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

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Acknowledgements

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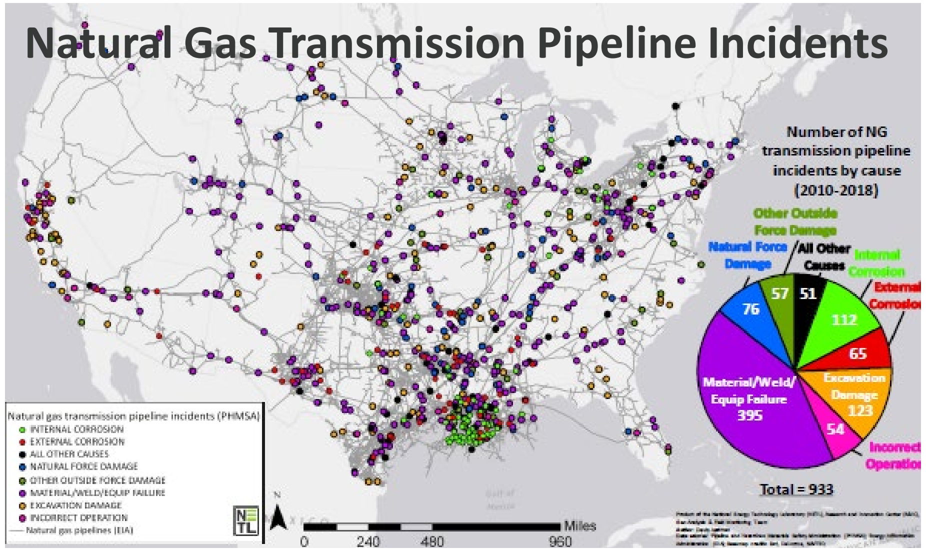
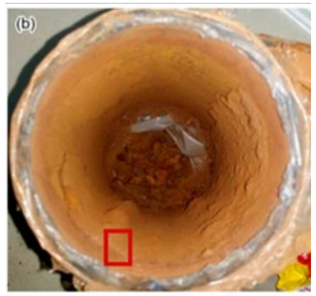
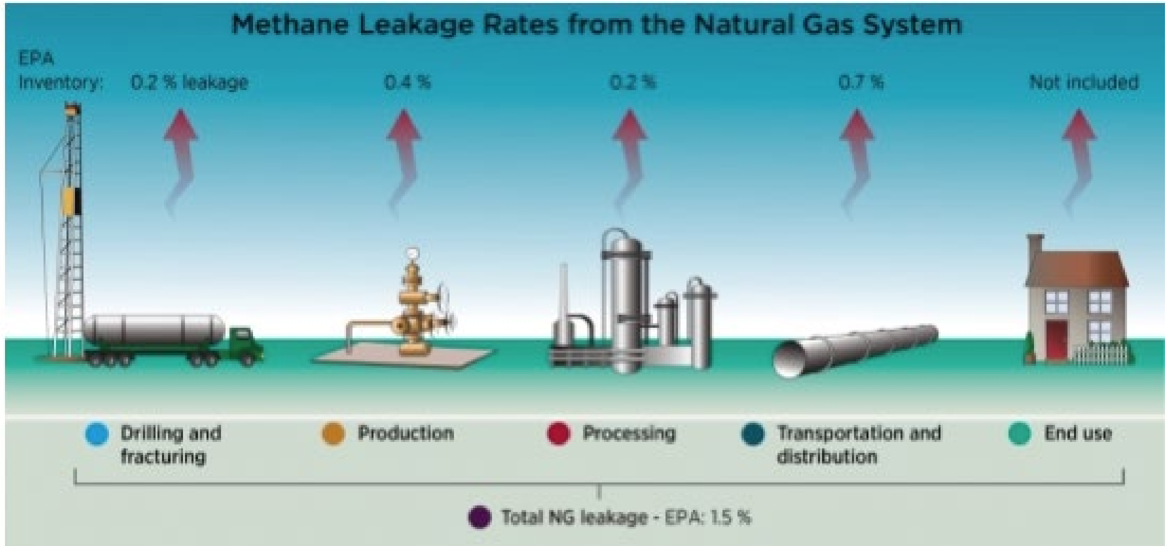
Natural Gas Infrastructure - Challenges



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

Internal corrosion





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

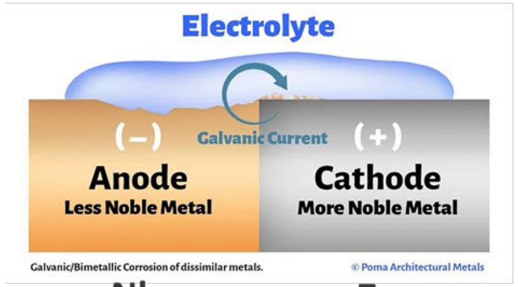
- **Methane emissions**
- **Internal corrosion**

- **Cost-effective refurbishment of in-service pipes**

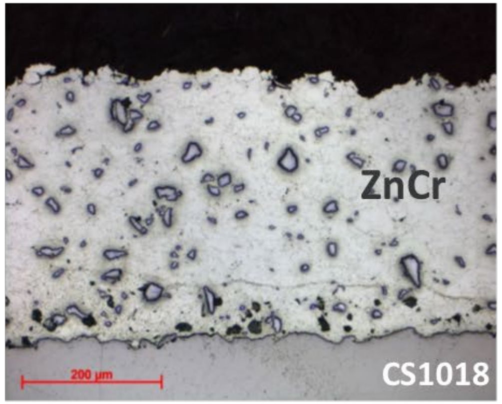
- **Hydrogen compatibility**
- **Remote monitoring**

Mitigation – NETL Approach

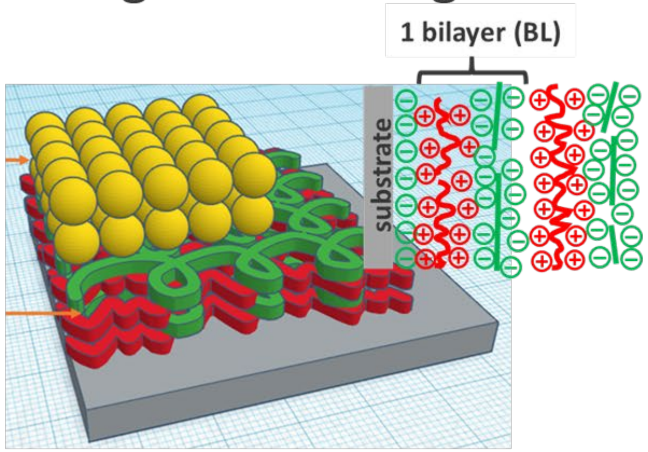
Metallic Coatings



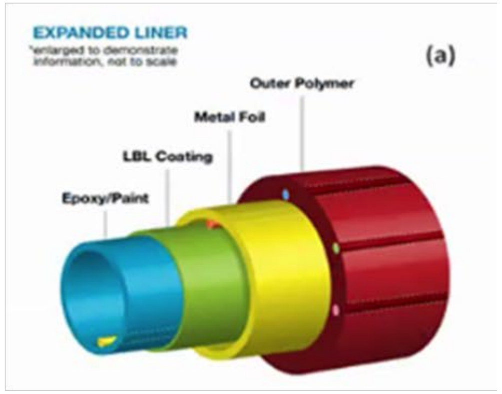
Nb Zn

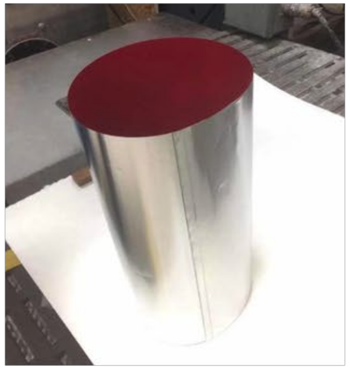


Multilayer Organic Coatings



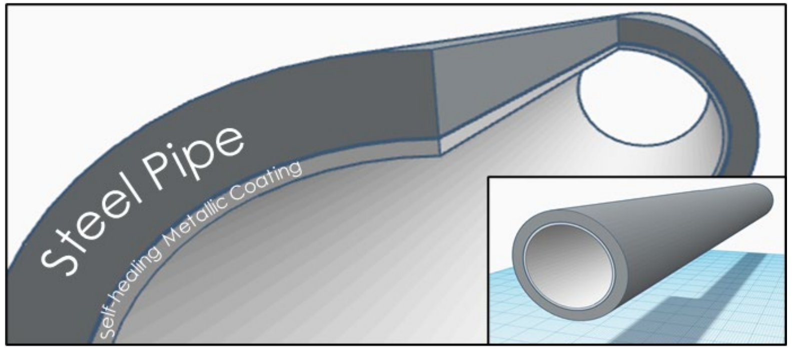
Composite Liners

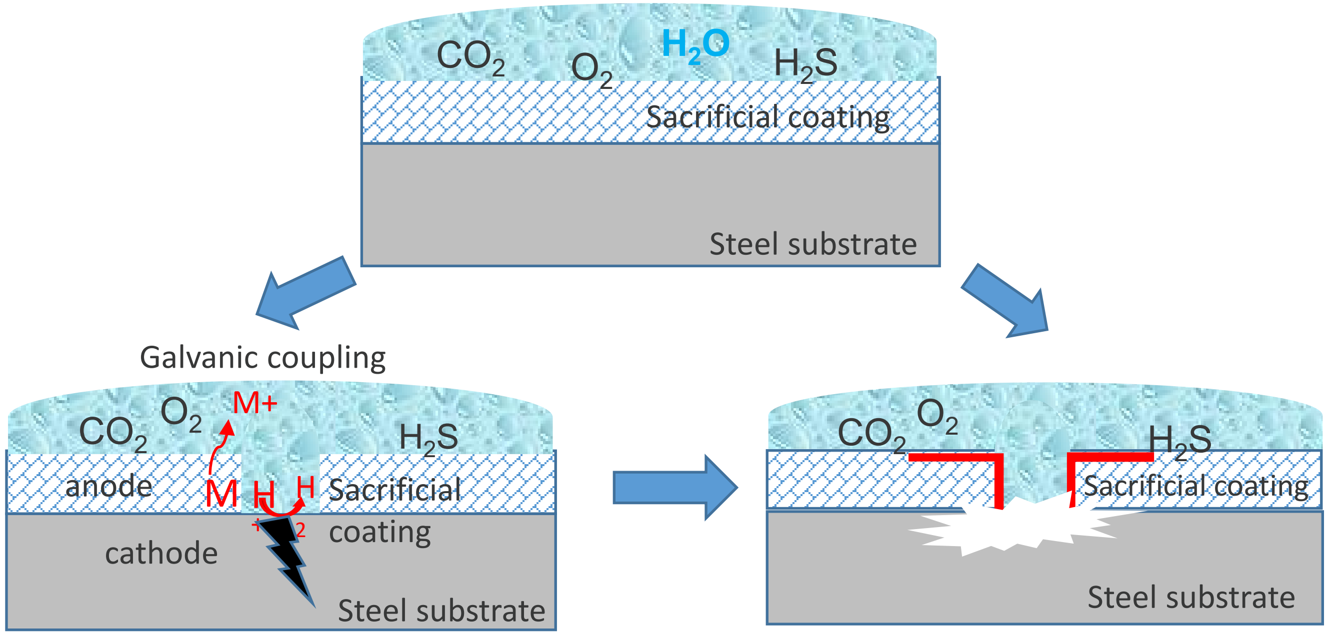




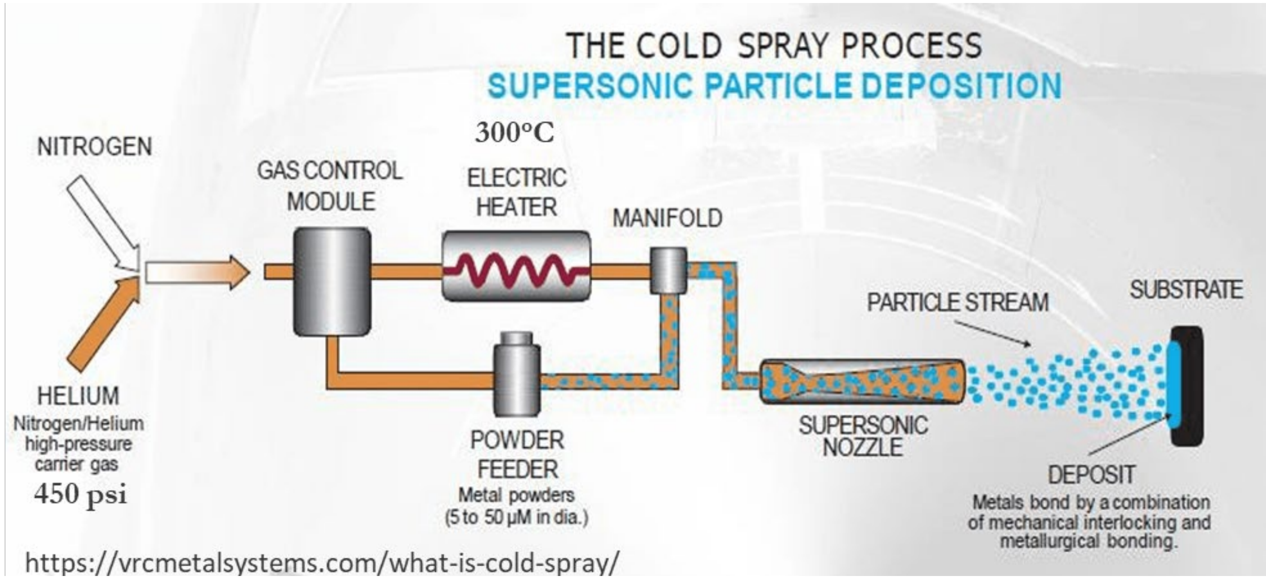
Sacrificial (and Self-healing) Metallic Coatings

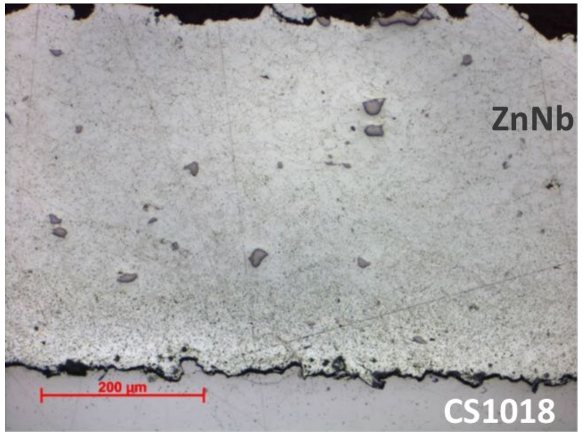
- Sacrificial coatings are used for corrosion protection.
- Zinc is a common sacrificial coating.
- However, Zn corrodes too fast in NG pipeline conditions.
- Can we slow Zn corrosion inside NG pipelines?
- Can we form *micro galvanic cells* to control Zn corrosion?

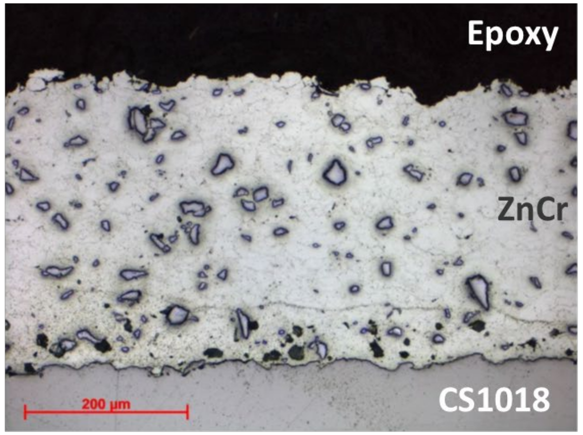




Cold Spray Coating Technology







Coatings	Thickness (μm)	Gas Temperature (°C)	Gas Pressure (PSI)	Porosity (%)
ZnNb	428 ± 5.1	300	450	≈ 0.32 ± 0.13
ZnCr	304 ± 7.0	300	450	≈ 0.5 ± 0.28

Electrochemical Results: Cold Spray Coatings Immersed In a CO_2 Saturated NaCl Solution

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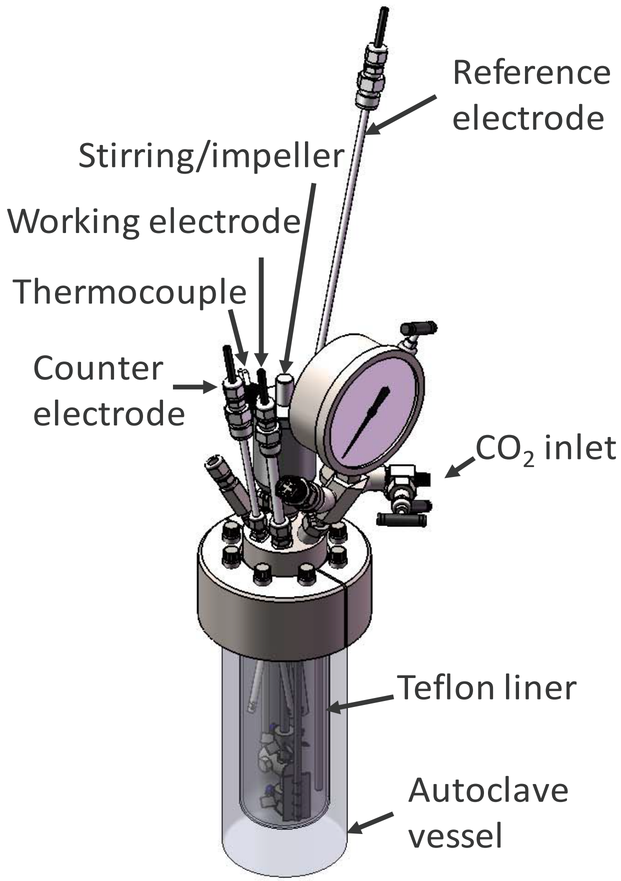
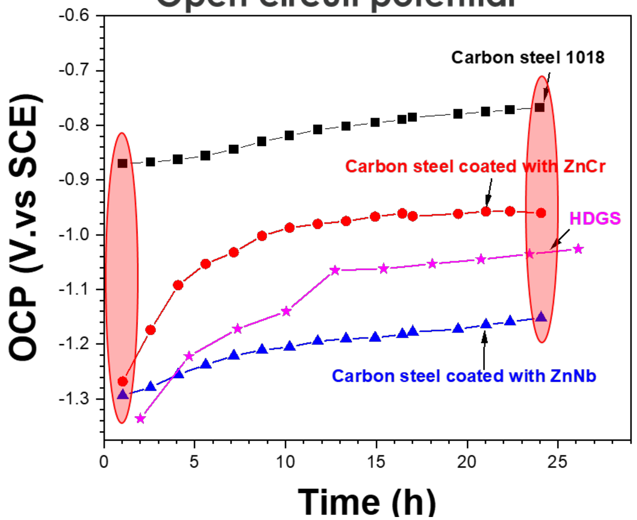
Electrochemical Reaction Autoclave (ERAC)

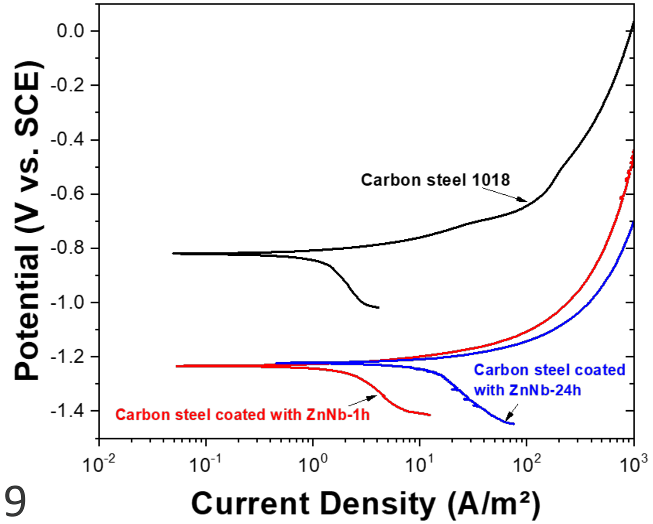


p_{CO2} = 4 bar, T=40°C, 3.5 wt% NaCl, pH_{in} = 3.87, pH_{fin} = 3.9

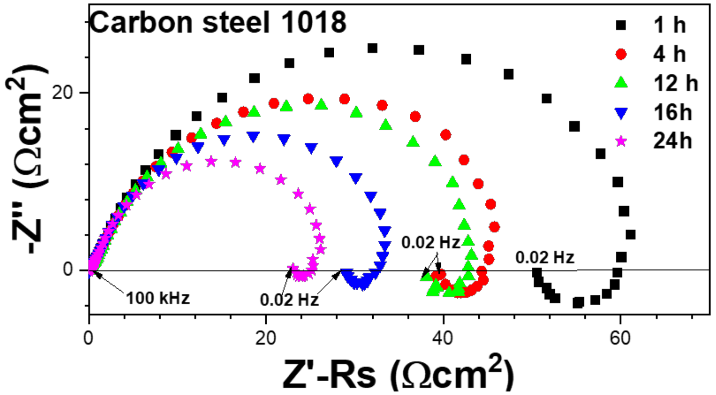
Open circuit potential



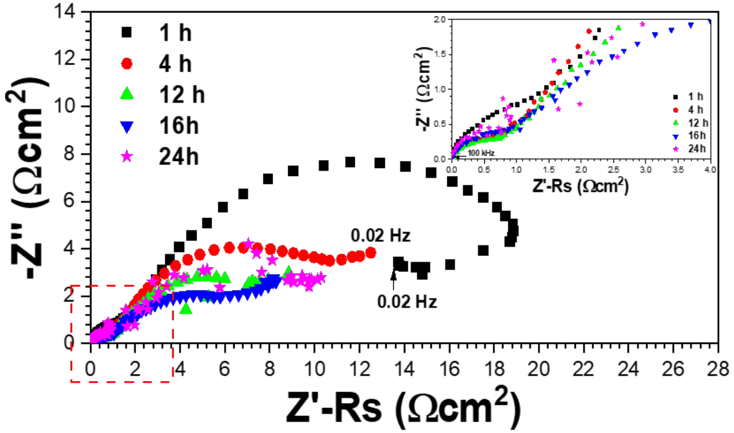
Potentiodynamic polarization curves carbon steel coated with ZnNb



Electrochemical Impedance Spectroscopy (EIS)



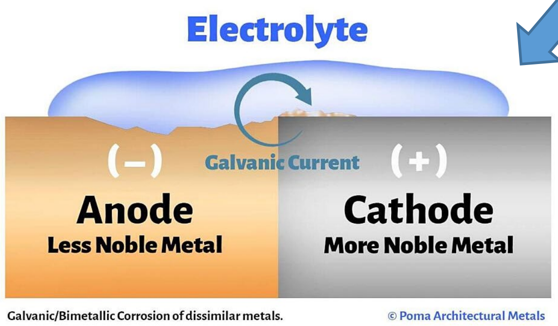
Carbon steel coated with ZnNb



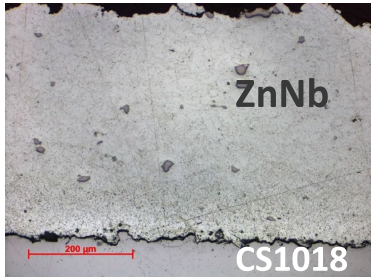
Corrosion Mechanism of ZnNb

$Zn^{2+} + 2e^- \leftrightarrow Zn \quad E_0 = -0.76\ V$

$Nb^{3+} + 3e^- \leftrightarrow Nb \quad E_0 = -1.099\ V$



Nb Zn



Corrosion of Zn and formation of $ZnCO_3$

Chemical reaction

$CO_2 \leftrightarrow + H_2CO_3$

$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$

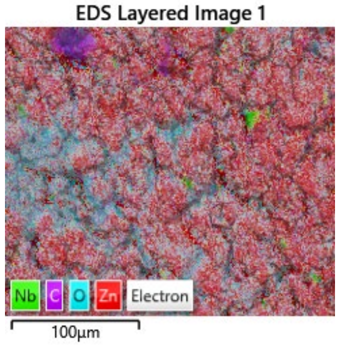
Electrochemical reaction

$Zn \leftrightarrow + Zn^{2+} + 2e^-$

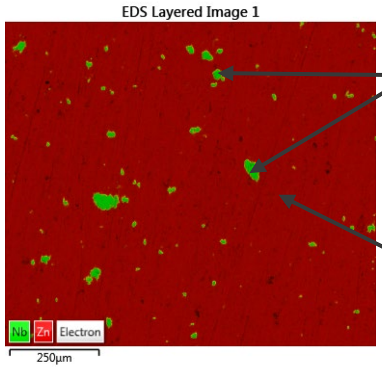
$2H^+ + 2e^- \leftrightarrow H_2$

Chemical reaction

$Zn^{2+} + CO_3^{2-} \leftrightarrow ZnCO_3$



Formation of galvanic cell



At the anode (Nb):

$Nb \leftrightarrow Nb^{3+} + 3e^-$

At the cathode (Zn):

$2H^+ + 2e^- \leftrightarrow H_2$

- Surface of Zinc >> surface of Nb (A_{Zn}/A_{Nb}) ~34.7

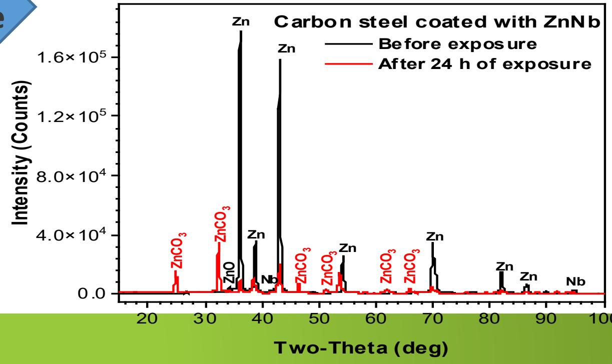
- At OCP : $I_{anode} = I_{cathode}$

Oxidation rate >> reduction rate

$i_{anode} >> i_{cathode}$

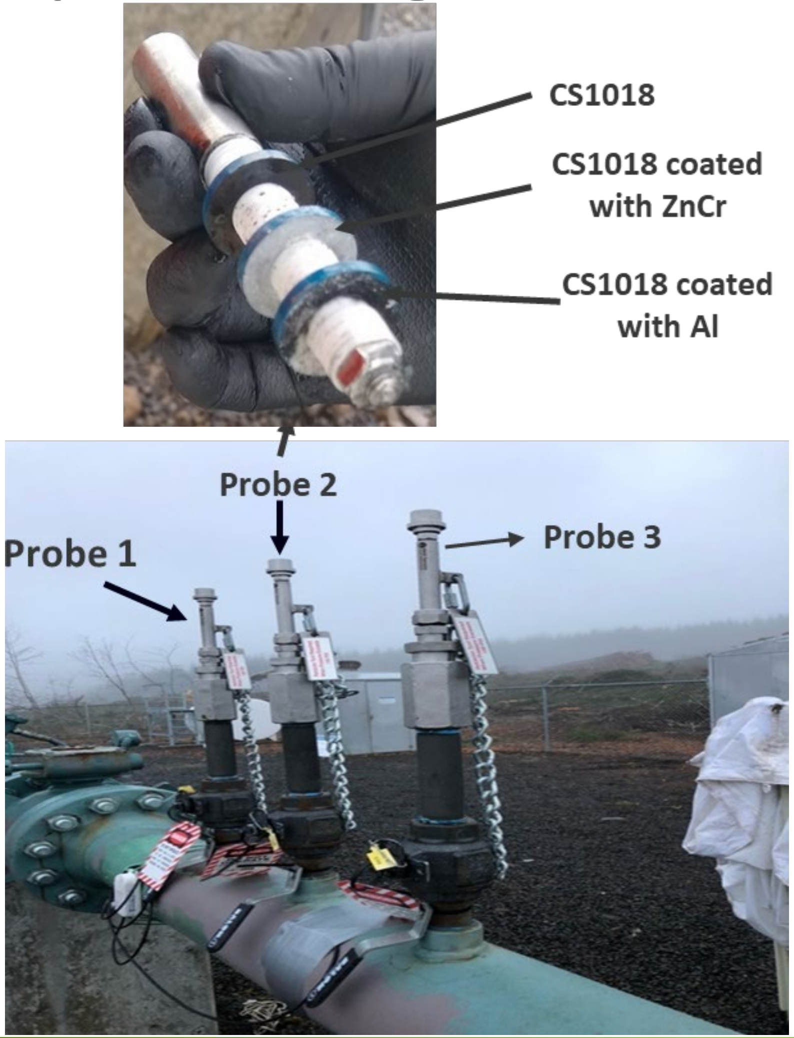
Accelerate dissolution of Nb

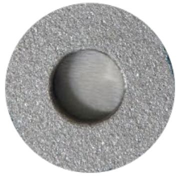
With the time

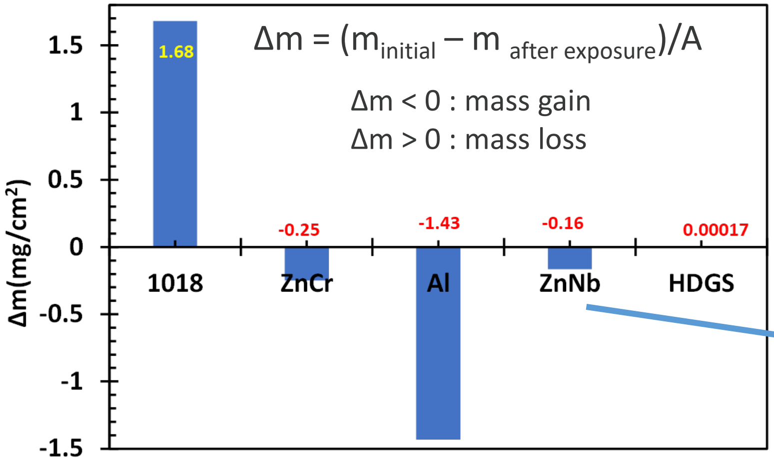


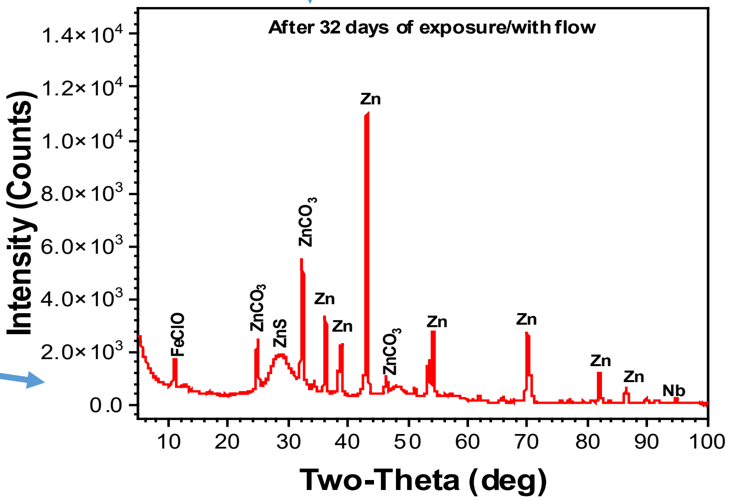
Field Test at NW Natural Gas Storage Facility

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



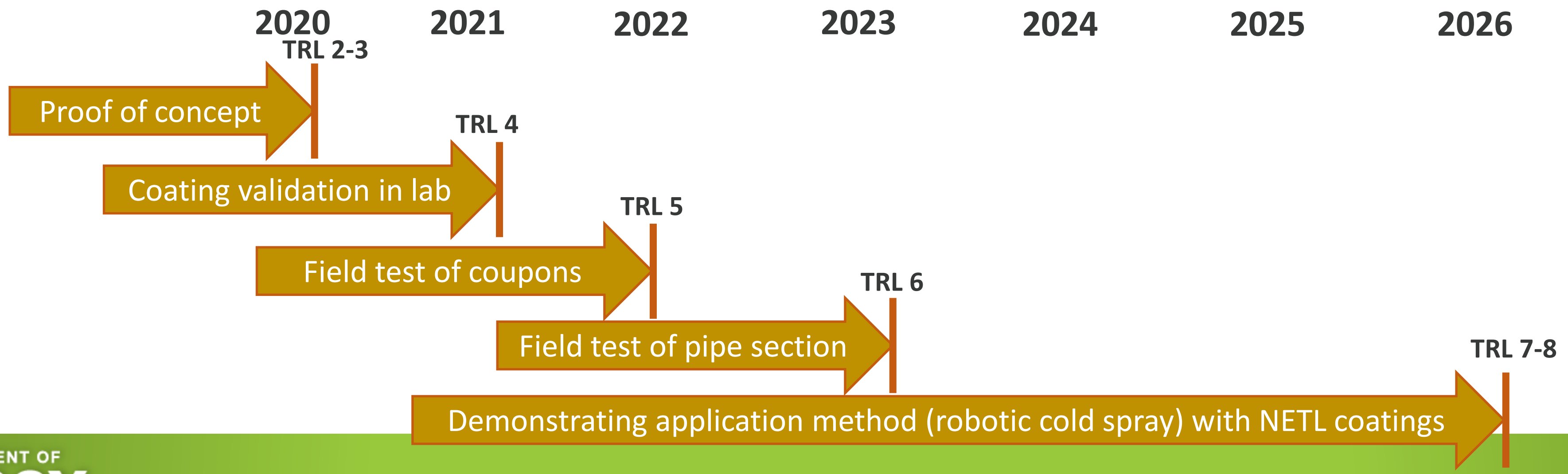
Alloys	CS1018	CS1018 coated with ZnCr (cold spayed coating)	CS1018 coated with Al (Thermal spayed coating)	CS1018 coated with ZnNb (cold spayed coating)	Hot dip galvanized steel (GS)
Before exposure					
After 32 days of exposure					





Metallic Coating Technology Maturation

Performance Attributes	03/2022	03/2023	03/2024	Timeline and Steps to TRL 7&8
Corrosion rate mm/y	<0.025 mm/y	<0.01 mm/y	<0.01 mm/y	Lab and field tests
Adhesion of coating on steel substrate				ASTM C633 – Adhesion bond bar testing and / or MIL-J-24445A Lug shear test , Field test
Hydrogen permeation rate	Calculated (<10^{-14} mols/m $Pa^{0.5}$ s)	<10^{-14} mols/m $Pa^{0.5}$ s	<10^{-14} mols/m $Pa^{0.5}$ s	Laboratory test
Application method – Robotic cold spray	TRL 4	TRL 4	TRL 5	Developed at ULC Technologies
Cost including robotic deposition	<$1M per mile	<$1M per mile	<$1M per mile	Cost analysis
Summary	TRL 5	TRL 6	TRL 7	3/31/2026



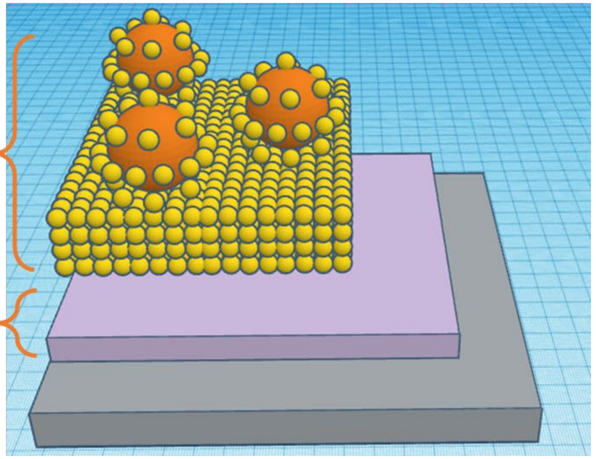
Multilayer Organic Coatings

Different layers serve different purposes

After testing multiple configurations, a multilayer design was chosen.

(top) superhydrophobic coating blocks CO_2 and/or NaCl

(bottom) primer layer blocks water vapor



Why multilayer?

only superhydrophobic top (corroded)

only primer bottom (corroded)

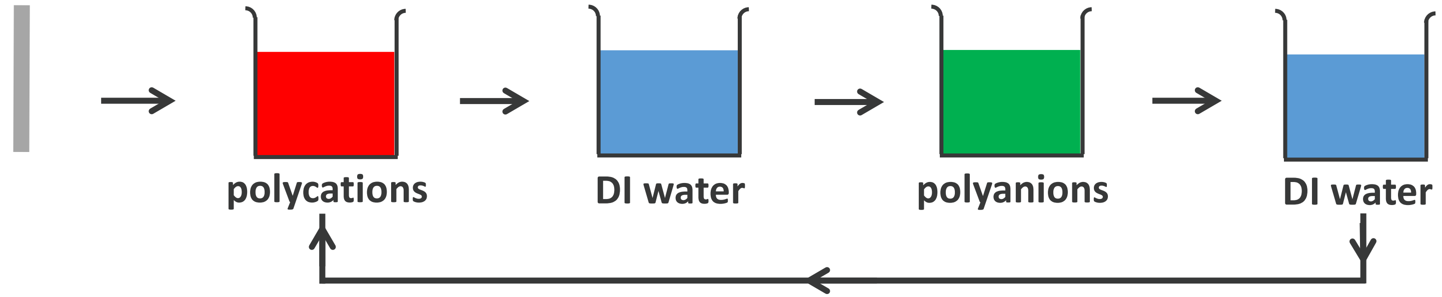
combine top and bottom (inhibited corrosion)

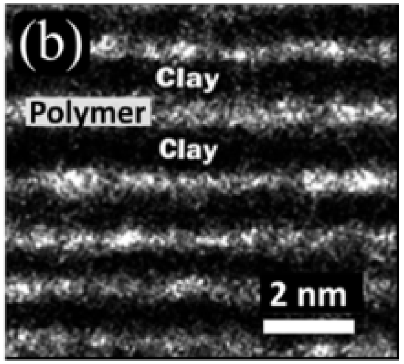
How was the multilayer coating made?

LbL (layer-by-layer) assembly is ideal for combining different materials together.

Typically, positively charged components and negatively charged components are alternately deposited one layer at a time.

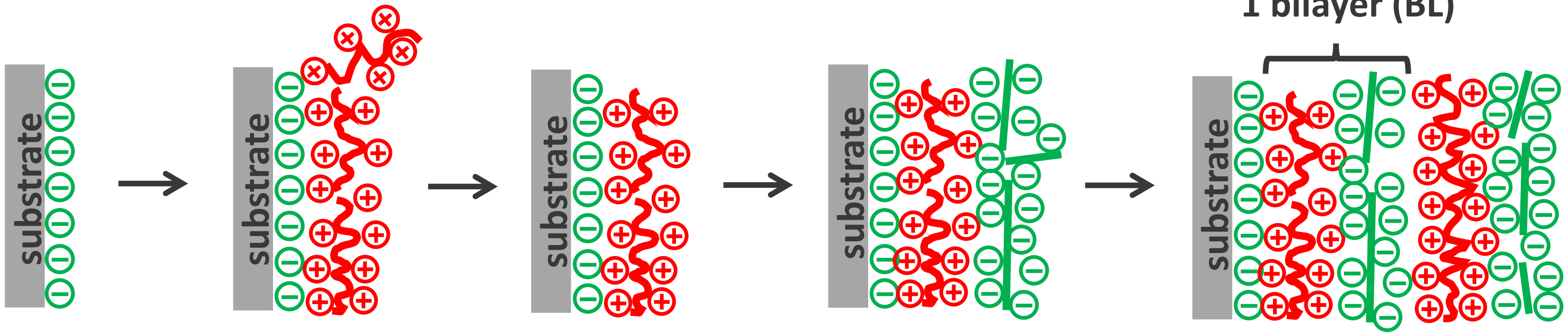
Process





Hagen D. A. *RSC Advances* **2014**, 4, 18354.

Corresponding structure



Decher G. *Science* **1997**, 277, 1232.

- **Thin and light**

Reduce material cost

- **Customizable**

Avoid using toxic component

- **Structural control**

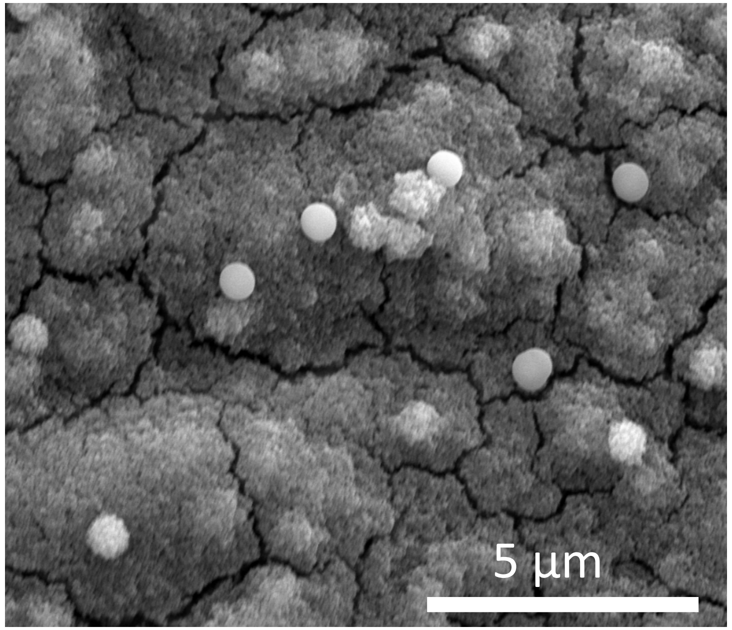
Fine tuning at nanoscale

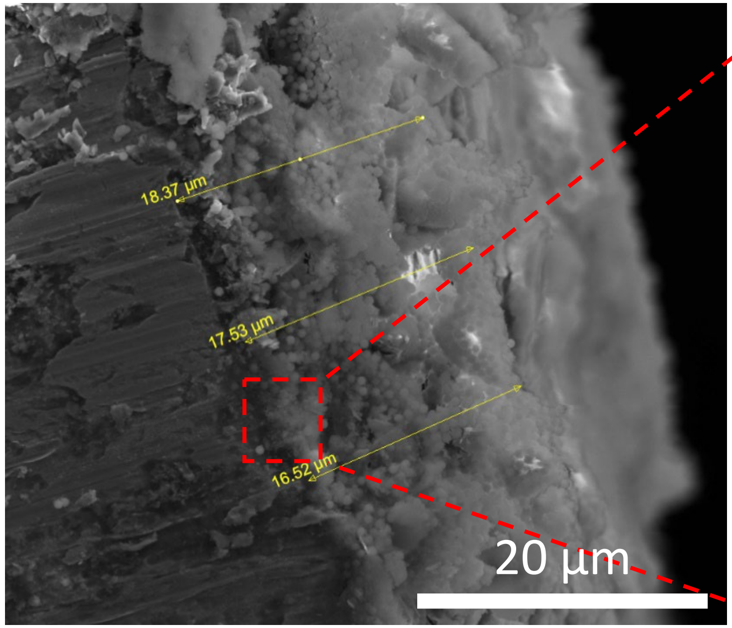
Surface morphology

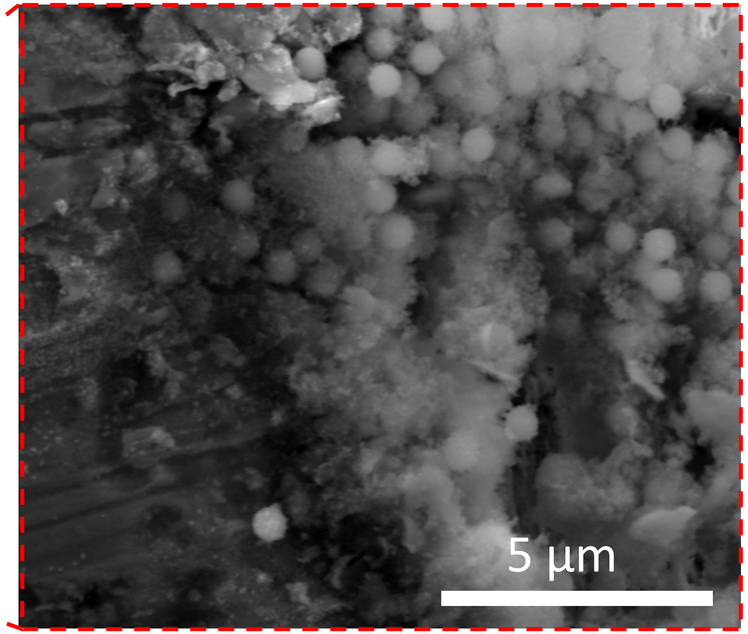
The microscopically rough surface allows *hydrophobic* material to form a *superhydrophobic* surface.

Surface

Cross-section







rough surface with
60 and 600 nm SiNPs

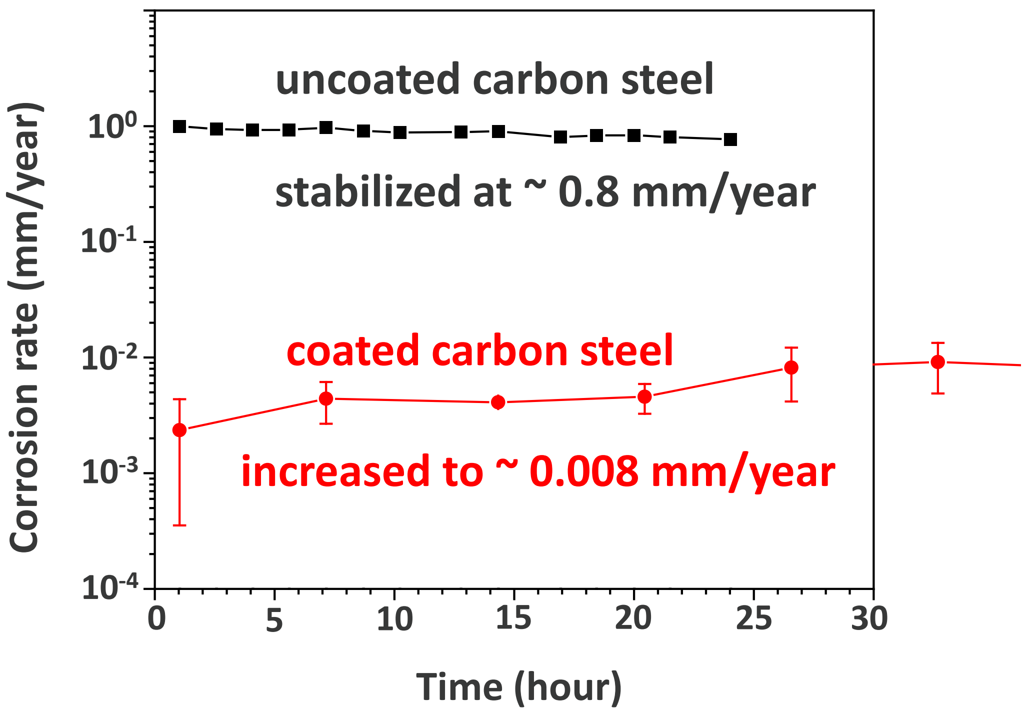
thickness ~16 µm

mix&matched SiNPs

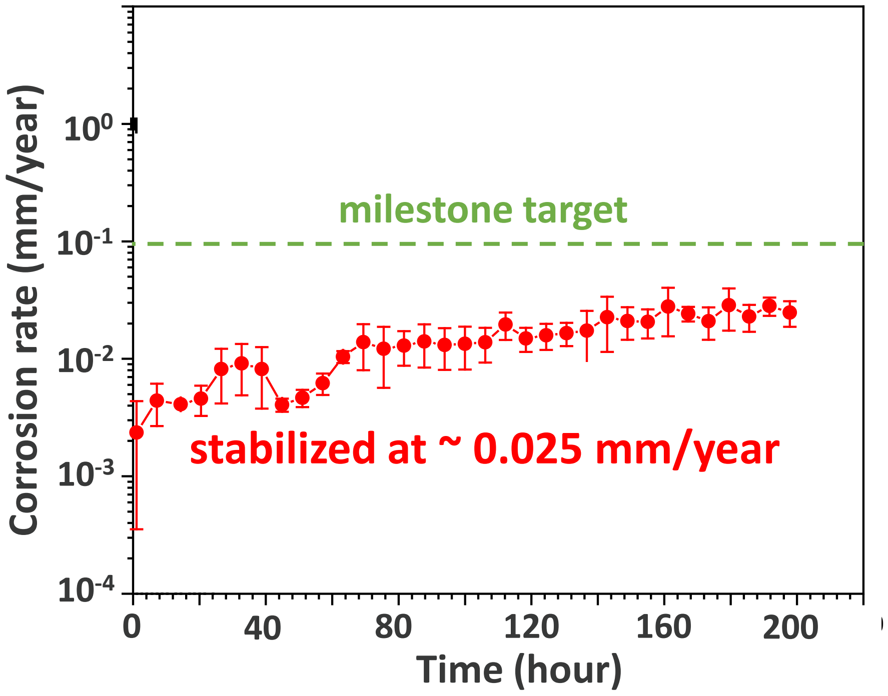
Anti-corrosion performance in CO_2+NaCl+H_2O

The corrosion rate was analyzed using linear polarization resistance.

short term test



long term test



Achieving a corrosion rate lower than the milestone target of 0.1 mm/year

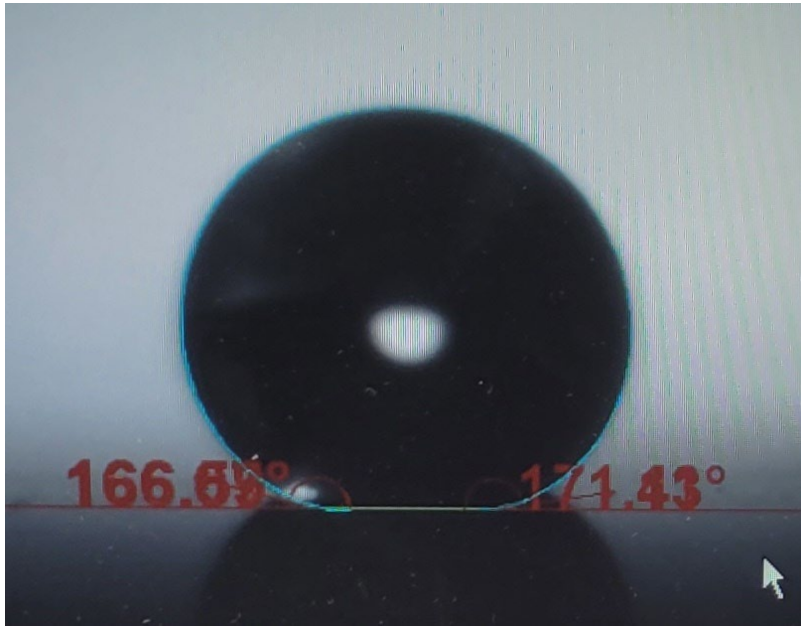
Testing temperature=20 ^oC; 3.5wt% NaCl; CO_2 bubbling.

Mechanical test

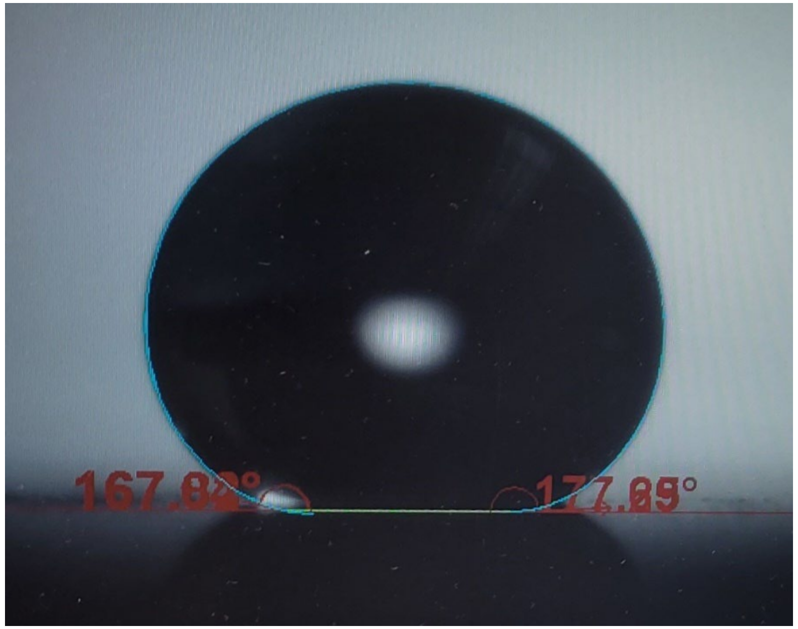
The durability of coating was tested according to ASTM D3359 (scratch and then peel with adhesive tape).

the coating remained superhydrophobic

before



after



Multilayer Organic Coatings – Technology Maturation

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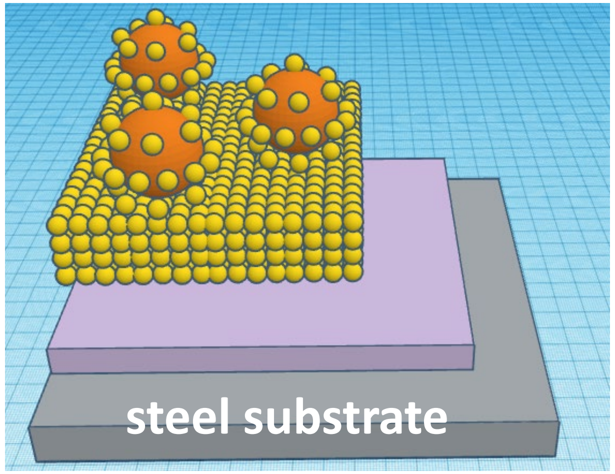
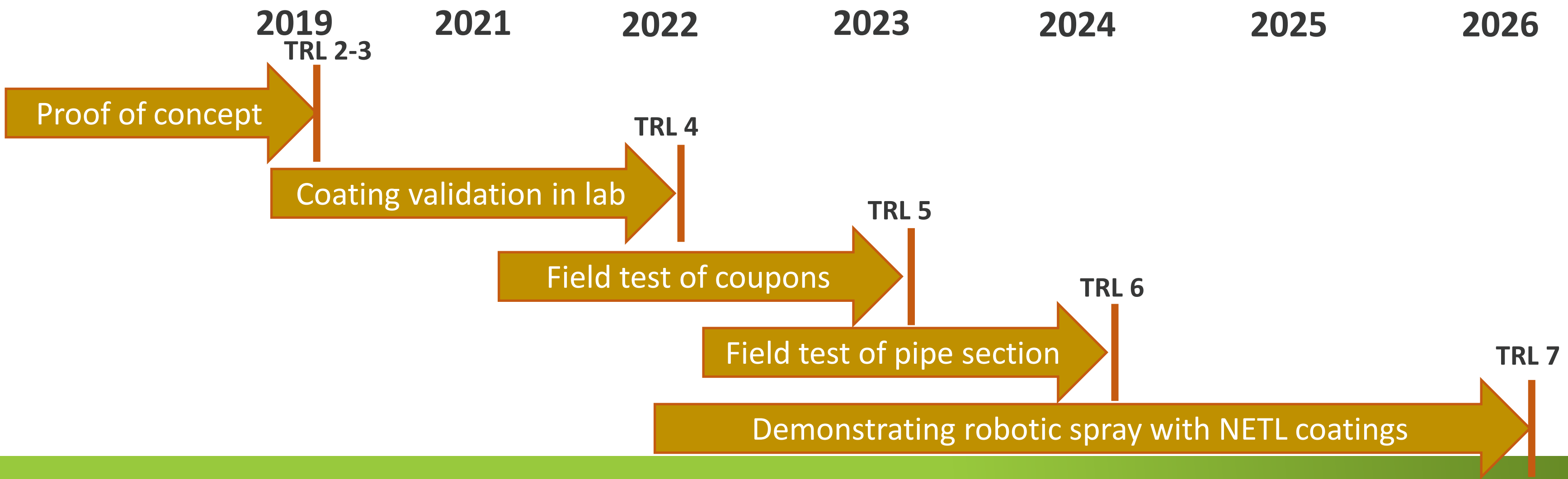
(top) superhydrophobic coating blocks CO_2 and NaCl

(bottom) primer layer blocks water vapor



- Improve the corrosion resistance by incorporating gas barrier layers.
- Enhance the applicability by reducing the number of layers and by adopting spray coating.
- Reduce the environmental impact by switching to a non-fluorinated silane.

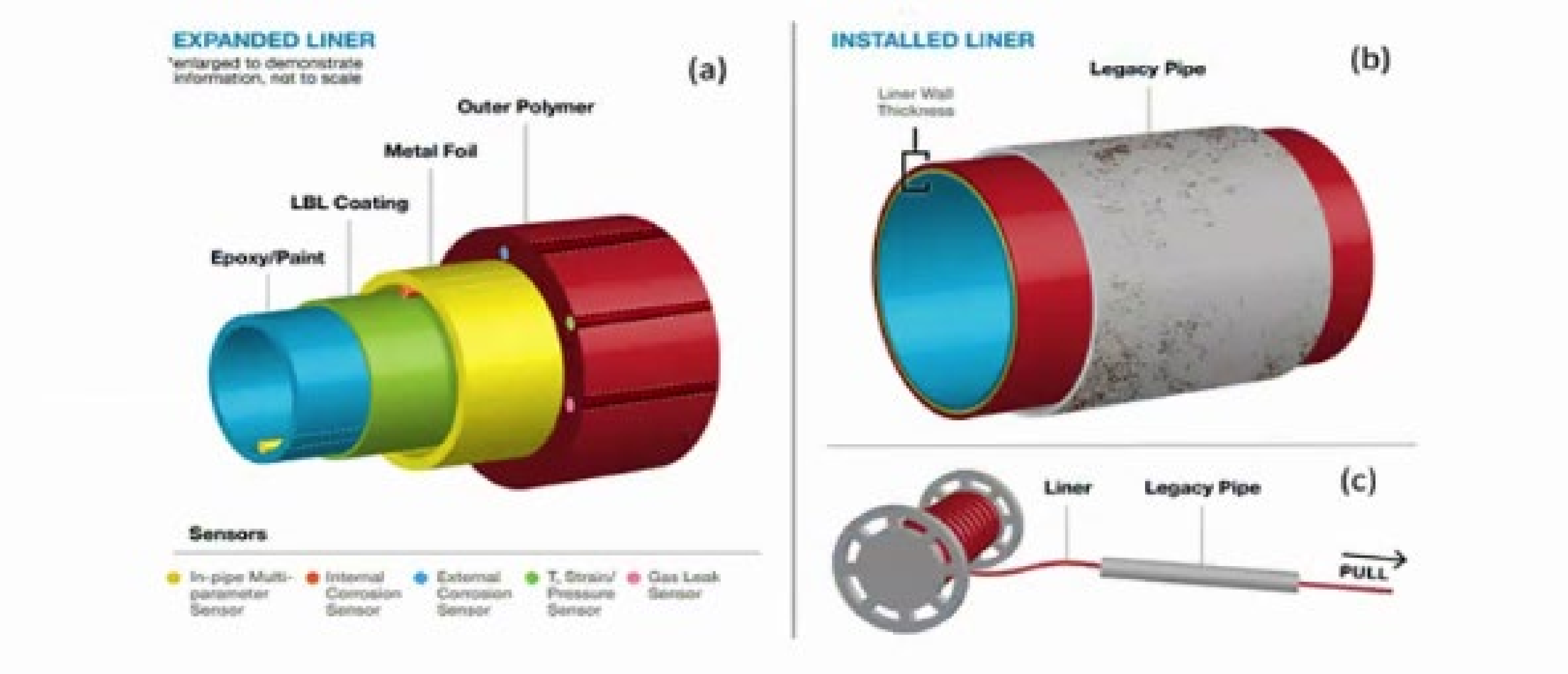
Performance Attributes	Performance Results By 03/30/2022	EY22	EY23	Timeline and Steps to TRL 7&8
Hydrophobocity	-	>165°	>165°	Lab test
Corrosion rate	0.1 mm/y - Lab	0.025 mm/y - Lab	Field test - coupon	Lab and field tests
Durability	-	Passed ASTM D3359	Field test - coupon	ASTM D3359 and field test
Lifetime				Lab/field tests
Cost	Estimate <$0.5M per mile			Cost Analysis
Summary	TRL 3	TRL 4	TRL 5	03/30/2026



Corrosion protective composite liners

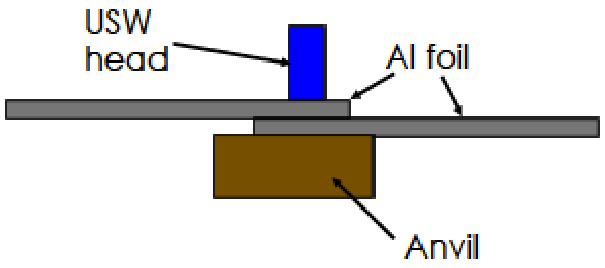
❖ **Continuous metal layer barrier for methane and hydrogen leak.**

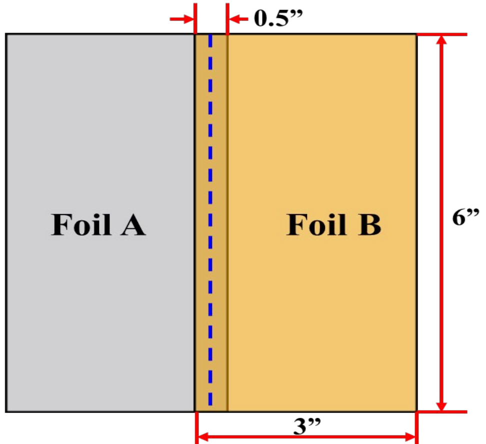
- Composite liner: internal polymer layer, metal foil layer, external polymer layer.
- Internal polymer layer—provide protection from natural gas corrosion
- Metal foil layer—significantly reduce gas (methane, hydrogen) leak.
- External polymer layer—provide mechanical strength.

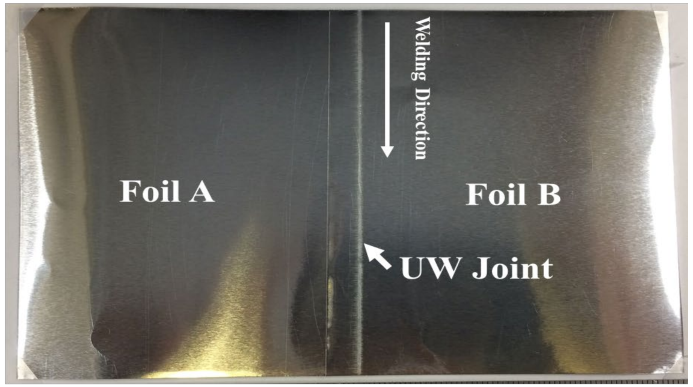


Pipeline shaped liner prototype: foil layer

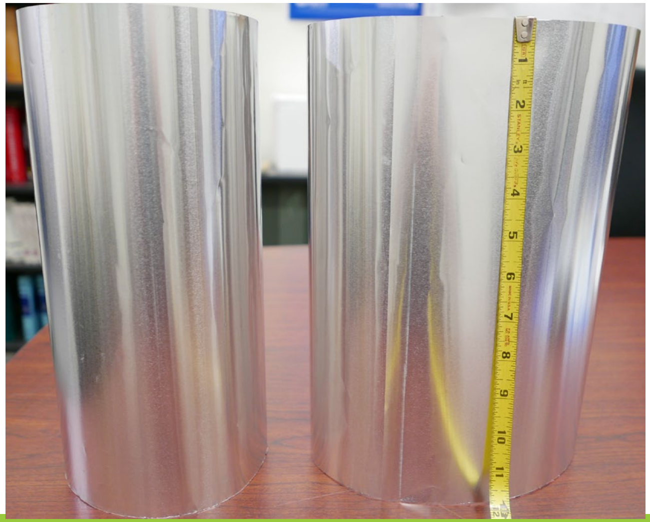
- Continuous ultrasonic welding

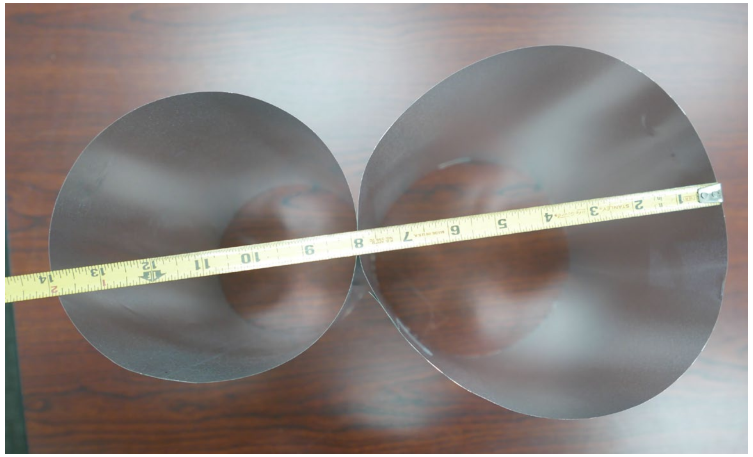




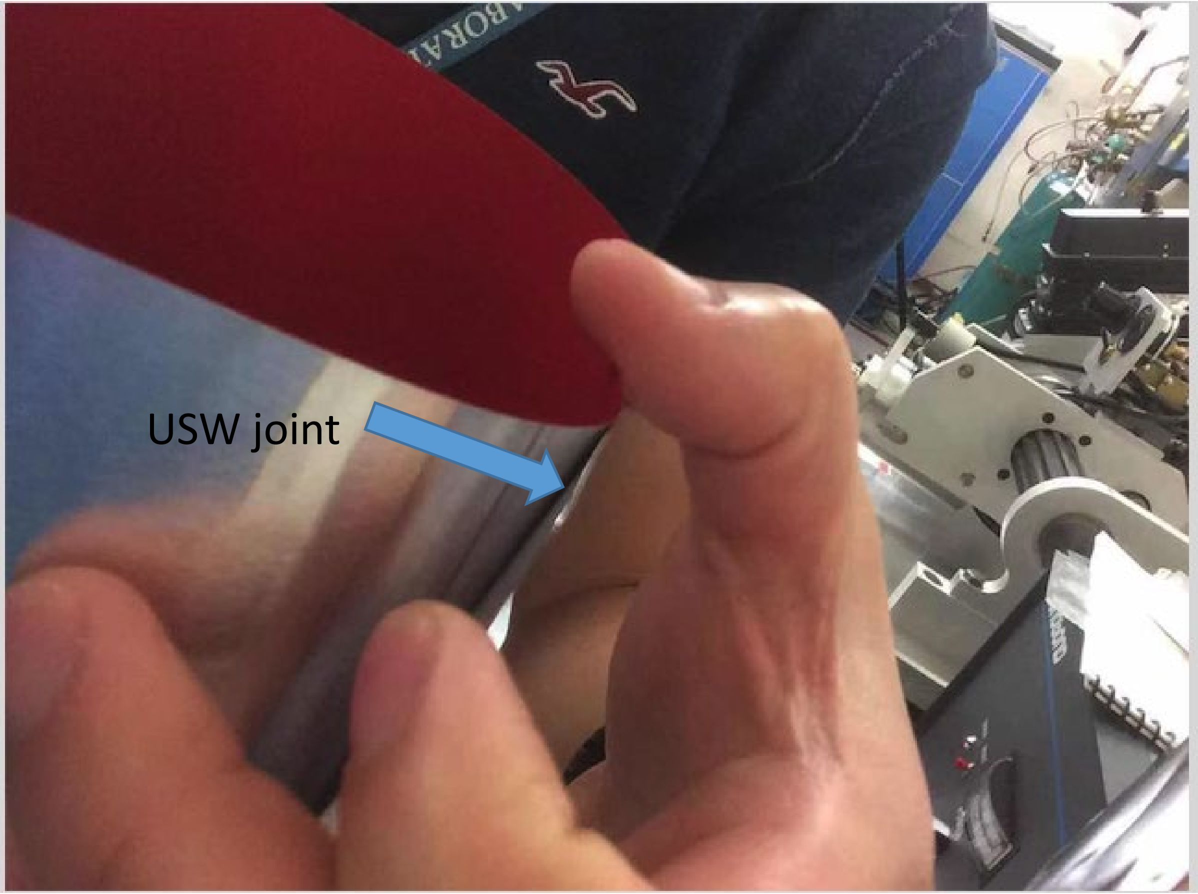


- 1 foot long, 6’’ and 8’’ diameter pipe shaped liner.





Pipeline shaped liner prototype: foil + inner polymer



Inner polymer layer material

1. Akzo Nobel BarRust 236

- Commercially available polymer coating for oil pipelines
- Fusion bonded epoxy

2. Oceanit Coating

- Preliminary results show promising bonding between coating and foil substrate
- Preliminary peel test confirms the durability of the coating
- Coating on the steel substrate survived with pigging process

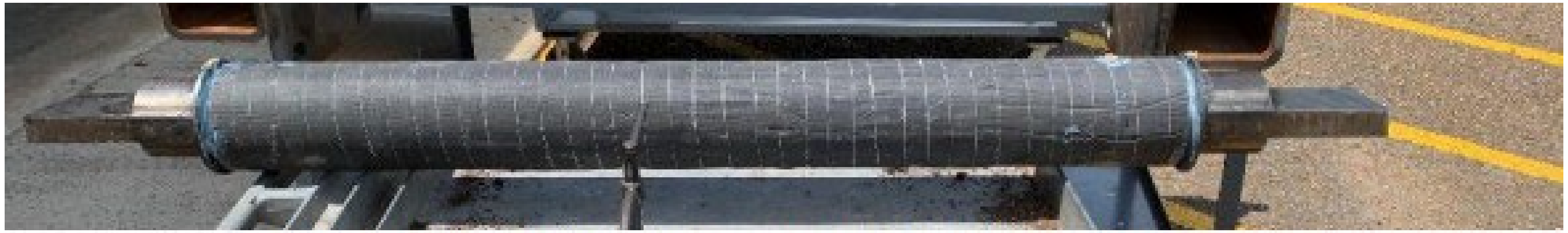
3. Layer by layer organic coating developed by NETL

- Successfully applied onto thicker aluminum coupons
- Passed preliminary peel test
- Coupons ready for in-house corrosion test

Plan: Perform adhesion and corrosion tests of all three coatings and down select.

Proposed outer layer solution

Overwrapping with polymer or fiber reinforced polymer



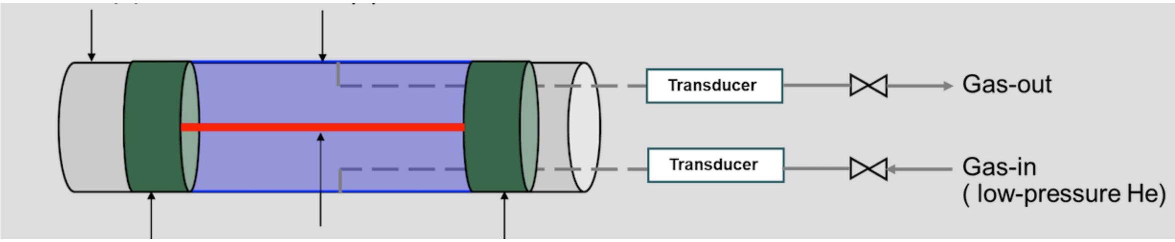
Overwrapped braided composite over metal substrate

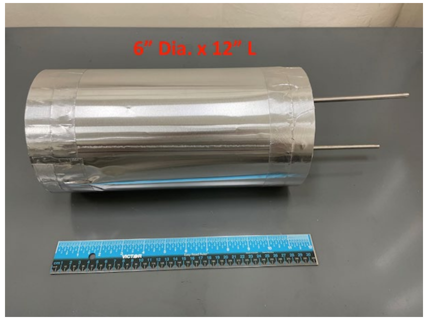
Steps:

1. Insert the rod into Aluminum foil layer.
2. Overwrap the composite layer over the foil layer.
3. Coil the wrapped liner structure on a ~~s~~pool.
4. Transport the wrapped liner structure to site.

Performance tests

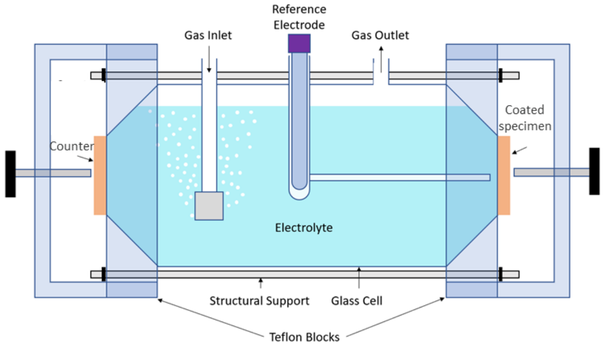
Pressure test





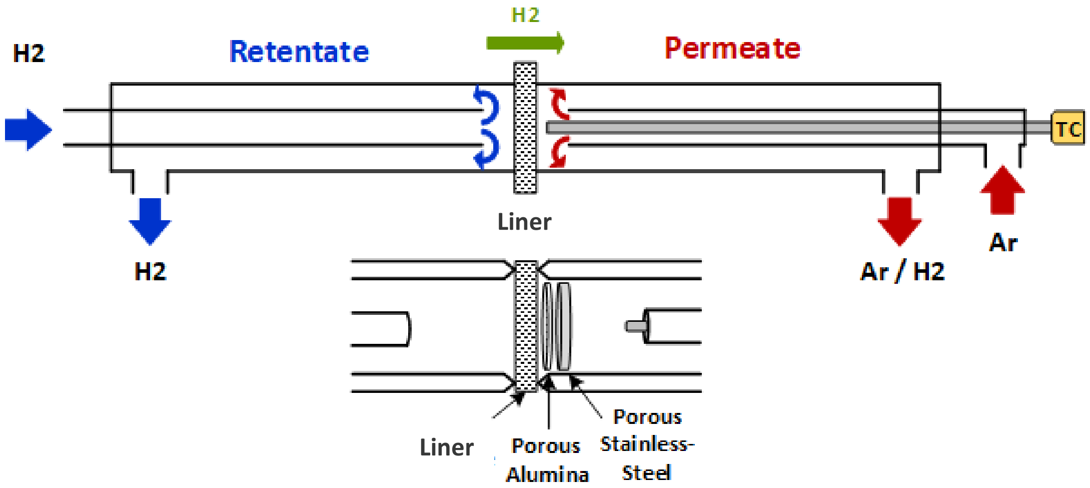
Able to detect He gas leak and locate the leak location

Corrosion test



- Environment: CO_2 Saturated 3.5% NaCl, simulated natural gas environment.
- Tests: Open circuit potential (OCP)
  Linear polarization resistance (LPR)
  Electrochemical Impedance Spectroscopy (EIS).

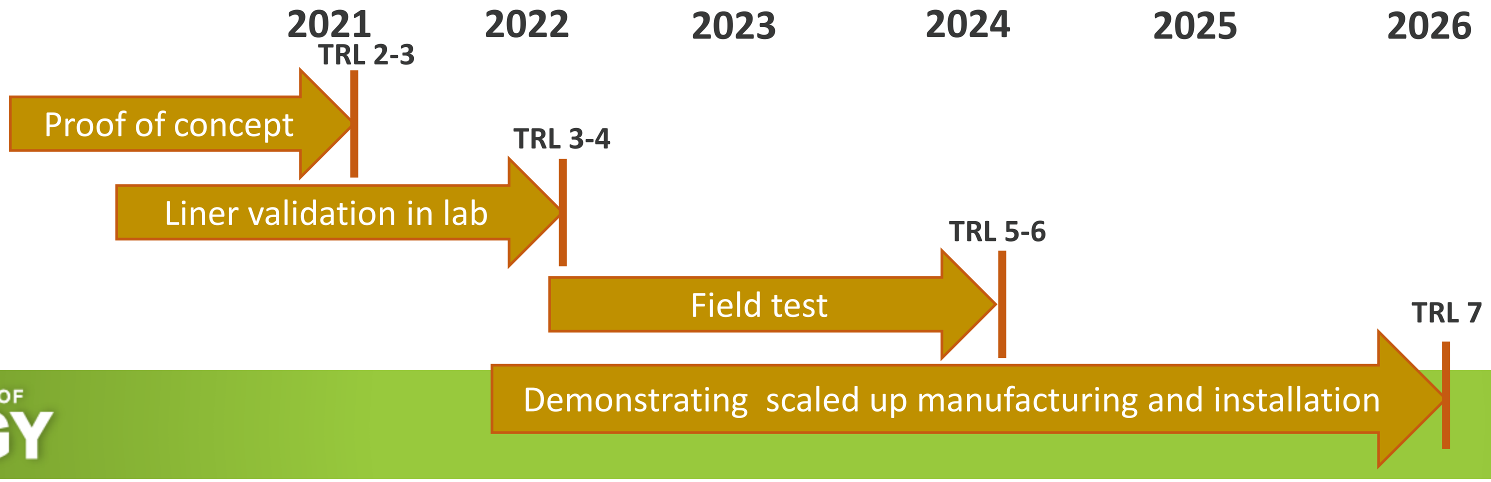
Gas permeation test



Corrosion cell schematic: Teeter, Lucas, Ziomek-Moroz, Margaret, Tylczak, Joseph, and Grant Crawford. "ZnCr and ZnNb Cold Spray Coatings." Paper presented at the CORROSION 2021, Virtual, April 2021.

Liner Technology Maturation

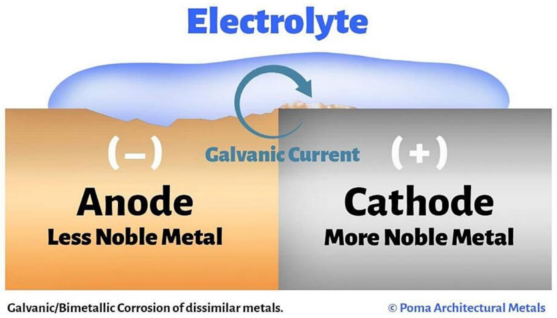
Performance Attributes	03/2022	03/2023	03/2024	Timeline and Steps to TRL 7&8
Corrosion rate mm/y	-	<0.01 mm/y	<0.001 mm/y	Lab and field tests
Application thickness	Calculated (<5 mm), not demonstrated	<5 mm	<5 mm	Lab and field tests
Hydrogen permeation rate	Calculated ($<10^{-14}$ mols/m $Pa^{0.5}$ s)	$<10^{-14}$ mols/m $Pa^{0.5}$ s	$<10^{-14}$ mols/m $Pa^{0.5}$ s	Laboratory test
Spoolable	-	-	Yes	Lab and field demo
Lifetime (based on corrosion rate)	-	5 years	>50 years	Lab/field tests
Cost including installation	$0.73M per mile /$0.41M per mile	-	-	Cost analysis
Summary	TRL 3	TRL 4	TRL 5-6	3/31/2026



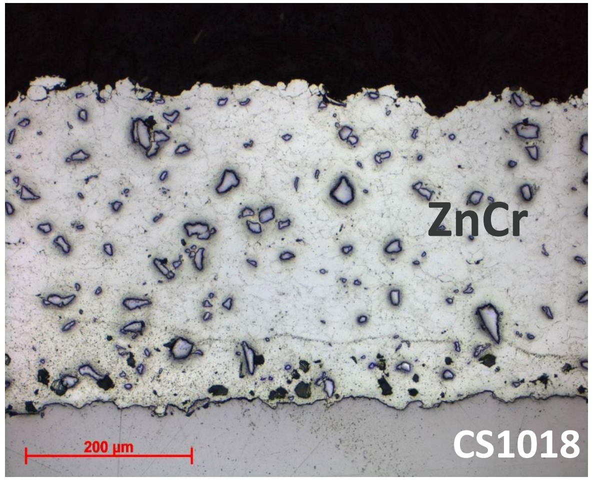
Materials for Mitigating Internal Corrosion, Methane Emissions, and Hydrogen Embrittlement

NATIONAL ENERGY TECHNOLOGY LABORATORY

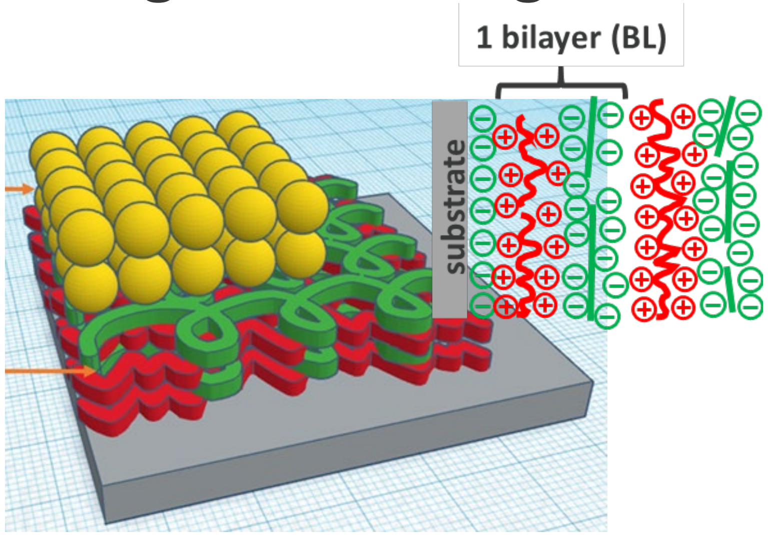
Metallic Coatings



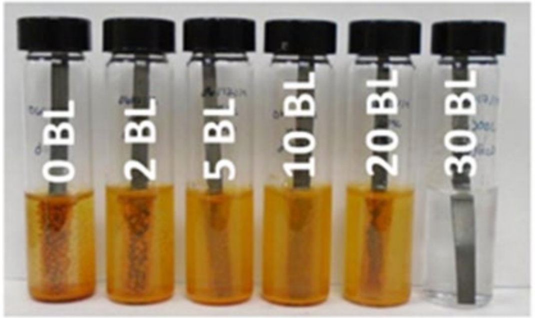
Nb Zn



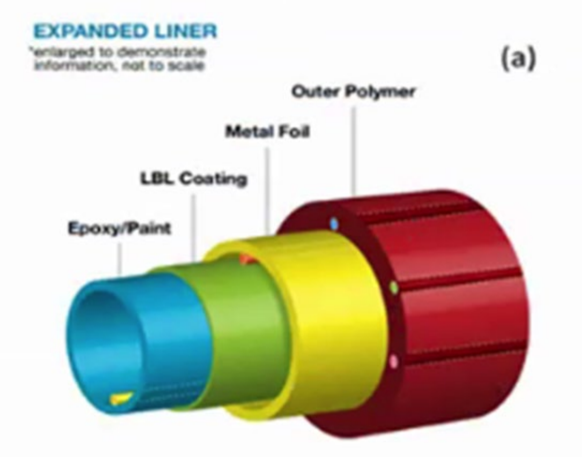
Multilayer Organic Coatings



1-month



Composite Liners



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

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