Development of Advanced Pipeline Materials: Metallic Coatings and Composite Liners

Task 3 Natural Gas Infrastructure FWP 1022424

Project Number 1611133

Margaret Ziomek-Moroz, Joseph Tylczak, Ömer Doğan

U.S. Department of Energy/National Energy Technology Laboratory, Research & Innovation Center

U.S. Department of Energy

National Energy Technology Laboratory

Oil & Natural Gas

2020 Integrated Review Webinar

NATIONAL ENERGY TECHNOLOGY LABORATORY

Overview of Advanced Pipeline Materials Project

- Project Funding: EY20: $775, 000
- Overall Project Performance Dates: April 1, 2019-March 31, 2022
- Project Participants: NETL/ Research & Innovation Center (RIC), DNV-GL, Oak Ridge National Laboratory (ORNL), Oregon State University (OSU), South Dakota School of Mines and Technology

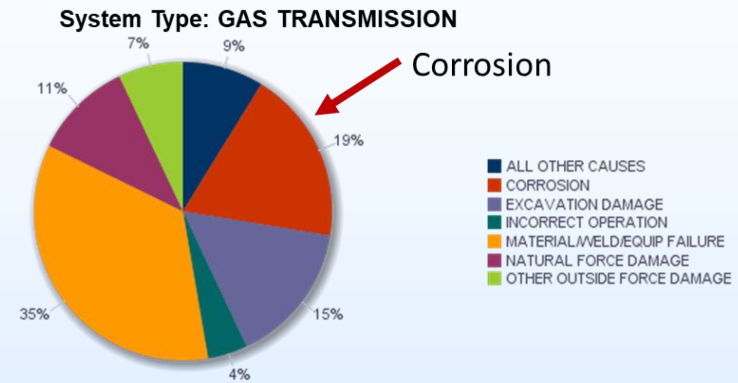
Overview: Advanced Pipeline Materials, continued

Overall Project Objectives

Develop **removable liners** and easy-to-deposit **long-lasting, self-healing, affordable coatings** for natural gas, hydrogen/ natural gas blends, and hydrogen transport capable of:

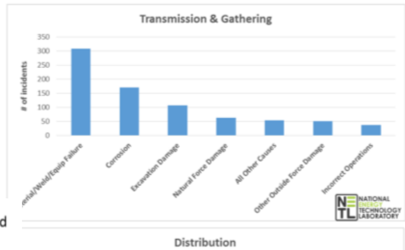
- Preventing corrosion in metal pipelines
  - » Reducing corrosion rate of pipelines below 0.1 mm/ year to be monitored by advanced sensors
- Preventing methane emissions

PHMSA Pipeline Incidents: Count (2000-2019)



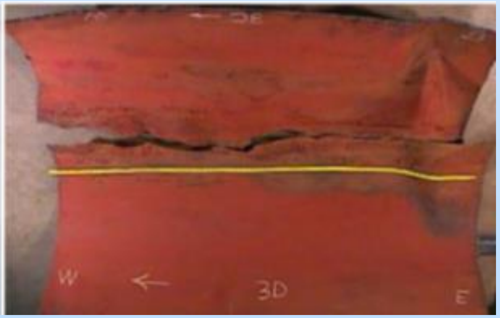
Top 3 Incident Causes for each system:

Transmission & Gathering:
1. Material/Weld/Equip Failure
2. Corrosion
   1. Internal
   2. External
3. Excavation Damage



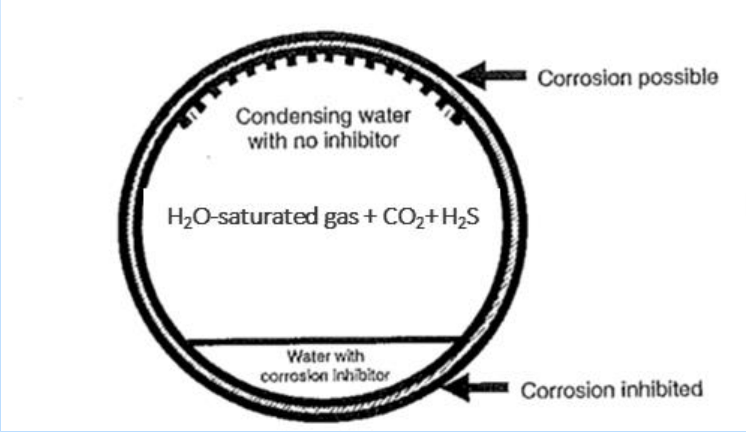
Source: Justman, Rose & Bauer, NETL, 2017. Data analyzed from U.S. DOT PHMSA Incident data

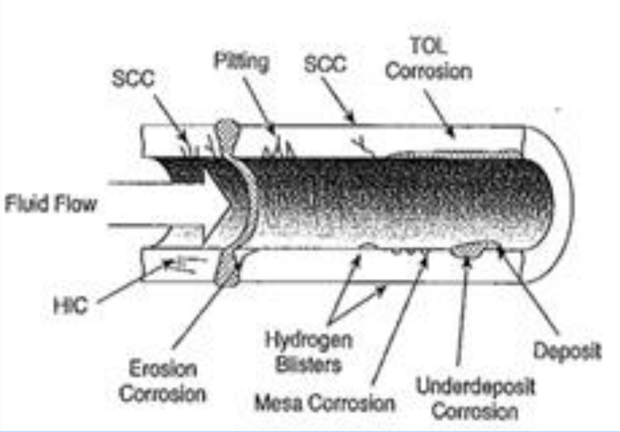
Improved pipeline reliability

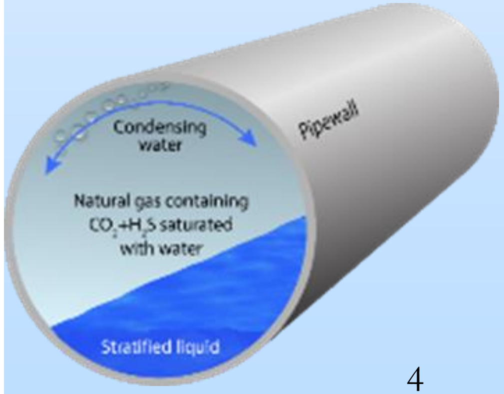


Background: Advanced Pipeline Materials

- Water is the primary cause of corrosion
  - Transmission pipelines are nominally dry, but water is regularly found in lines
- CO_2 is the 2nd most important contributor to corrosion
  - A natural gas transmission pipeline might be expected to have a partial pressure of 310 kPa (45psig) of CO_2
- Solution to this problem: **Coatings & liners** to protect internal pipeline against corrosion by preventing permeation of corrosive species







Approach to Mitigating Internal Pipeline Corrosion & Methane Emission: Coatings and Liners

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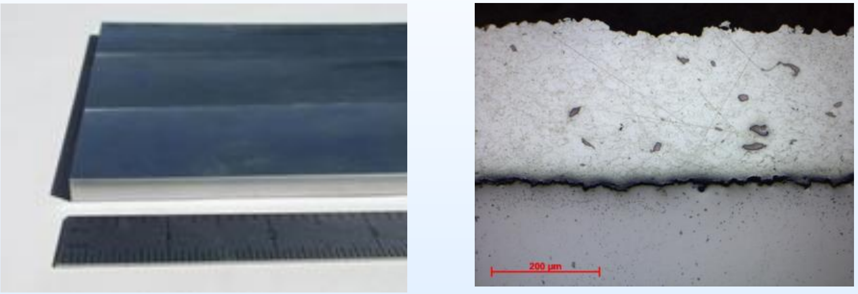
Corrosion Protection through Internal Pipeline Coatings (Subtask 3.1PI: Joseph Tylczak)

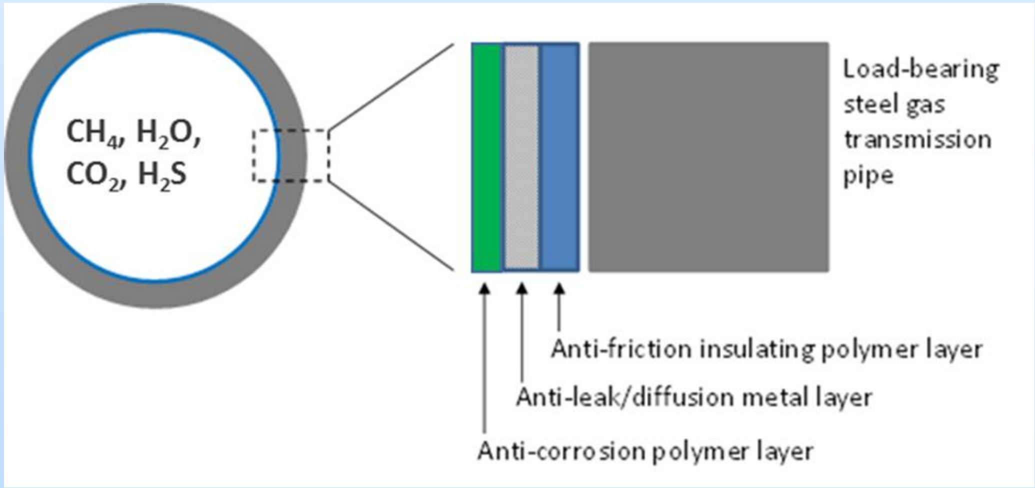
Developing and Demonstrating Zn-Metal Binary Coatings



Binary coatings

Corrosion Protection through Liners (Subtask3.2 PI: Ömer Doğan)

Developing and Demonstrating Multi-Layered Composite Liners for Insertion into Pipe.

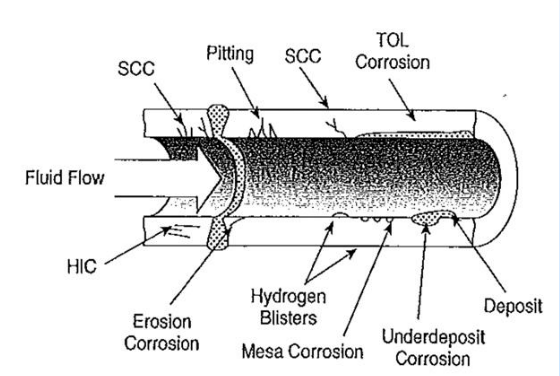


Background: Metallic Coatings for Corrosion Protection

- Corrosion is a thermodynamic process returning iron back to its lower energy state. A simple battery is an example of a corrosion process with voltage and current being the result.
  - The corrosion process can be limited by a counter voltage being impressed on the corroding metal.
- Corrosion can also be kinetically limited by the formation of a passive layer on a surface.
  - Aluminum oxide on aluminum is an example of this stable film protecting the metal.
- Use of a sacrificial alloy on a steel pipe surface is an example of the first process to limit the corrosion.
- Alloying the sacrificial alloy to generate a protective oxide (or carbonate) is an example of the second process.

We are combining these processes with the sacrificial metal coating work to make a self repairing/healing, protective layer.

Cathodic protection, including sacrificial metal (anode) are commonly used to protect external pipeline surfaces; the Challenge is to determine feasibility and methodologies for protecting internal surfaces in NG pipeline environments against different forms of corrosion.



Gas Distribution	Major Gas Impurities	Current pipeline material	Major Corrosion Issues
Natural gas and NG/H_2 blends	CO_2, H_2O, H_2S	API 5L steel	Uniform, localized corrosion, hydrogen–induce corrosion
CO_2	H_2O, O_2, SO_2	API 5L steel	Uniform and localized corrosion
H_2	H_2S	API 5L steel	Hydrogen damage and hydrogen induced cracking

Technical Approach: Task 3.1-Corrosion Protective Metallic Coatings Development

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Date	Milestone
3/31/2021	Selection of the most promising Zn-metal binary coatings
3/31/2021	Determination if Zn binary alloys do not produce sufficient electrical potential to generate atomic hydrogen on API 5L steels under pipeline conditions inducing hydrogen embrittlement (HE) and crack initiation.
3/31/2021	Evaluation of crack growth rate on notched samples under pipeline conditions
3/31/2022	Successful evaluation of the selected binary coating in the field.
3/31/2023	Demonstrate a coated natural gas pipeline that features a low corrosion rate (< 0.01 mm/year) under actual field conditions.

Metric Coated	State of Art	Project Target
Coated Steel Corrosion Rate	0.1 mm/y	<0.01 mm/y

Metallic Coatings: Progress

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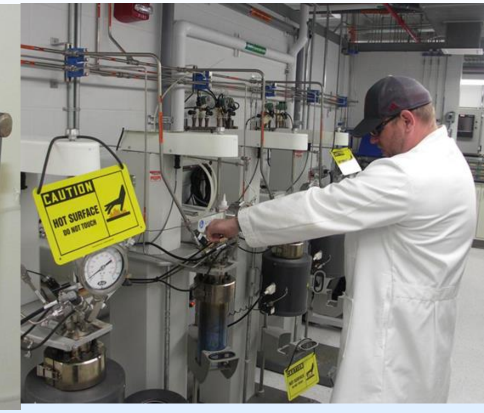
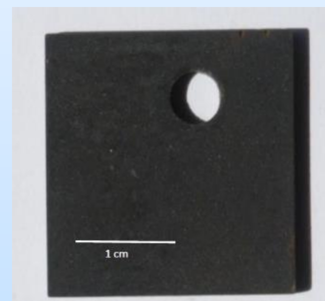
Key Accomplishment

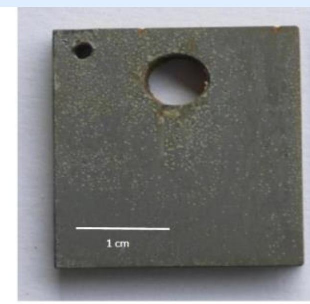
- **Demonstrated the effectiveness of Zn and Al as sacrificial anode to protect API 5L X-65 steel in simulated NG pipeline environment**
  - Corrosion rate determination of each metal in the galvanic couple.



Material	Temp, ° C	Gas	Pressure, atm(g)	Corrosion, mm/y	Sacrificial anode corrosion, mm/y
X65	40	air	0	0.12	
X65	40	CO_2	0	0.16	
X65	40	CO_2	3	0.94	
Al	40	CO_2	3	0.04	
Zn	40	CO_2	3	0.09	
X65-Coupled to Al	40	CO_2	3	0.01	0.78
X65-Coupled to Zn	40	CO_2	3	0.01	0.10



X-65 after immersion in 3.5% NaCl In CO_2, 45 psig, 40 °C



X-65 coupled to Zn or Al after immersion in 3.5% NaCl In CO_2, 45psig, 40 °C

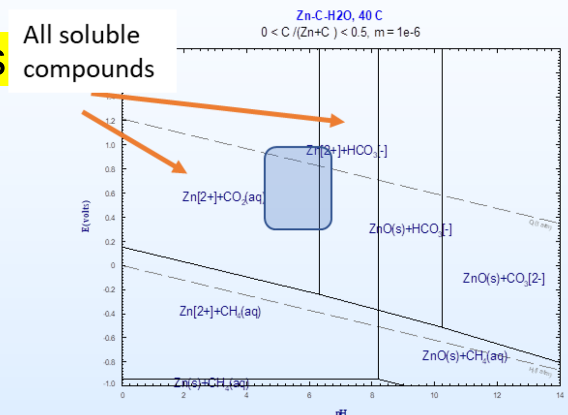
Zn is more suitable than Al as sacrificial coating.

Metallic Coatings: Progress, continued

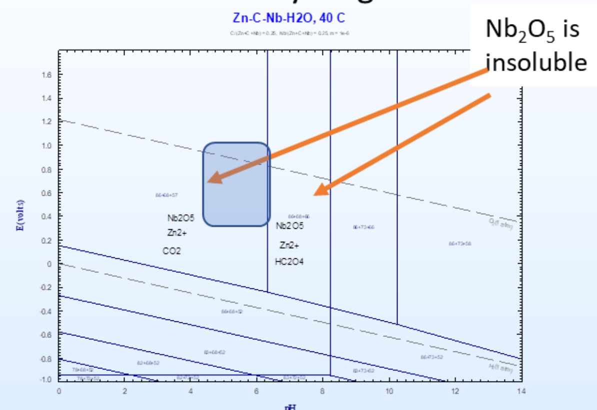
Key Accomplishment

- Designed a zinc-based alloys with better corrosion performance than pure zinc using FactSage and ThermoCalc thermodynamic databases
  - Corrosion performance confirmed by electrochemical corrosion screening test

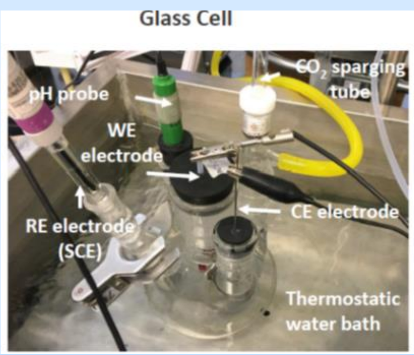
Zn alloy diagram

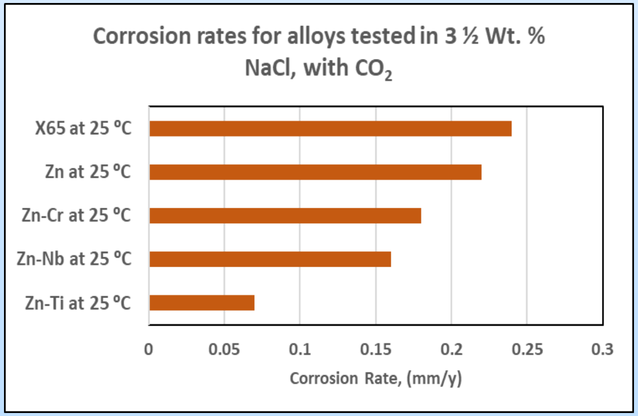


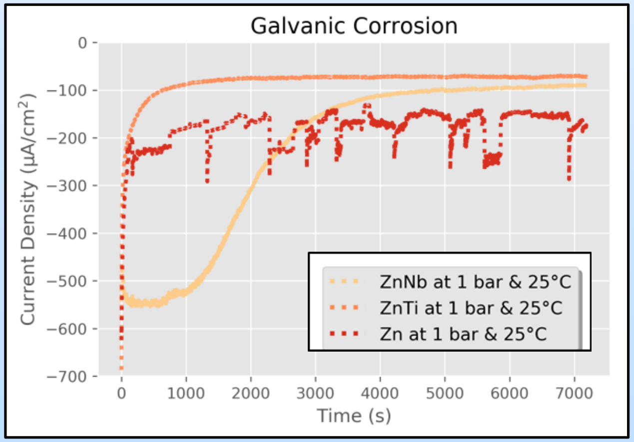
ZnNb alloy diagram



Zn-Nb alloy shows compounds that could form protective scales in the pH range of interest (pH of ~4 to 6.5), rather than soluble ions.







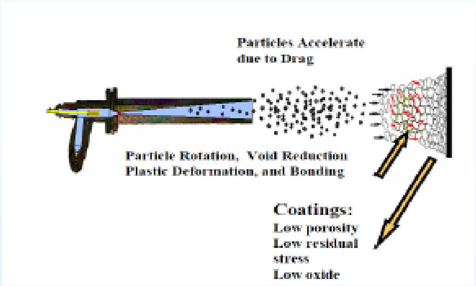
- Improved corrosion resistance at 25 °C, in CO_2 saturated 3.5% NaCl
- Lower corrosion and galvanic corrosion currents

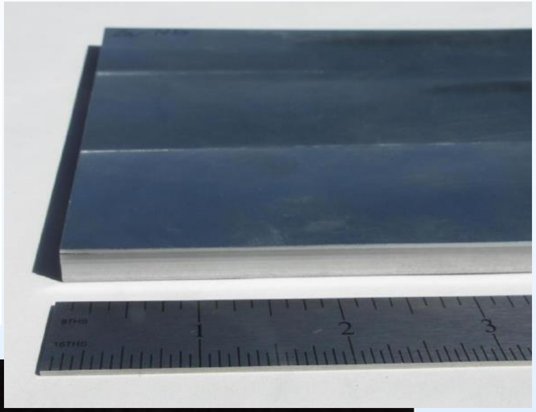
Metallic Coatings: Progress, continued

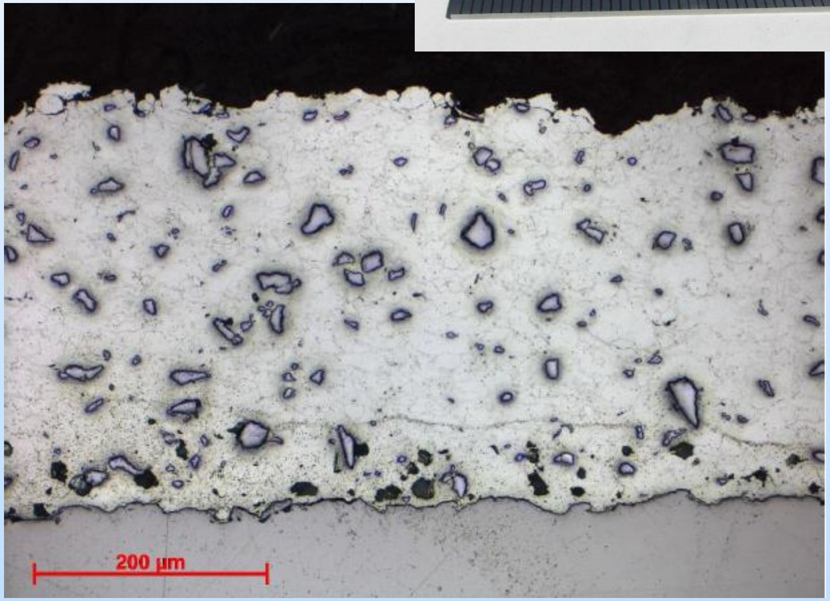
Key Accomplishment

Successfully demonstrated cold spraying as a method to deposit Zn-binary alloy coating on X65.

- Cold spray is a scalable industrial process. Solid state process powders are accelerated in supersonic gas jet. Upon impact powders undergo plastic deformation and adhere to the surface. Uniform coating are achieved by controlled scanning the substrate with the nozzle.







Cold spray deposition at the South Dakota School of Mines

Immersion tests: Autoclave 3 bar pressure

Coating

Steel side

ZnCr ZnNb ZnTi samples

Immersion testing at NETL

Metallic Coatings: Progress, continued

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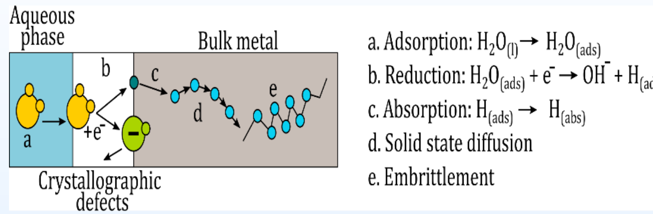
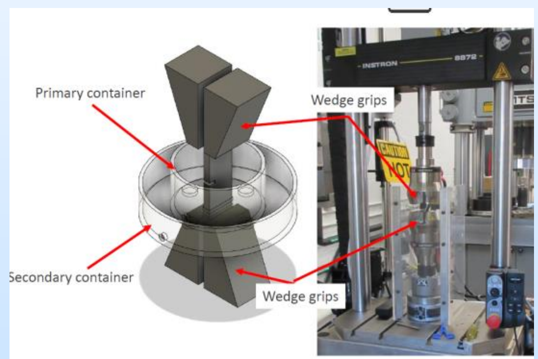
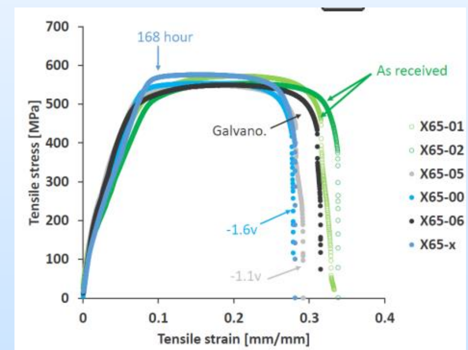
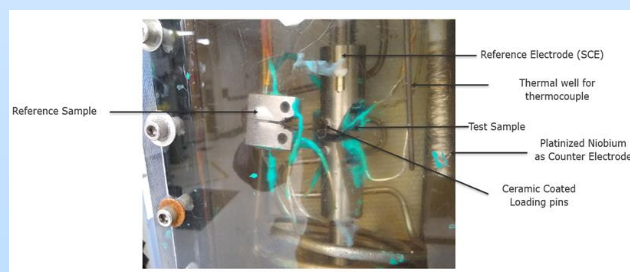
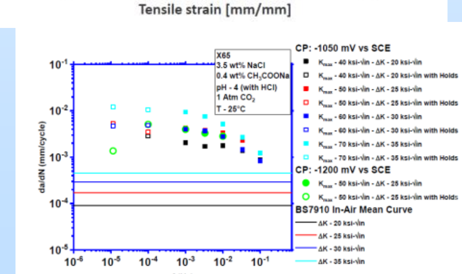
- **Hydrogen Embrittlement Challenge:** Atomic hydrogen generated during dissolution of pipeline steel, dissociation of hydrogen present in natural gas can cause hydrogen embrittlement that can result in catastrophic failures of pipelines.
- **Key finding**:
  - <u>Smooth tensile samples</u>: No evidence of hydrogen embrittlement was found from ex-situ mechanical testing of X-65 electrochemically pre-charged with hydrogen.
  - <u>Notched samples</u>: In-situ hydrogen charging increased fatigue crack growth rate compared to uncharged sample ((experimental work in collaboration with DNV-GL)











It appears that investigating in-situ crack initiation will improve data reliability.

<u>No HE crack initiation no catastrophic HE failure</u> If NETL self-healing coatings prove to be non-permeable, they will block hydrogen entry into steel and prevent HE inside pipe

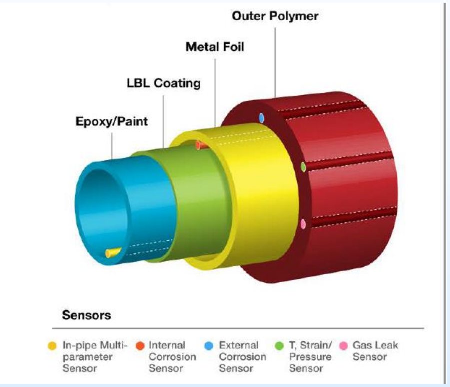
Metallic Coatings: Focus

- EY20 Binary Metallic Coatings Corrosion: Binary coatings of ZnCr, ZnTi and ZnNb are evaluated for their protectiveness by evaluating susceptibility to general corrosion, localized corrosion, and hydrogen-assisted corrosion in simulated natural gas environments.
  - Milestone: Selection of the most promising binary coating.
- EY20- Hydrogen Embrittlement Effects: Galvanic potential between model sacrificial Zn alloys and American Petroleum Institute's (API) pipeline steel will be measured. Hydrogen permeation rate values for API steel in brine solutions and crack propagation will be measured.
  - Milestone: Determination if Zn model alloys produce sufficient electrical potential to generate atomic hydrogen on API 5L steels in pipeline conditions and evaluation of crack growth.
- EY21-Binary Metallic Coating Field Testing: Demonstrate coating interior section of pipe. Test panel, with the selected binary coating for installation in a natural gas pipeline system.
  - Milestone: Initiate field test of selected binary coating.
- EY22 - Sacrificial Coating Optimization: Using the results from the field testing, the composition of the advanced sacrificial coating will be refined for longer operational life and ease/cost of application.
  - Milestone: A lower cost coating will be prepared for field evaluation.

Technical Approach: Subtask 3.2 Composite Liners Development

Milestones

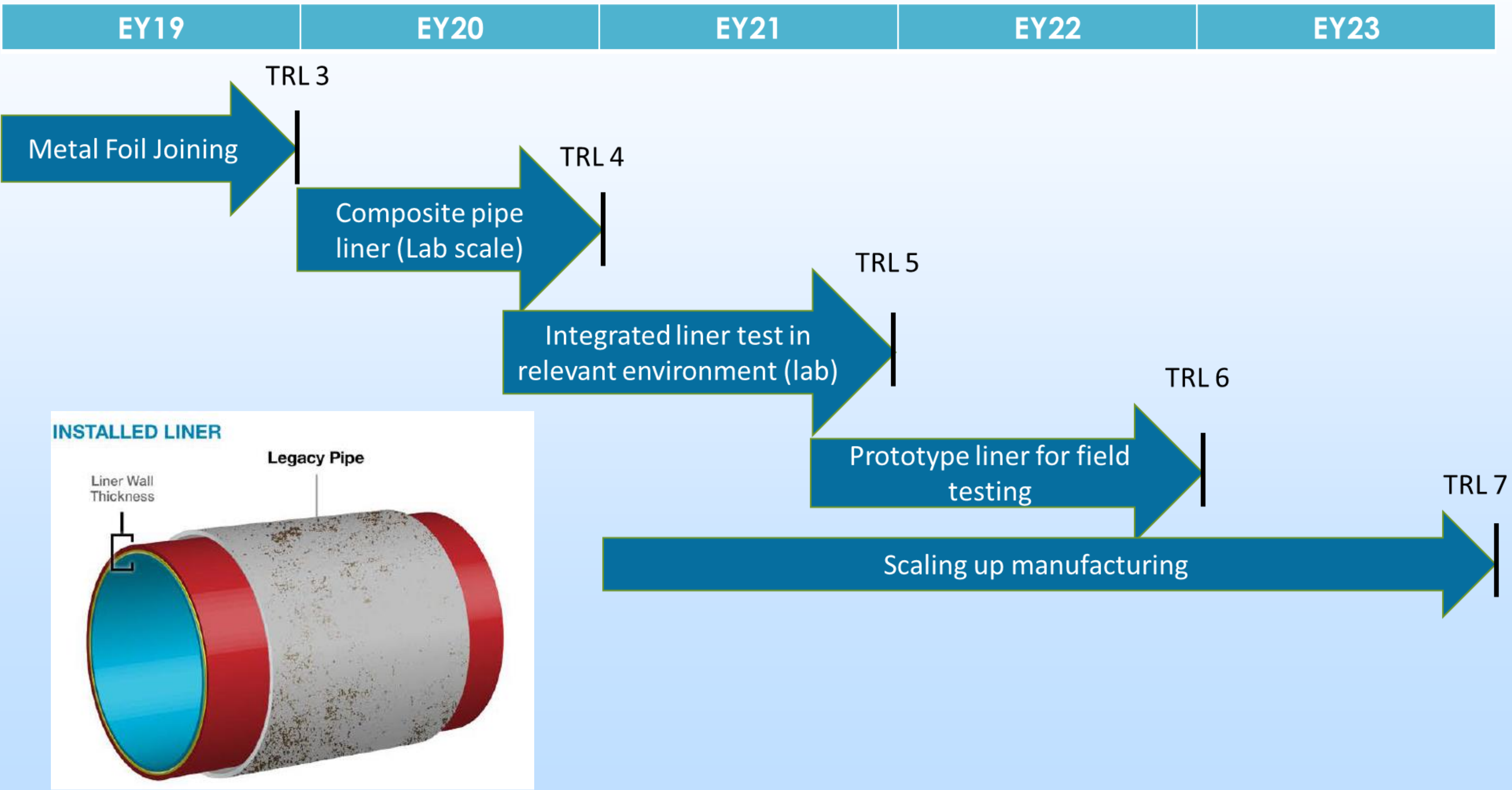
03/31/2020	Demonstrate joinability of a thin metal foil
03/31/2021	Demonstrate that a metal foil liner shape can be made using the joining methodology,
03/31/2022	Manufacture a prototype metal liner for a natural gas pipeline
03/31/2023	Manufacture a prototype composite liner that can be installed and tested in the field.



Metrics / Success Criteria

Metric	State of the Art	Proposed
Corrosion rate	0.01 mm/year	<0.001 mm/year
Coating integrity and pipeline heath monitoring	Point sensors, Costly, Infrequent inspection	Real-time distributed monitoring for >100km with <1m spatial resolution, 5-fold cost reduction
Hydrogen permeability	10^{-10} mols/m $Pa^{0.5}$ s	$<10^{-14}$ mols/m $Pa^{0.5}$ s
Cost	$1M-$10M per mile	$0.73M per mile ($0.41M per mile)

Composite Liner Technology Maturation

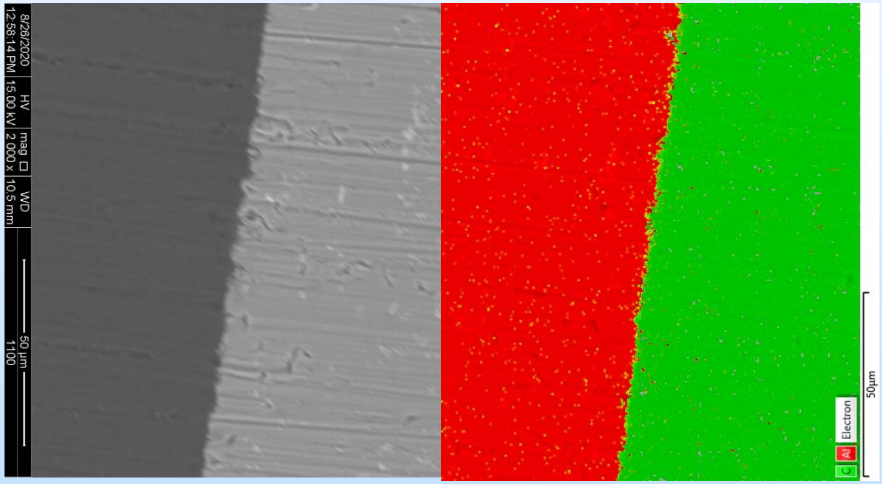


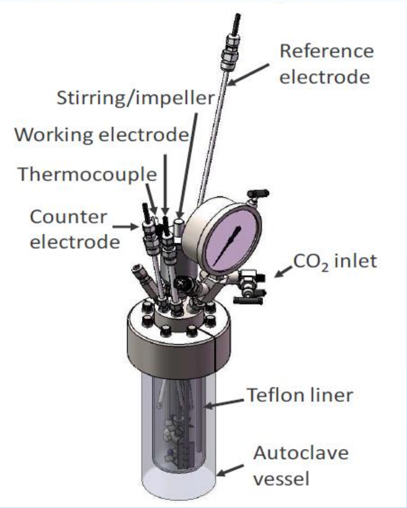
Composite Liners Progress: Why is Al a Good Choice for Foil in Composite Liner

- Inexpensive

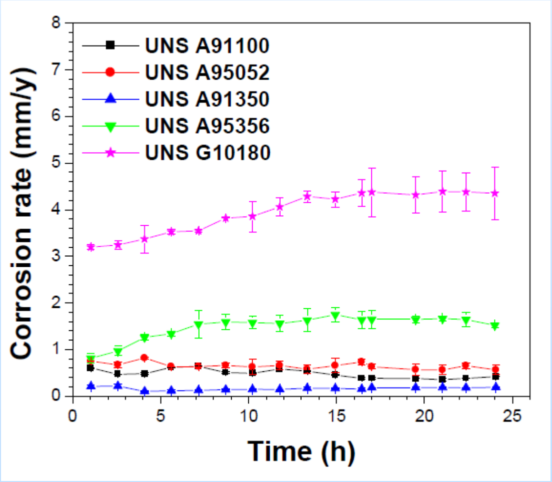
Key Accomplishment

- Al that does not contain electrically-conductive inclusions **is resistant to localized corrosion and has low corrosion rate** in 3.5% NaCl saturated with CO_2 at 40 °C and 4 bar CO_2.





NETL's Electrochemical Reaction Autoclave for performing in-situ electrochemical experiments at high pressures and temperatures in corrosive environments



Demonstrated that Al can be resistant to localized corrosion in chlorides that are pitting agents.

Composite Liners: Progress

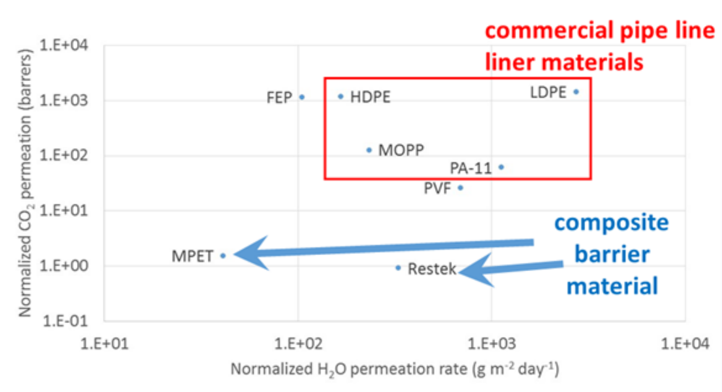
Key Accomplishments

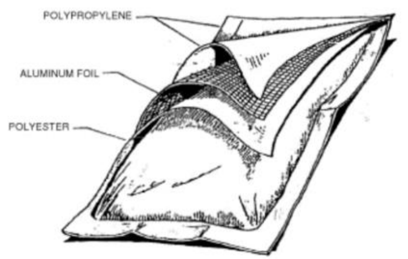
Demonstrated concept feasibility. Metal-Polymer layered composites were more resistant to CO_2 and methane permeation compared to polymer control samples representative of commercial pipeline liner materials in use today.

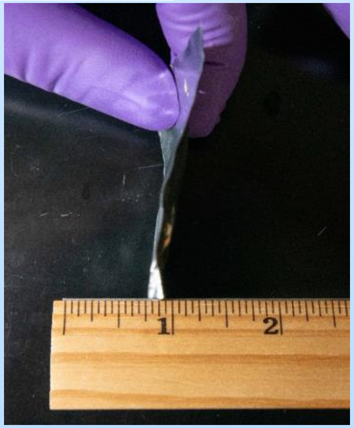
Key Finding

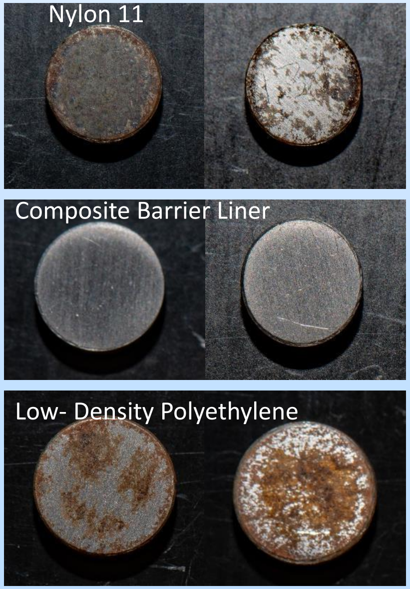
- **No apparent corrosion of steel coupons when protected by composite barrier liner, being exposed to a corrosive environment (wet carbon dioxide) at either ambient or elevated pressures.**
- **No apparent permeation of gases into the commercial barrier liner sample bags during the experiment for up to four weeks.**

NETL gas permeation apparatus

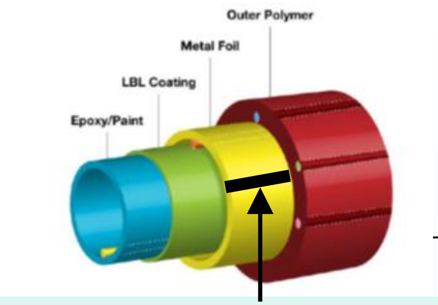








Challenge: Manufacturing Metal Foil "Pipe"
Solution: Joining

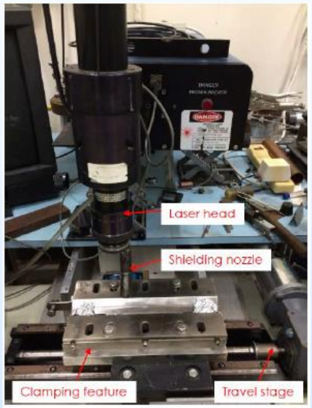


Length-wise joint along foil to create foil "tube or pipe"

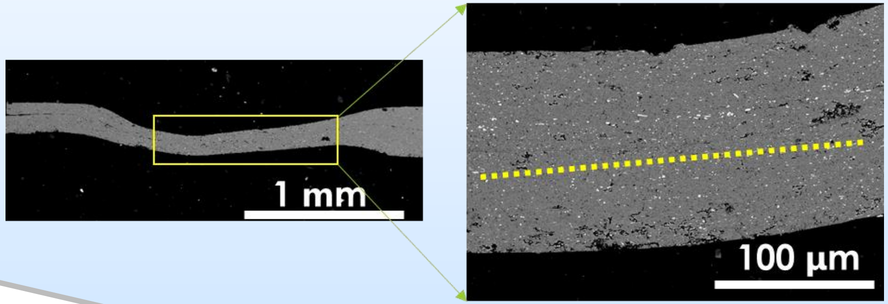
Laser and ultrasonic welding techniques were investigated to join aluminum foils in collaboration with ORNL

<ins>FY19/20 Key accomplishment</ins>:

Demonstrated that thin metal foils can be joined without defects



Laser Welder



Ultrasonic Welder

Weld quality	Good	Good
Weld speed (m/min)	0.5-2.5	0.4-4
Setup	Clamping is critical to joint quality	No clamping required
Effect on microstructure	Formation of fusion zone, and heat affected zone	No obvious microstructure alteration
Shield gas	Argon	None
Safety	Laser might be harmful	Not harmful to operator

Composite Liners: Focus

- EY20 - Demonstration of a joining method to fabricate a continuous metal liner: The successful joining method from EY19 is implemented to produce short liners of different diameters (seam tubes and pipes using aluminum foil) in a laboratory scale. Ability of the joining technique to be used as a continuous process will be assessed.
  - Milestone: Demonstrate that a metal foil liner shape can be made using the joining methodology and that the liner including the joint forms a barrier to methane and water molecules.
- EY21-22- Scaling Up the Joining Method to Fabricate Prototype Liners: In collaboration with an industrial partner, an effort to scale up the joining technology will be undertaken. The goal of this effort will be to develop a method that can produce a continuous, defect free metal liner prototype for a natural gas pipeline.
  - Milestone: Manufacture a prototype metal liner for a NG pipeline using a process that is scalable to continuous production.

NETL Coatings and Liners for Industry

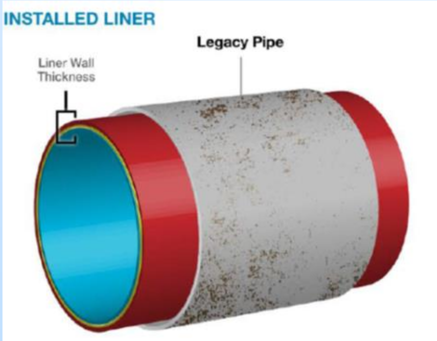
- To validate that NETL Coatings and Liners work, NETL is planning field testing
    - Recently, NETL and GTI have discussed potential place for testing metallic coatings in natural gas
- Transport of Natural Gas/ Hydrogen blends in existing natural gas pipelines will require field testing of NETL coatings and liners.
    - NETL researchers working on this project are involved in developing NETL/ RIC Hydrogen Program, in which liners and coatings are very important.
- Once demonstrated through field trials, NETL Coatings and Liners can be transferred to the industry. Products developed in this project will provide a foundation for modifying these materials for working in other environments.

Pipeline Material Technology: Summary

- **Sacrificial metal coatings of interior of line pipe.**
  - Demonstrated that coatings will protect pipeline steel in a pipeline environment in the laboratory
    - Hot dipping zinc on steel is an industrial process
  - Effects of electrochemically generated hydrogen on steel pipelines are being explored; however
    - Initial data indicate no hydrogen embrittlement on ex-situ hydrogen pre-charged samples after tensile test and increased crack propagation in notched samples electrochemically charged in-situ with hydrogen in fatigue tests
- **Improved sacrificial coatings**
  - Designed and created new coatings that show superior performance in the laboratory on-going testing
  - Coatings have been successfully applied via Cold Spray technique
- **Composite Liners**
  - Demonstrated that addition of a metal layer in a polymer matrix is responsible for this improved performance
  - Demonstrated that thin metal foils can be joined without defects
  - Demonstrated that inclusion free Al can be resistant to localized corrosion in chlorides that are pitting agents.

Pipeline Material Technology: Summary, continued

- **Expected project outcomes upon completion** :
  - Material technologies that mitigate methane leakage through reliable pipeline corrosion protection
  - Enabling flexible pipeline corrosion protection
  - Materials and processes for pipeline manufactures



Publication list: 9 papers, 10 presentations, 1 patent application

Appendix

Organization Chart

- **National Energy Technology Laboratory**
  - **Research & Innovation Center**
    - **Materials Engineering & Manufacturing Engineering Directorate**
      - **Structural Materials Team Members** working on the Advanced Pipeline Materials Development Project focusing on *Materials Development and Design* :
      - *Joseph Tylczak- 3.1 Subtask* Coatings PI: area of expertise-*metallurgy*
      - *Ömer Doğan*-3.2 Subtask Composite Liners PI; area of expertise-materials science and engineering
      - *Margaret Ziomek-Moroz*, Task 3 PI: area of expertise: *corrosion science and engineering*
      - *Peter Hsieh*, area of expertise-*materials science and engineering*
      - **Functional Materials Team**: *David Hopkinson,* area of expertise: *chemical engineering*
      - **NETL/ Leidos Research Support** *Members* with expertise in materials science and engineering: *Zineb Belarbi, Kyle Rozman, Kaimiao Liu*, *Fangming Xiang;* **NETL/ORISE Postdoctoral Researcher:** *Lucas Teeter –Ph.D. in materials science and engineering*

External Collaborators: DNV-GL, Oak Ridge National Laboratory (ORNL), Oregon State University (OSU), South Dakota School of Mines and Technology

Progress Chart

Development of Advanced Pipeline Materials: Metallic Coatings and Composite Liners