

Pipeline Materials Technologies for Mitigating Corrosion, Methane Emissions, and Hydrogen Embrittlement



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FWP 1022424 Task 3



2024 Resource Sustainability Project Review Meeting

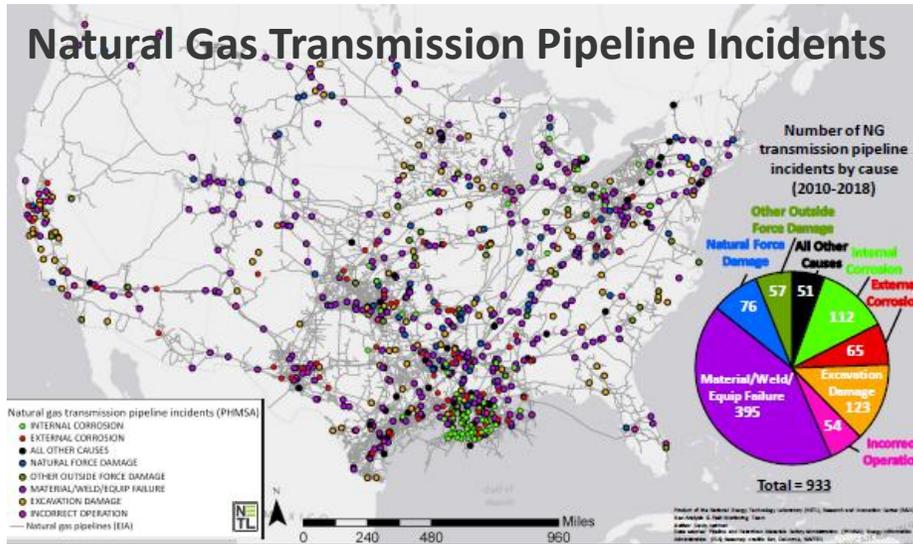
Acknowledgements

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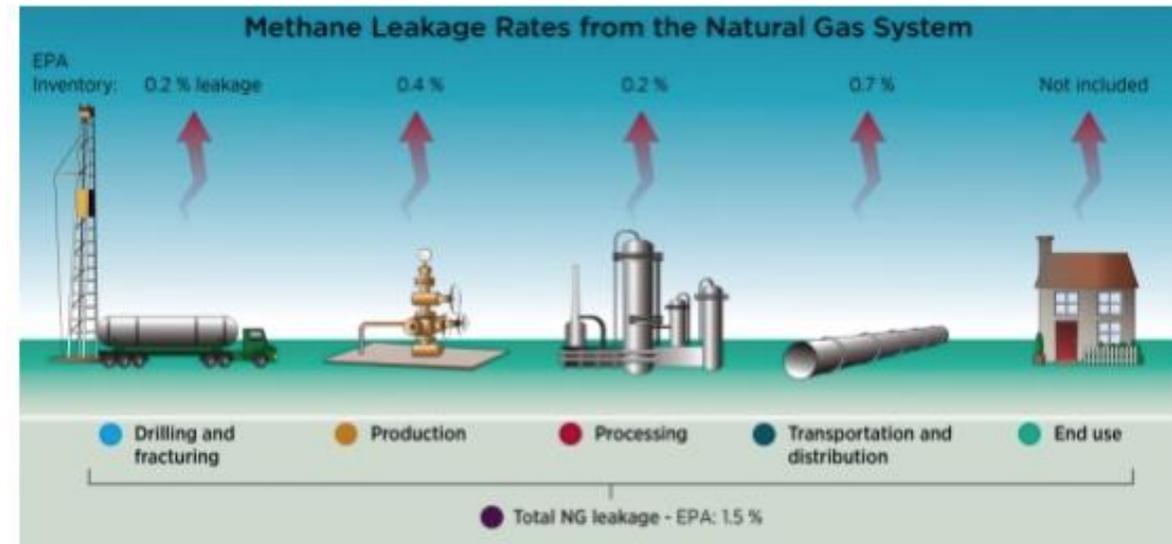
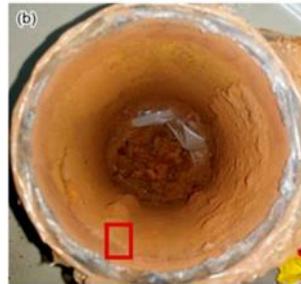
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Natural Gas Infrastructure – Materials Challenges



Internal corrosion



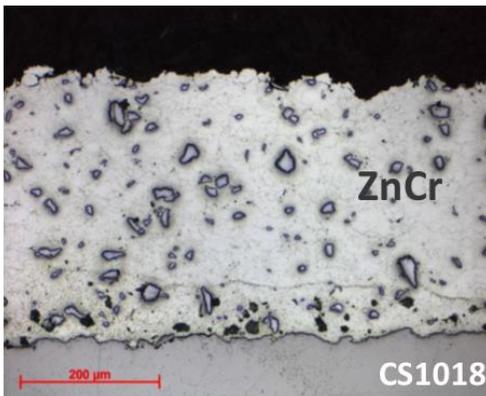
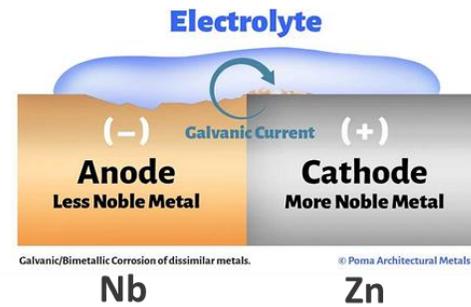
<https://www.news.ucsb.edu/2014/013953/americas-leaky-natural-gas-system-needs-fix>

Justman, Rose & Bauer, NETL, 2017. Data analyzed from U.S. DOT PHMSA incident data

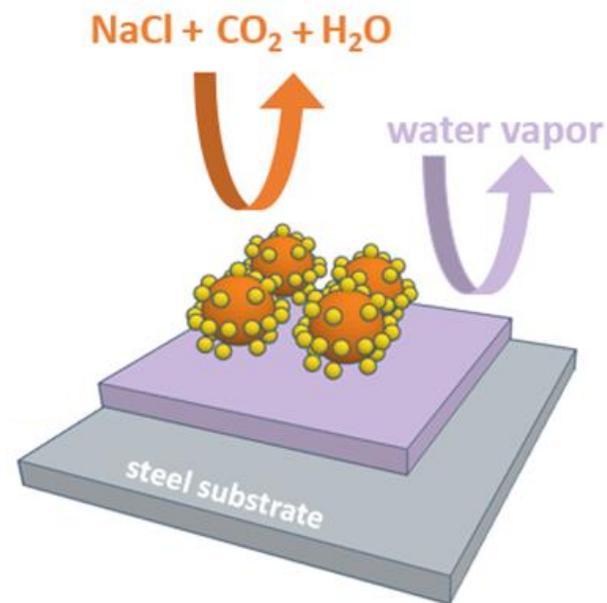
- Methane emissions
- Internal corrosion
- Cost-effective refurbishment of in-service pipes
- Hydrogen compatibility
- Remote monitoring

Mitigation – NETL Approach

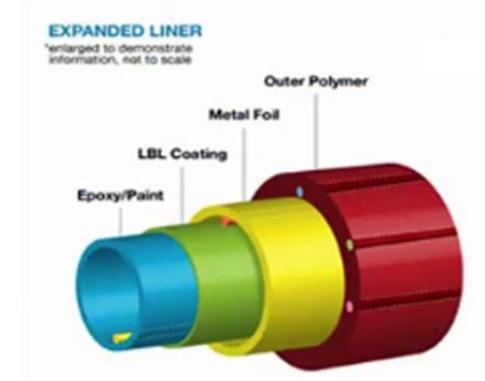
Self-Healing Metallic Coatings



Superhydrophobic Anti-Corrosion Coatings

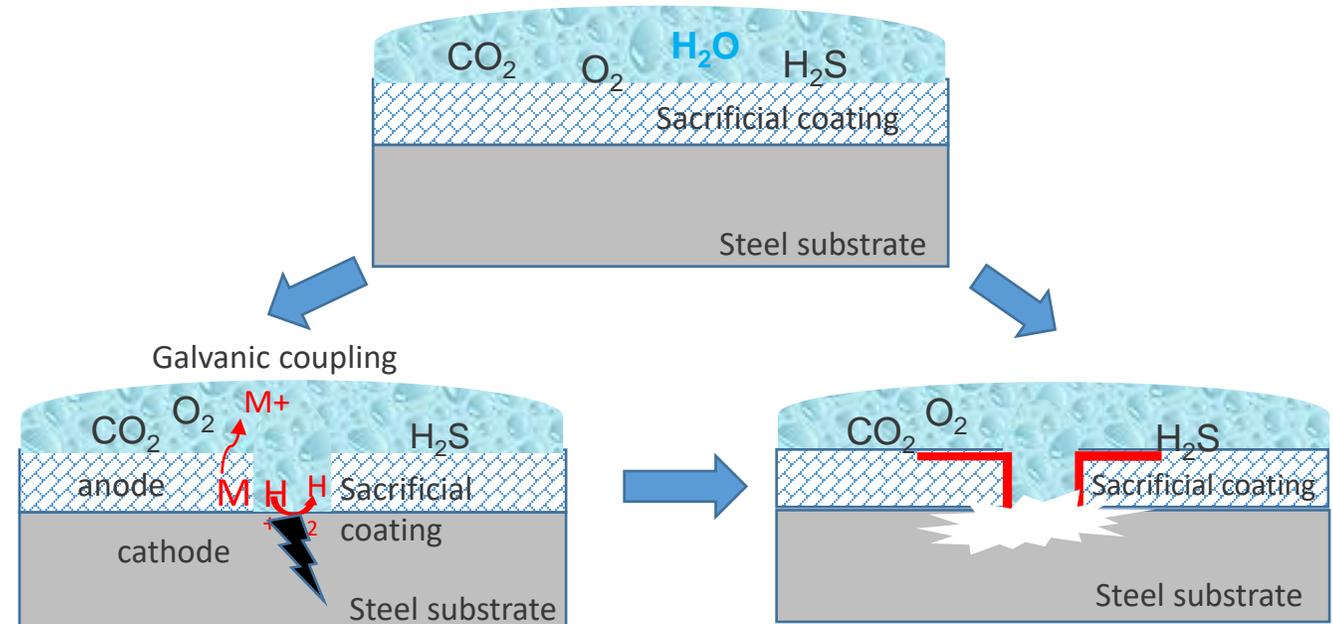
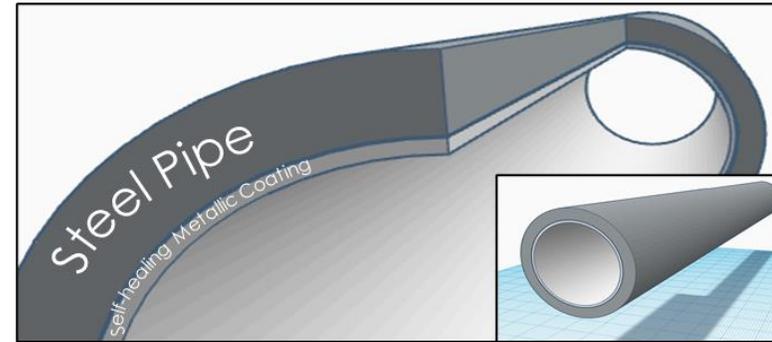


Composite Liners



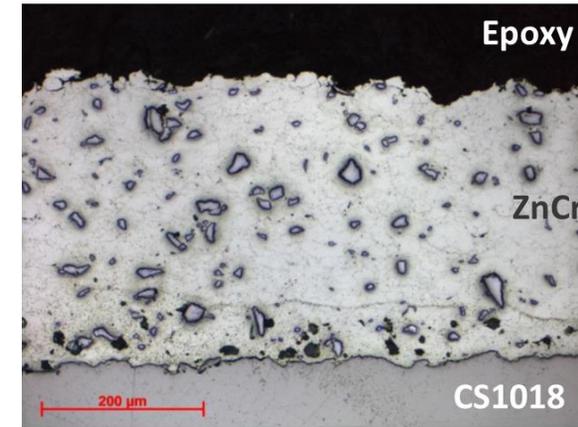
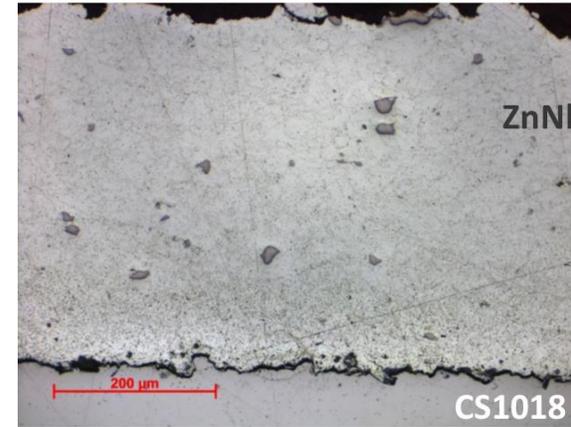
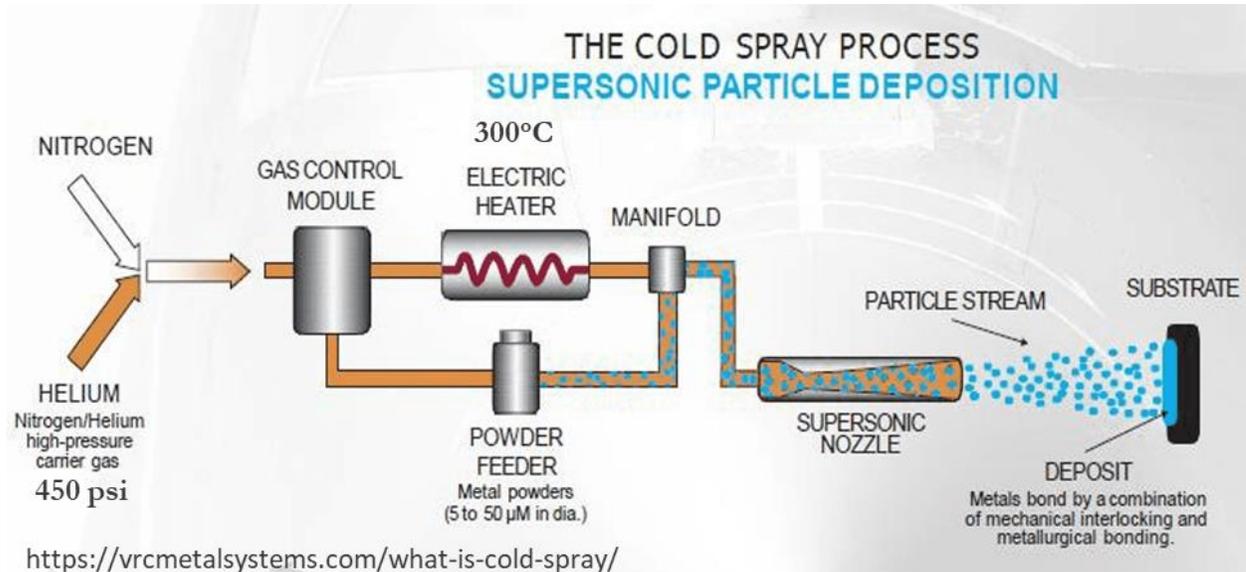
Self-Healing Metallic Coatings

- Sacrificial coatings are used for corrosion protection.
- Zinc is a common sacrificial coating.
- However, Zn corrodes too fast in NG pipeline conditions.
- Can we slow Zn corrosion inside NG pipelines?
- Can we form *micro galvanic cells* to control Zn corrosion?



Self-Healing Metallic Coatings

Cold Spray Coating Technology

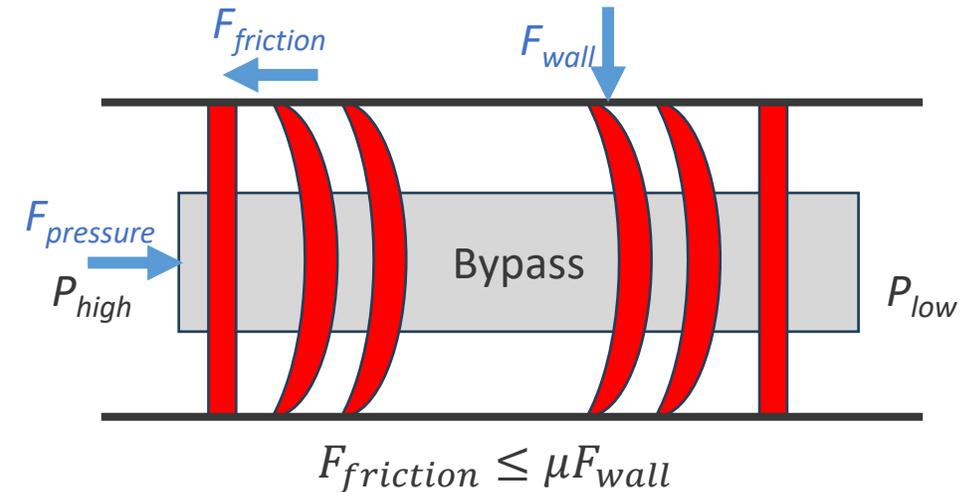
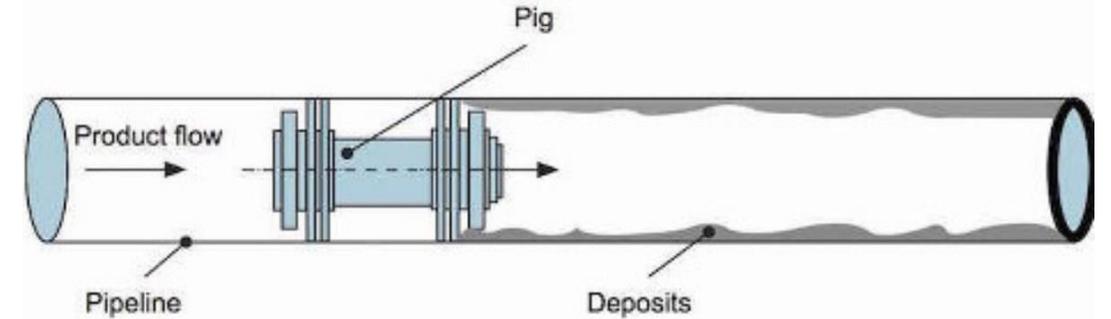


Coatings	Thickness (μm)	Porosity (%)
ZnNb	428 ± 5.1	$\approx 0.32 \pm 0.13$
ZnCr	304 ± 7.0	$\approx 0.5 \pm 0.28$

Self-Healing Metallic Coatings - Mechanical Testing

Forces imparted by pigging on cold-sprayed self-healing coatings

- Most forces on coatings during the pigging process will be:
 - Wall (compressive)
 - Friction (shear)
- Testing for **shear adhesion** and **wear properties** will determine the viability of these coatings to mechanical pigging.



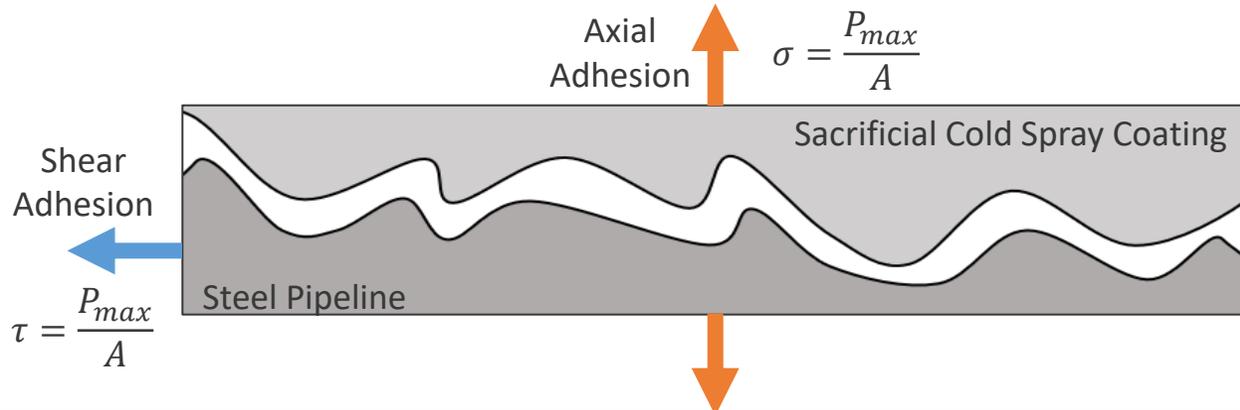
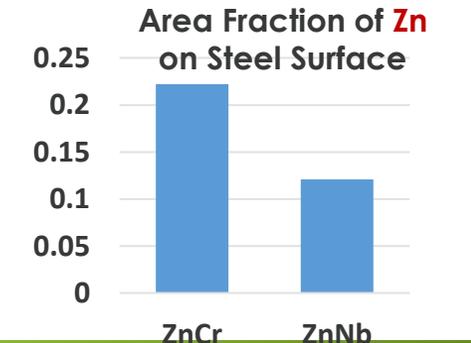
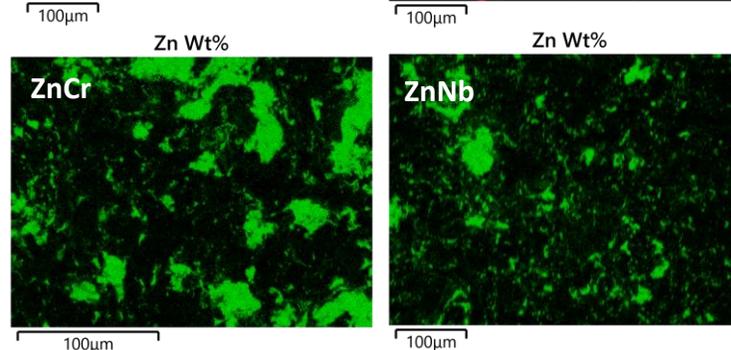
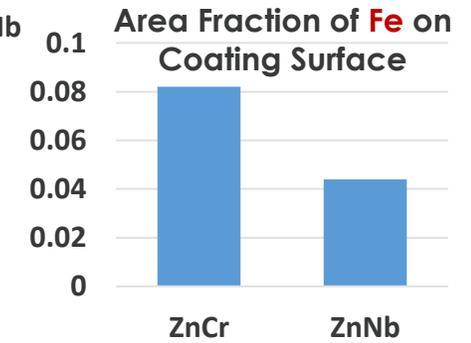
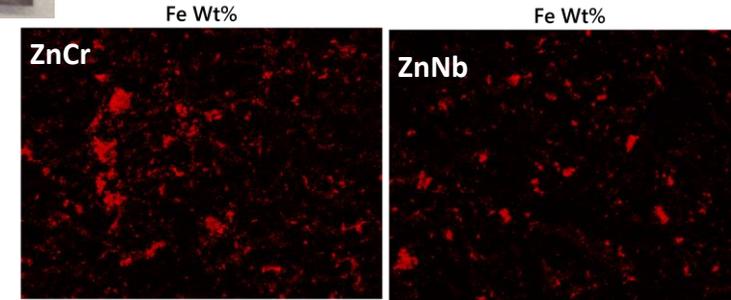
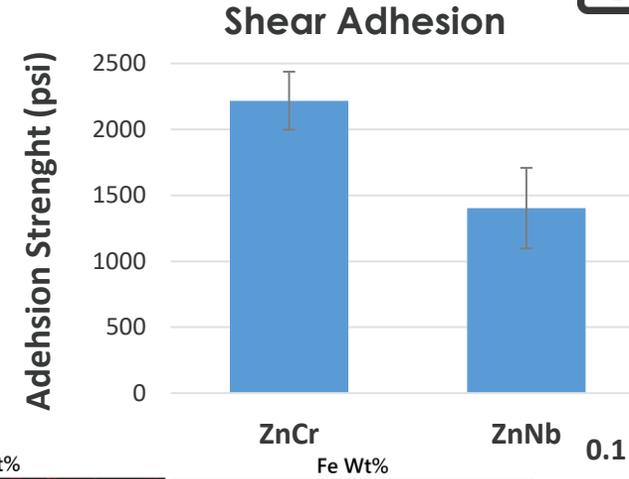
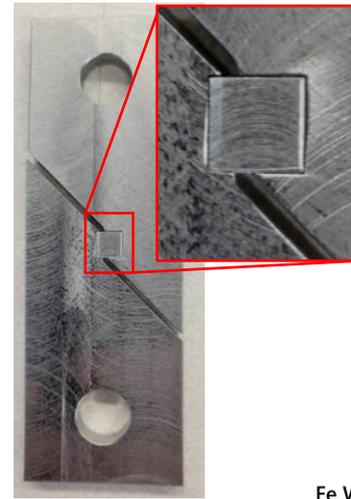
$$\tau = \frac{P_{max}}{A} \text{ [MPa] (PSI)}$$

$$\text{wear} = \frac{CW_x}{\rho S_x} \text{ [mm}^3\text{/Nm]}$$

Self-Healing Metallic Coatings

Shear Adhesion Testing

- Most forces on coatings during the pigging process will be friction (shear).
- Shear testing clevises were fabricated, and results were tabulated for both maximum shear strength (modified ASTM B 831).
- Fracture surfaces were imaged for elemental composition on both fracture surfaces.
- Shear adhesion appears to correlate with area fraction of elements left on opposing surfaces.
- Shear adhesion and axial adhesion measurements were not correlated.



Self-Healing Metallic Coatings

Pin-on-Drum Wear Test

- Wear properties of the zinc cold spray coatings is similar though slightly higher than pure zinc.
- The wear rate of zinc and the zinc cold spray coatings is approximately three times that of the underlying X65 pipeline material.

$$\text{wear} = \frac{CW_x}{\rho S_x} \left[\text{mm}^3 / \text{Nm} \right]$$

where:

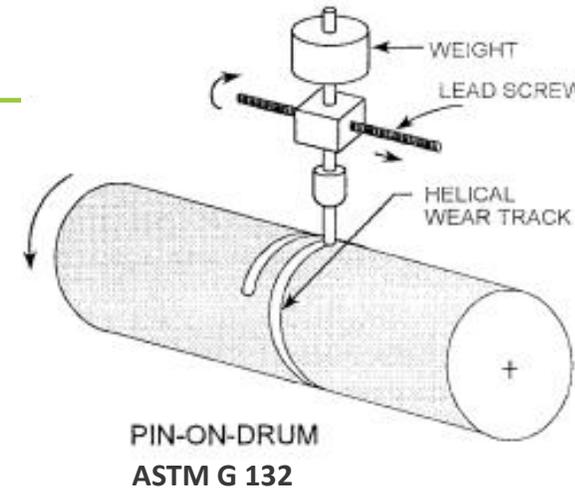
W_x = mass loss of the test specimen

S_x = mass loss of the reference specimen

ρ = density of the test specimen, known or measured to three sig figs g/cm^3 (mg/mm^3)

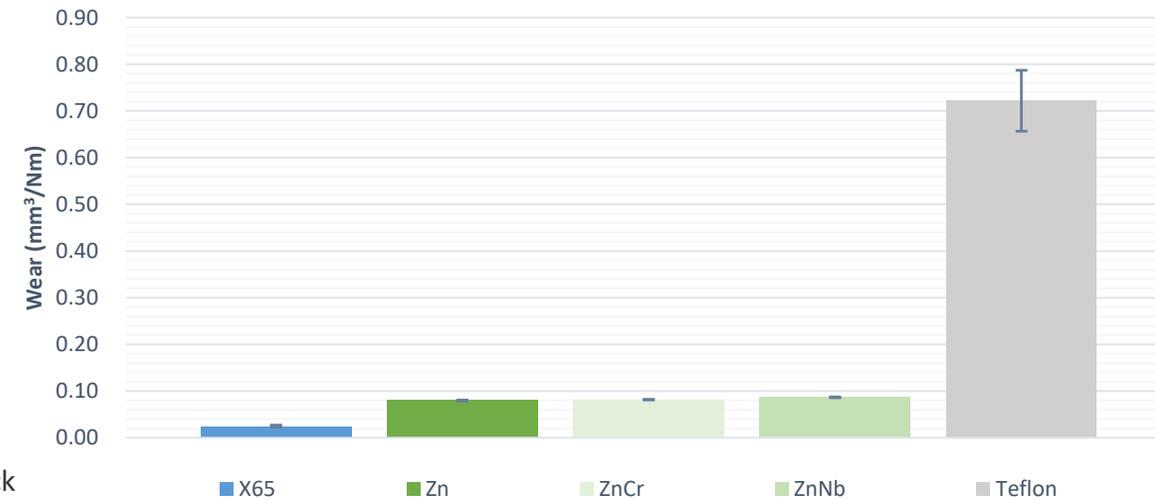
C = reference constant equal to the mean mass loss (mg) of the reference pin per unit track length (m) per unit load (N), for the abrasive type and test parameters used. (The ratio $C:S_x$ functions as a normalizing factor).

The value of the constant C for a given reference material and abrasive is determined from a large number of tests, preferably in several machines and/or locations



Testing Conditions

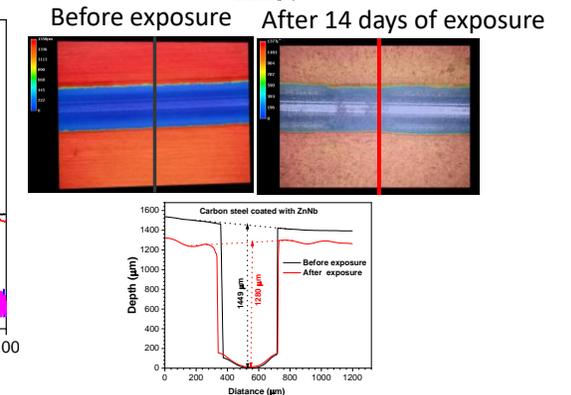
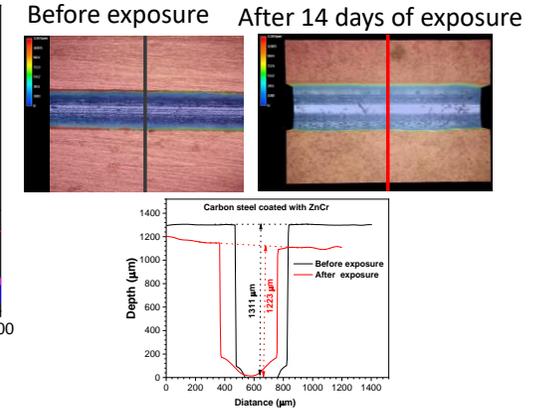
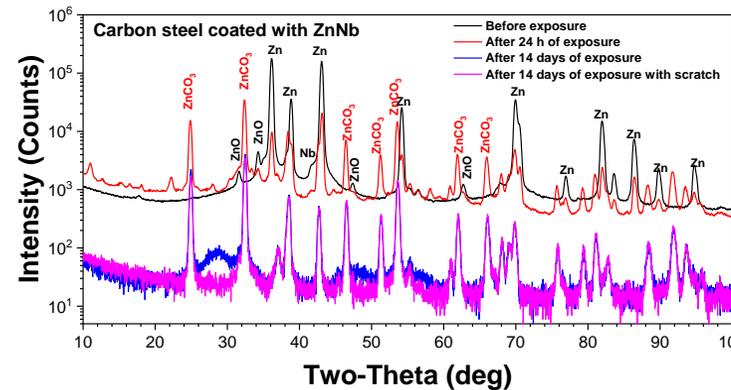
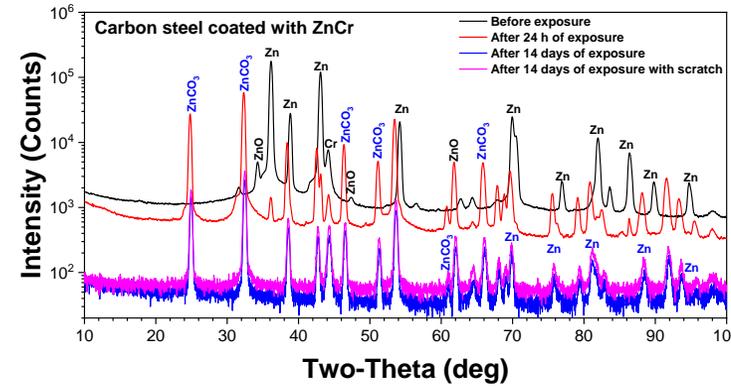
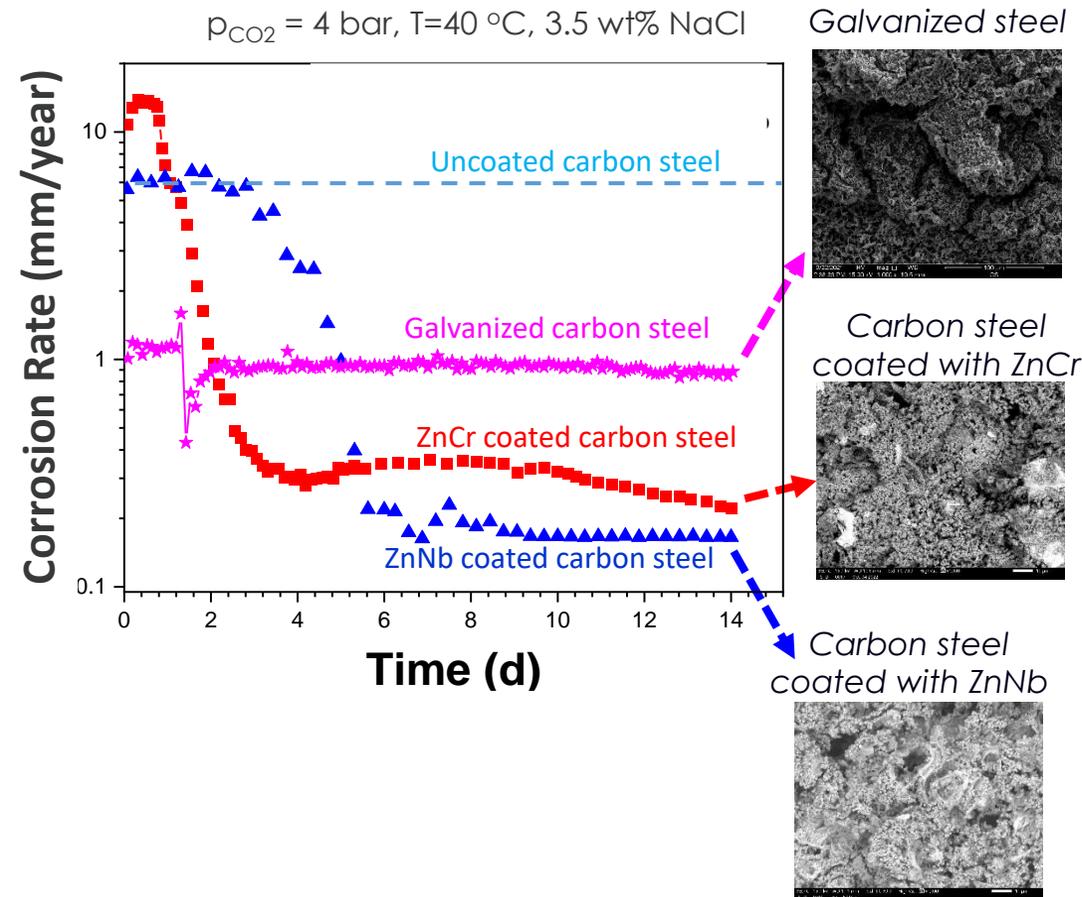
Abrasive	Force, N	distance, m
150 grit SiC	65.47	3.2



Self-Healing Metallic Coatings

✓ Laboratory corrosion test

✓ Self-healing properties

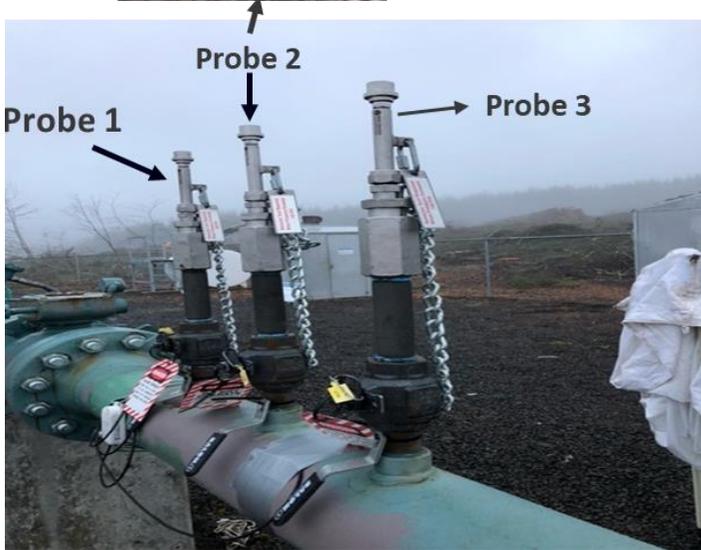
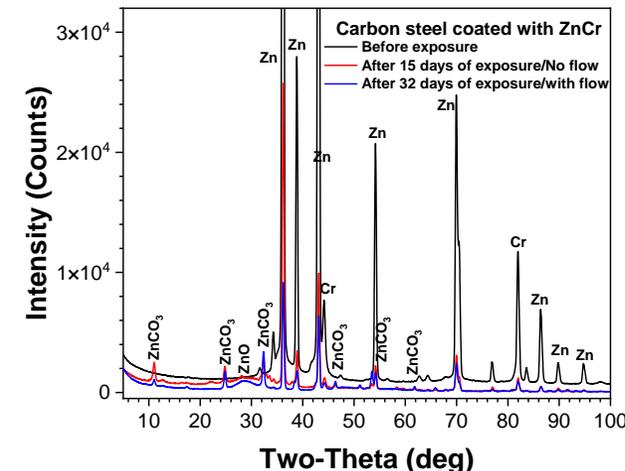
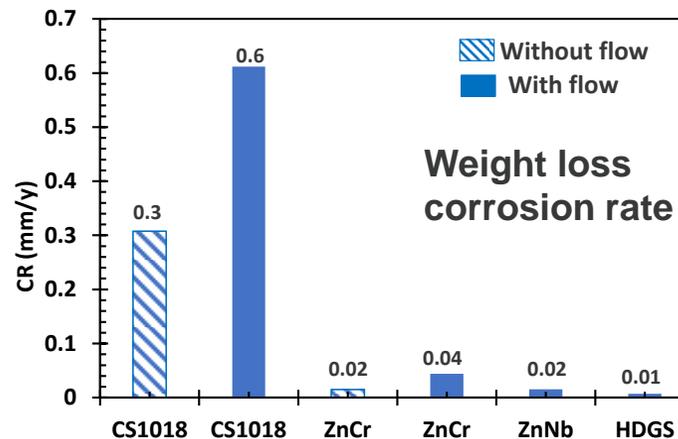


Z. Belarbi et al., "Binary Sacrificial Coatings for Internal Corrosion Protection of Natural Gas Transmission Pipelines," in ECS Meeting Abstracts MA2022-01-0686, 2022.

Self-Healing Metallic Coatings – Coated Coupons in Pipeline

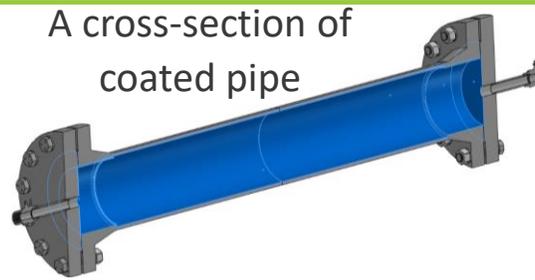
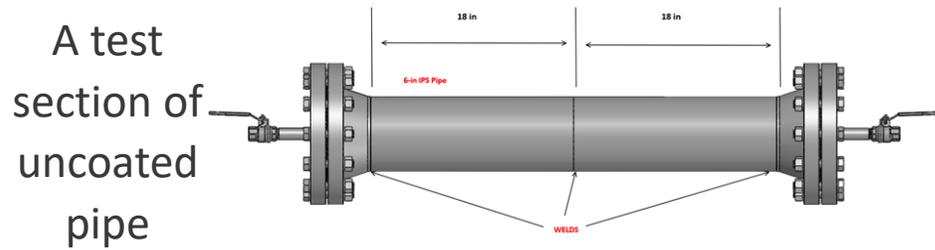
Field Test at NW Natural Gas Storage Facility - TRL 5

Probes removed after 32 days of exposure to natural gas under flow



Coating	SEM Image	EDS Image	C Ka1,2	Zn La1,2	Cr Ka1	O Ka1	S Ka1
CS1018 coated with ZnCr after 32 days of exposure with flow	SEM showing ZnCr coating and corrosion product	EDS showing ZnCr coating and corrosion product	25µm	25µm	25µm	25µm	25µm
CS1018 coated with ZnNb after 32 days of exposure with flow	SEM showing ZnNb coating and corrosion product	EDS showing ZnNb coating and corrosion product	25µm	25µm	25µm	25µm	25µm
Galvanized steel after 32 days of exposure with flow	SEM showing Zn coating and corrosion product	EDS showing Zn coating and corrosion product	50µm	50µm	50µm	50µm	50µm

Self-Healing Metallic Coatings – Coated Pipe Test (TRL 6)

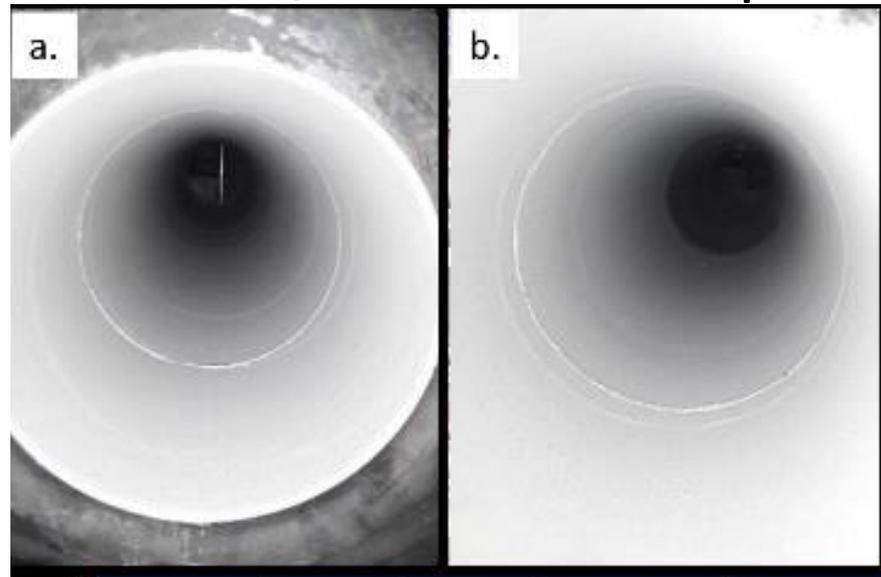


Field Test Parameters	Specification
Line pressure	500 psi to 1000 psi*
Flow Rate	Stagnant condition
Natural Gas Characteristics	Untreated (corrosive)
Test duration	90 days
Pipe diameter	6 inches
Pipe length	3 feet

Cold spray setup at VRC Metal Systems

Pipe inner surface with Zn-Cr top-coat

Pipe inner surface with Zn-Nb top-coat



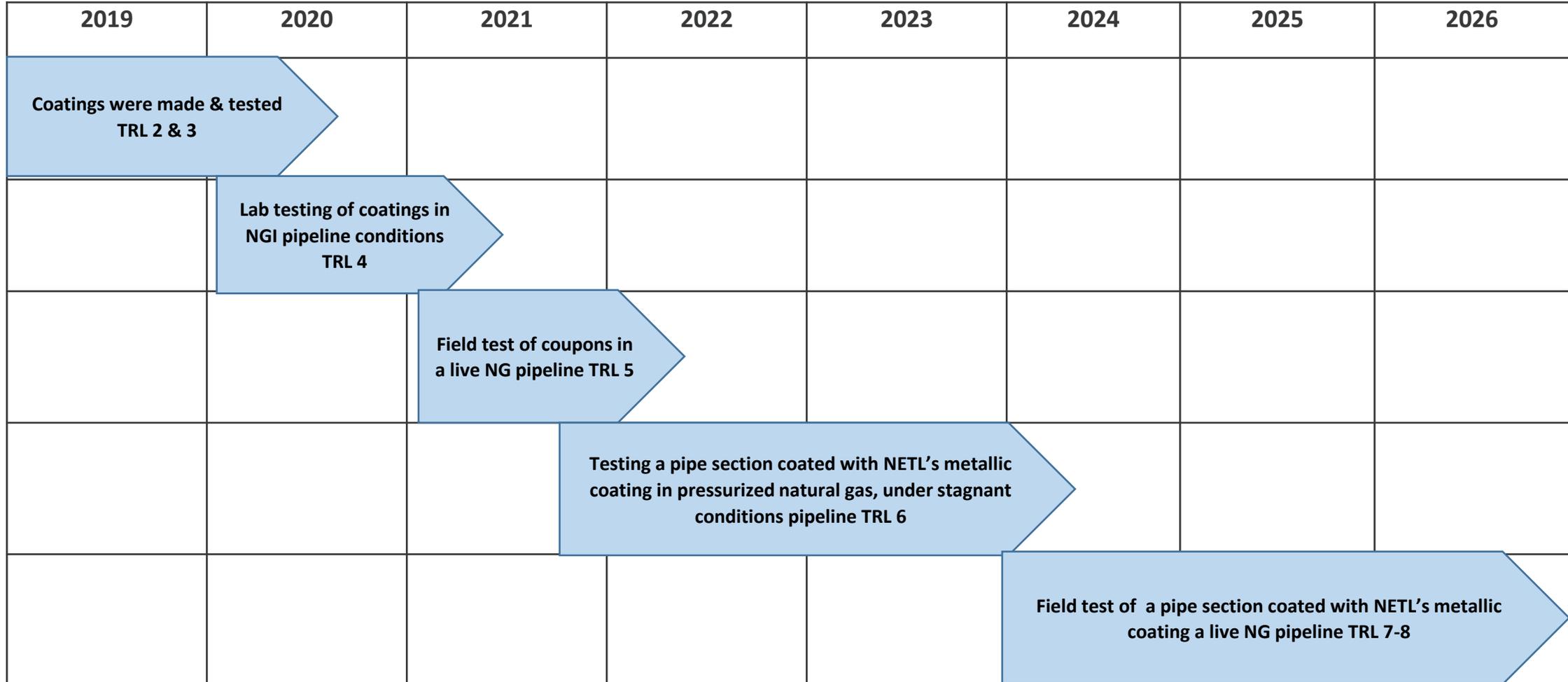
c.	Initial Diameter (In.)	Final Diameter (In.)	Deposition/ Layer (In.)	Total Deposition (In.)	Target Deposition (In.)
	6.048	5.998	0.0017	0.025	0.012-0.016
	6.048	6.02	0.0016	0.014	0.012-0.016



Field Test at NW Natural Gas Company:
 Gas Being Injected Into Test Sample Pipe (right of pipe - Red Hose) to Purge of Air. Verification of 100% Gas on Vertical Vent Pipe with Gas Detector (left of pipe), Indicating Air Purged.

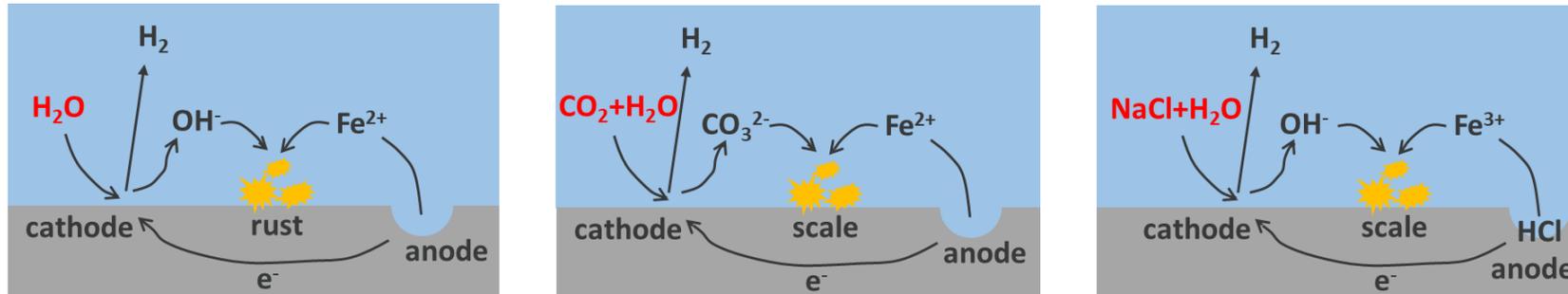
Self-Healing Metallic Coatings

TRL Evaluation & Timeline

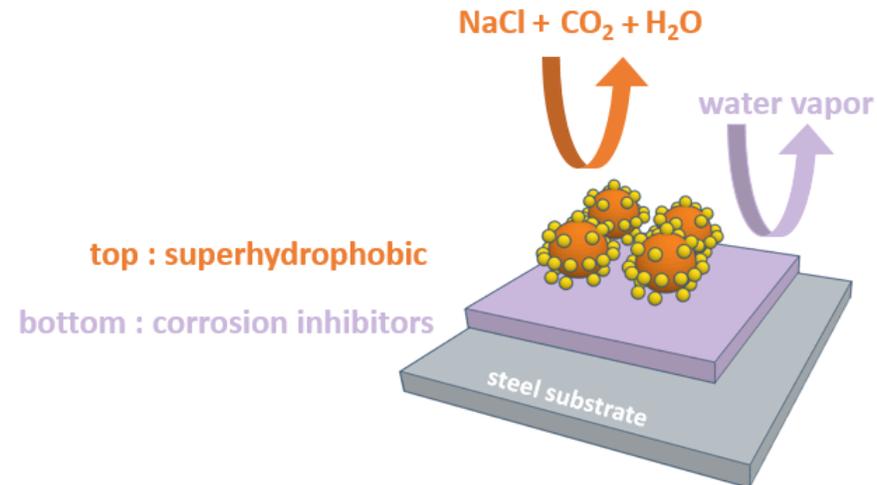


Superhydrophobic Anti-Corrosion Coatings

Three major corrosive species: H_2O , CO_2 , and $NaCl$

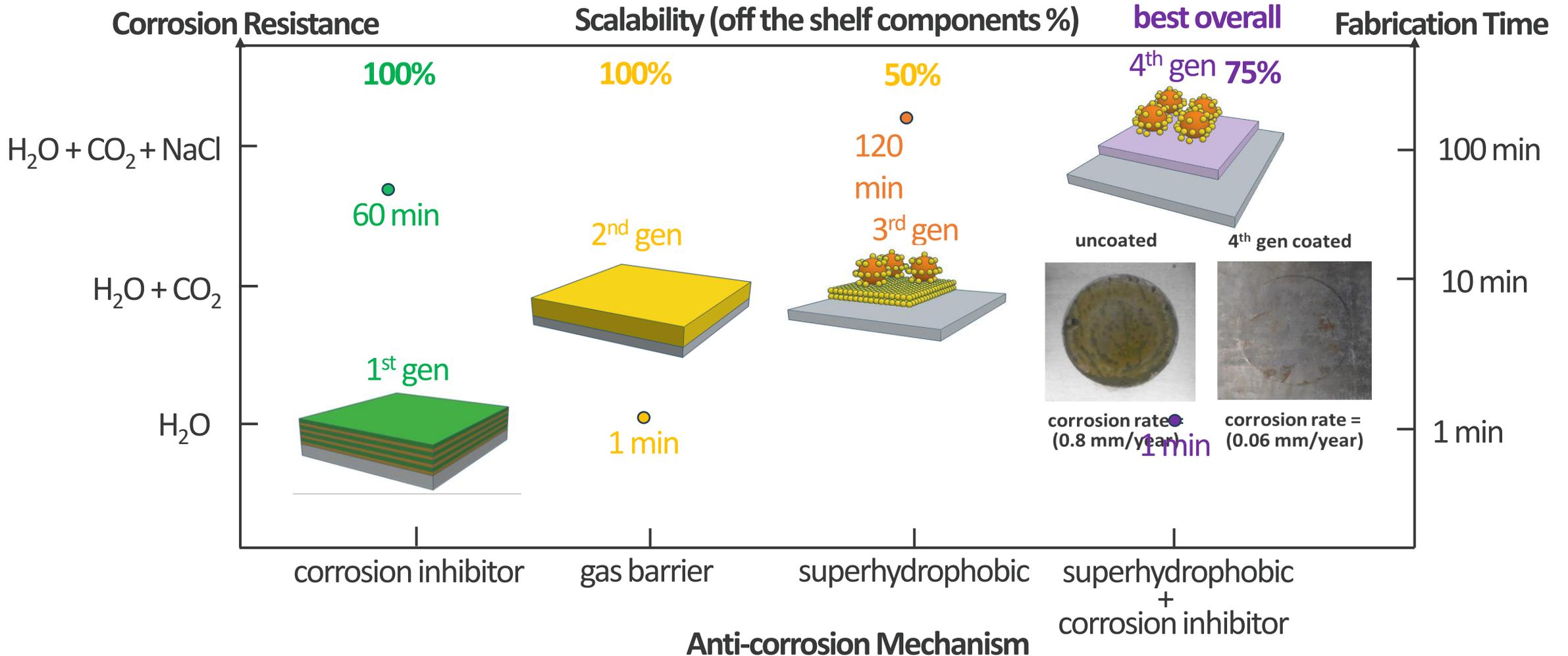


To the best of our knowledge, no existing material can handle all three corrosive species at once. A multilayer coating was developed, with each layer tackling a specific set of corrosive species.



Superhydrophobic Anti-Corrosion Coatings

Evolution of anti-corrosion coatings developed by NETL

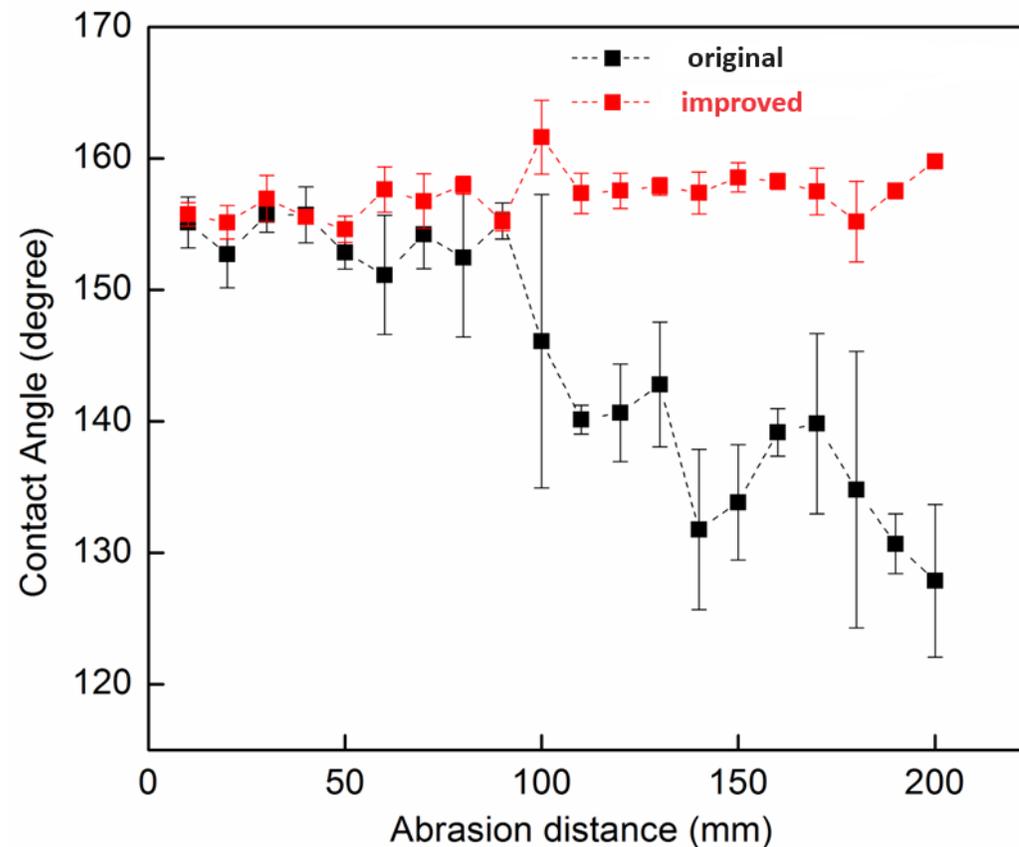
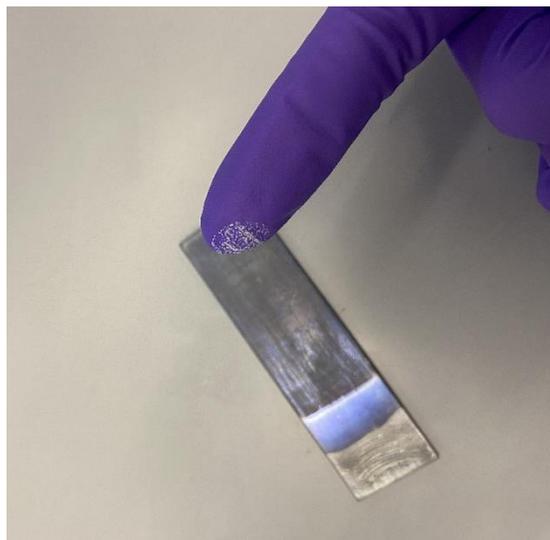


Superhydrophobic Anti-Corrosion Coatings

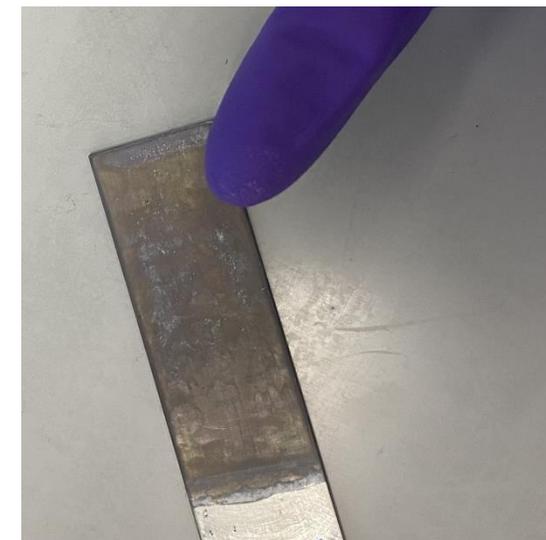
Improve mechanical property

Improving mechanical property without lowering hydrophobicity (contact angle), which can be critical for surviving the field test.

original



improved



dragged across a 600 grit sand paper over different distance

Superhydrophobic Anti-Corrosion Coatings

Field test sample preparation and installation

X65 steel washers were prepared using the new recipe with improved mechanical property.

bare steel



primed



coated



load on sample holder



installation

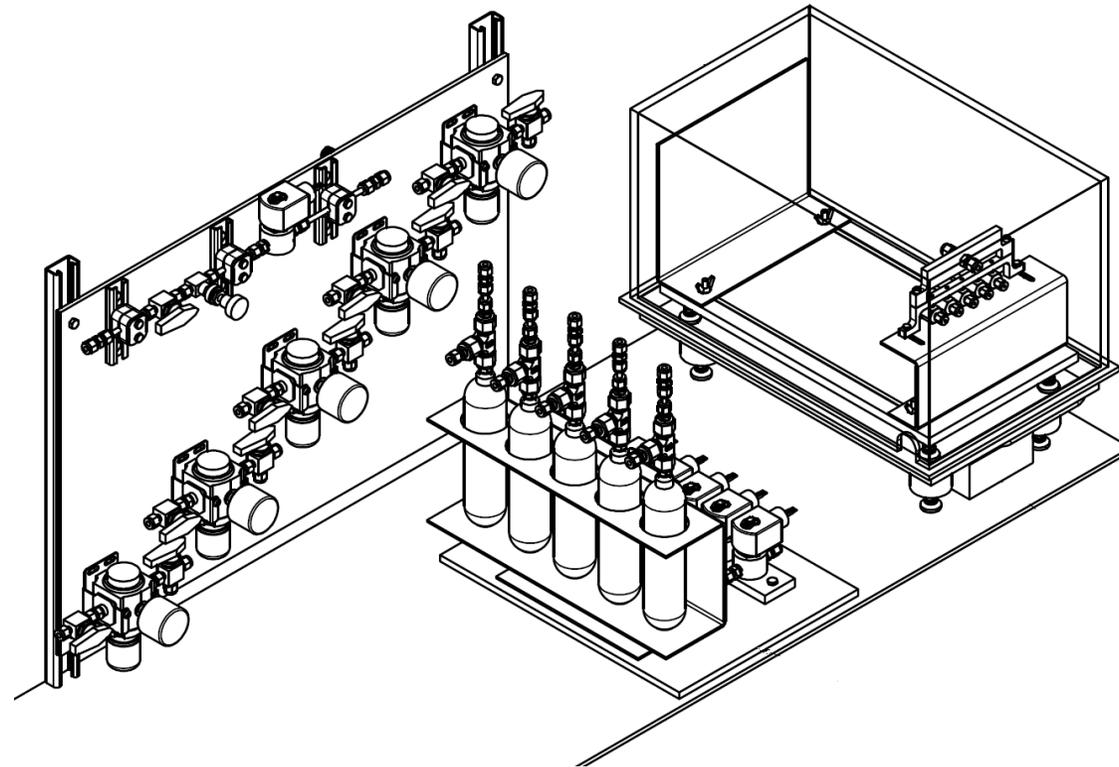


NW Natural Gas Company

Superhydrophobic Anti-Corrosion Coatings

Automation

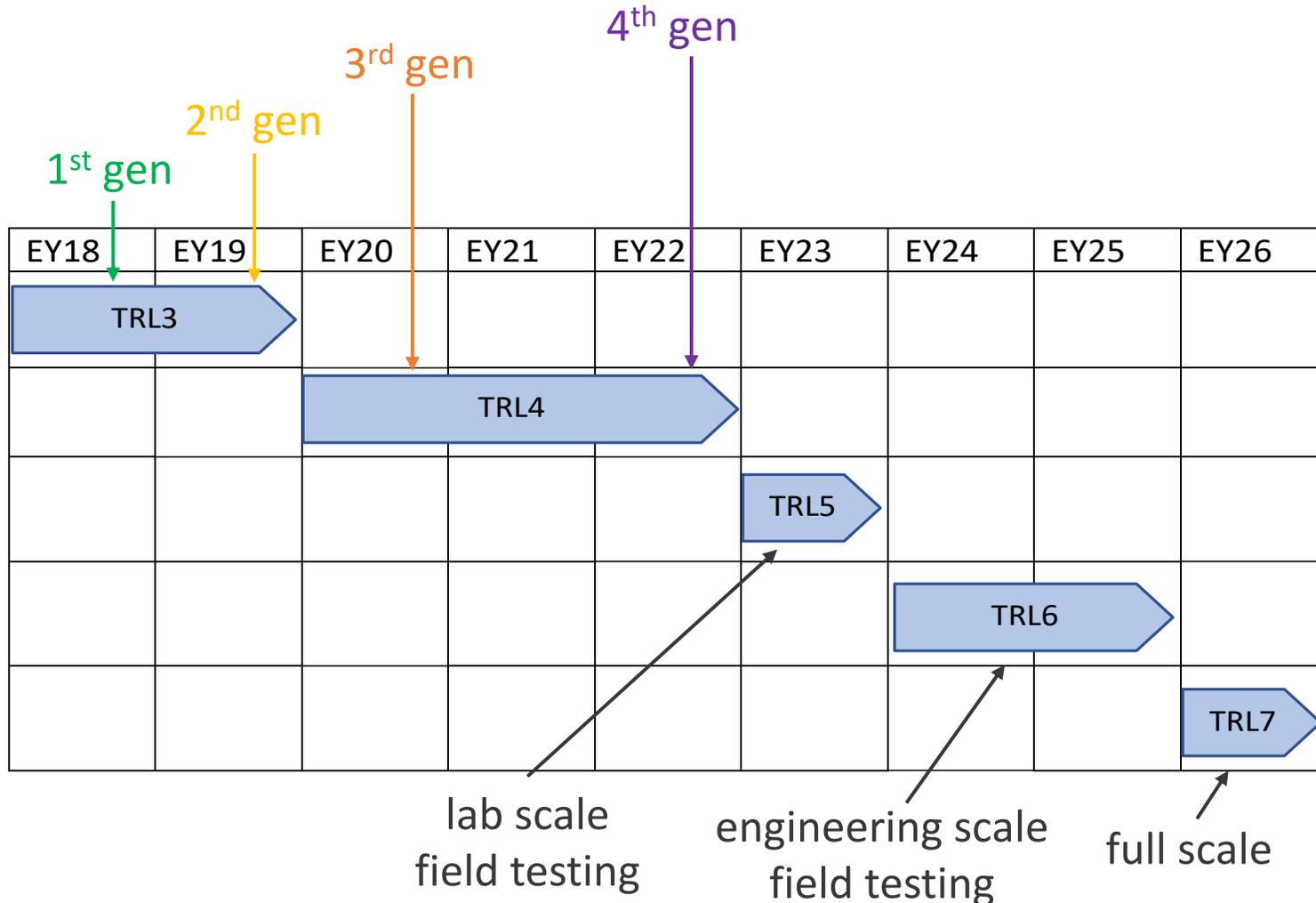
A multi-head spraying system was commissioned to automate the fabrication process and improve reproducibility.



The development in coating composition and fabrication process could further improve scalability.

Superhydrophobic Anti-Corrosion Coatings

Conclusions and future plan



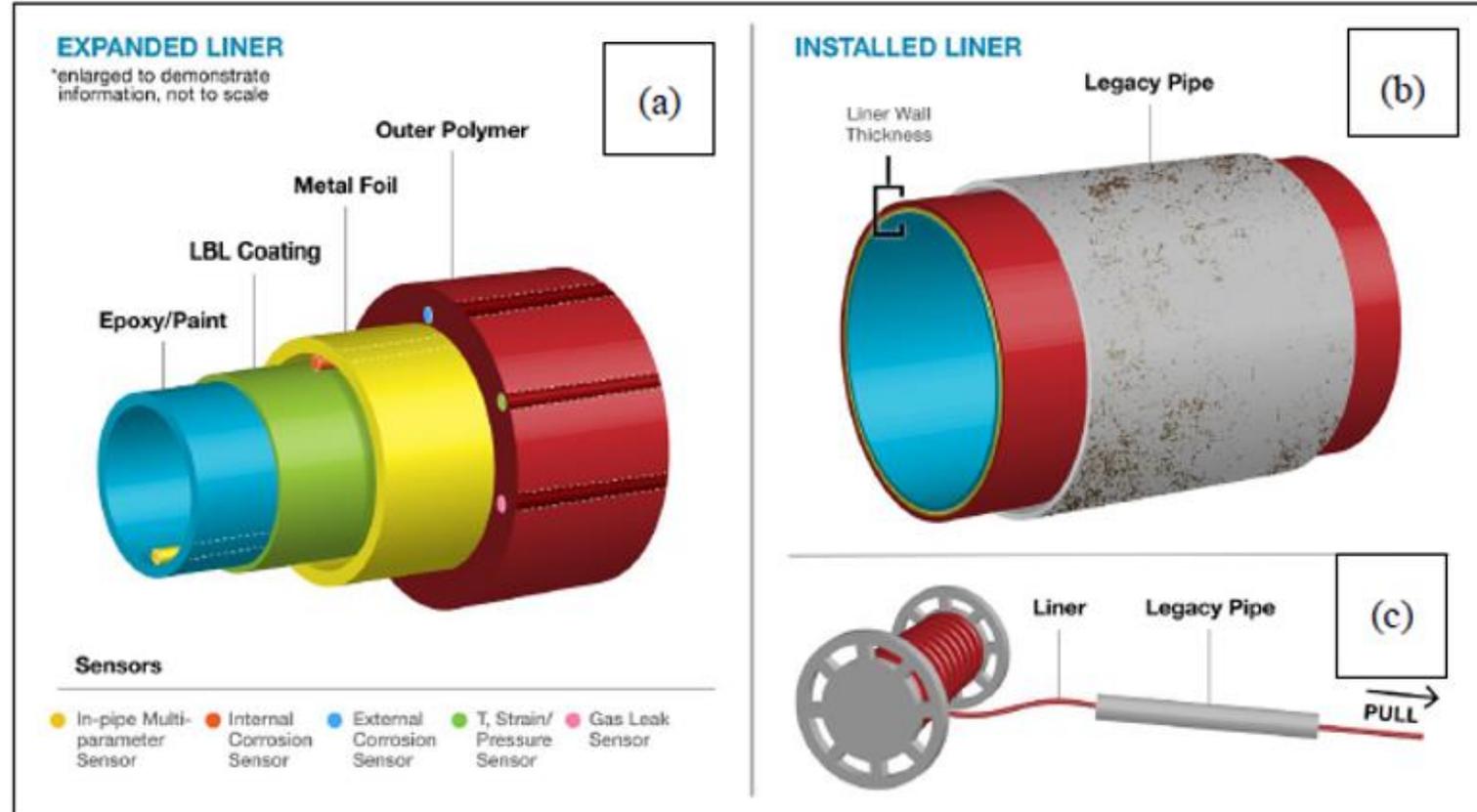
Expected Completion Date	Milestone Description
09/30/2020 ✓	Complete fabrication and corrosion testing of at least two steel coupons with defect-free multilayer coatings.
03/31/2021 ✓	Demonstrate a defect-free, corrosion resistant multilayer coating under continuous CO ₂ bubbling.
03/31/2022 ✓	Demonstrate a multilayer superhydrophobic corrosion-protective coating that can reduce the corrosion rate of carbon steel (API 5L X65 grade) to < 0.1 mm/year under realistic conditions in the laboratory .
09/30/2024	Demonstrate a coated sample that can reduce the corrosion rate of carbon steel (API 5L X65 grade) to < 0.01 mm/year in a live natural gas pipeline.

Passed the internal invention review board; filing a patent application

Goal: simple, scalable, strong, and cost effective

Composite liner for mitigating pipeline corrosion and gas permeation

Liner prototype development with collaborators – Progress and ongoing efforts



An illustration of sensor-embedded composite liner.

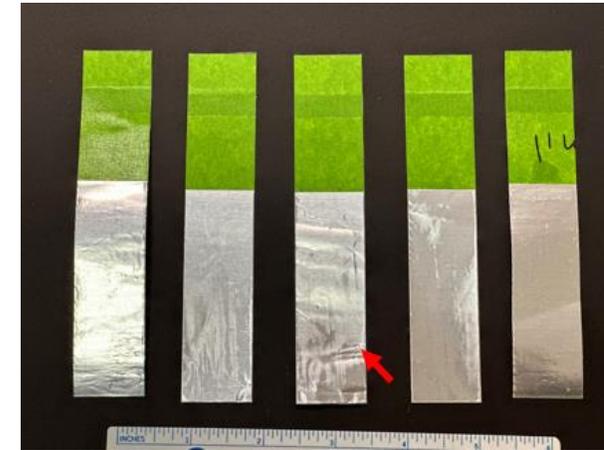
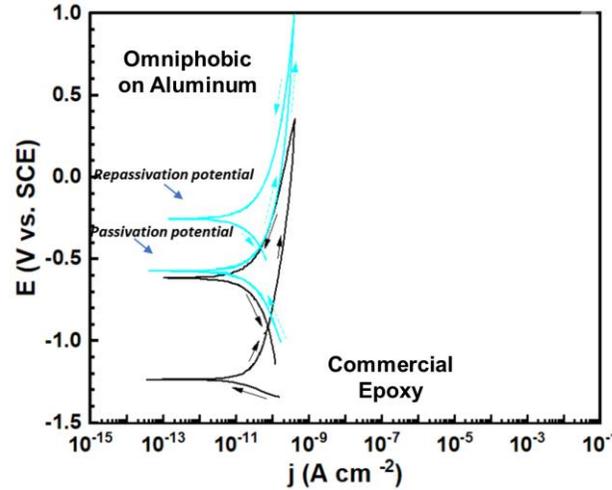
(a) Expanded view showing the individual layers of the liner.

(b) The liner is shown in the existing pipe after installation. (c) Installation process.

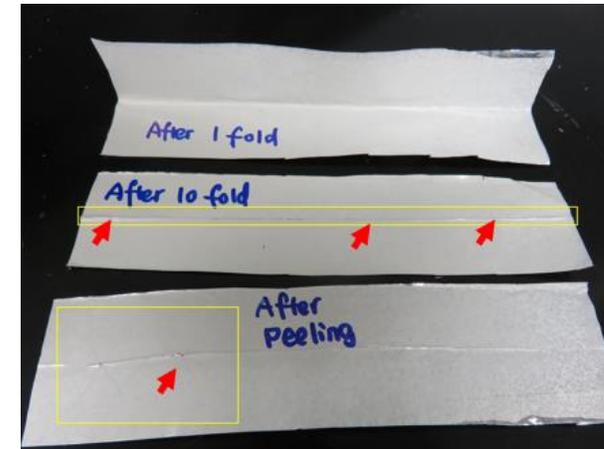
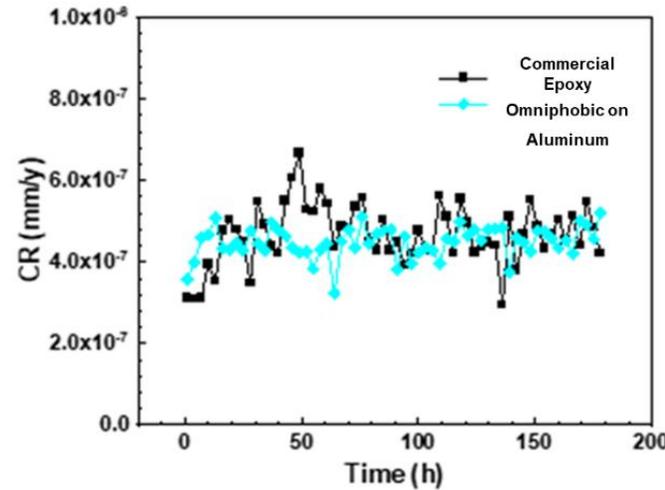
Composite liner for mitigating pipeline corrosion and gas permeation

Inner layer development with collaborators – Progress and ongoing efforts

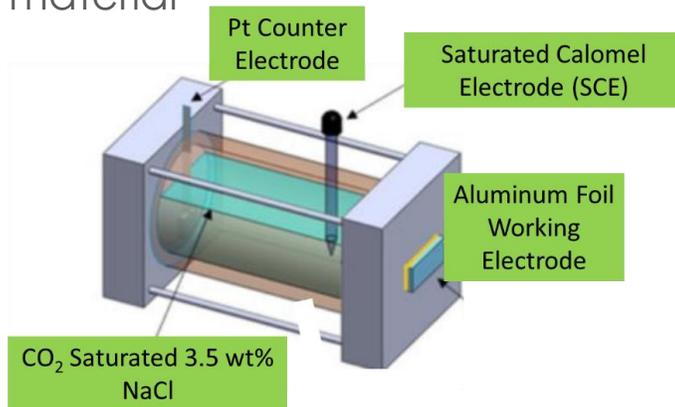
- Collaborating with Oceanit to develop inner polymer layer for corrosion resistance
- Polyurethane-based “Oceanit A” coating outperformed alternative coatings
 - Lower corrosion rate
 - Higher bonding strength
- Oceanit A coating of 16 – 20 μm thickness selected as inner layer material



Minimal delamination observed on Oceanit A coating after peel test



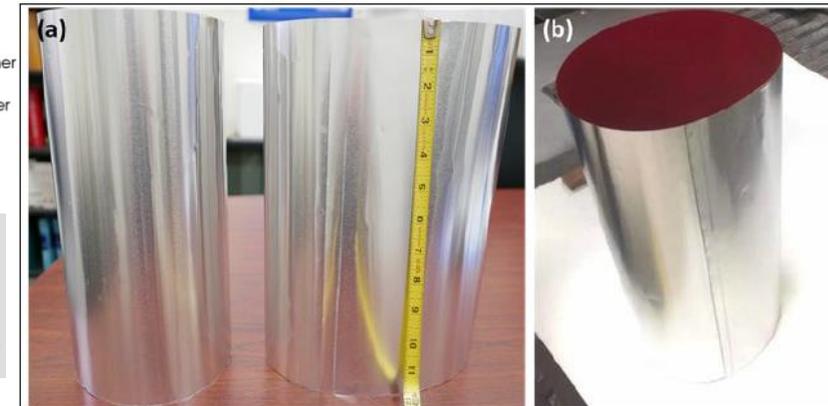
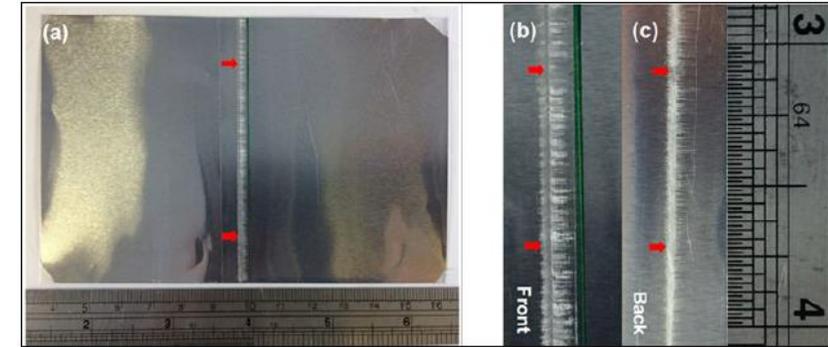
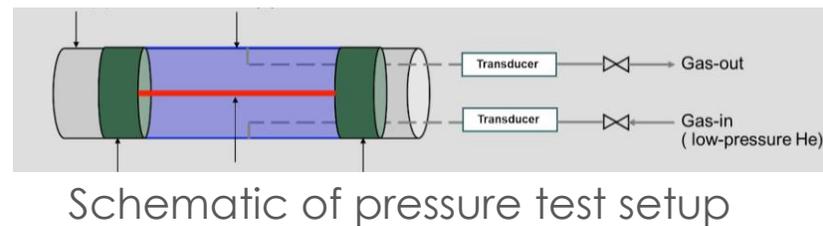
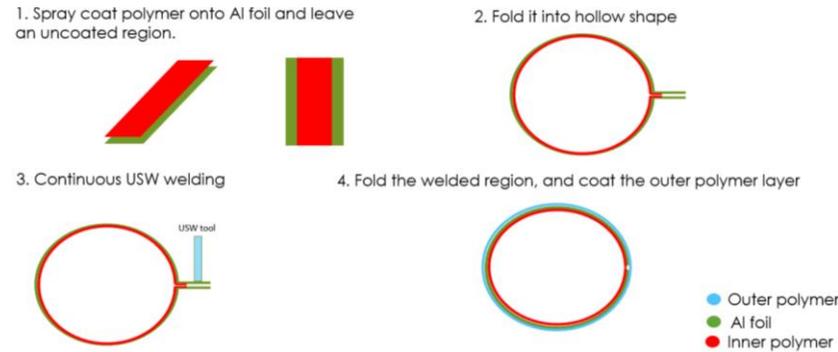
Significant delamination observed on BarRust 236 commercial epoxy coating after peel test



Composite liner for mitigating pipeline corrosion and gas permeation

Middle layer development with collaborators – Progress and ongoing efforts

- Collaboration with ORNL
 - Improve scalability of Al foil ultrasonic welding to form liner with pipe geometry
 - Pressure testing of liner prototype
- Welding tests ongoing to improve flexibility of joined Al layer using thinner/softer foil
- Experimental rig suitable for pressure testing liner prototype ETA Q3 2024



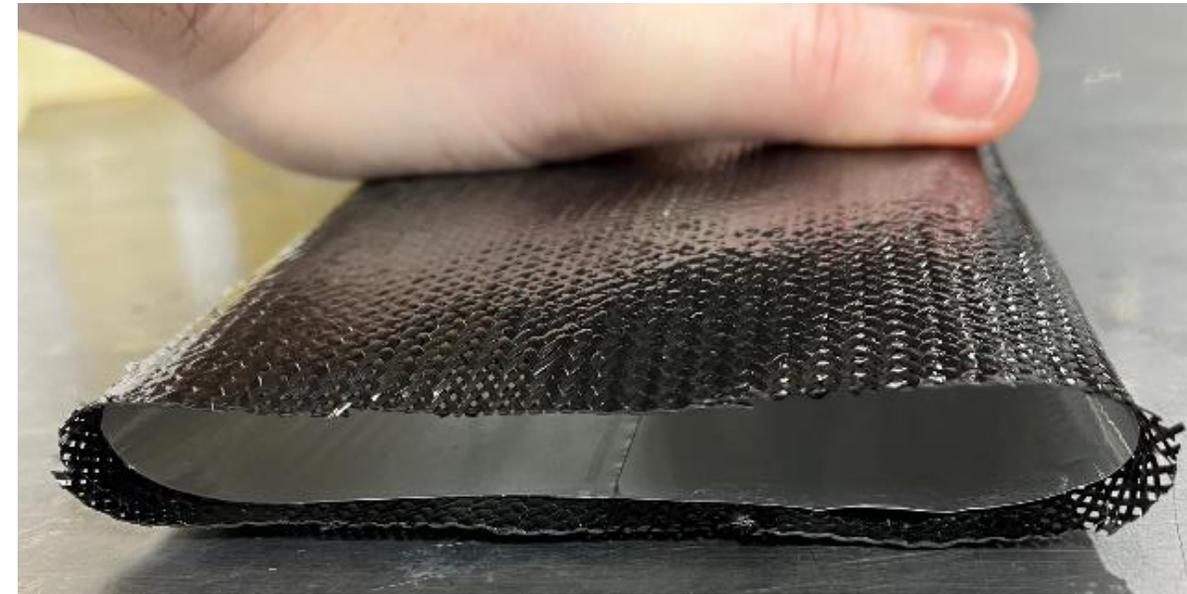
Composite liner for mitigating pipeline corrosion and gas permeation

Outer layer development with collaborators – Progress and ongoing efforts

- Collaborating with DBTech to develop outer polymer layer for mechanical strength
- Evaluating feasibility of two elastomeric resin-infused carbon fiber composite layer designs
 - Pre-cured (cured at plant)
 - Prepreg (cured in field via steam treatment)
- Demonstrated resin adherence to Al foil layer prevents creasing when folded



Resin-infused biaxial carbon fiber composite layer

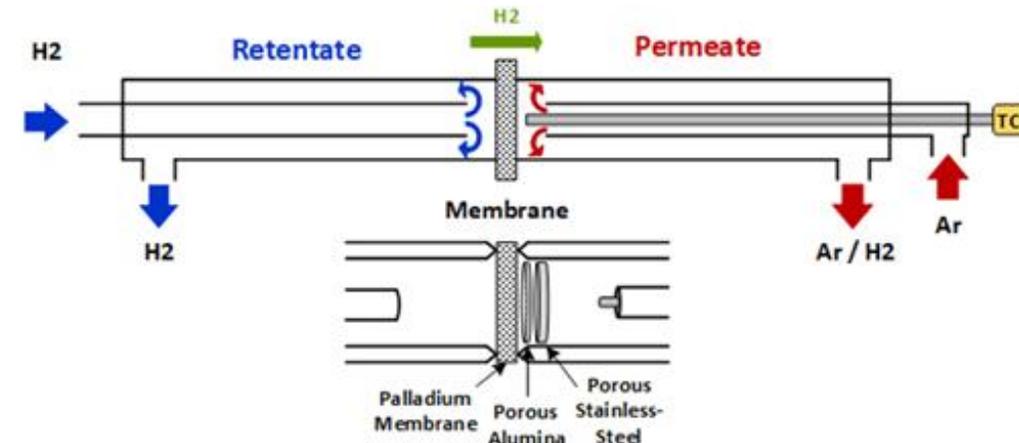
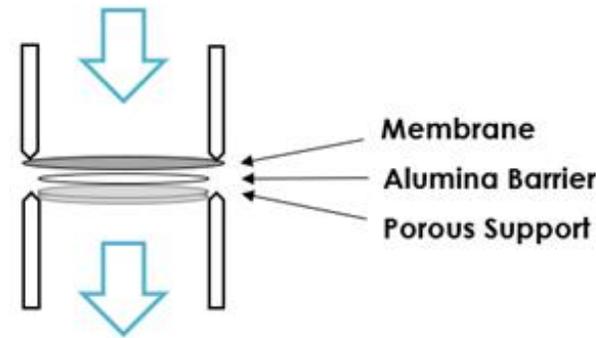


Adherence of resin to middle Al foil layer imparts minimum bending radius, preventing creasing when folded

Composite liner for mitigating pipeline corrosion and gas permeation

Hydrogen permeation testing of liner materials – Progress and ongoing efforts

- No hydrogen permeation through welded foil detected at pressures up to 145 PSIG
- Seamless and welded foils had comparable rates of pressure increase
- Future efforts will focus on permeation testing of welded foils and foils with omniphobic coating at higher pressures (1000 psig)

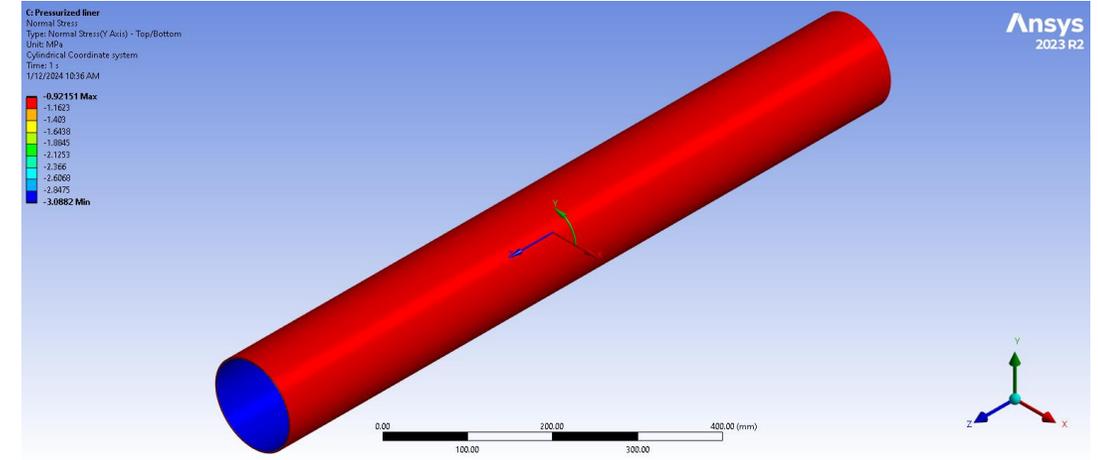


Composite liner for mitigating pipeline corrosion and gas permeation

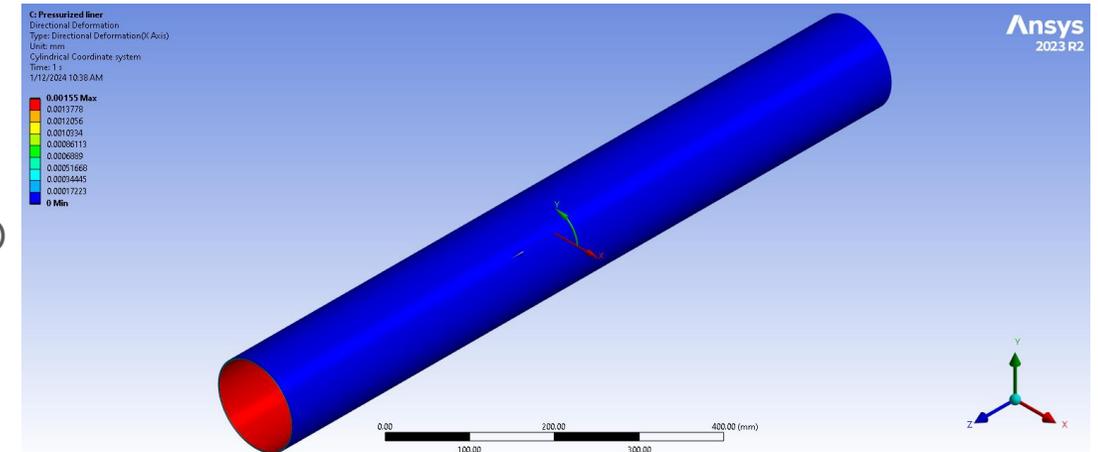
FEA simulation of liner stress/strain state during operation – Progress and ongoing efforts

- Preliminary Ansys simulation results predict stress/strain of pressurized liner
- Future efforts will characterize performance of liner under different operating conditions and stresses associated with storage, installation, etc.

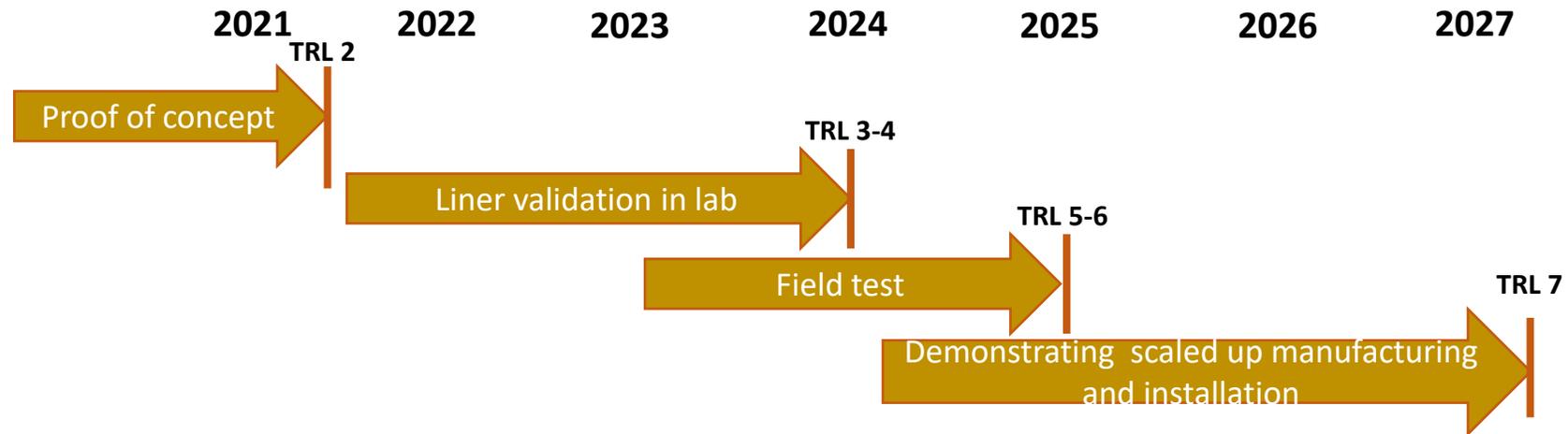
Axial stress in 3D



Hoop stress in 3D

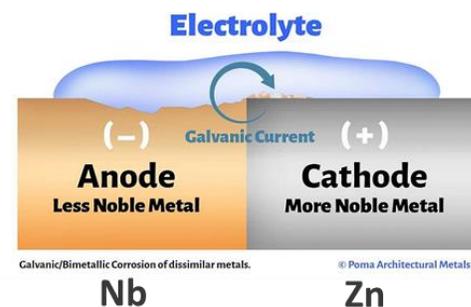


Composite liner technology maturation

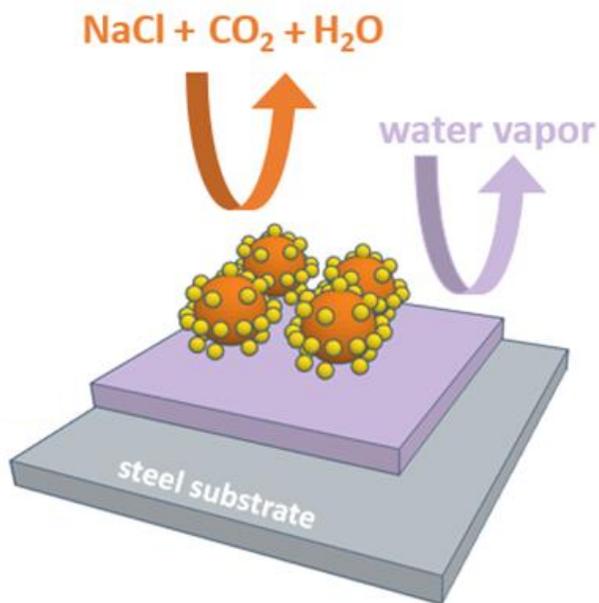


NETL's Coating and Liner Technologies for Pipelines

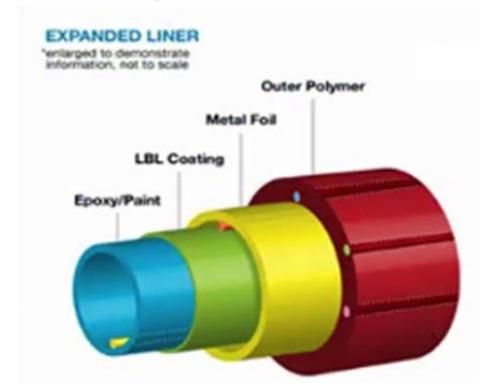
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Composite Liners



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