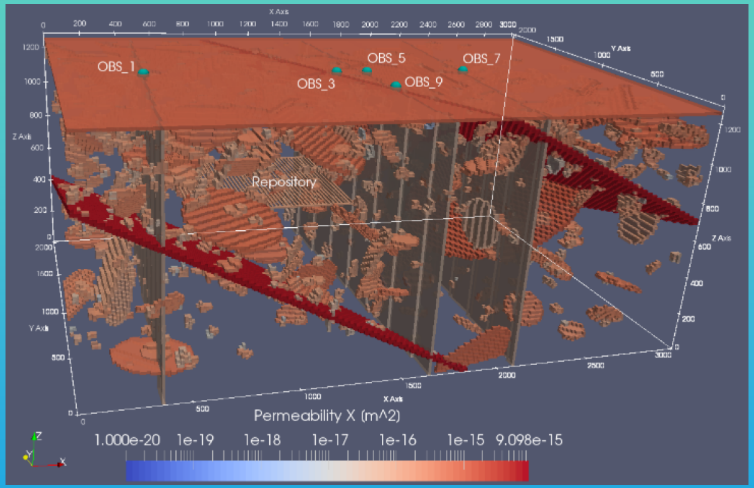
Spent Fuel and Waste Science and Technology (SFWST)



Cold Spray and Coatings – Repair and Mitigation

NEI Used Fuel Management Conference

May 3-5, 2022, Las Vegas, NV

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Sandia National laboratories

Ken Ross

Pacific Northwest National Laboratories

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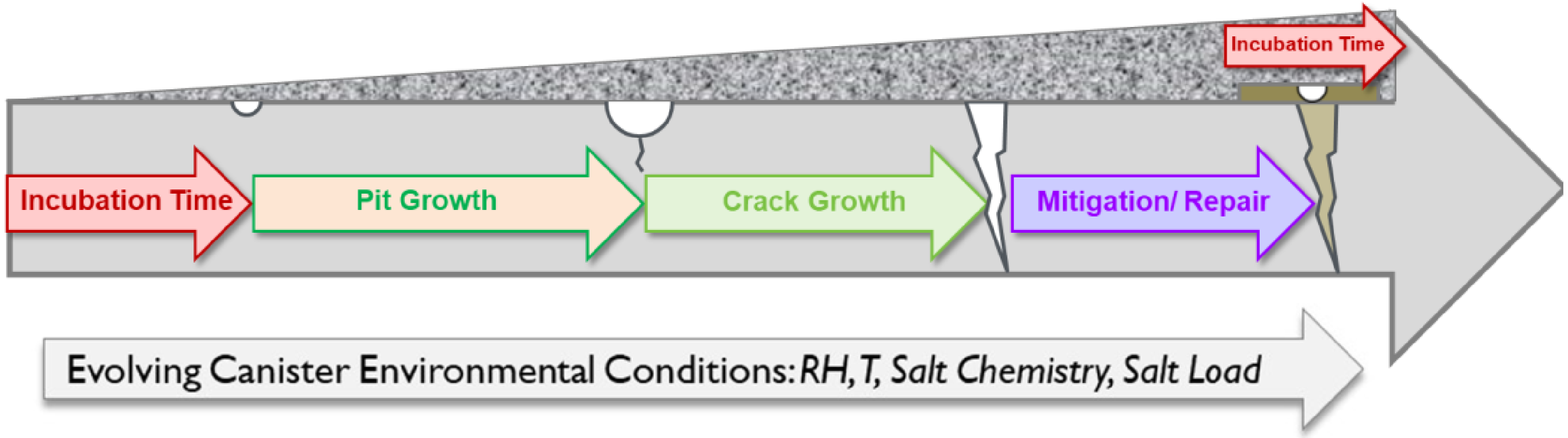
Dry Storage Canister SCC: Current work

Sandia's Role:

1. **Defining the canister surface environment**
2. **Importance of canister environment for pitting/SCC**
3. **Crack growth rate studies**
4. **Mitigation and Repair Strategies**



Current focuses:

1. Deposited salt characteristics/compositions
2. Mg-chloride brine evolution
3. Canister Deposition Field Demonstration
4. Corrosion in more realistic environments
   - Diurnal cycles in T/RH
   - Inert dust
   - Additional anions (e.g., NO_3, SO_4)
5. Pit-to-crack transition—environmental and material dependencies
6. CGR –moving towards atmospheric testing
7. Cold spray/coatings

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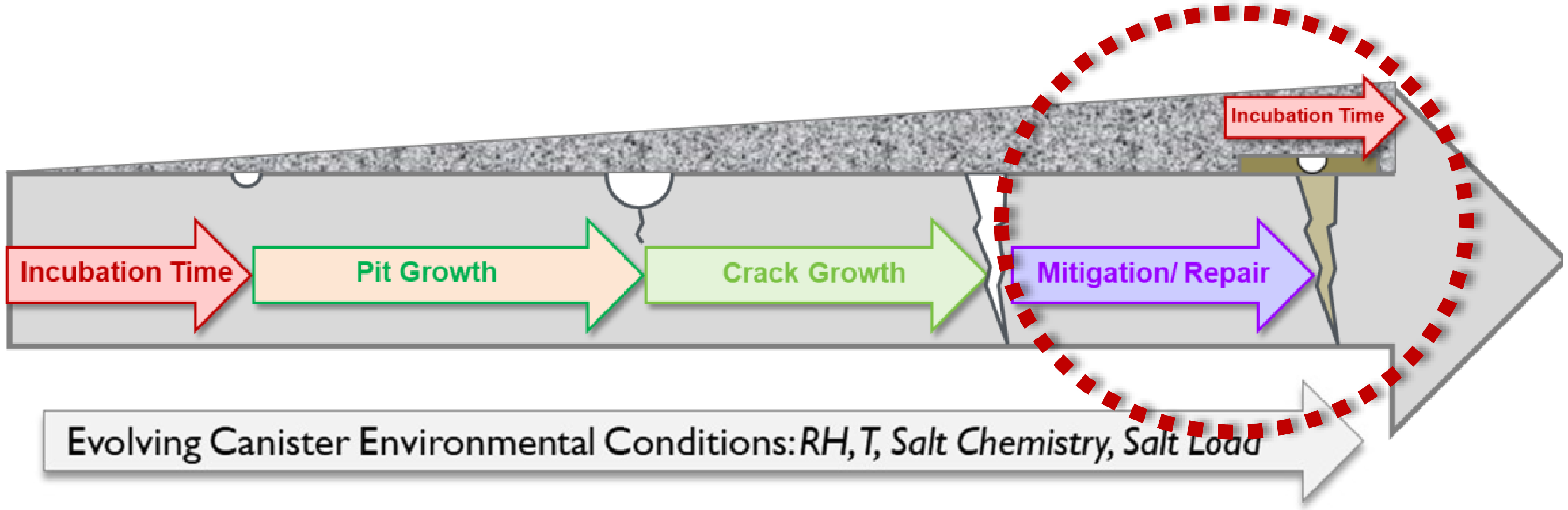

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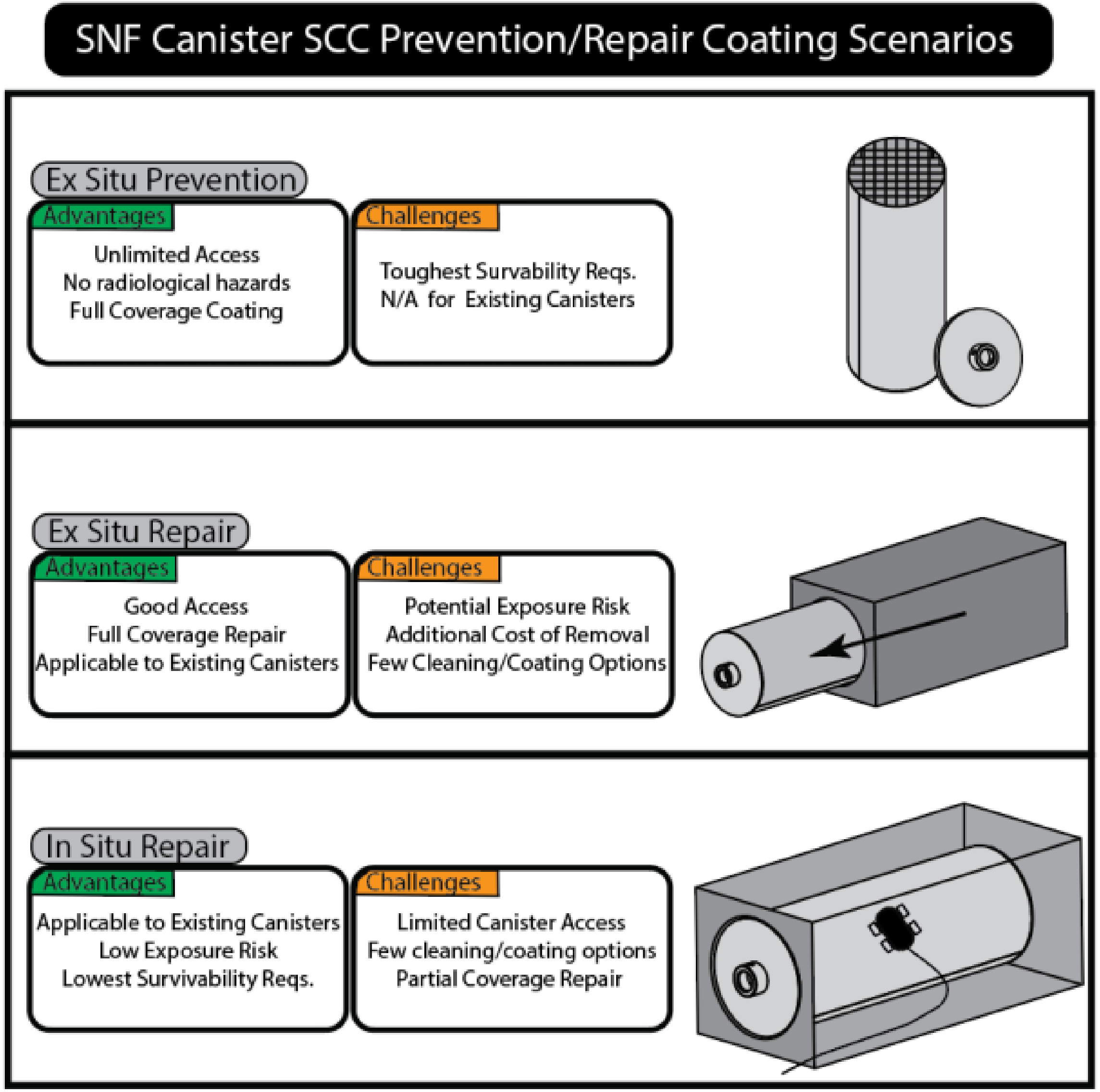
Mitigation and Repair: Canister Coatings Evaluation



1. Collaborative effort with industrial partners
   - *Based on FY20 coatings report*

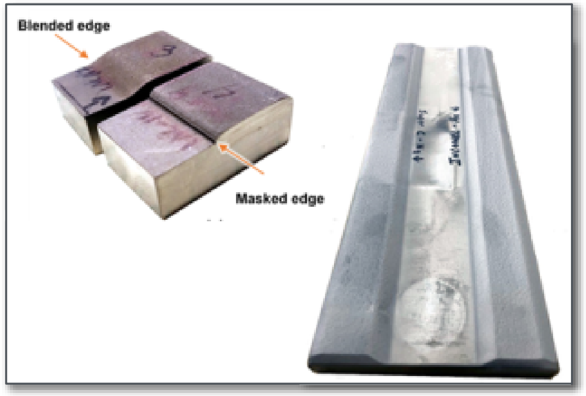
Initial Scoping Report


SAND2020-7916R

Corrosion-Resistant Coatings for Mitigation and Repair of Spent Nuclear Fuel Dry Storage Canisters

Spent Fuel and Waste Disposition

2. Collaboration with PNNL to evaluate cold spray as a potential mitigation and repair strategy



SNL-Industrial Collaboration– Initial coatings for evaluation

Coating types:

4 collaborating companies, 11 variants

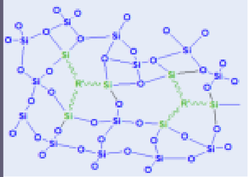
- *176 samples for analysis (coated on rough and smooth finish)*

1 Gentoo - 1

2 Gentoo - 1 + Zn-rich Primer

3 Gentoo - 2

4 Gentoo - 2 + Zn-rich Primer

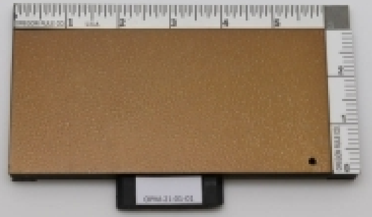


5- variants of Gentoo with and without Zn-rich primer

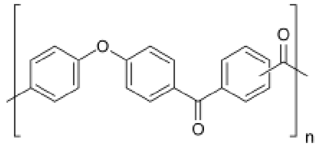
Durable ceramic hybrid inorganic/polymer coating with/without galvanic protection

5 Zn-rich Primer

1 OXPEKK resin

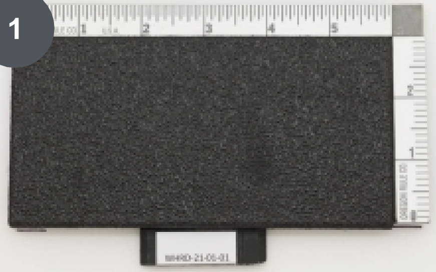


2 OXPEK-Sulfonated



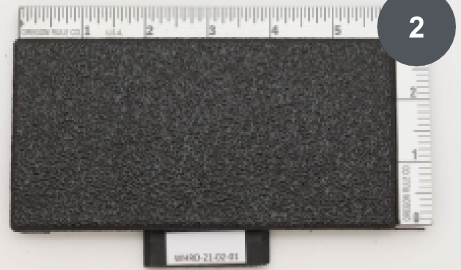
2- variants of Polyetherketoneketone (OXPEKK).
High temperature thermoplastic with high radiation resistance

1



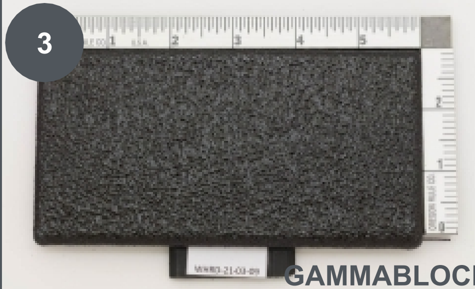
CRACKSTOP

2

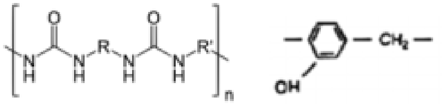


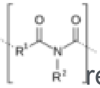
GAMMABLOCK

3



GAMMABLOCK *PLUS*

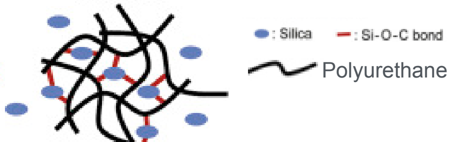




3- variants of modified polyimide, polyurea, phenolic resins. Durable, chemically inert and can include additives to increase corrosion resistance

1

CLADCO



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

SNL-Industrial Collaboration–Surface Roughness Characterization

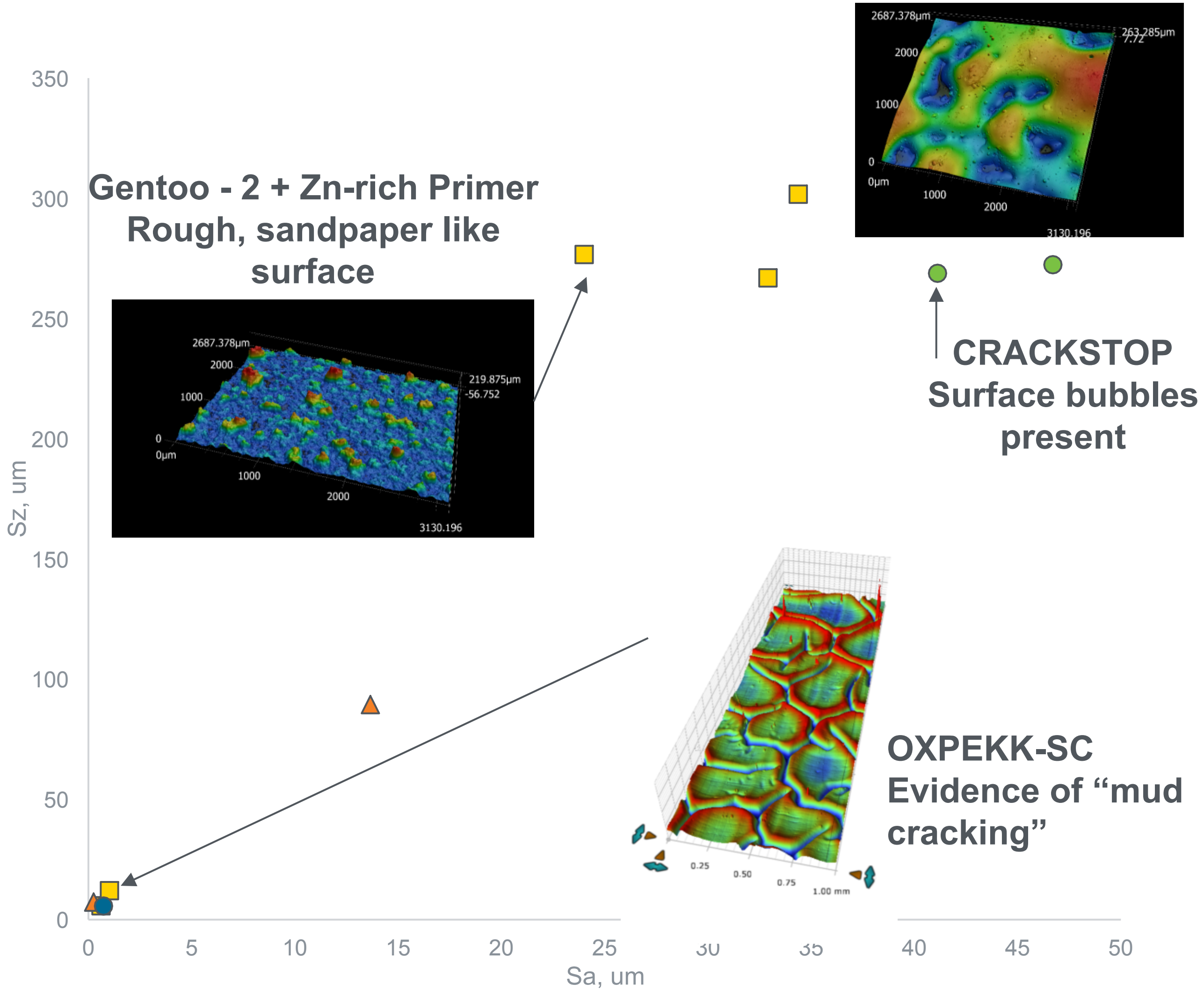
What does the surface look like and are there significant features that may impact performance?

- Surface roughness measured through profilometry
- Two primary groups (related to the coating thickness)
  1. Contained large, rough surface features
  2. Smooth

- Several had evidence of bubbles or gasses being entrenched (gasses are emitted during the curing processes)
  - Outgassing tests will be performed to identify species

The impact of roughness will be assessed:

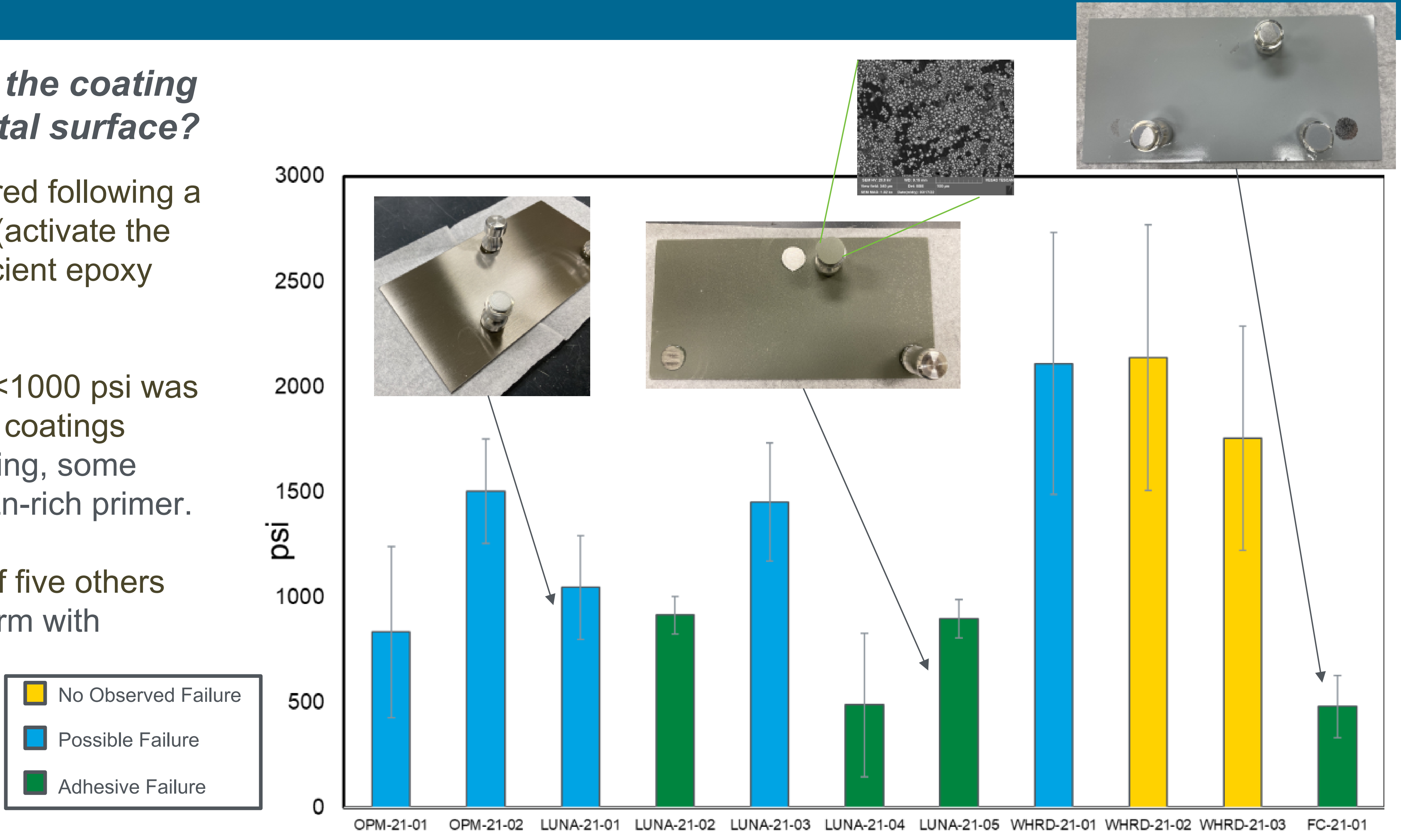
- Sites for brine pooling
- Increase dust accumulation



SNL-Industrial Collaboration – Adhesion Characterization

How well does the coating stick to the metal surface?

- Adhesion measured following a plasma cleaning (activate the surfaces for sufficient epoxy adhesion)
- Adhesive failure <1000 psi was observed for four coatings
  - Ceramic coating, some contained a Zn-rich primer.
- Possible failure of five others
  - Need to confirm with SEM/EDS

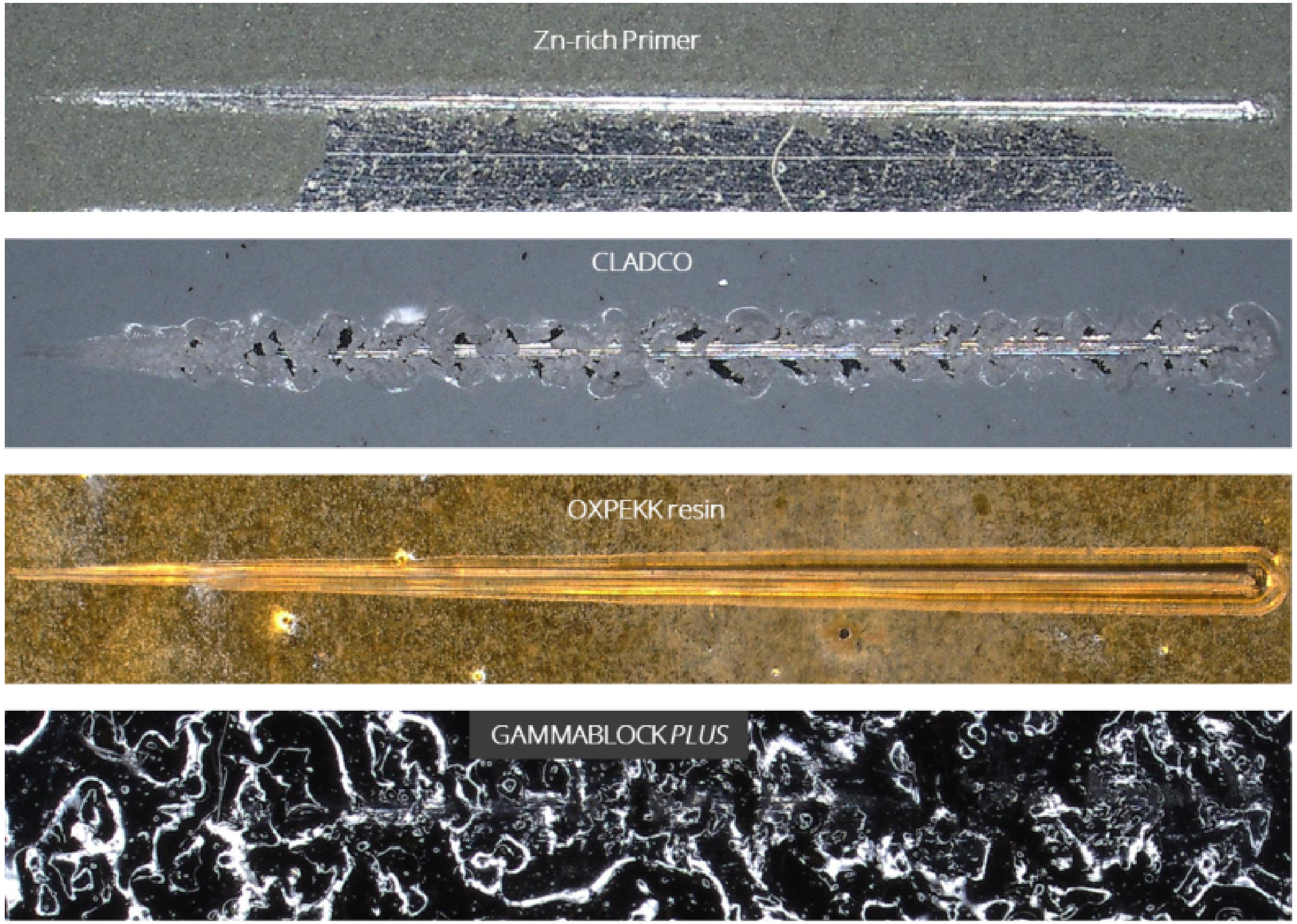


SNL-Industrial Collaboration – Scratch Characterization

What is the mechanical strength of the coating?

- Scratch (tribology) evaluated for all coatings

- Different failure types were observed based upon the properties of the coating.
  - **Ceramic coatings:** generally failed in fragment and experience brittle failure
  - **Organic coatings:** underwent elastic deformation
  - **WHRD Coating:** minimal deformation – never failed to the base metal



Brittle failure in ceramic coatings

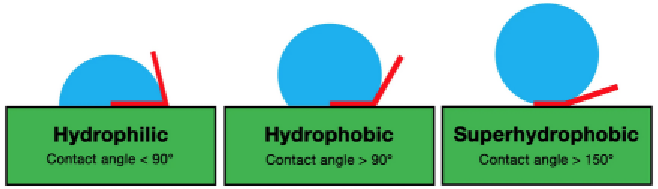
Elastic deformation polymeric coatings

Minimal deformation observed in WHRD samples

SNL-Industrial Collaboration– Chemical Characterization – contact angle

How hydrophobic is the coating?

- Water contact angle was measured with a droplet of fluid on the coating surface
  - DI water, 76 % RH brine, and 40 % RH brine
- Generally contact angles were > 90 % suggesting hydrophobic coatings
  - Contact angle increased with increasing ionic strength
- Surface roughness interferes with comparison across different coatings, therefore surface tensiometry measurement will be performed



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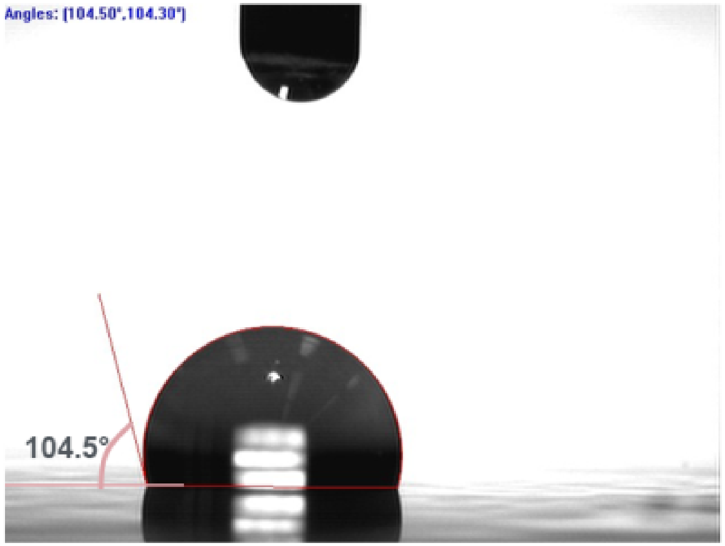
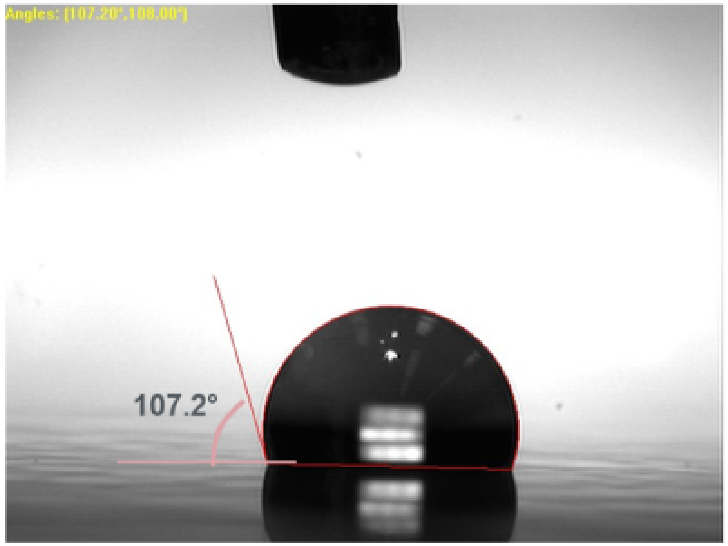
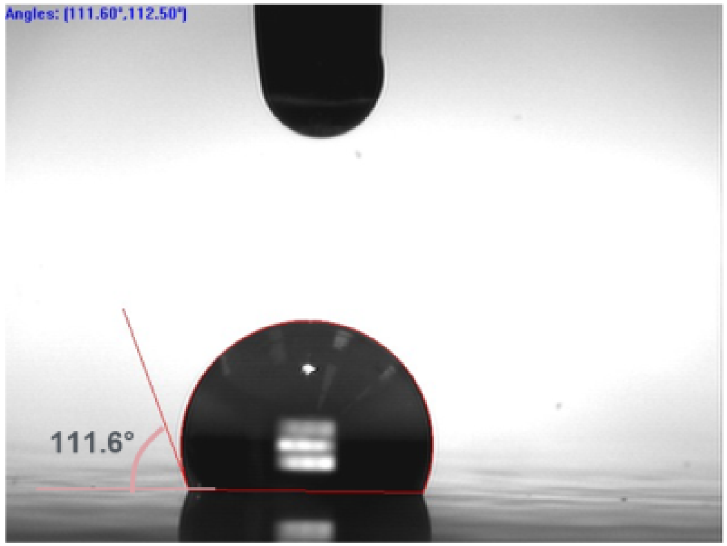


DI water



76 % RH Brine



40 % RH Brine

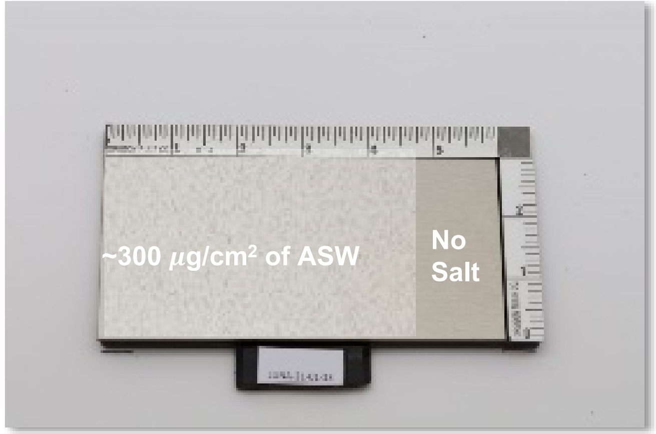
SNL-Industrial Collaboration– Ongoing Characterization

Water Permeation

- Brine permeation and potential coating degradation are being measured through electrochemical impedance spectroscopy (EIS).
- Baseline measurements for exposure in 0.6 M NaCl are currently being acquired over a 1 month open circuit exposure in full immersion.
- Future work will also assess atmospheric exposures.

Atmospheric Exposure

- Coatings are deposited with artificial seawater and aged in an accelerated corrosion environment (76% RH, 40 ºC) for 30-90 days.
  - Physical and chemical properties will be evaluated post-exposure.



Chemical Outgassing

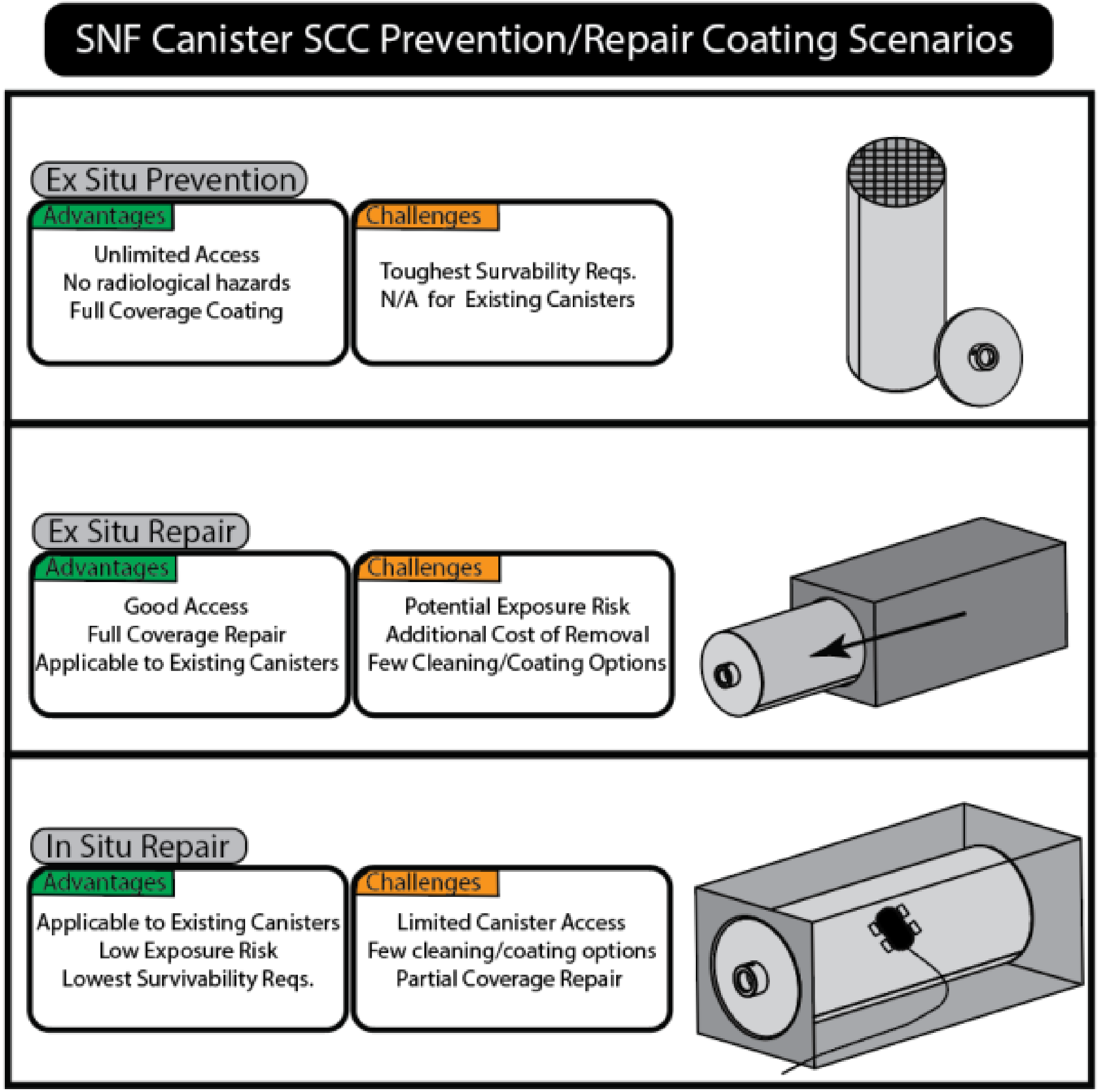
- Thermogravimetric analysis will be performed on a fragment of each sample to track thermal degradation.
  - In the event that a large mass change is observed, additional tests will be performed to identify the outgassed species.

Summary: Initial Gaps Identified and Future Work - Coatings

Coatings

- Private industry has developed many corrosion resistant coatings for a wide variety of applications, none exist for SNF canisters
- Under evaluation for SNF canisters here are:
  - Thermoplastics
  - Polymeric composites
  - Hybrid organic-inorganic ceramic coatings
- In-depth characterization is required to verify viability and to ensure coatings “do no harm” if implemented
  - ***<u>Gaps:</u>***
  - Needs to be a **clearly defined acceptance criteria** to assess the viability of a given coating technology
  - Demonstration of **long term corrosion resistance** under canister relevant environmental conditions is needed
  - **Thermal and radiolytic stability** in under long-term conditions

Mitigation and Repair: Canister Coatings Evaluation



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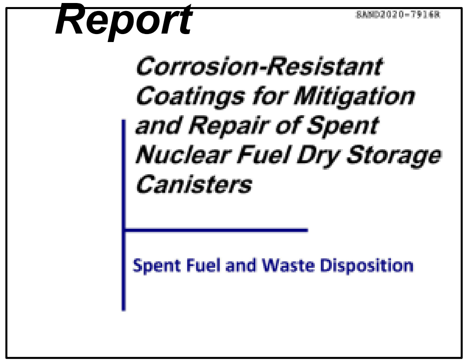
Initial Scoping Report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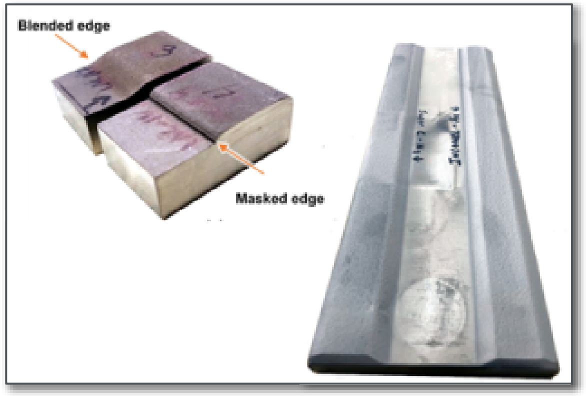
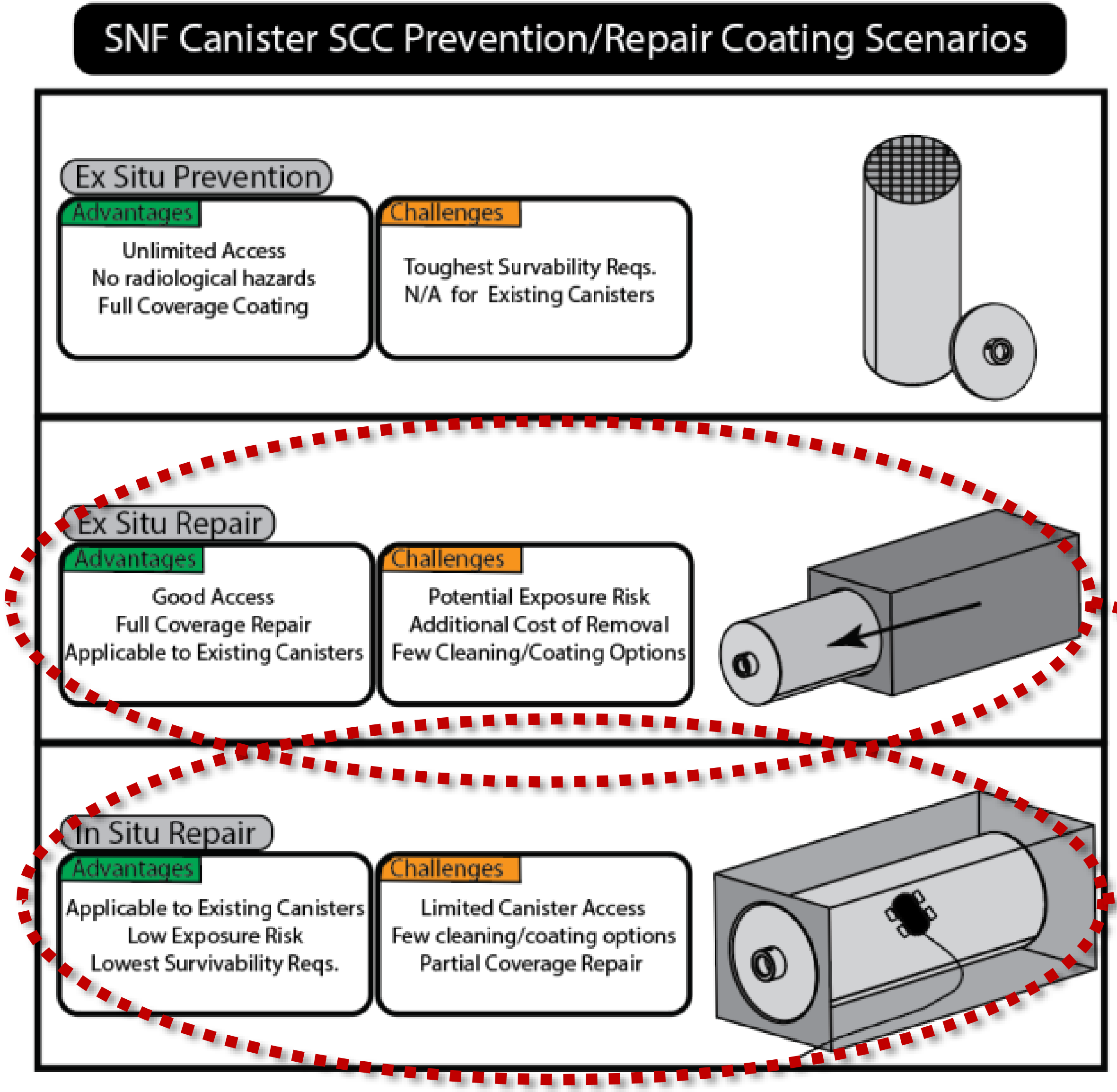


Mitigation and Repair: Cold Spray (CS)



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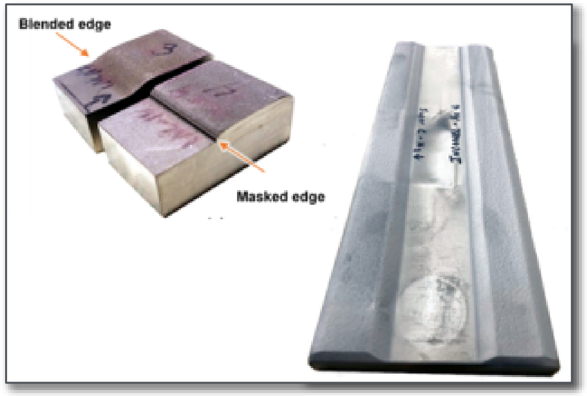


CS Focus → Patch Application for

Potentially vulnerable or damaged areas

SNL – PNNL collaboration:
Cold Spray – Materials and Corrosion concerns

SS 304L base material

Cold Spray:
- Nickel
- Super C
- Inconel 625

→
- CS susceptibility
- Galvanic potential?

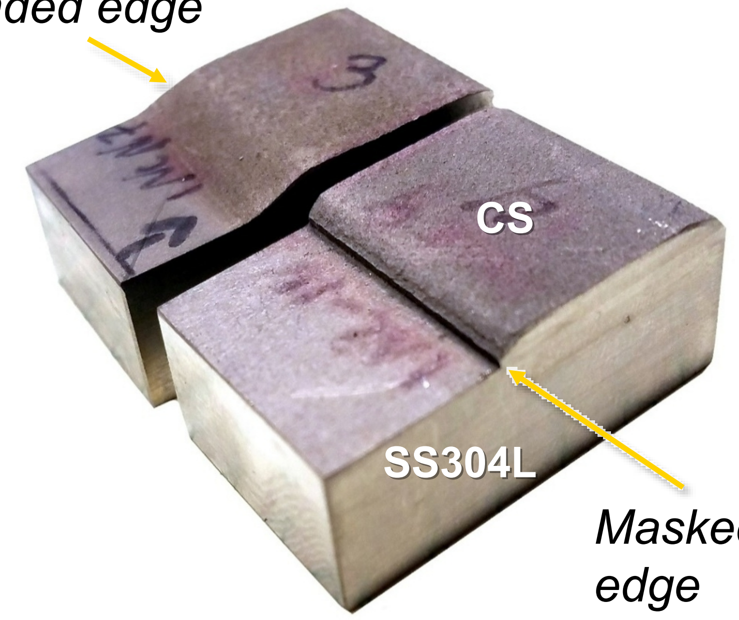
Interface:
- Blended
- Masked

→
- Coating Coverage at Interface
- Residual Stresses

Accelerating Gas:
- Nitrogen
- Helium

→
- Porosity
- Cost/Sustainability

Cold Spray Samples with Edge Processing



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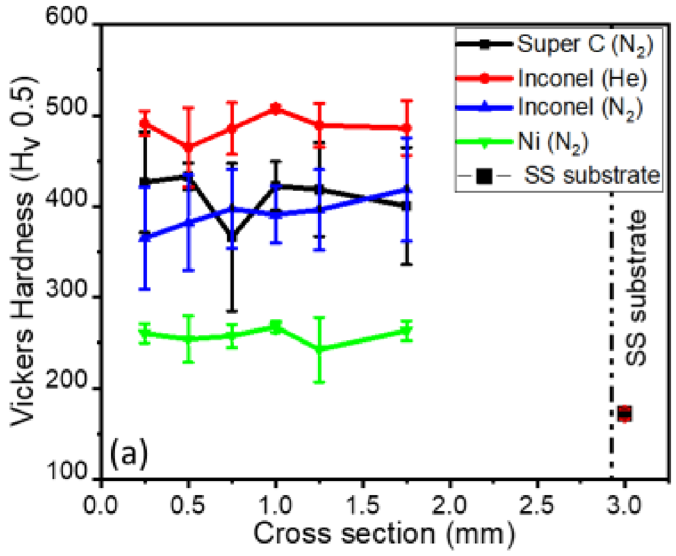
Mitigation and Repair: Cold Spray – Material Characterization

Cold Spray Matrix

CS Material	Interface	Process Gas
Inconel 625	Blended	He
Inconel 625	Blended	N
Inconel 625	Masked	N
Nickel	Blended	N
Nickel	Masked	N
Super C	Blended	N

Initial Hardness Measurements:

- *Vickers microhardness as a function of depth (RT)*
  - *Near-top surface to SS304L substrate.*



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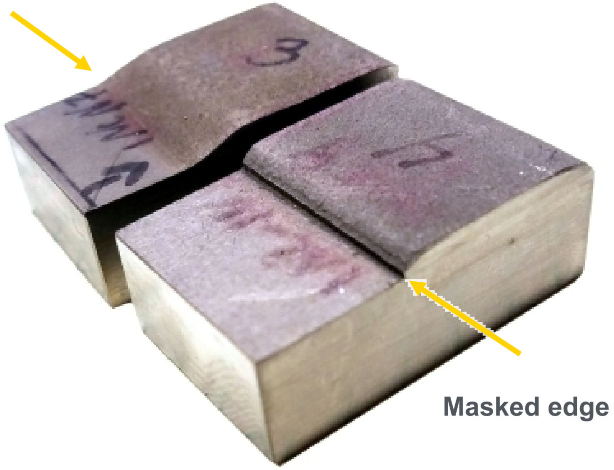

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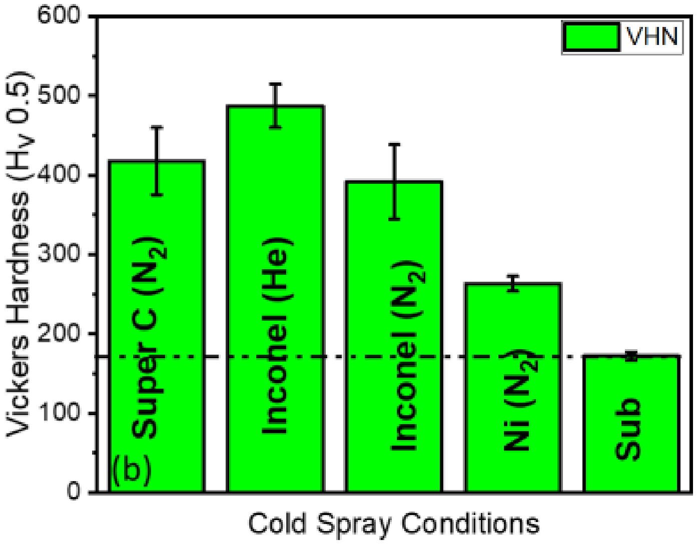

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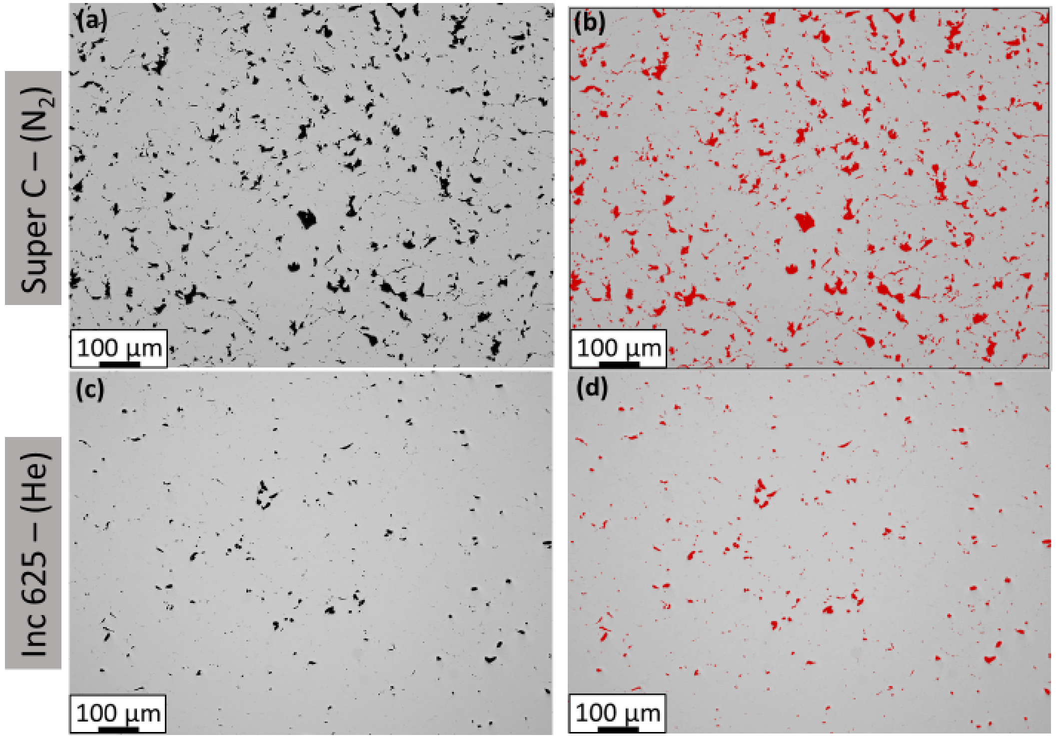
Nickel	Masked	N
Super C	Blended	N

Porosity Measurements:

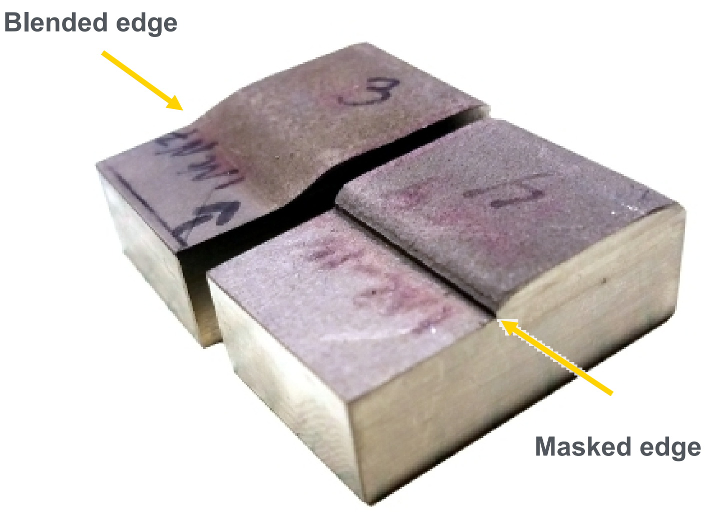
- *Calculated from image processing of bright field optical measurements*
- *Influenced by carrier gas type*



** Note: surface finished to mirror polish for measurements*

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 Samples with Edge Processing



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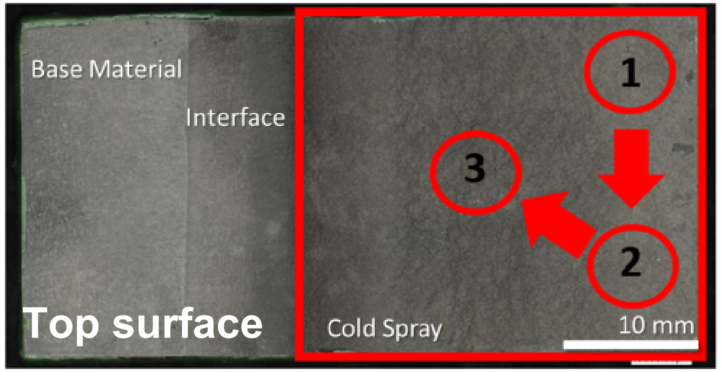
PNNL M3 Report 2021

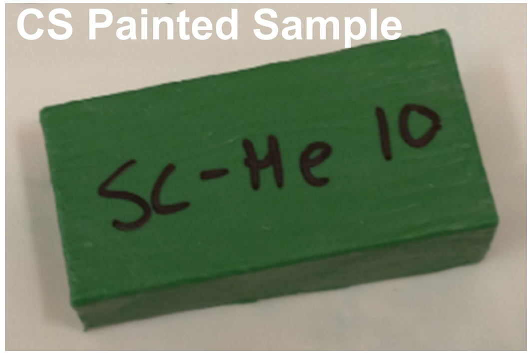
Mitigation and Repair: Cold Spray – Accelerated Testing

Corrosion Testing Matrix

CS Material	Interface	Process Gas	Electrochemical Testing (ASTM G5)			Pitting Test
			As Sprayed	600 grit	1200 grit	(ASTM G48)
Inconel 625	Blended	He	X	X	X	X
Inconel 625	Blended	N	-	-	-	X
Inconel 625	Masked	N	X	X	X	X
Nickel	Blended	N	-	-	-	X
Nickel	Masked	N	X	X	X	X
Super C	Blended	N	X	X	X	X



Sample for ASTM G-5 Testing



Sample for ASTM G-48 Testing

<u>Accelerated Corrosion Testing for Cold Spray Optimization:</u>

ASTM G-5: (potentiodynamic polarization)

- *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*

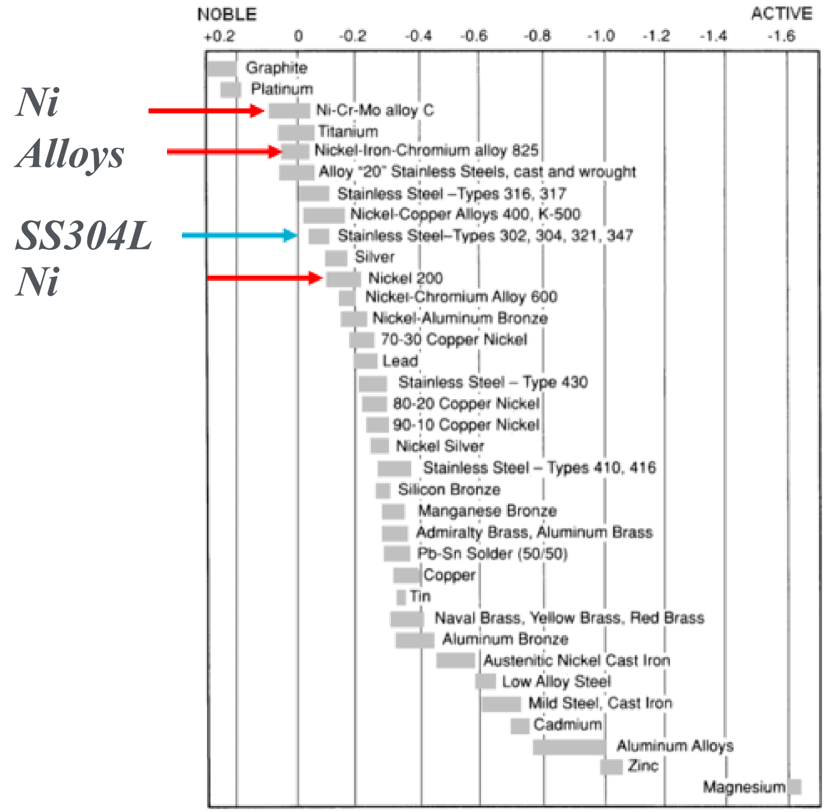
ASTM G-48: (accelerated pitting)

- *6% by mass Ferric Chloride*
- *Full Immersion 24 h at 22 ^{o}C*
- *Entire top surface tested*
  - *Other surfaces painted, as sprayed condition*

SNL – PNNL collaboration:
Cold Spray – Accelerated Corrosion Testing

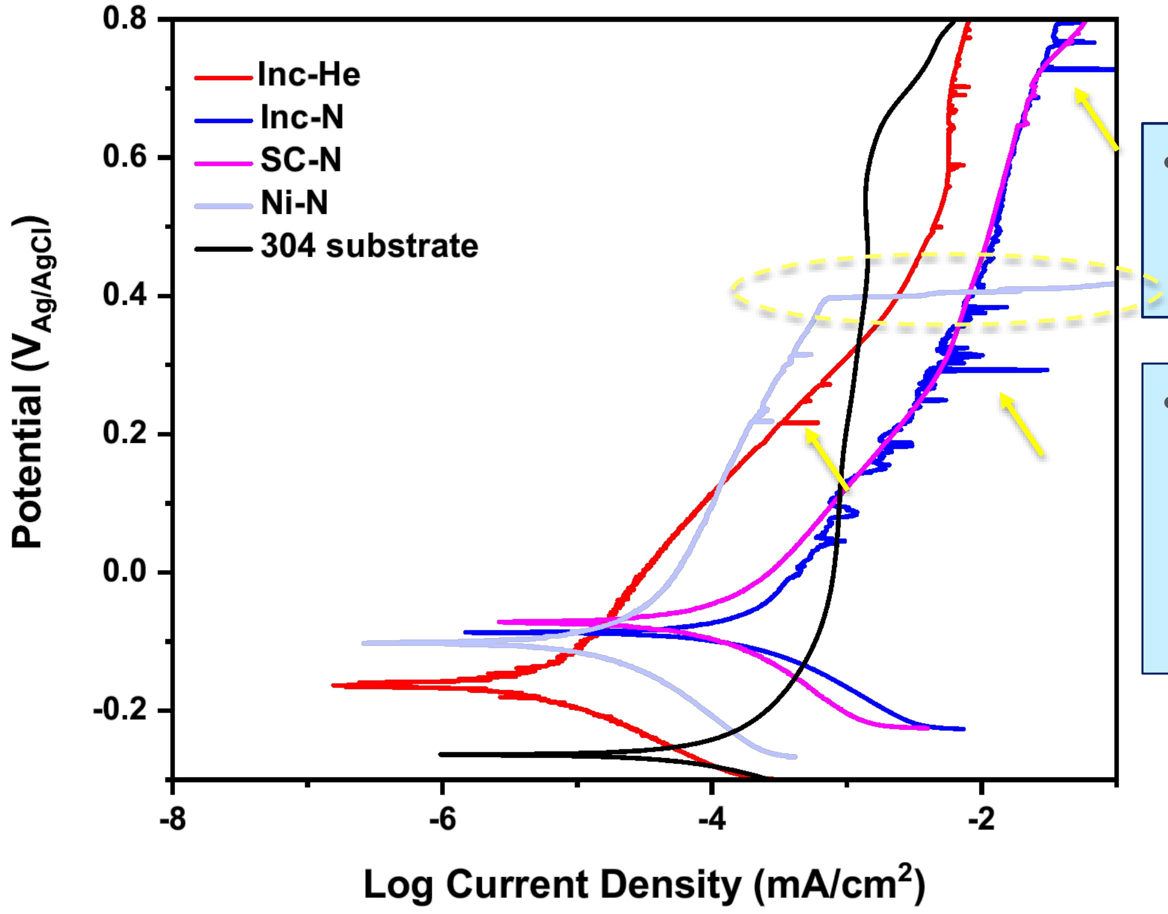
Scan Parameters:

- *0.6 M NaCl*
- *1 h Open circuit potential followed by anodic polarization, 0.1667 mV/s*



Galvanic Series in Seawater

ASTM G-5: potentiodynamic polarization in 0.6 M NaCl



- ***Metastable pitting observed***

- ***Ni CS breakdown at much lower potential***

SNL – PNNL collaboration:
Cold Spray – Accelerated Corrosion Testing

ASTM G-5: potentiodynamic polarization in 0.6 M NaCl

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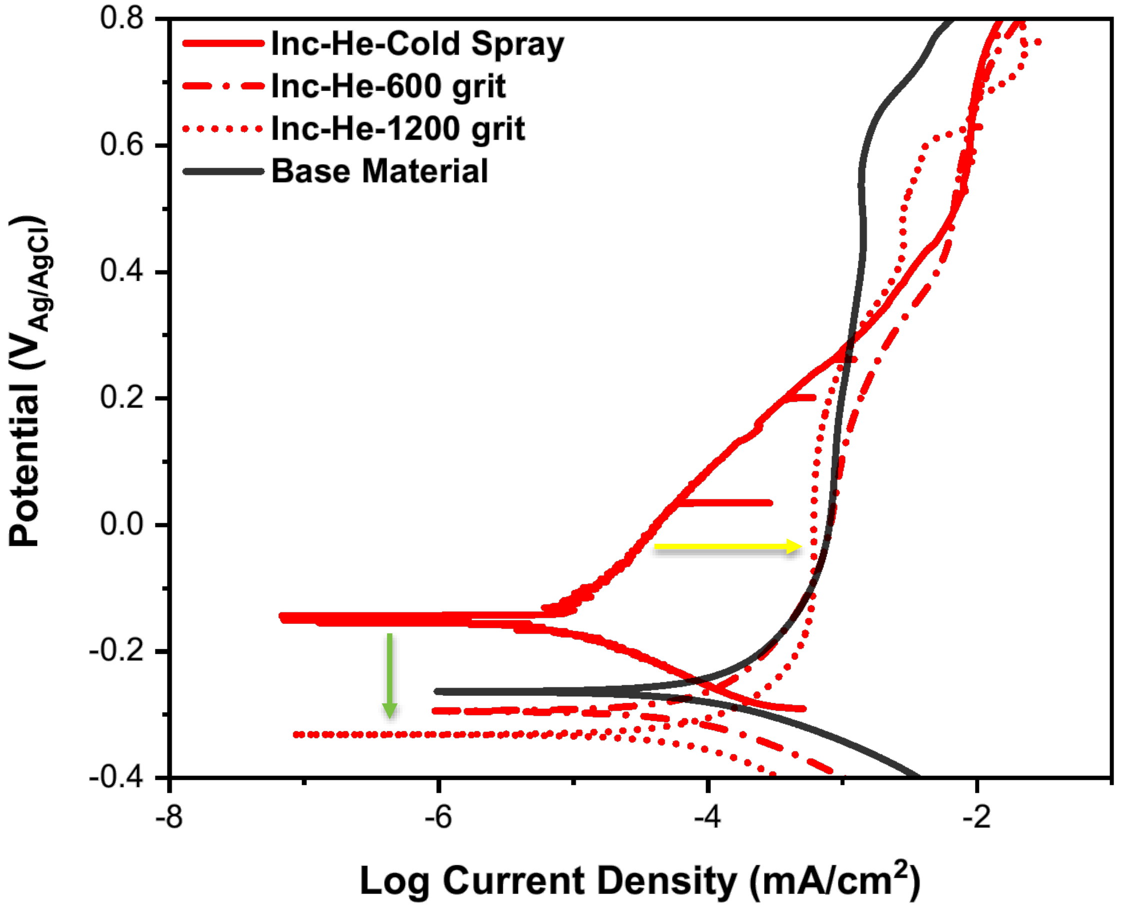
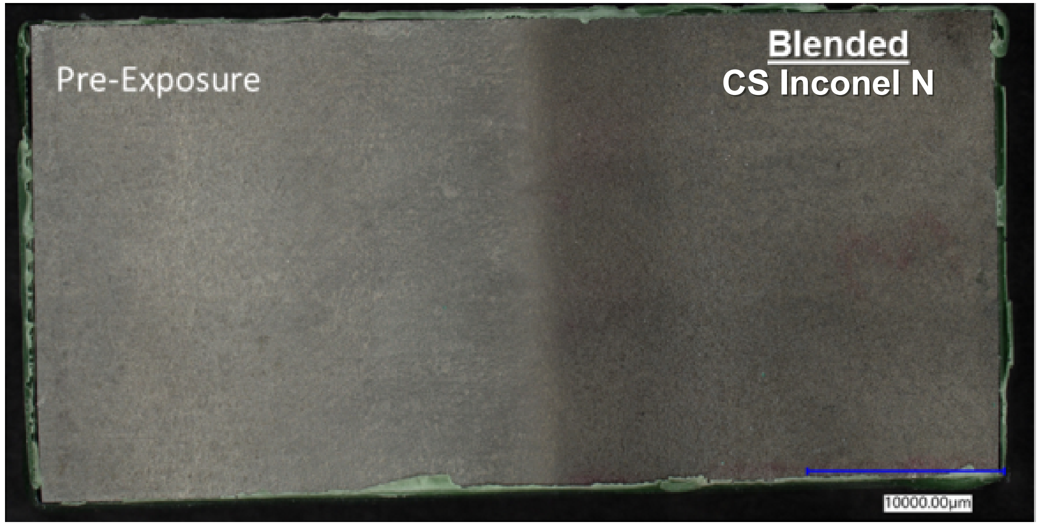
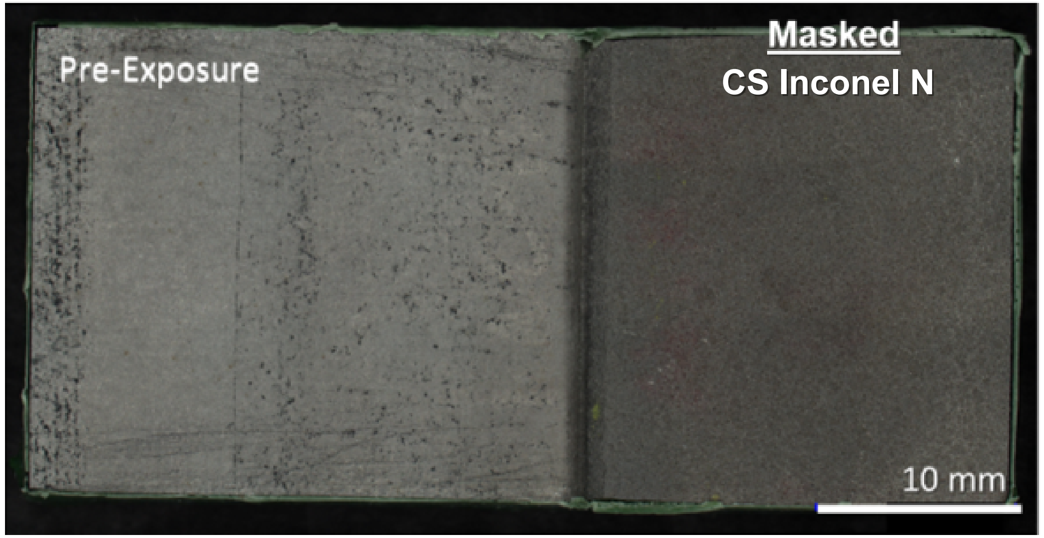


- ***Metastable pitting reduced when polished (dotted red)***

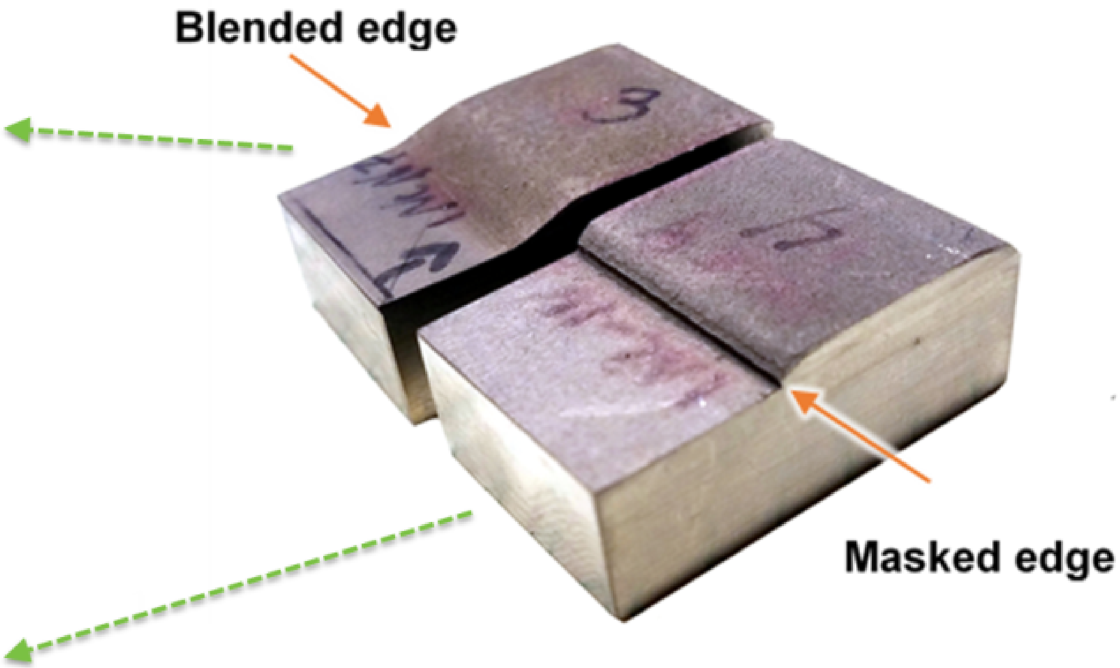
- ***OCP drops when polished (expected)***

SNL – PNNL collaboration:
Cold Spray – Accelerated Corrosion Testing





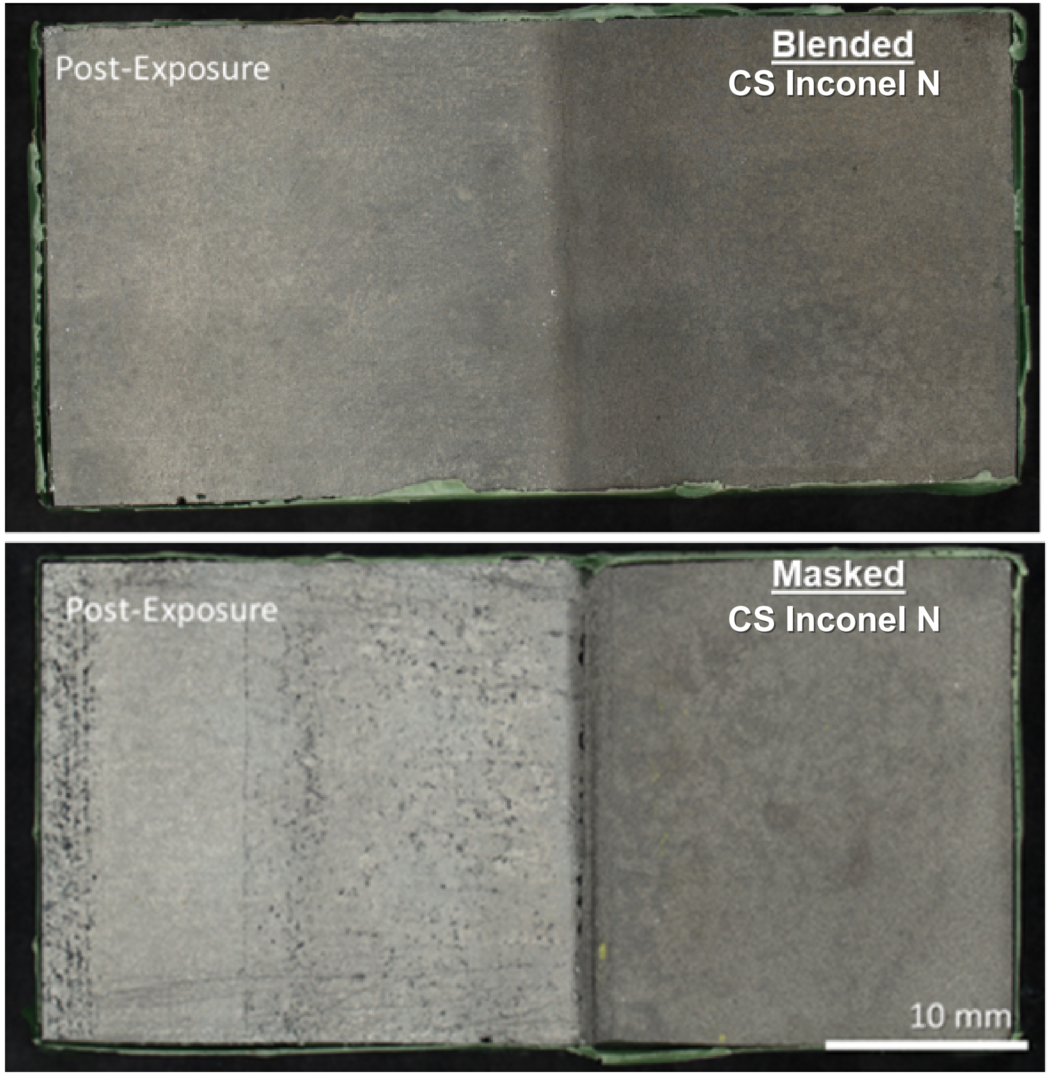
ASTM G-48: (accelerated pitting) in $FeCl_3$



Exposure Conditions:

- *6% by mass Ferric Chloride, Full Immersion 24 h at 22 ^{o}C*
- *Entire top surface tested (Other surfaces painted, as sprayed condition)*
- ***Accelerated testing** conditions to identify potential vulnerabilities*

SNL – PNNL collaboration:
Cold Spray – Accelerated Corrosion Testing – Edge Type



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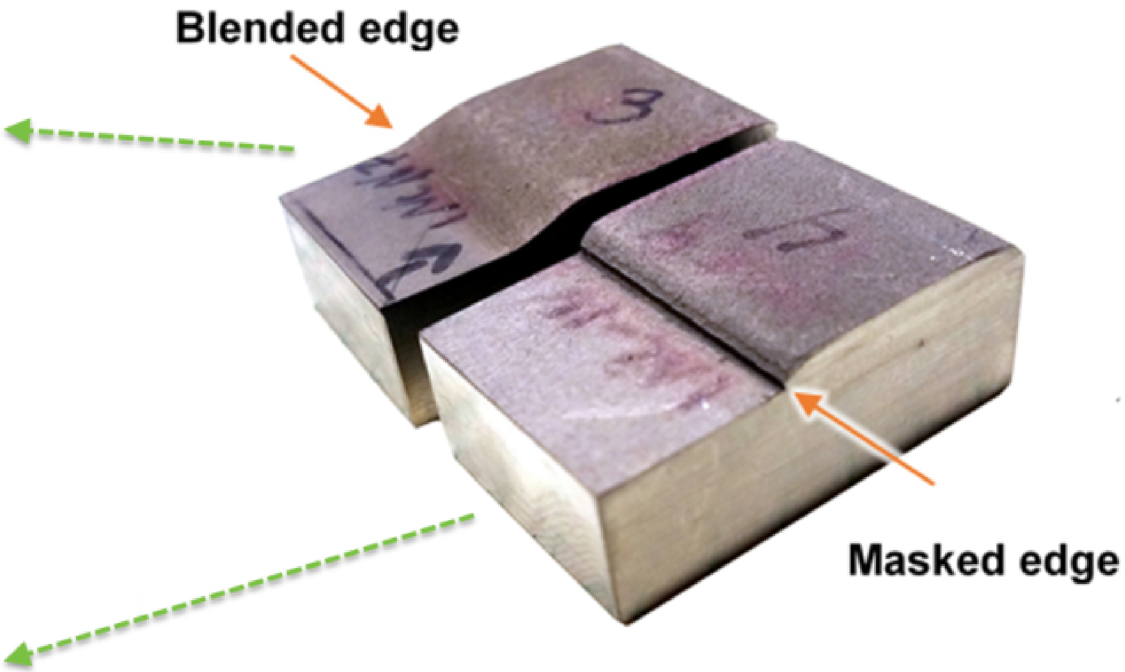

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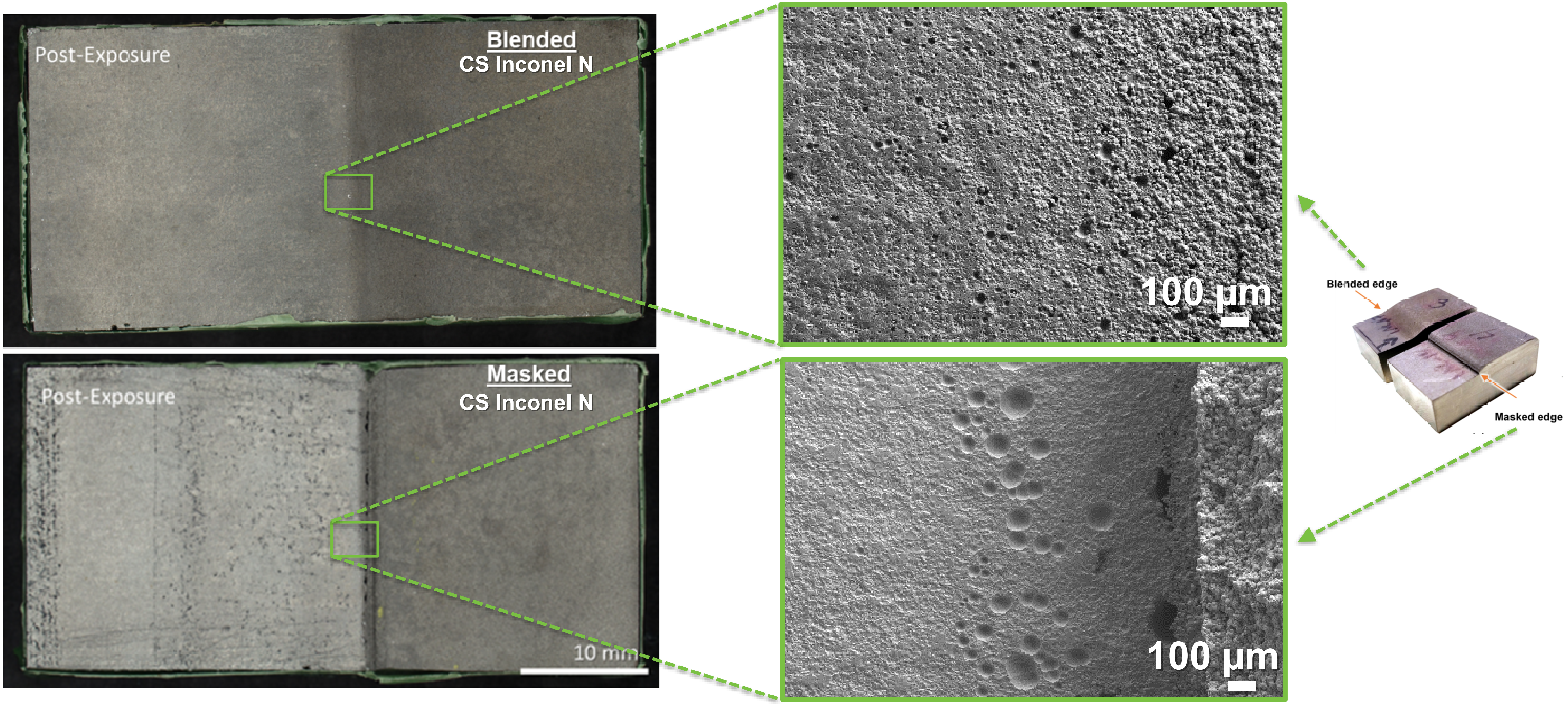

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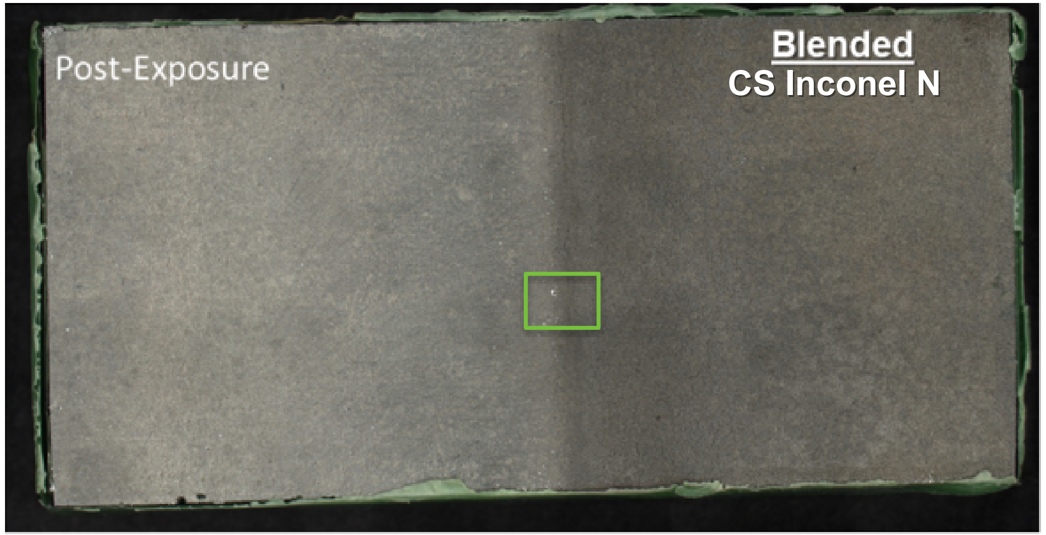
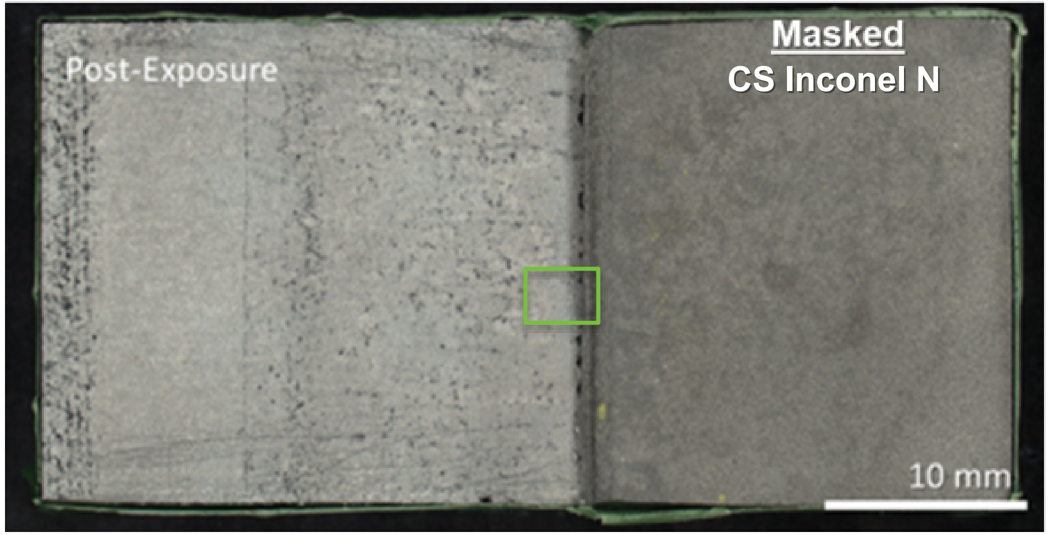
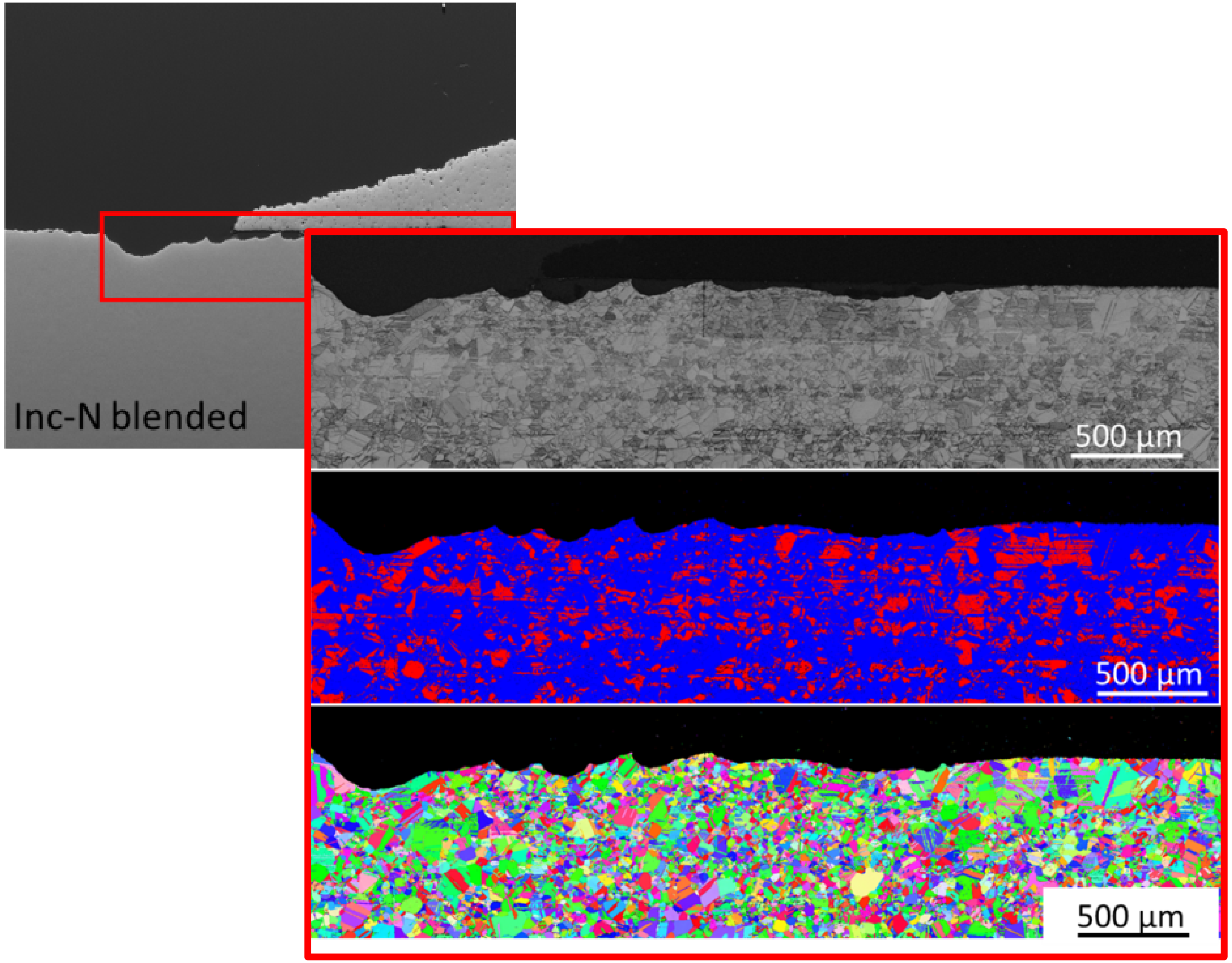
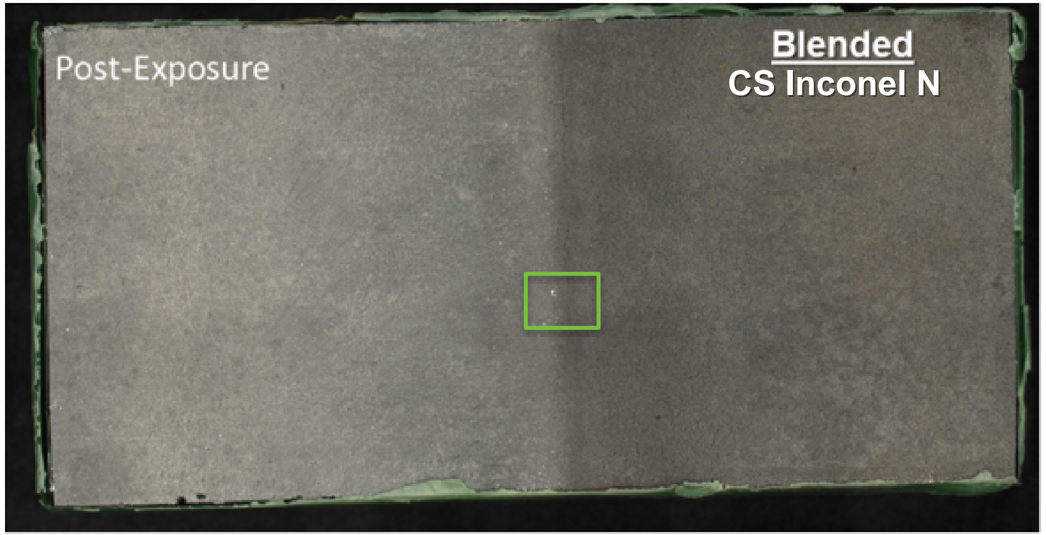
Cold Spray – Accelerated Corrosion Testing - Edge Type

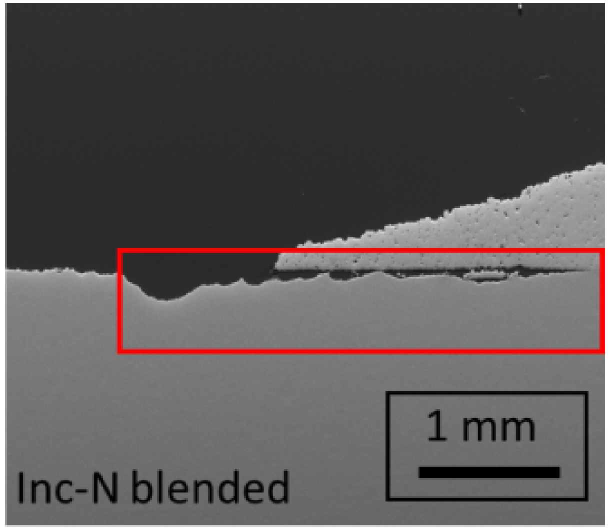


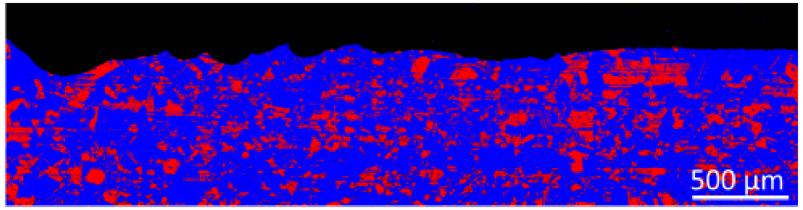


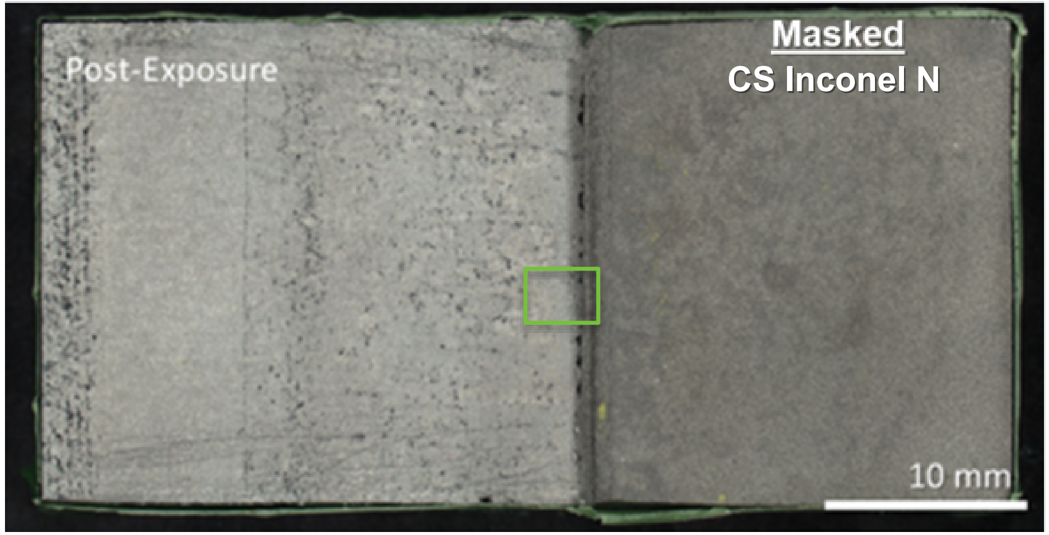


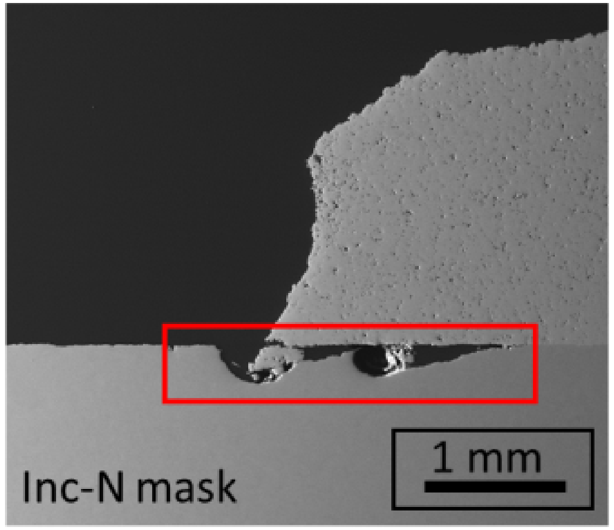
SNL – PNNL collaboration:
Cold Spray – Accelerated Corrosion Testing - Edge Type

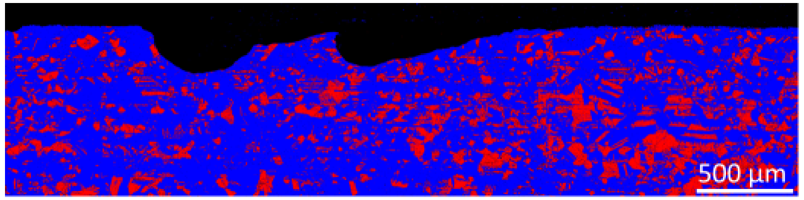






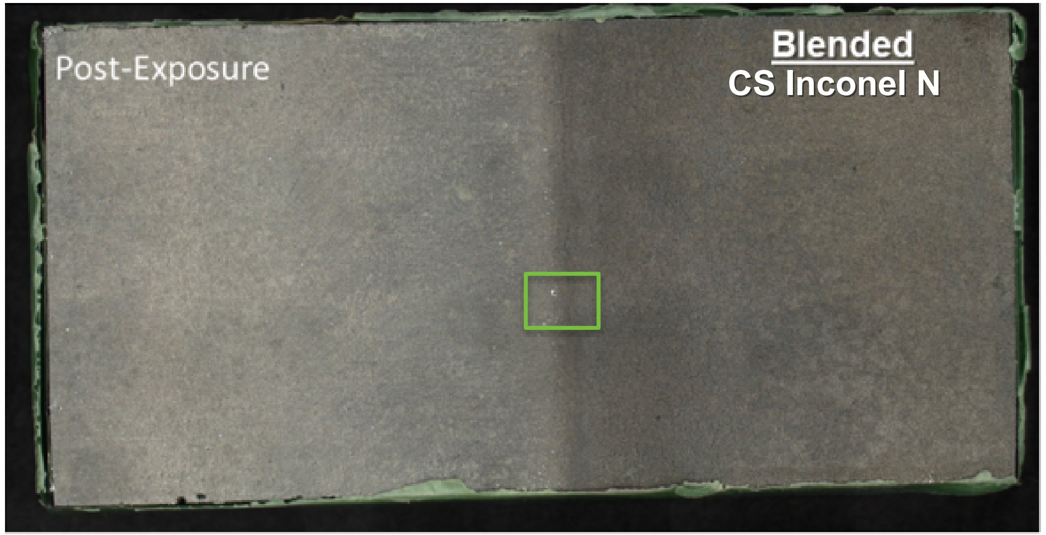


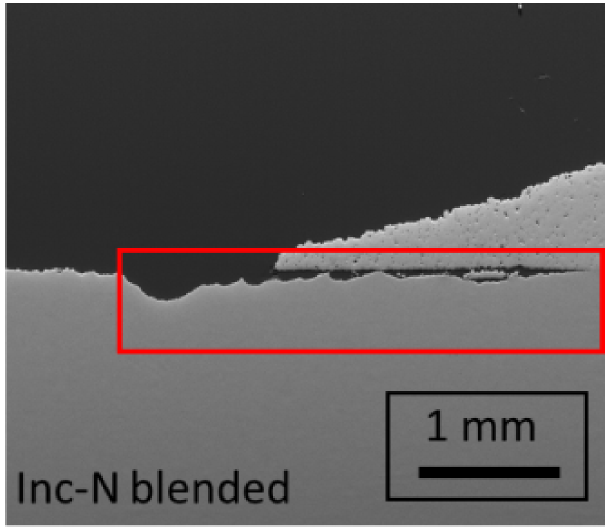


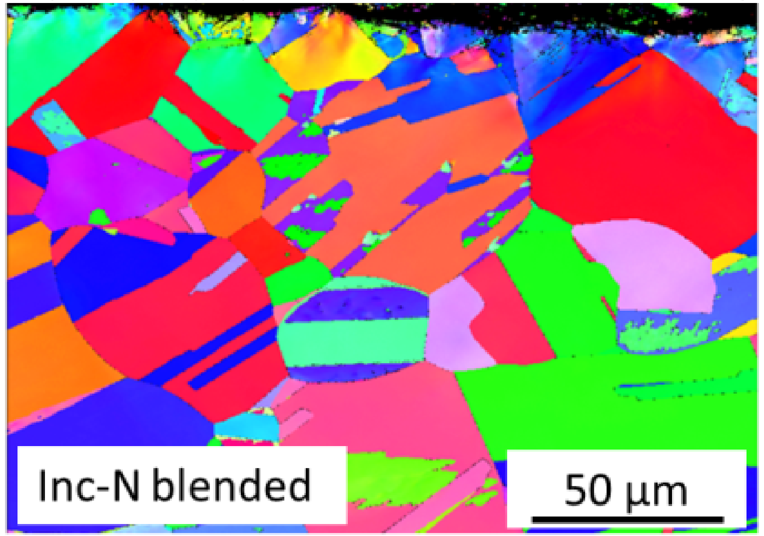


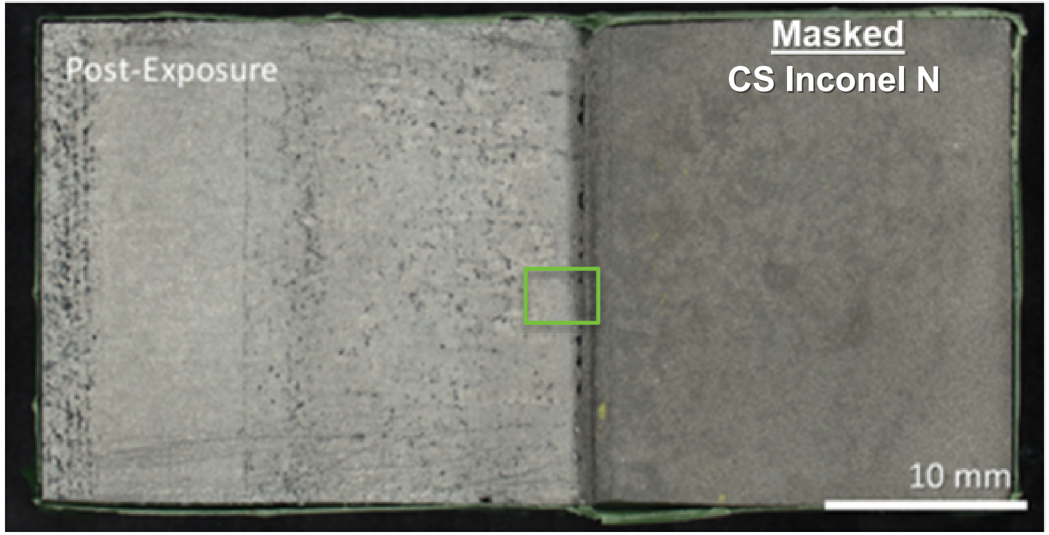
SNL – PNNL collaboration:
Cold Spray – Accelerated Corrosion Testing - Edge Type

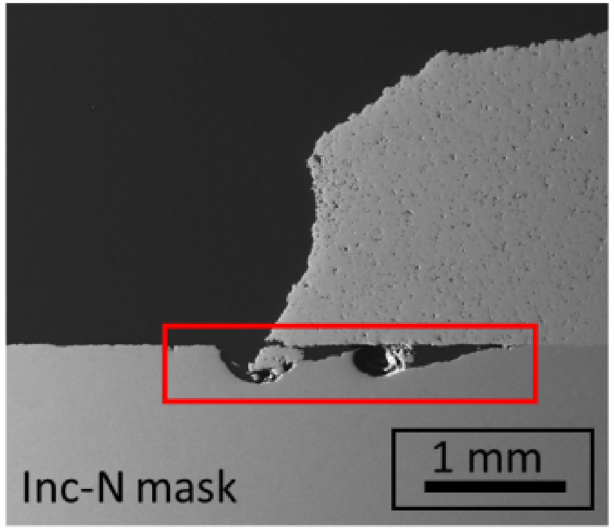
EBSD of interface far from corrosion attack (uncorroded region)

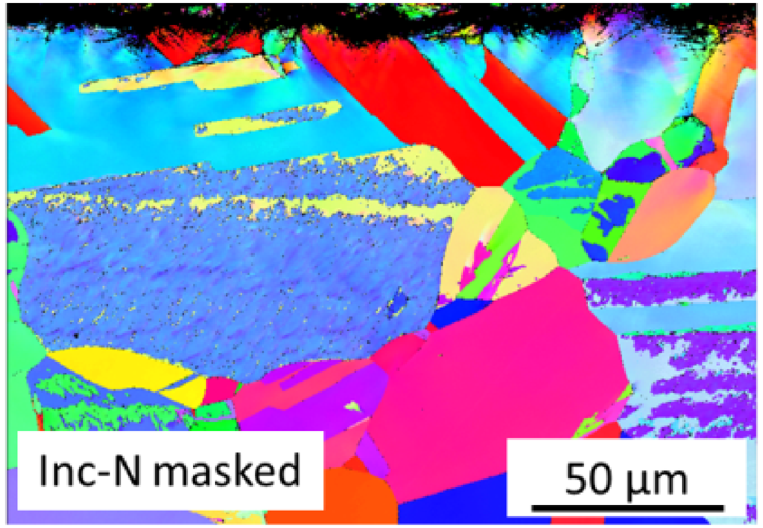








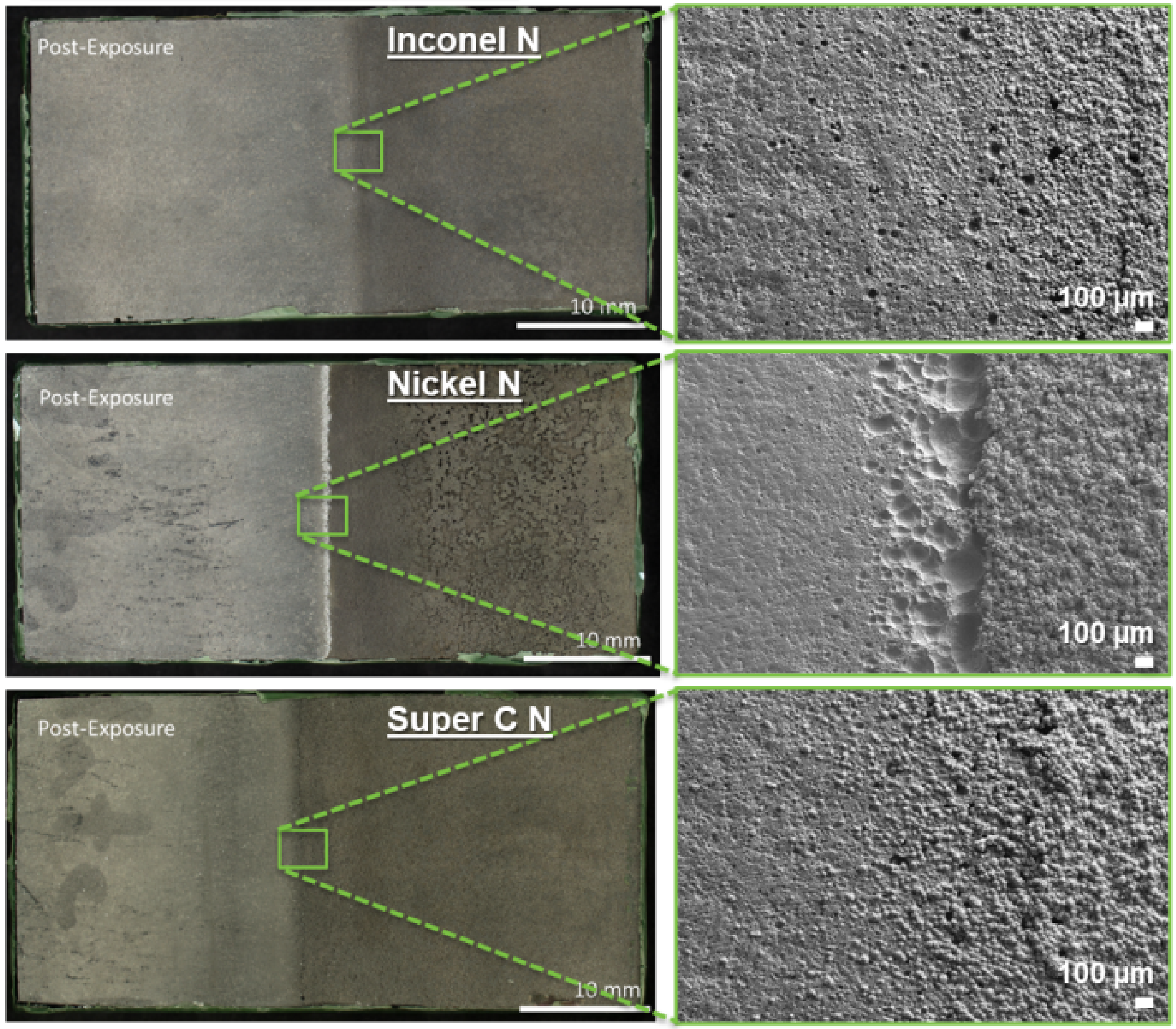




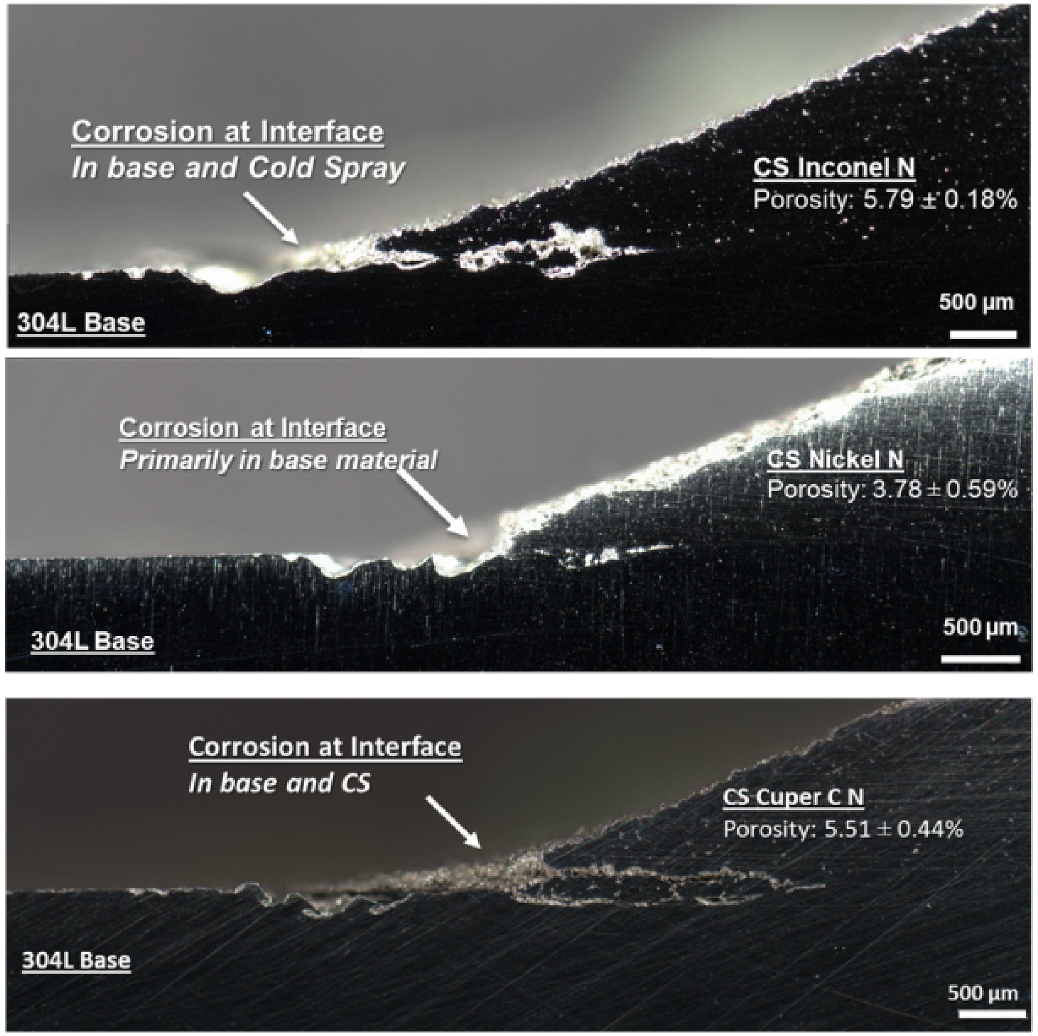
*** Far from interface – deformation layer still intact – likely influences corrosion at interface**

SNL – PNNL collaboration:
Cold Spray – Accelerated Corrosion Testing – Material Selection

Post ASTM G-48 Exposure

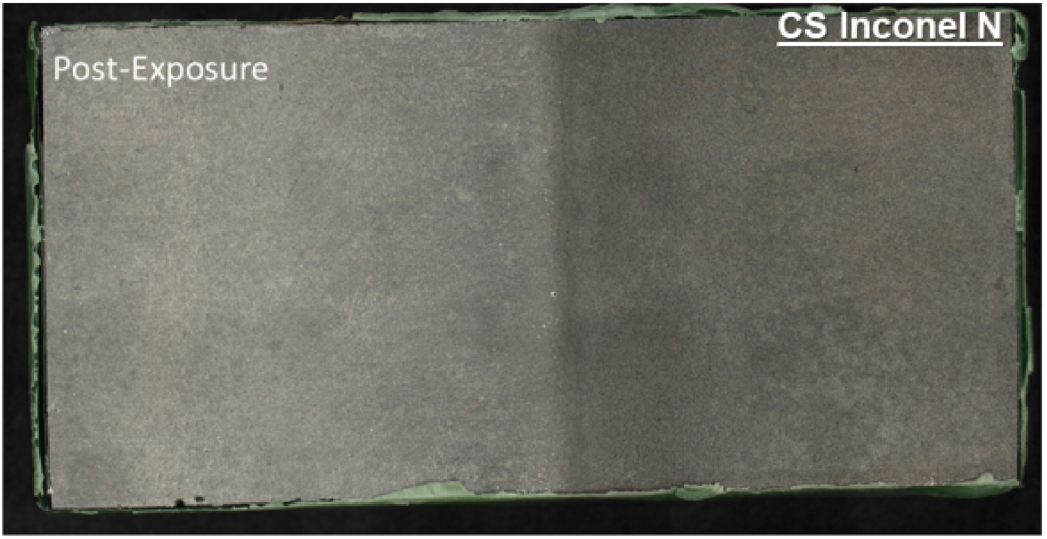


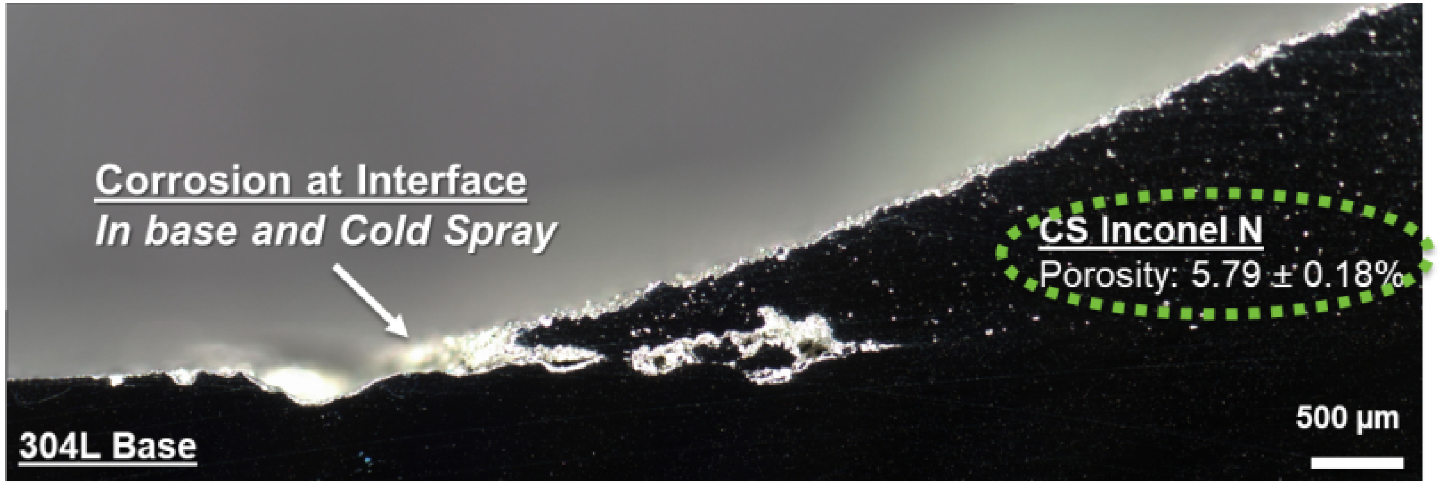
Cross section Post Exposure

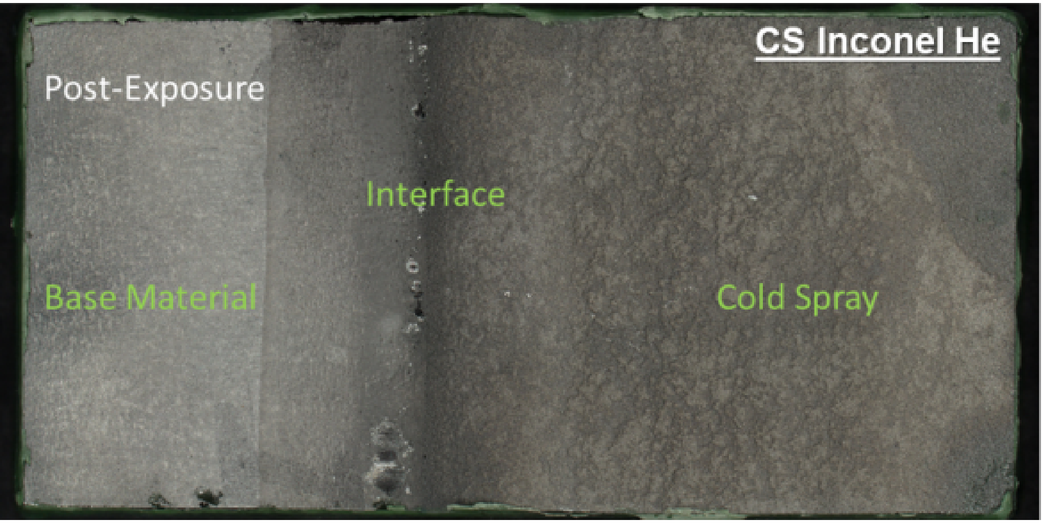


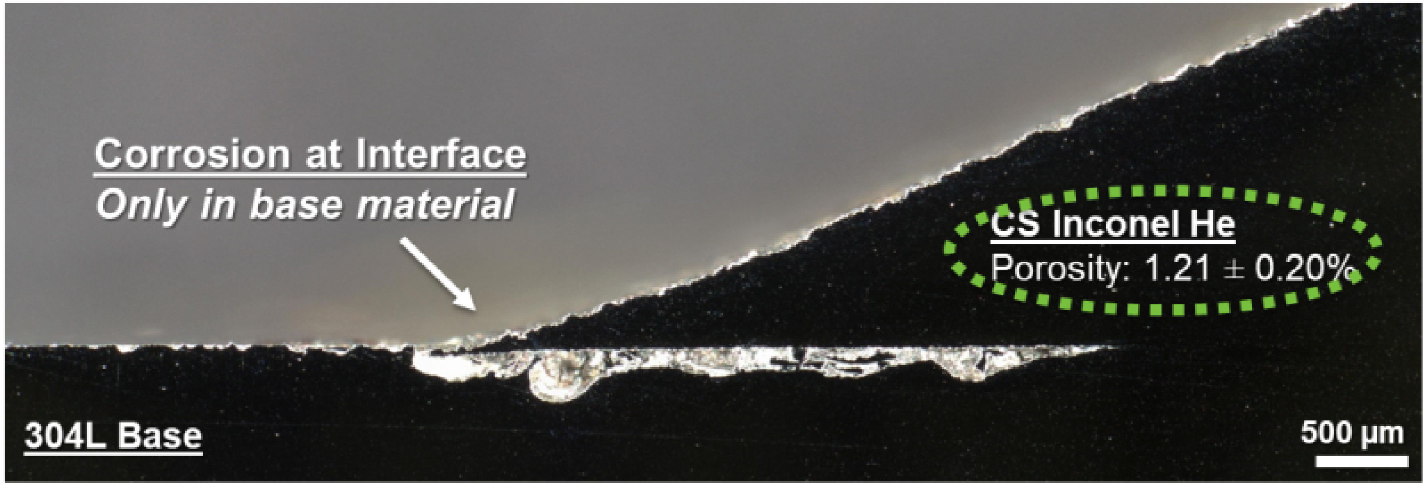
**** Attack at interface influenced by sample porosity and material***

SNL – PNNL collaboration:
Cold Spray – Accelerated Corrosion Testing – Processing Gas









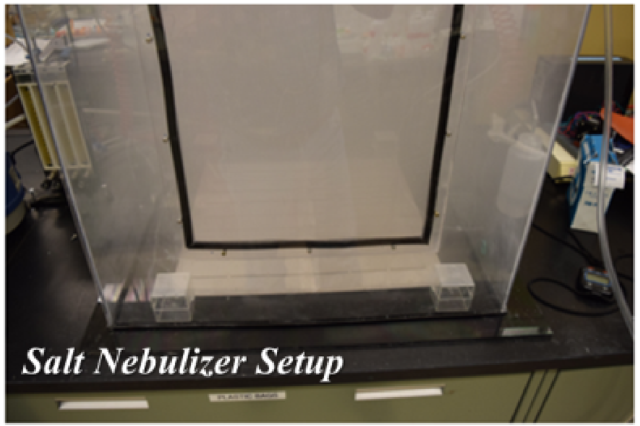
**** Process gas can influence porosity and thus corrosion at the interface***

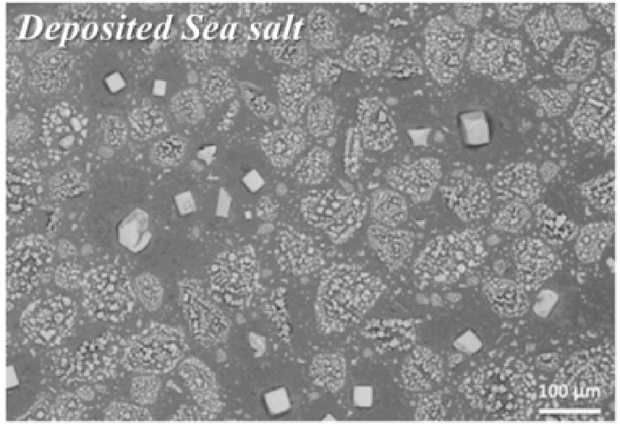
SNL – PNNL collaboration:
Cold Spray – Atmospheric Corrosion Testing

Deposited 300 µg/cm^2 of Artificial Sea Water on CS Surface

Three Atmospheric Exposure Conditions

1. Static 40% RH; 35 °C
2. Static 75% RH; 35 °C
3. Cyclic – at right

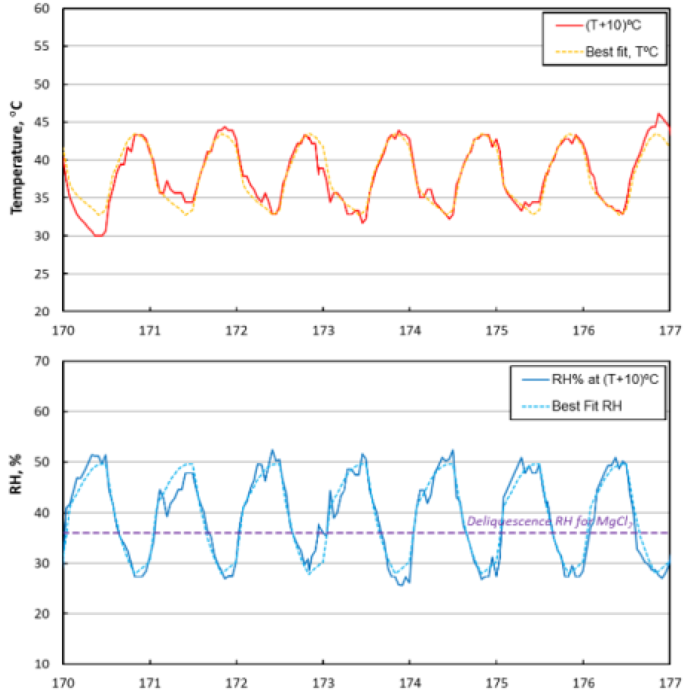




Note: Exposure conditions 1 and 3 below NaCl deliquescence RH, whereas 2 is above (influences brine composition and volume)

Hour	Temperature, °C	RH, %
2	41.68	30.33
4	36.45	41.68
6	35.27	43.92
8	34.35	46.69
10	33.69	48.68
12	32.74	49.54
14	33.44	49.57
16	38.24	40.98
18	40.55	34.62
20	42.69	30.62
22	43.51	27.82
24	42.97	29.15

Diurnal T and RH fluctuations

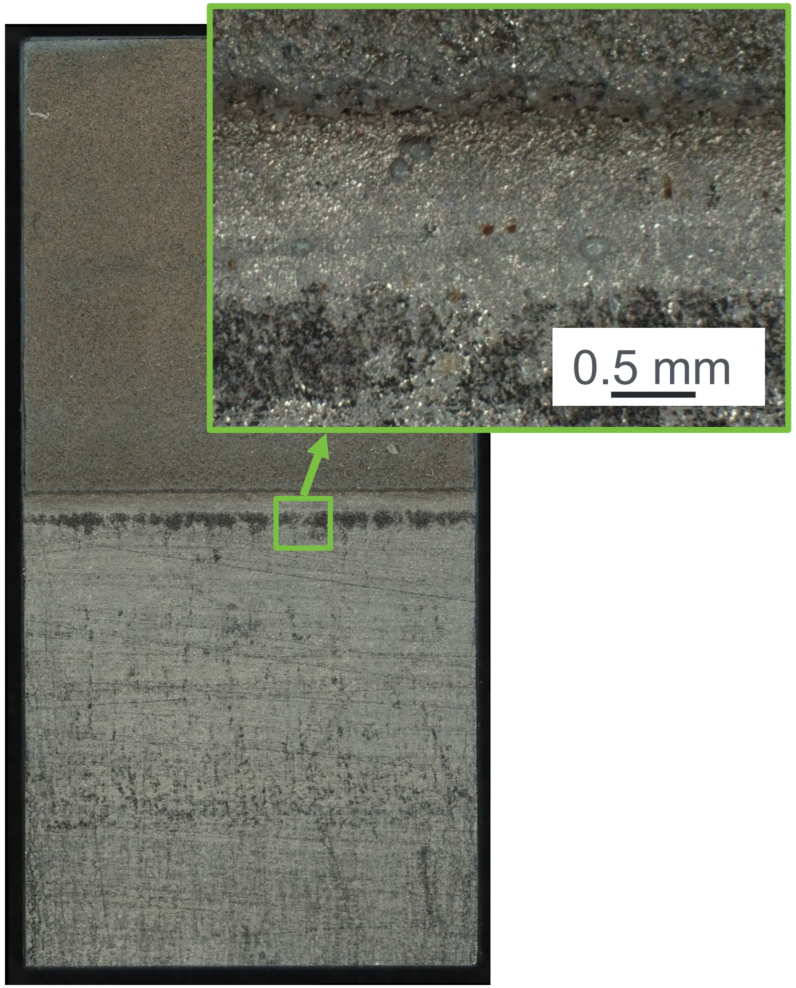


Cyclic atmospheric conditions developed from Arkansas Nuclear 1 ISFSI (SNL 2021 M2)

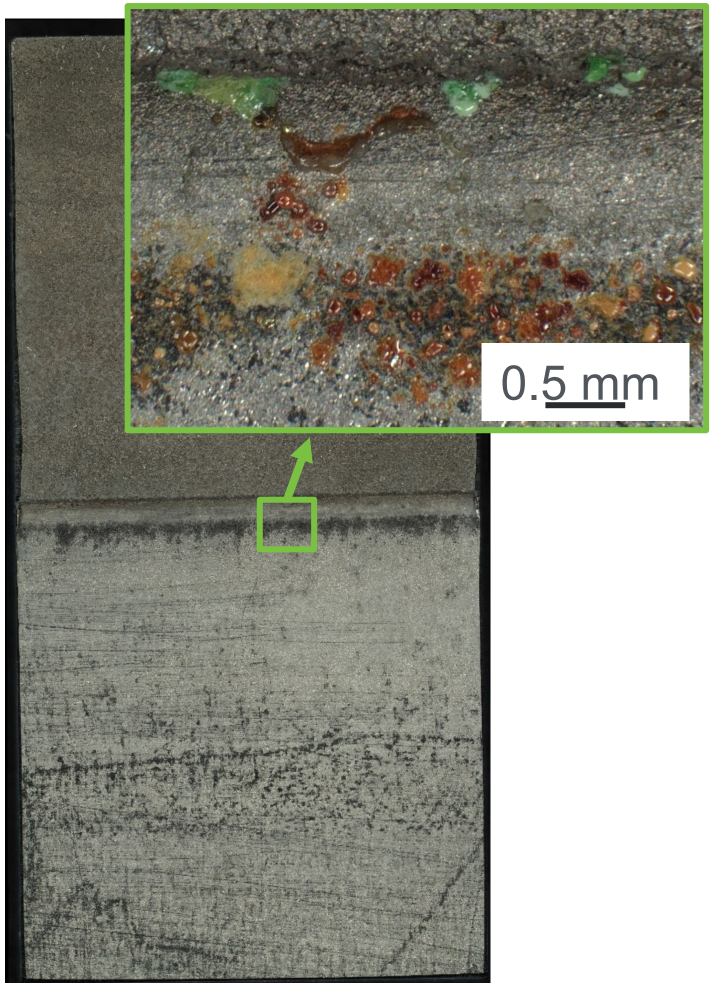
SNL – PNNL collaboration:

Cold Spray – Atmospheric Corrosion Testing

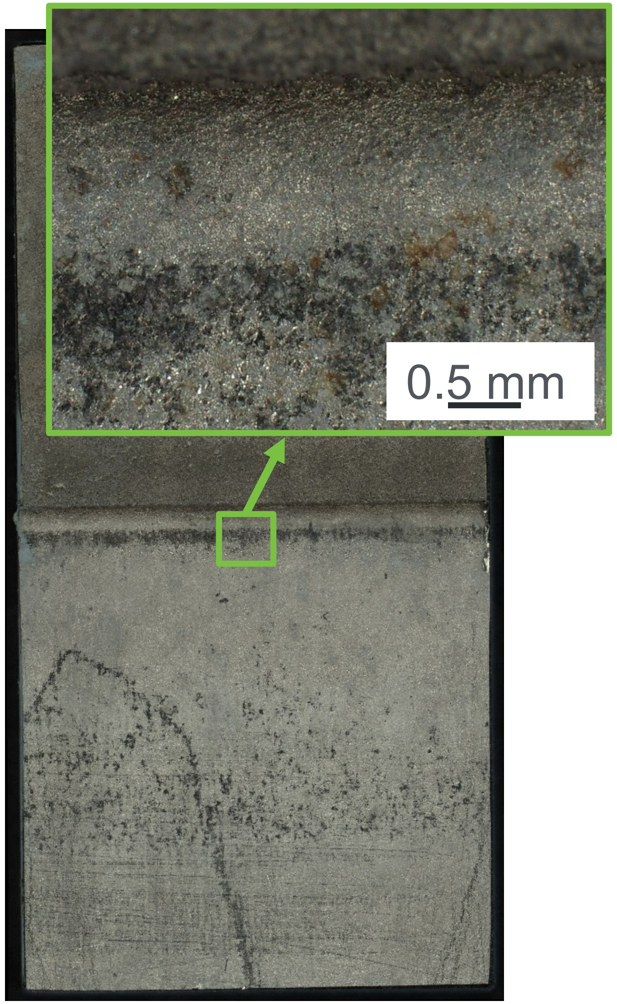
Attack at interface observed, initial optical observations show enhanced attack at higher RH – exposure ongoing



1) 40% RH



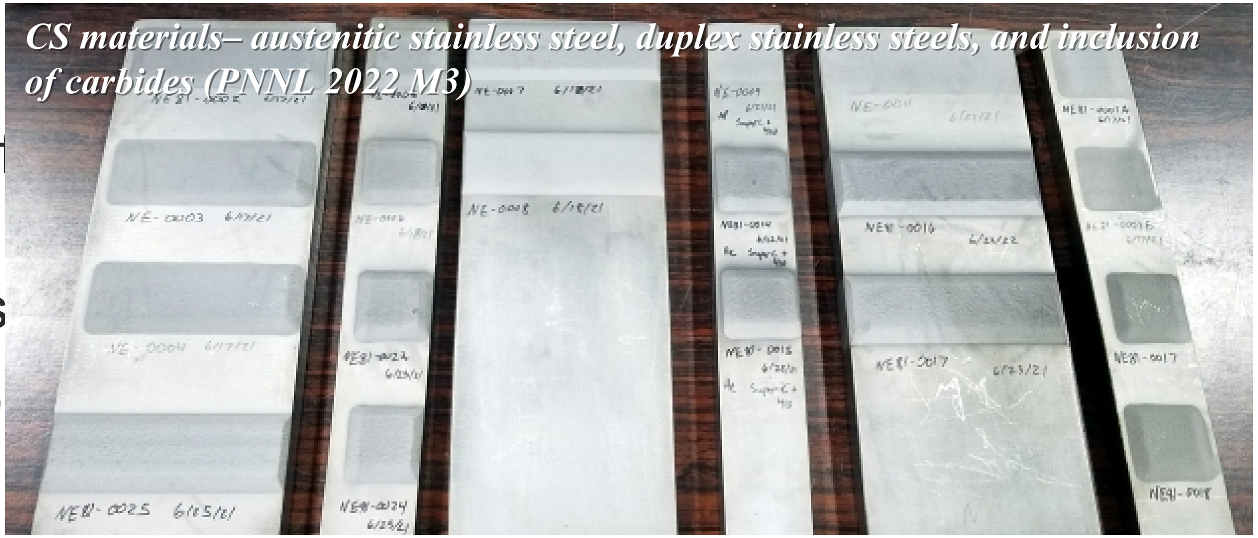
2) 75% RH



3) cyclic

Summary: Initial Gaps Identified and Future Work - CS

- **Cold Spray**
  - Material selection for cold spray is signi
    interface or defect)
  - Process carrier gas can influence poros
  - Edge processing can influence corrosio
  - ***<u>Gaps:</u>***
    - ***Understand and develop methods to reduce potential vulnerabilities at the CS-base interface***
    - ***Understand influences of deformation*** *(and potential microstructural transformation) – compressive residual stress at interface not significant to limit corrosion under accelerated testing conditions*
    - ***Enhance materials selection*** *– can galvanic influences be reduced?*
    - ***Optimize processing*** *– can gas selection or CS powder mixing reduce porosity, increase hardness, and enhance corrosion resistance?*
    - ***Long term behavior of CS in environment of interest*** *– have initiated this testing, but need further information (under stress, other chemistries, etc.)*



CS materials– austenitic stainless steel, duplex stainless steels, and inclusion of carbides (PNNL 2022 M3)

Acknowledgements

We would like to acknowledge the contributions of the following Sandians: Ryan Katona, Greg Koenig, Jason Taylor, Makeila Maguire, Luis Jauregui, and Sara Dickens.

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Questions?