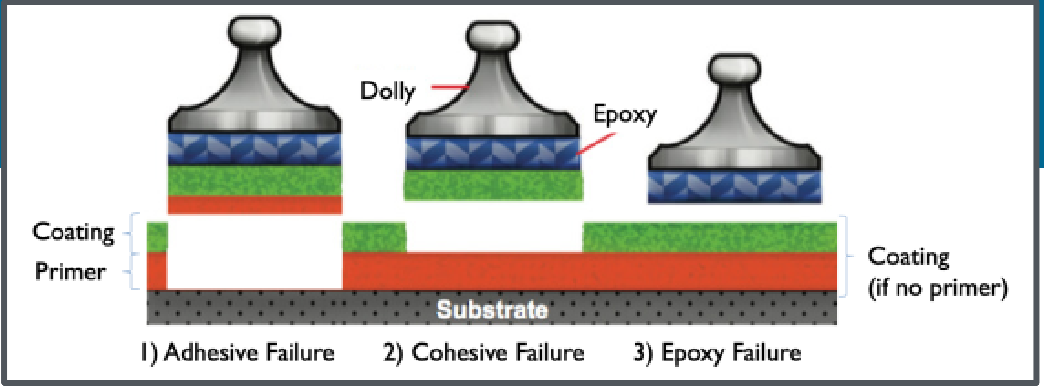


OPM-21-02-02 Baseline had evidence of "mud cracking"



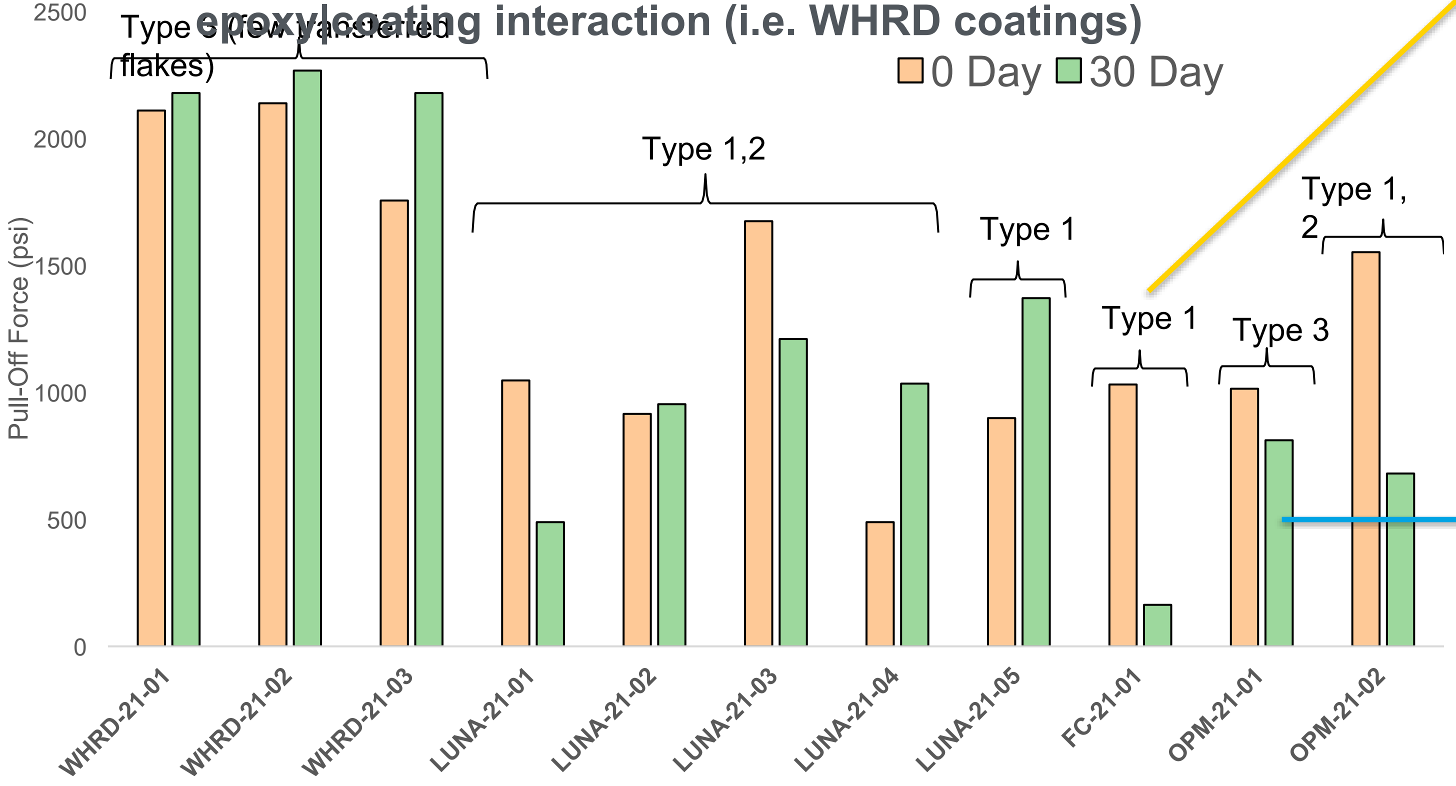


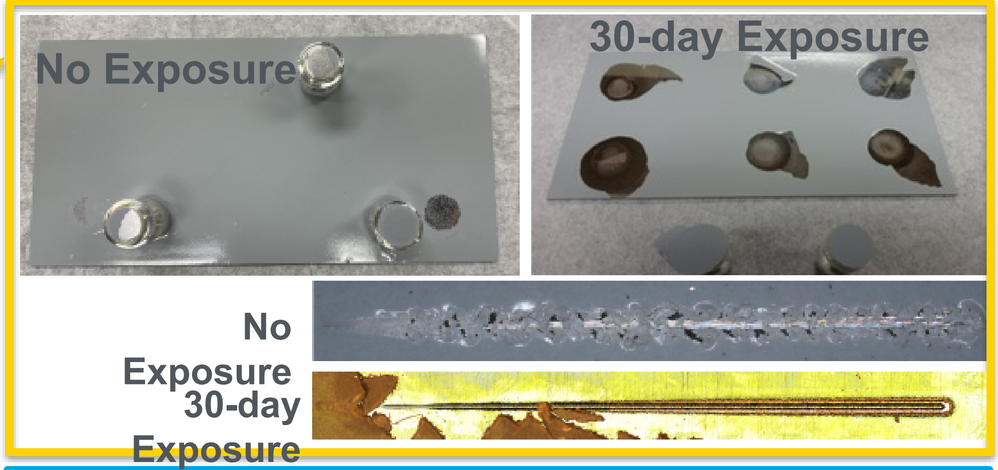
Adhesion and Scratch

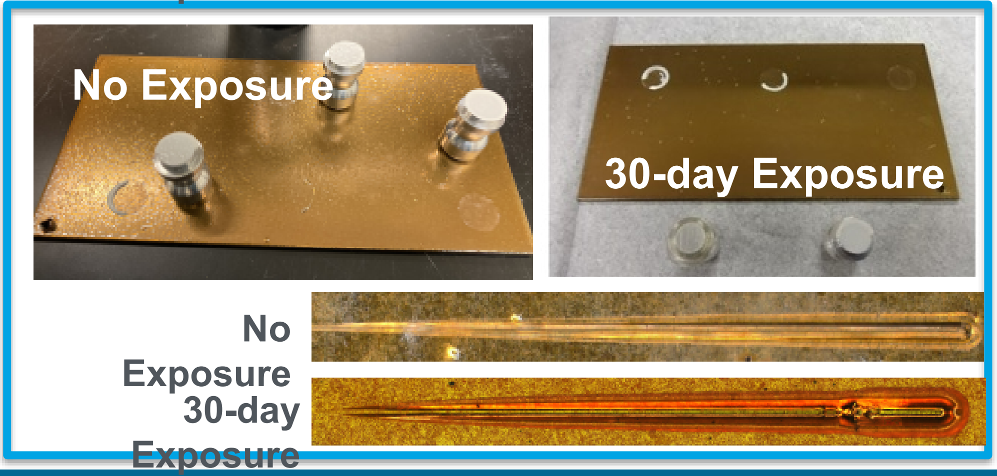


The adhesive strength of…

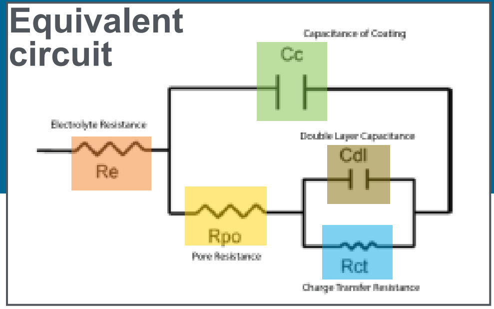
- **Ceramic coatings generally decreased following atmospheric exposure.**
  - **In most cases, adhesive failure was observed**
- **Organic coatings generally did not fail to the substrate**
  - **Except OPM-21-02**
  - **Increase in pull-off pressure was likely due to increase in epoxy/coating interaction (i.e. WHRD coatings)**





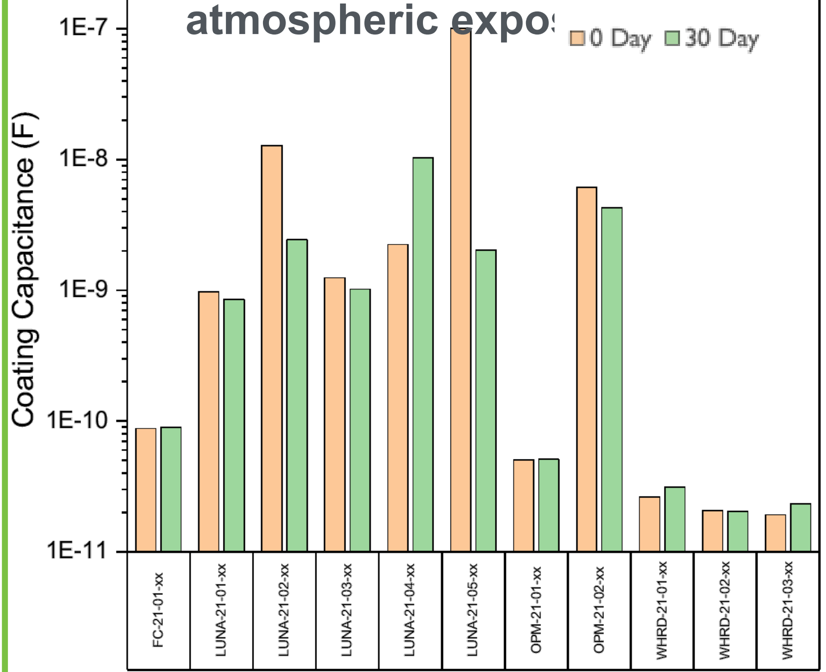


Electrochemical Impedance Spectroscopy



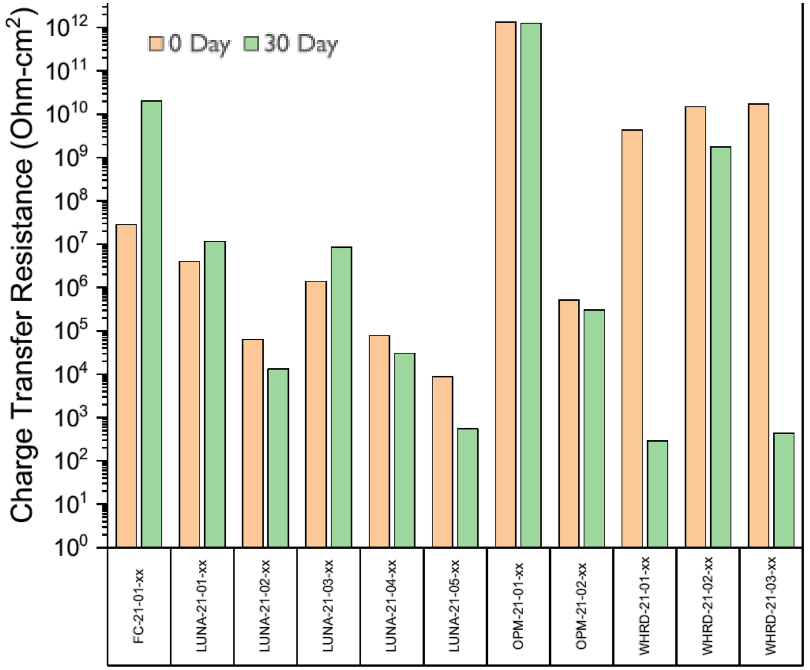
EIS evaluates the impedance of an electrochemical system as a function of the frequency of an applied a.c. wave. EIS is a common method to evaluate coating performance

Evaluate changes in water permeability before and after atmospheric exposure



- Permeation of water into coating causes increased capacitance, but so can oxidation.
- Therefore OPM-21-02 and the LUNA coating with the Zn-rich primer showed highest C_C values

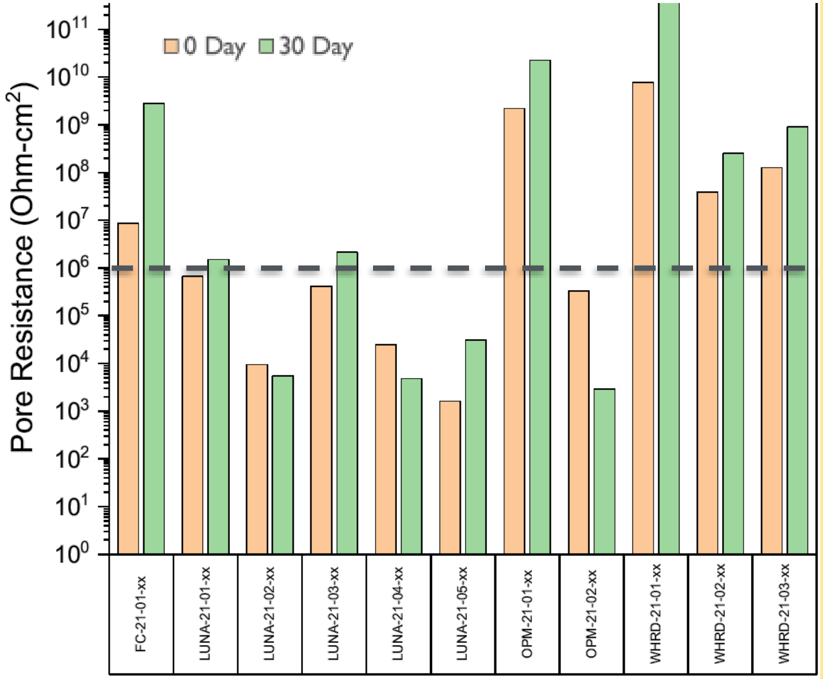
Evaluate corrosion resistance of coating system



R_{CT} is most direct analogue to corrosion resistance. High R_{CT} ≈ Low Corrosion Rate

- Large changes in R_{CT} in WHRD-21-01 and WHRD-21-03
- OPM-21-01 and FC-21-01 had highest R_{CT} after exposures

Evaluate resistance to ion transport



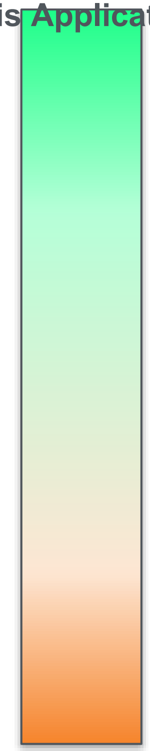
- $\geq 10^6$ Ωcm^2 is considered a protective coating
- Criteria generally met by all coatings except for coatings with Zn-rich primer (different mechanism of protection) and OPM-21-02 (degradation and exposed SS).

Amirudin, A., & Thierry, D. (1995). *Progress in Organic Coatings (26) 1-28.*

Initial Qualitative Assessment of Coating Viability

Changes in physical and chemical properties as a result of exposure can help indicate how a coating will perform over time.

Good Performance For This Application



Could Be Improved For This Application

Coating		Initial					Change as a result of exposure					Radiation Exposure	Thermal Exposure
		R_{CT}	R_{PO}	C_C	Adhesion	Scratch	R_{CT}	R_{PO}	C_C	Adhesion	Scratch		
Ceramic/Hybrid Coating	FC-21-01												
	LUNA-21-01												
	LUNA-21-02*	–	–	–			–	–	–				
	LUNA-21-03												
	LUNA-21-04*	–	–	–			–	–	–				
	LUNA-21-05*	–	–	–			–	–	–			FY23	FY23
Polymeric Coating	OPM-21-01												
	OPM-21-02												
	WHRD-21-01												
	WHRD-21-02												
	WHRD-21-03												

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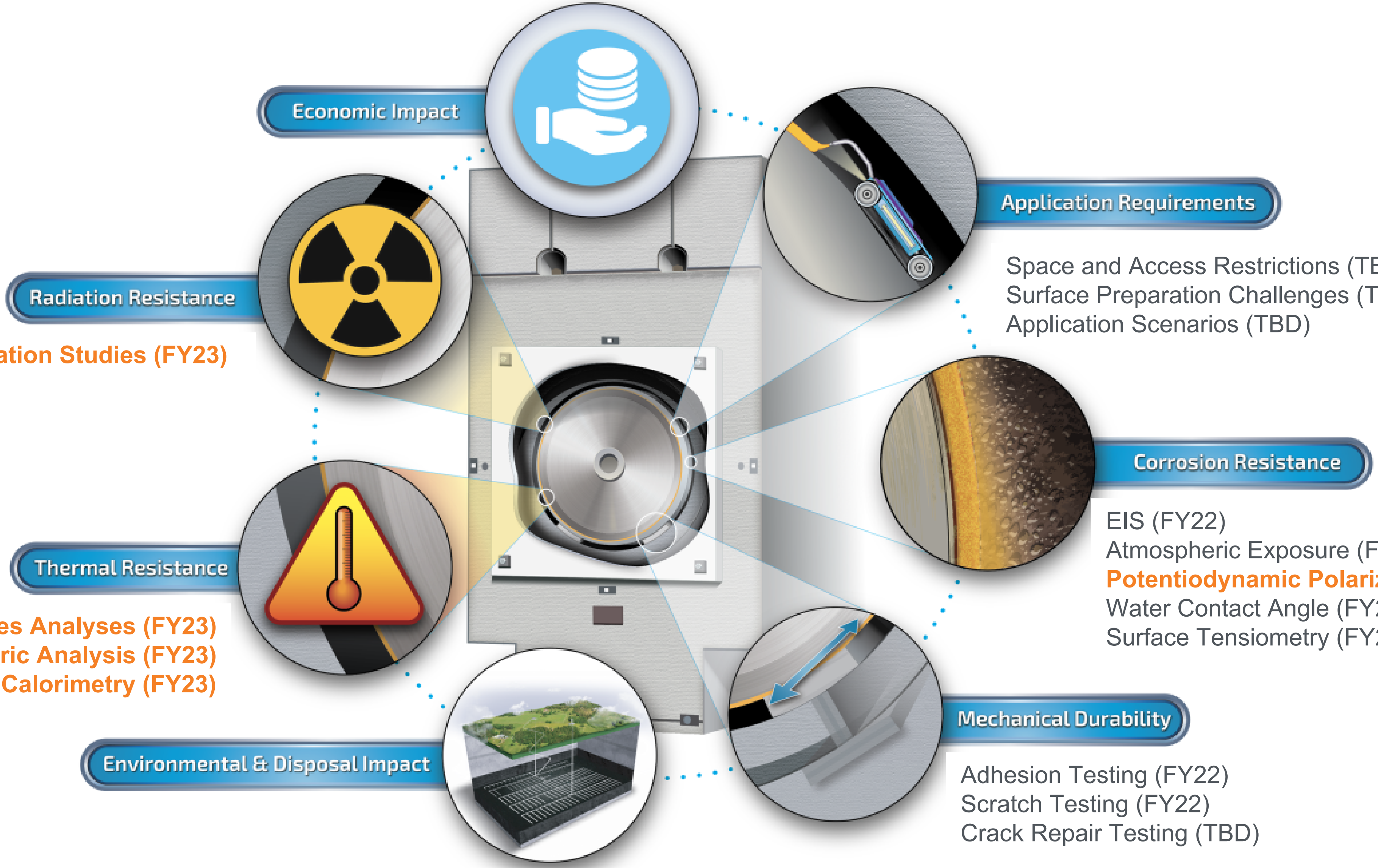
	LUNA-21-01												
	LUNA-21-02*	–	–	–			–	–	–				
													FY23
Polymeric Coating	OPM-21-01												
	OPM-21-02												
	WHRD-21-01												
	WHRD-21-02												
	WHRD-21-03												

Need to define performance criteria relevant to interim storage to guide screening decisions

Future Work



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Mechanical Durability

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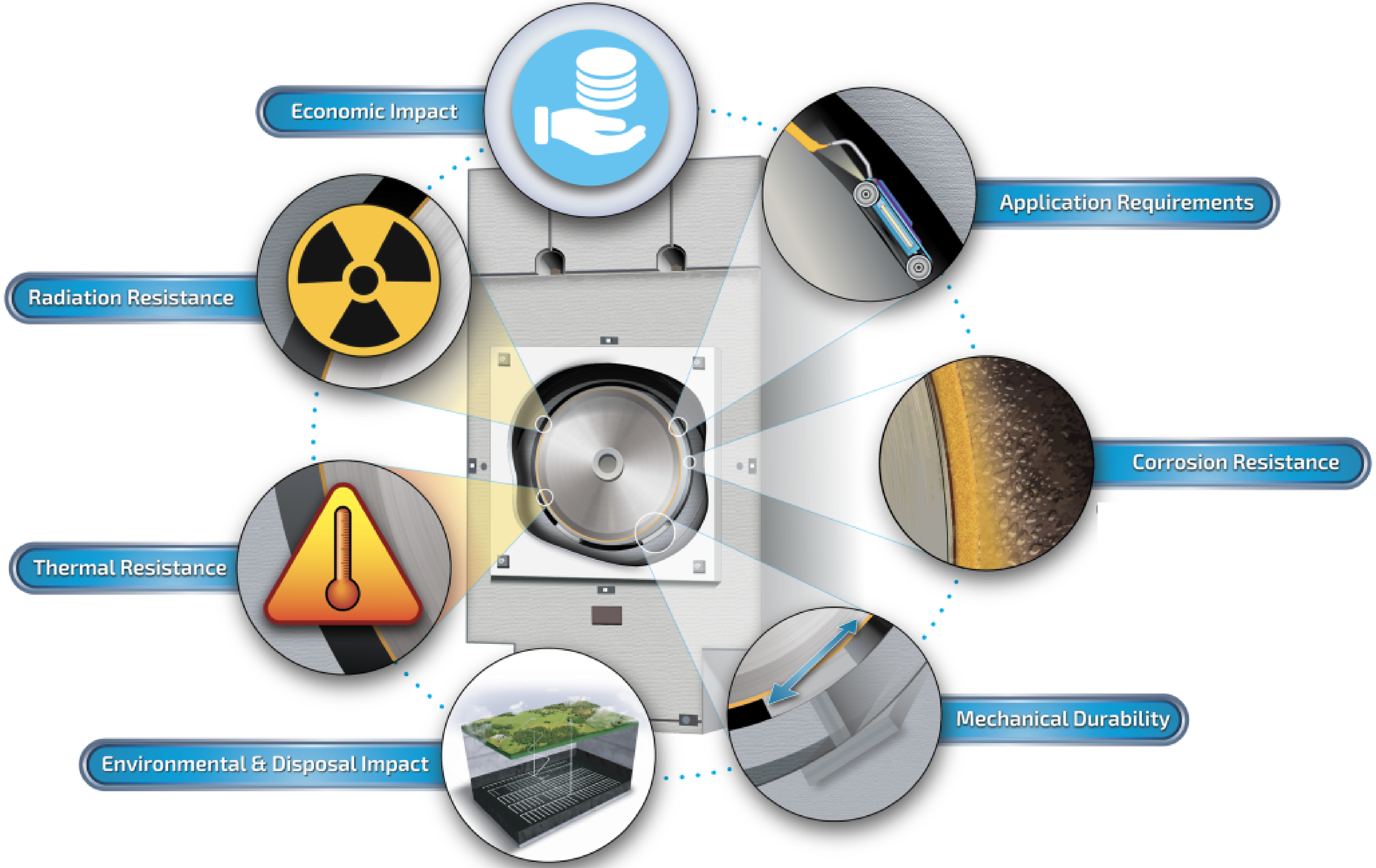
- Crack Repair Testing (TBD)

To Optimize M&R Technology, We Must Define Performance Metrics



Questions?

Cold Spray	Edge	Process Gas	Potentiodynamic Polarization		Accelerated Pitting Exposure	Atmospheric Exposure			Boiling $MgCl_2$ Exposure
			NaCl	$FeCl_3$		40 % RH, 35 °C	75 % RH, 35 °C	Cyclic	
Inc	Tapered	He	x	x	x	x	-	x	x
Inc	Tapered	N	x	x	x	-	-	x	x
Inc	Masked	N	-	-	x	x	x	x	x
Ni	Tapered	N	x	x	x	x	-	x	x
Ni	Masked	N	-	-	x	x	x	x	x
Ni	Tapered	He	-	-	x	-	-	-	-
Ni	Masked	He	-	-	x	-	-	-	-
SC	Tapered	N	x	x	x	x	x	x	-
SC	Tapered	He	-	-	x	-	-	-	-
SC	Masked	He	-	-	x	-	-	-	-
SS316 + 25% CrC 410	Tapered	N	-	-	x	-	-	-	-
SS316 + 25% CrC 410	Tapered	N	-	-	x	-	-	-	-
SS316 + 25% CrC 410	Tapered	N	-	-	x	-	-	-	-

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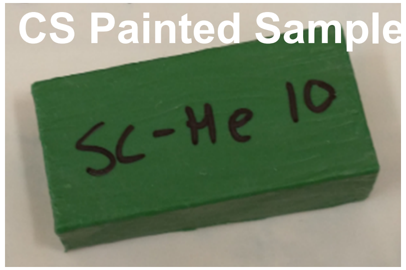
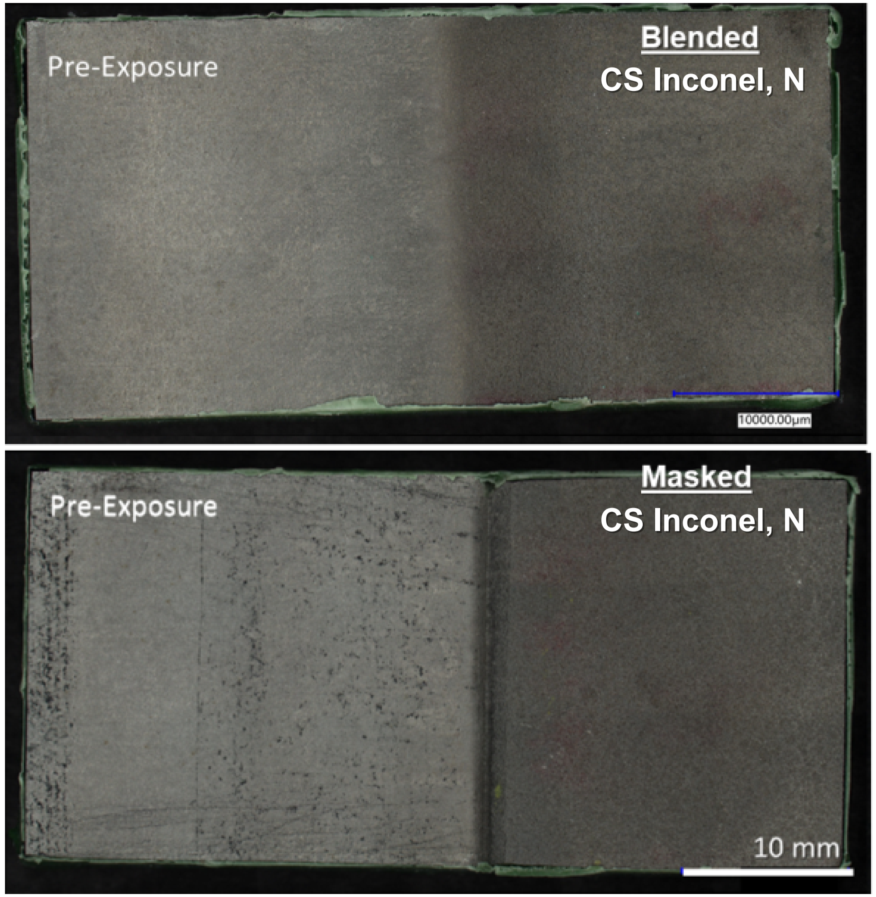
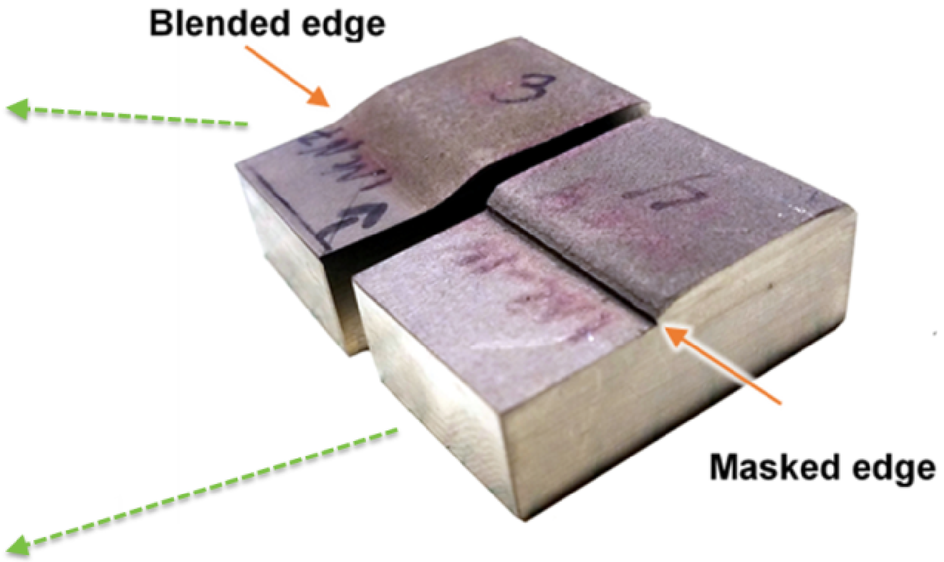
- *6% by mass Ferric Chloride*
- *Full Immersion 72 h, 22 ^{o}C*
- *Entire top surface tested*
    - *Other surfaces painted*



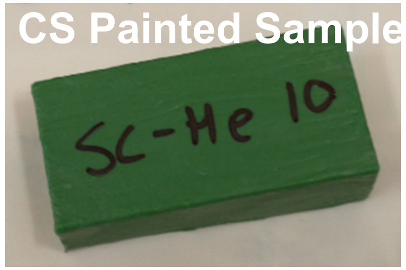


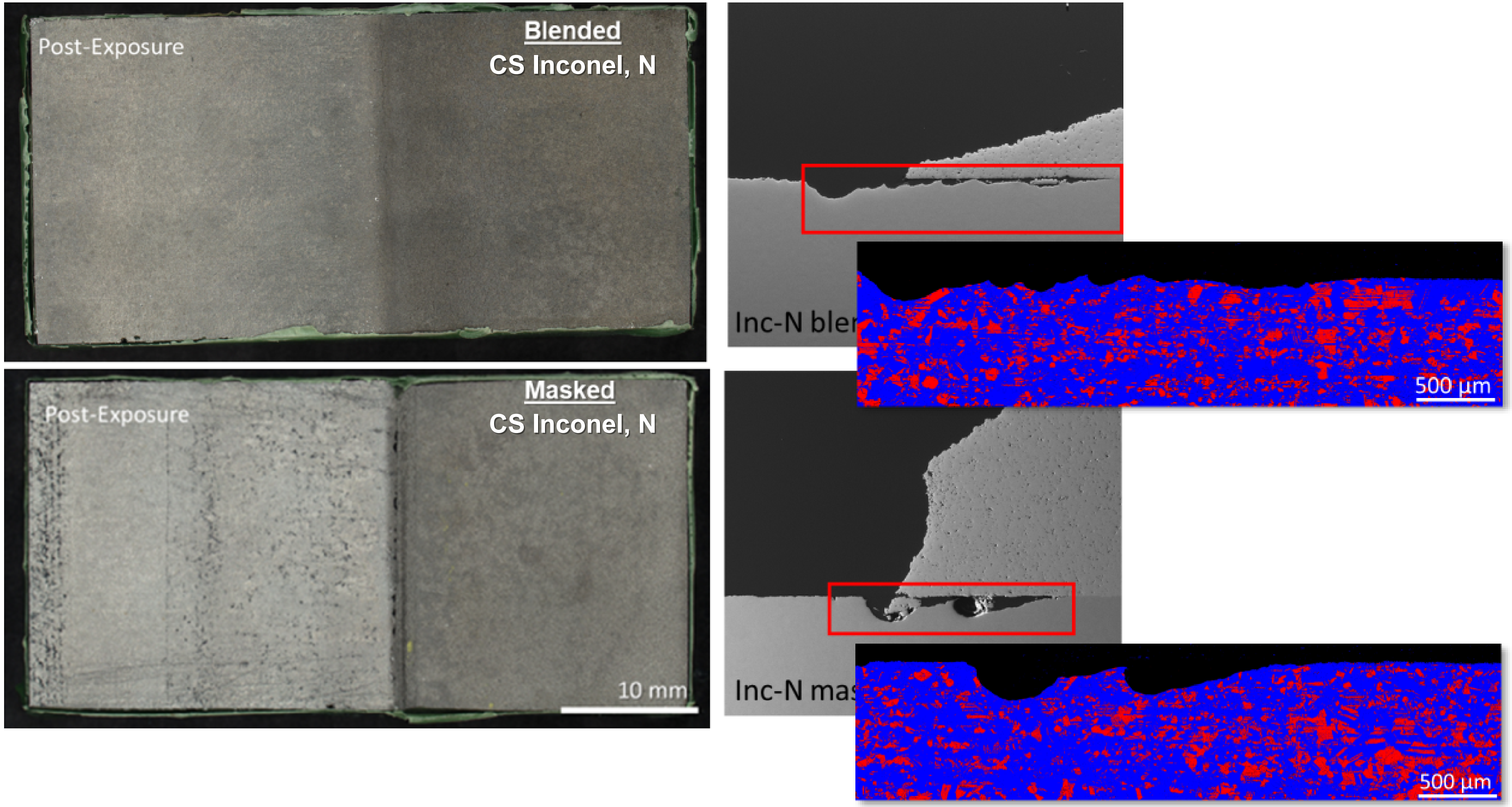


Cold Spray – Accelerated testing for optimization

Pitting Characterization:

- *6% by mass Ferric Chloride*
- *Full Immersion 72 h, 22 °C*
- *Entire top surface tested*
  - *Other surfaces painted*





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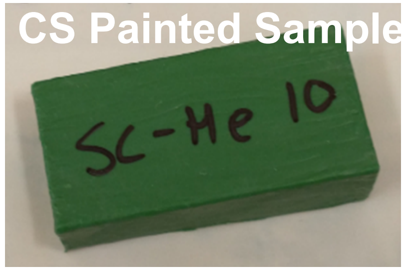
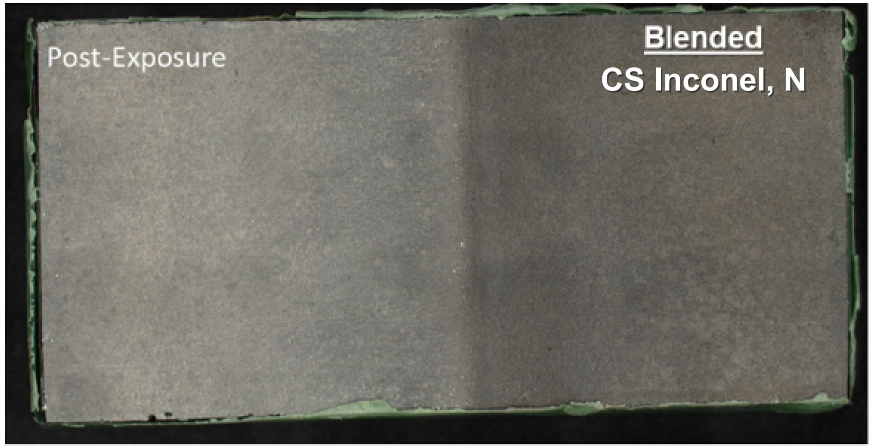
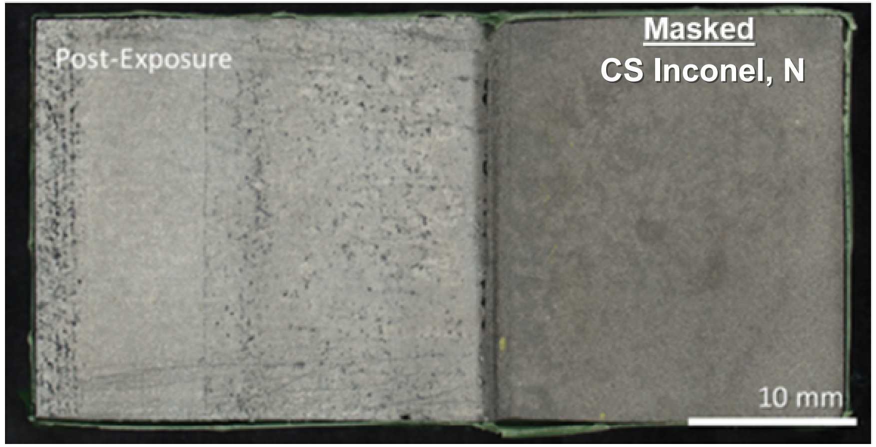
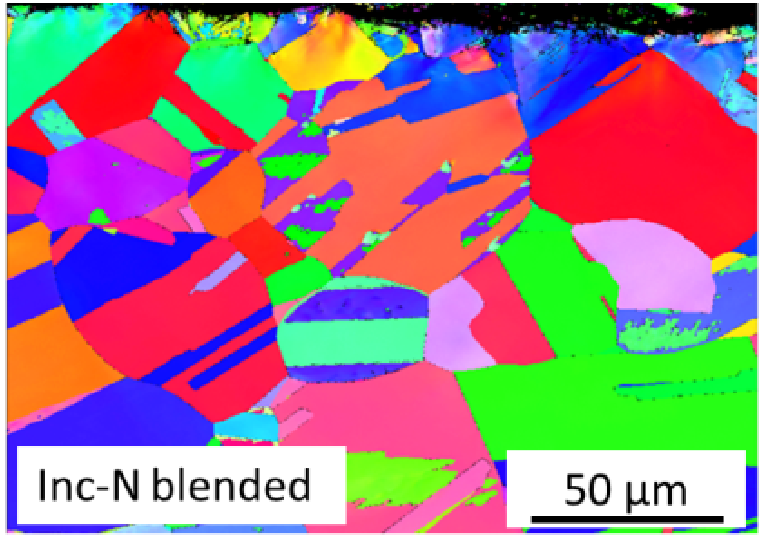
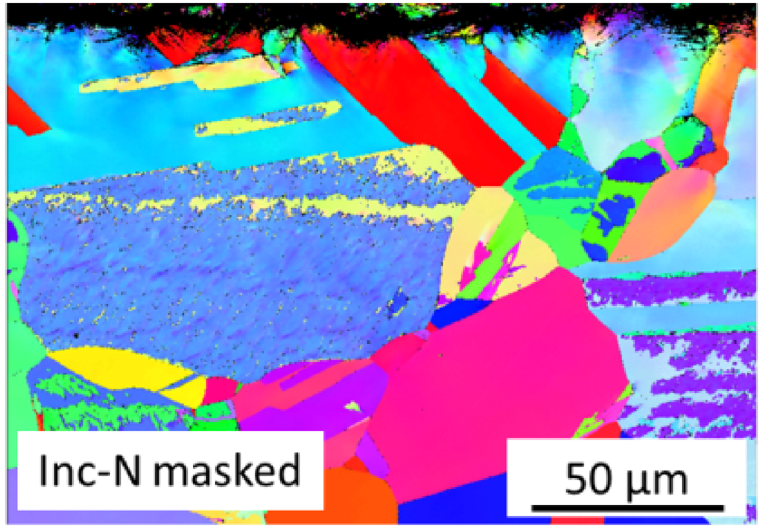






EBSD of interface far from corrosion attack (uncorroded region)





Cold Spray – Summary and Moving Forward

Summary of initial optimization:

1. *Metastable pitting in full immersion is reduced when the cold spray coating surface is polished*
2. *The morphology of the edge interface (tapered vs masked) influences the resultant corrosion morphology*
3. *The porosity (due to carrier gas) of the cold spray coating influences the extent of corrosion damage*
4. *Initial observations of accelerated testing as compared to more relevant atmospheric testing indicate similar damage morphologies*

Future work/ questions:

1. *Further testing under relevant conditions*
2. *What qualifies as "good enough" for a mitigation and repair strategy?*
    - *How can we optimize coatings with initial observations, and how will we know when they meet sufficient requirements?*
3. *How does cold spray behave on a pre-corroded or pre-exposed surface?*
    - *What surface preparation is necessary, if at all?*