

# **Development of Advanced Pipeline Materials: Metallic Coatings and Composite Liners**

Task 3 Natural Gas Infrastructure FWP 1022424

Program: 1611133 – Emissions Mitigation

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Ömer Doğan (PI), Kyle Rozman, Lucas Teeter, Kaimiao Liu, Fangming Xiang

U.S. Department of Energy/National Energy

Technology Laboratory, Research & Innovation Center

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U.S. Department of Energy

National Energy Technology Laboratory

2021 Carbon Management and Oil and Gas Research Project Review Meeting

August 2021

# Presentation Outline

- Overview of Advanced Pipeline Materials Project
- Background & Objectives
- Approach to Mitigate Internal Corrosion & Methane emission: Coating and Liners
- Pipeline Material Technology: Summary

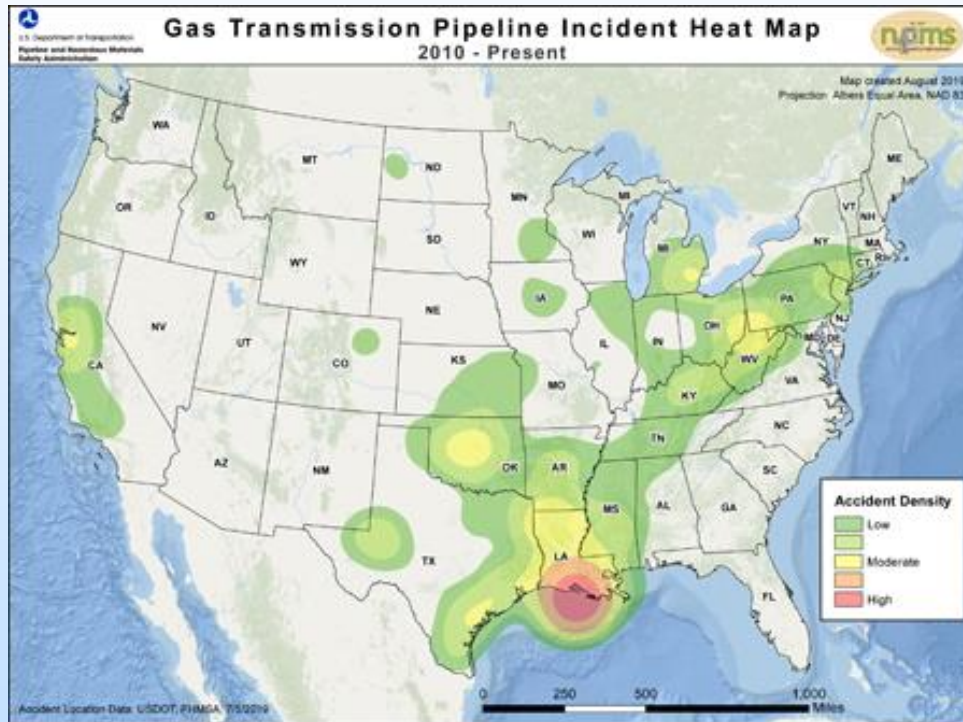
# Overview of Advanced Pipeline Materials Project



- Project Funding: EY21: \$882K
- Overall Project Performance Dates: April 1, 2021-March 31, 2024
- 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

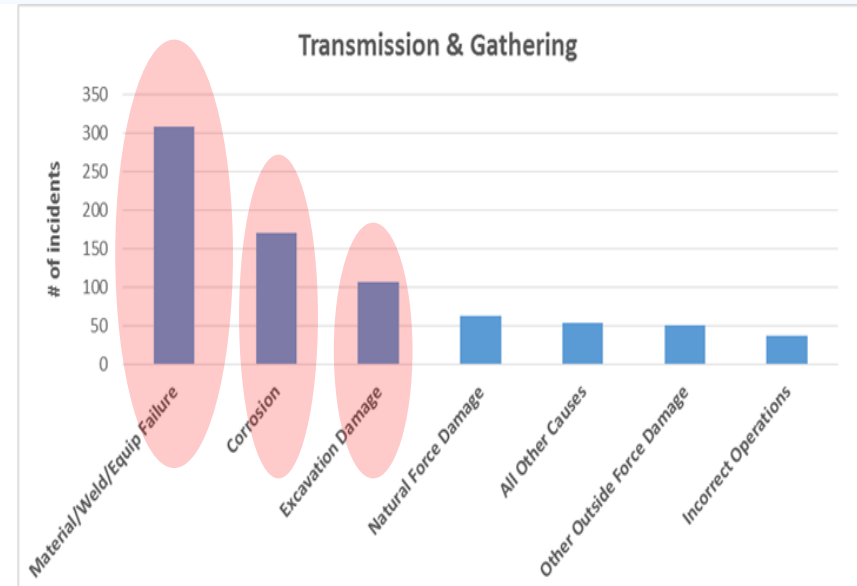
# Overview: Advanced Pipeline Materials, Continued

The U.S. Department of Transportation reported numerous case histories of corrosion problems and failures in wet in gas pipelines.

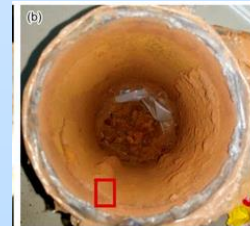


Incident Density of Gas Transmission Pipeline Incidents\*

Top three incident causes in transmission & gathering system (1998-2017)\*\*



Internal corrosion



External corrosion



Excavation damage



\*<https://www.phmsa.dot.gov/incident-reporting/accident-investigation-division/accident-maps>

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

# Objectives: Advanced Pipeline Materials

## Overall Project Objectives

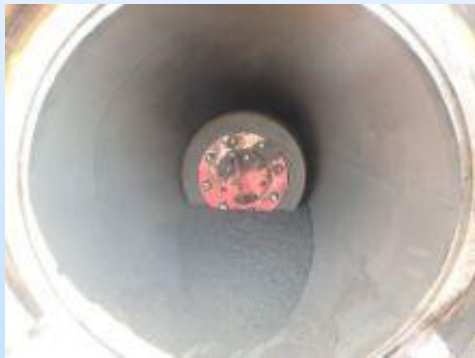
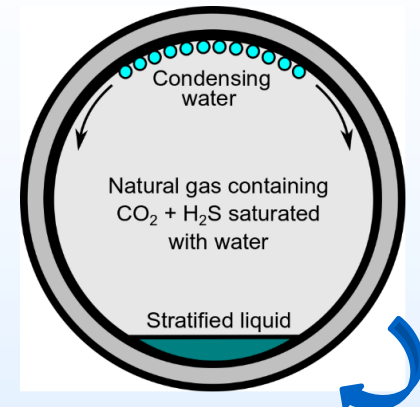
Develop **removable liners** and easy-to-deposit **long-lasting, self-healing, affordable coatings** for natural gas, hydrogen/ natural gas blends, and hydrogen transport, capable of:

- Preventing corrosion in metal pipelines
  - Reducing corrosion rate of pipelines below 0.1 mm/ year to be monitored by advanced sensors
- Preventing methane emissions
- Identifying an alloy/pipeline material with suitable mechanical and corrosion properties for transporting natural gas, H<sub>2</sub>, and CO<sub>2</sub>

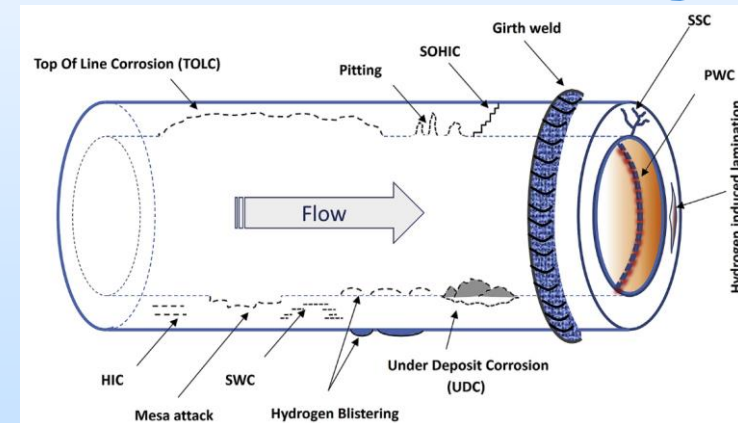


# Background: Advanced Pipeline Materials

- Water is the primary actor in causing corrosion inside the gas pipelines
- CO<sub>2</sub> is the second most important contributor to corrosion
  - A natural gas transmission pipeline might be expected to have a partial pressure of 310 kPa (45psig) of CO<sub>2</sub>



Heavy black powder deposits\*



Different form of internal corrosion in natural gas pipeline \*\*

- Solution to this problem: **Coatings & liners** to protect internal surface of pipeline against corrosion

\*<https://www.rosen-group.com/global/solutions/industry-case-studies/oil-gas/Case-Study-Black-is-Black.html>

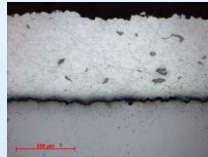
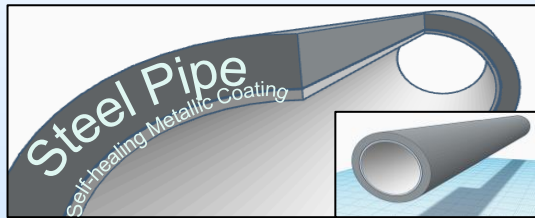
\*\*M. Askari et al., Journal of Natural Gas Science and Engineering, 71, November 2019, 102971



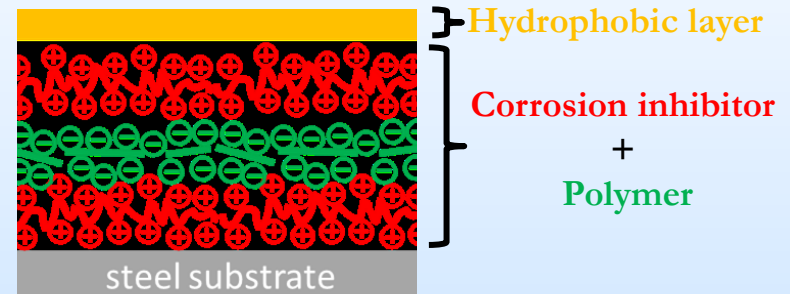
# Approach to Mitigating Internal Pipeline Corrosion & Methane Emission: Coatings and Liners

## Corrosion Protection through Internal Pipeline Coatings (Subtask 3.1)

- Corrosion Protection through Zn-metal binary materials

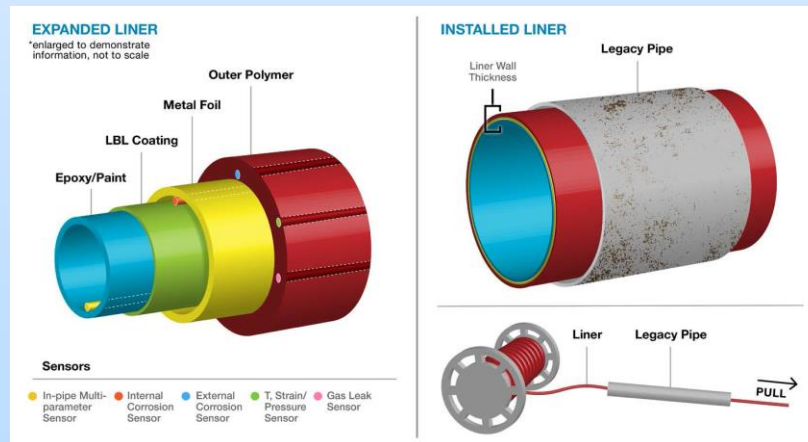


- Corrosion Protection through polymer -Based multilayer coatings



## Corrosion Protection through Liners (Subtask 3.2)

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



# Technical Approach: Task 3.1-Corrosion Protective Metallic Coatings Development



Date	Milestone
3/31/2022	Identify at least one binary metal binary coatings with the reliable self-healing properties.
3/31/2022	Demonstrate a corrosion-protective coating that can reduce the corrosion rate of carbon steel (API 5L X65 grade) to < 0.1 mm/ year under simulated pipeline test conditions in the laboratory.
3/31/2022	Demonstrate level of risk for H <sub>2</sub> embrittlement and level of uptake of H <sub>2</sub> for binary metallic coated alloys.
3/31/2022	Identify at least one promising alloy for a multi-purpose pipe transporting natural gas, H <sub>2</sub> , and CO <sub>2</sub> .
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.
09/31/2024	Technical support for successful demonstration of a coated natural gas pipeline that features a low corrosion rate (< 0.1 mm/ year) under actual field conditions as part of Subtask 7.4.

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





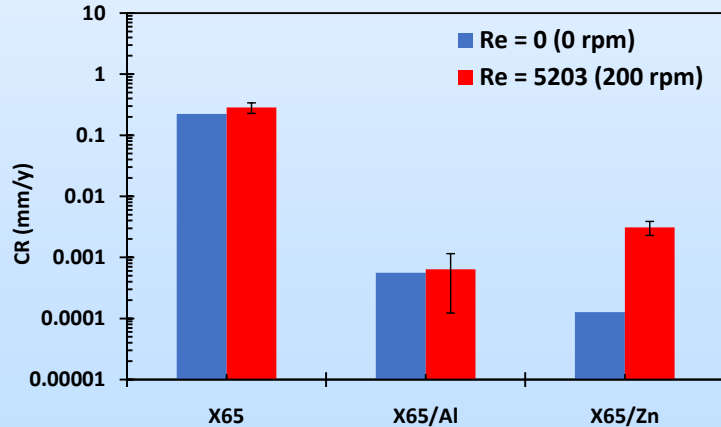
# Metallic Coatings: Progress

## Key Accomplishment

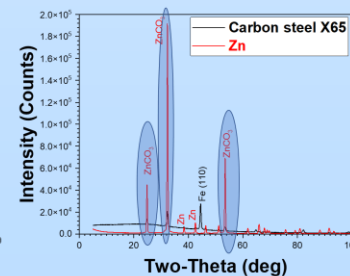
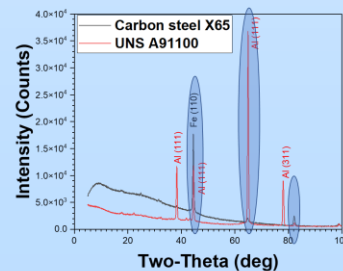
- Demonstrated the effectiveness of Zn and Al as sacrificial anode to protect API 5L X-65 steel in simulated NG pipeline environment



$p_{CO_2} = 45$  psig,  $T=40^\circ C$ , 3.5 wt% NaCl, 7 days



Re	Without galvanic coupling	Galvanic coupling with Al	Galvanic coupling with Zn
0			
5300			

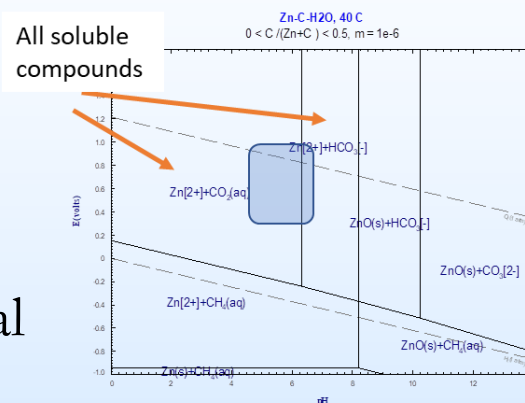


# Metallic Coatings: Progress, Continued

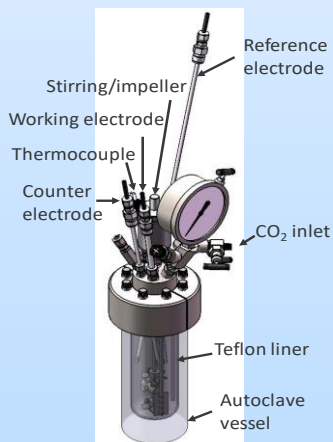
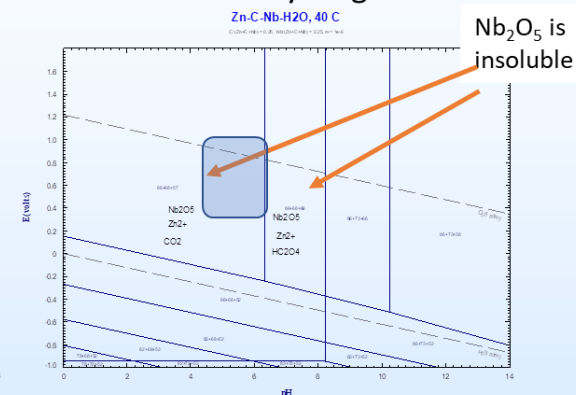
## Key Accomplishment

- Designed a zinc-based alloys with better corrosion performance than pure Zinc
- Corrosion performance confirmed by electrochemical corrosion screening test

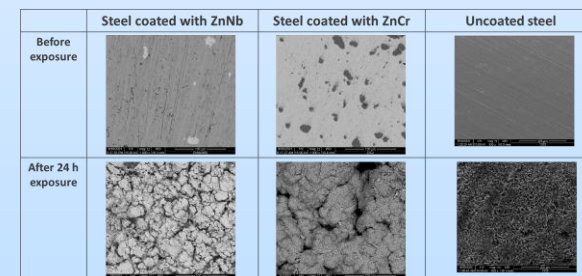
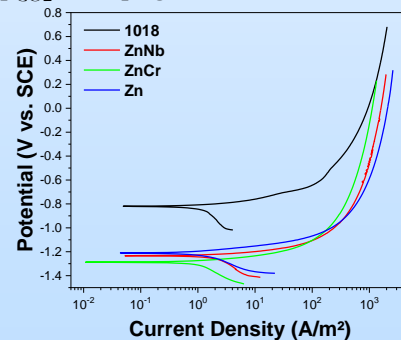
Zn alloy diagram



ZnNb alloy diagram



$P_{CO_2} = 45$  psig,  $T = 40^\circ\text{C}$ , 3.5 wt% NaCl



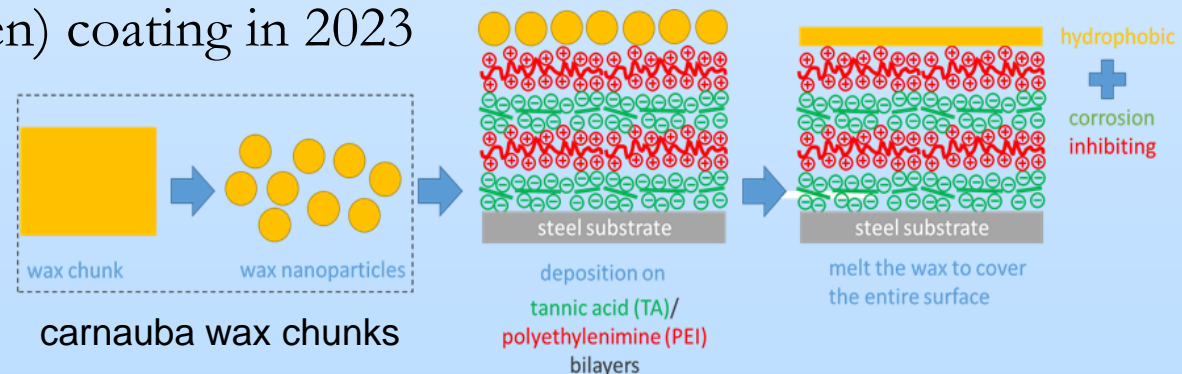
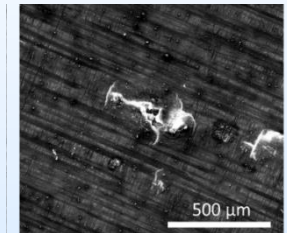
# Polymer-Based Multilayer Coatings: Progress, Continued

## Key Accomplishment

A new multilayer coating that combines corrosion inhibition and hydrophobicity was developed and tested:

- ✓ Wax top layer allows the multilayer coating to be hydrophobic and resistant against CO<sub>2</sub>-caused corrosion
- ✓ A low material cost of ~ \$0.3/ft<sup>2</sup>
- ✓ Currently at TRL 3, expecting a field test of the next generation (4<sup>th</sup> gen) coating in 2023

CO<sub>2</sub> + water

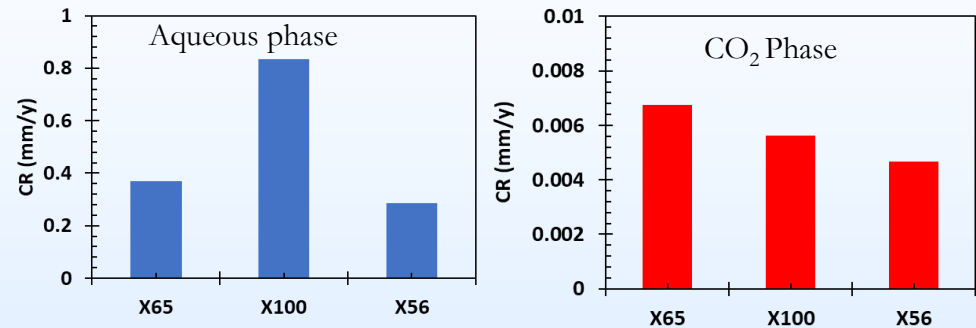


# Alloy for Multi-Purpose Pipe Transporting Natural Gas, H<sub>2</sub>, and CO<sub>2</sub>

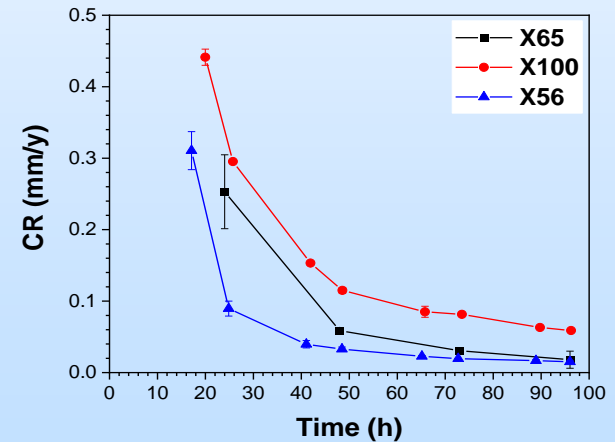
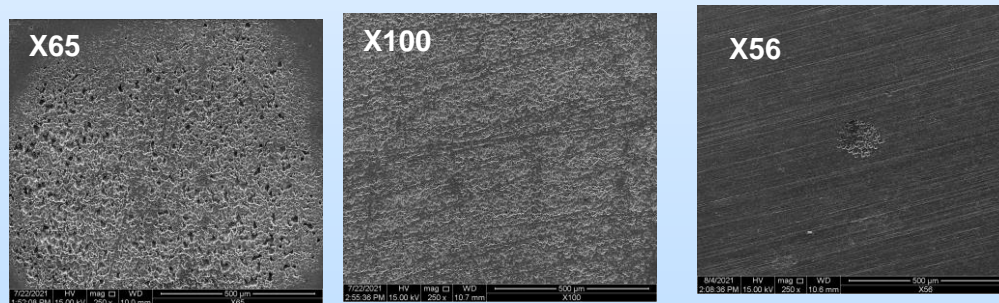
- **Key finding:**

- Tested multiple steel pipelines exposed to supercritical CO<sub>2</sub> environment : Carbon steel X56 showed low corrosion rates

100 barg, 30°C



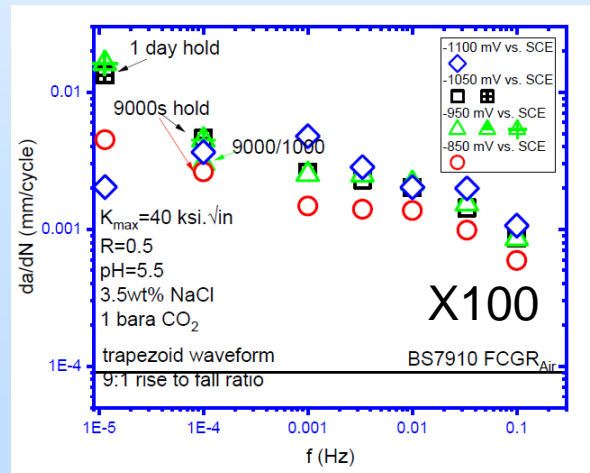
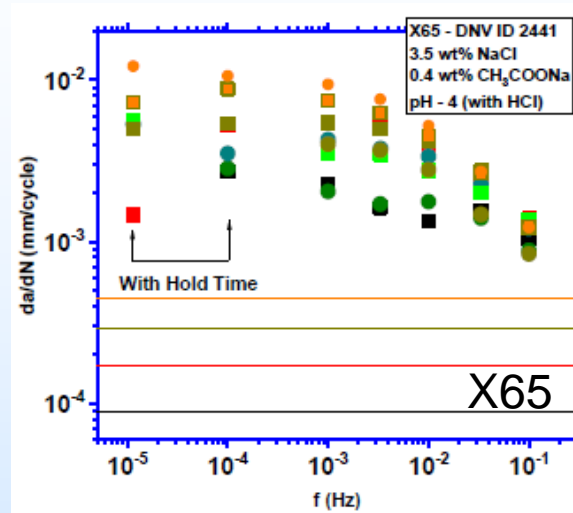
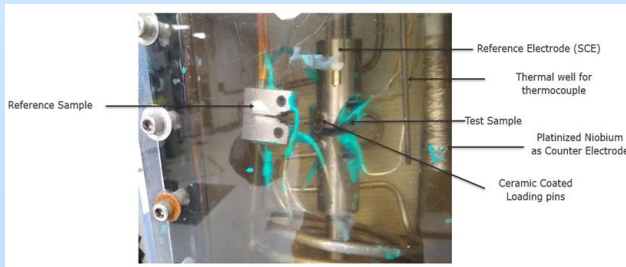
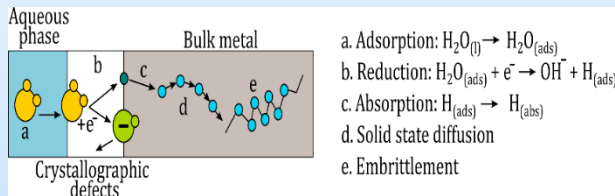
In-situ corrosion measurements





# Steel for Multi-Purpose Pipe Transporting Natural Gas, H<sub>2</sub>, and CO<sub>2</sub>

- Hydrogen Embrittlement**  
**Challenge:** Atomic hydrogen generated during dissolution (corrosion) of pipeline steel and dissociation of hydrogen present in natural gas can cause hydrogen embrittlement that can result in catastrophic failures of pipelines



## Key finding:

➤ Fatigue crack growth rate (FCGR): Both X65 and X100 showed a significant increase in FCGR under cathodic polarization conditions compared to in air testing.

➤ Both steels also showed an increase in FCGR with decreasing frequency.

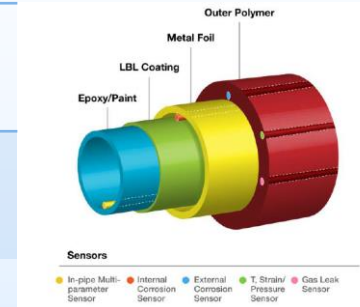
➤ These observations suggest that these steels are susceptible to environmentally assisted cracking

# Technical Approach: Subtask 3.2

## Composite Liners Development

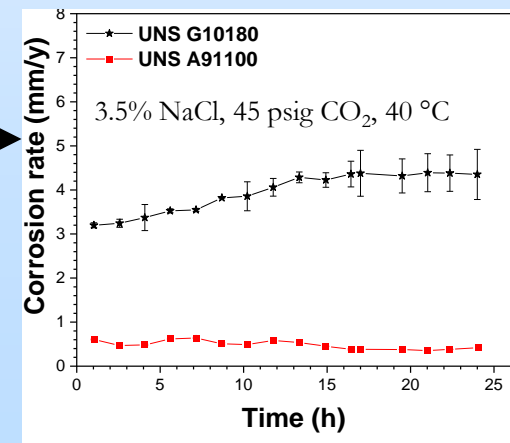
### Milestones

03/31/2022	Manufacture a prototype metal liner for a natural gas pipeline
3/31/2022	Successful pressure testing (no leaks) of a 1-foot section of a 6-inch diameter composite liner.
3/31/2023	Present a detailed description of the composite liner installation technology.
03/31/2024	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 health 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 <sup>0.5</sup> s	$<10^{-14}$ mols/m Pa <sup>0.5</sup> s
Cost	\$1M-\$10M per mile	\$0.73M per mile (\$0.41M per mile)





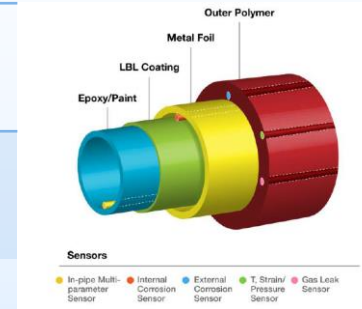
# Technical Approach: Subtask 3.2

## Composite Liners Development



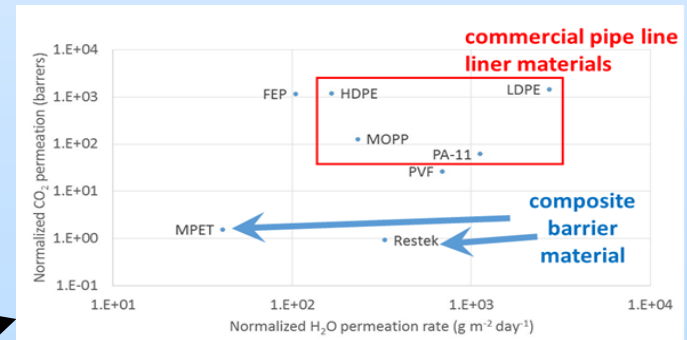
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### Metrics / Success Criteria

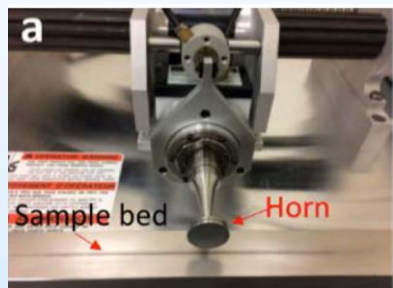
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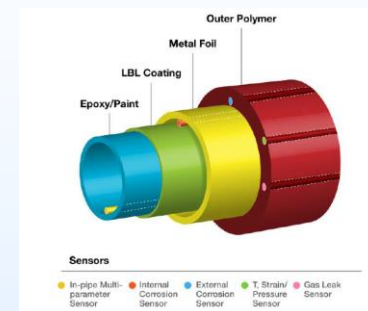
# Challenge: Manufacturing Metal Foil

## “Pipe” Solution: Joining

Ultrasonic welding techniques were investigated to join aluminum foils in collaboration with ORNL

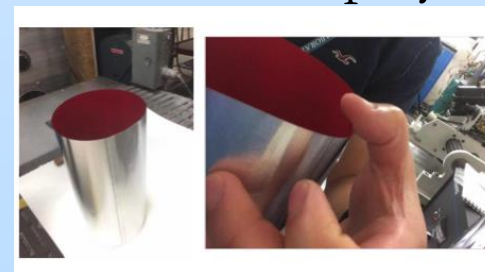
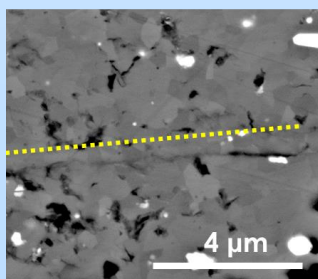


- No clamping system required for this setup, minimize foil wrinkle caused by clamping



### Key accomplishment:

- ✓ Demonstrated that thin metal foils can be joined without defects
- ✓ Aluminum foil only liner prototype welded with ultrasonic welding
- ✓ Liner prototype with interior coated with corrosion resistant polymer



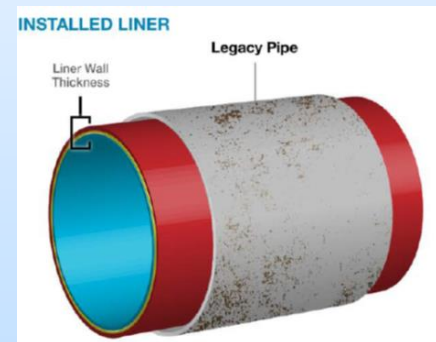
# Pipeline Material Technology: Summary



- ✓ **Sacrificial metal coatings of interior of line pipe**
  - Demonstrated that metallic coatings with self-healing properties will protect pipeline steel in a pipeline environment in the laboratory
  - Developed metallic coatings that show superior performance in the laboratory on-going testing
- ✓ **Alloy for multi-purpose pipe transporting natural gas, H<sub>2</sub>, and CO<sub>2</sub>**
  - Caron steel X56 shows good resistance for supercritical CO<sub>2</sub> corrosion. However, in order to use carbon steel X56 for a multi-purpose pipe transporting natural gas, H<sub>2</sub>, and CO<sub>2</sub>, the level of risk for H<sub>2</sub> embrittlement and level of uptake of H<sub>2</sub> for X56 needs to be investigated
- ✓ **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: 12 papers, 18 presentations, 1 patent application**

# Plans for Future Testing

## Corrosion Protection through Internal Pipeline Coatings

Date	Milestone
3/31/2023	Demonstrate a corrosion-protective coating that can reduce the corrosion rate of carbon steel (API 5L X65 grade) to $< 0.1$ mm/ year under realistic pipeline test conditions in the laboratory.
3/31/2023	Demonstrate a coated natural gas pipeline that features a low corrosion rate ( $< 0.01$ mm/year) under actual field conditions.
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## Corrosion Protection through Liners

3/31/2022	Successful pressure testing (no leaks) of a 1-foot section of a 6-inch diameter composite liner.
3/31/2023	Present a detailed description of the composite liner installation technology.
03/31/2024	Manufacture a prototype composite liner that can be installed and tested in the field.

# Appendix



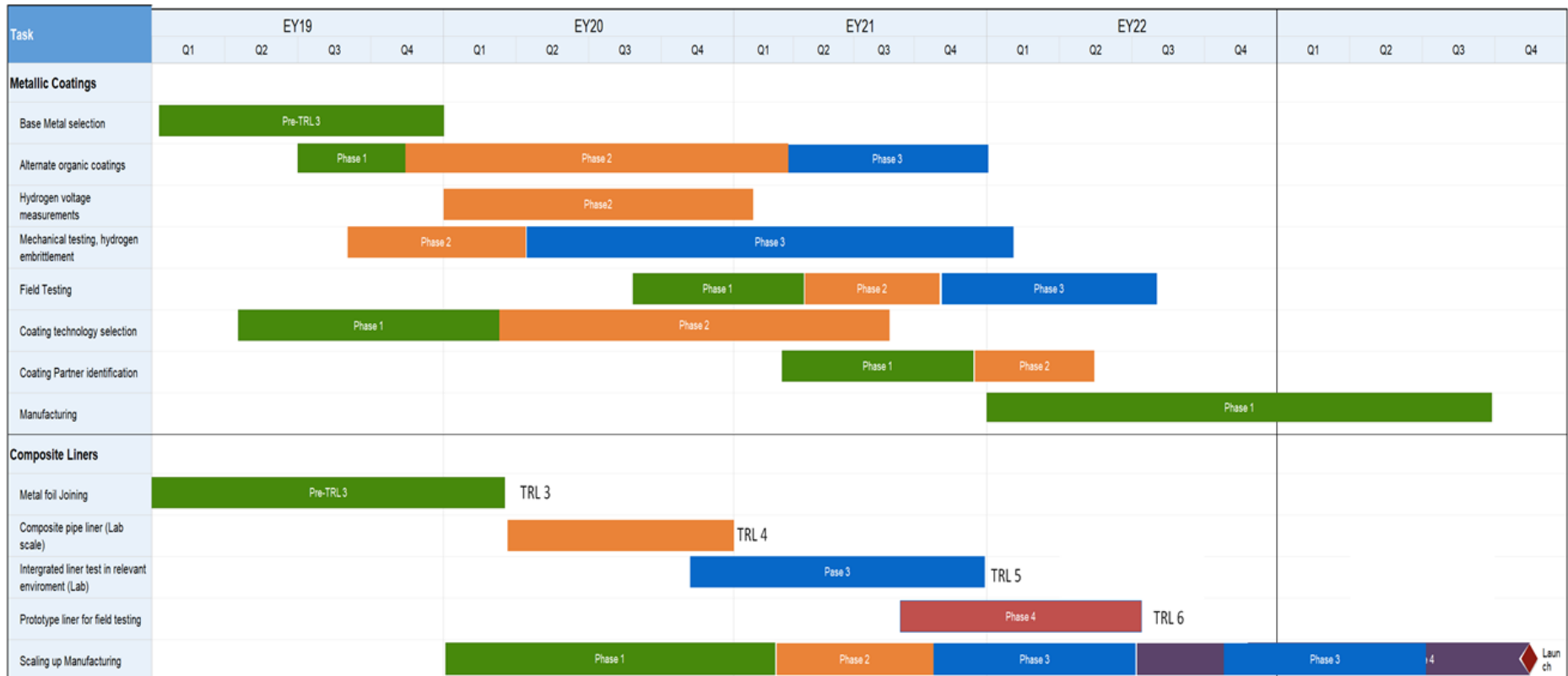
# Organization Chart



- **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*:
        - Ömer Doğan, PI-Task 3 ; area of expertise-materials 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, Lucas Teeter, Kyle Rozman, Kaimiao Liu, Fangming Xiang*
  - **External Collaborators:** DNV-GL, Oak Ridge National Laboratory (ORNL), Oregon State University (OSU), South Dakota School of Mines and Technology, GTI

# Progress Chart

## Development of Advanced Pipeline Materials: Metallic Coatings and Composite Liners



# Bibliography

## Peer-review publication

- 1- A. Rodriguez, J.H. Tylczak, M. Ziomek-Moroz, "Corrosion behavior of CoCrFeMnNi high-entropy alloys (HEAs) under aqueous acidic conditions," ECS Trans. 2017 77(11): 741-752
- 2- R. Feng, M. Ziomek-Moroz, J. H., Tylczak, P.R. Ohodnicki, "Corrosion of Carbon Steel in CO<sub>2</sub>-Saturated Brines Investigated by Rotating Disk Electrode and Scanning Vibrating Electrode Technique." ECS Transactions, 77(11), 809-822
- 3- A. Rodriguez, J. Tylczak, M. Gao, P. Jablonski, M. Detrois, M. Ziomek-Moroz, J. Hawk, "Effect of Molybdenum on the Corrosion Behavior of High-Entropy Alloys CoCrFeNi<sub>2</sub> and CoCrFeNi<sub>2</sub>Mo<sub>0.25</sub> under Sodium Chloride Aqueous Conditions," Advances in Materials Science and Engineering, (2018): 11 pages
- 4- A. Rodriguez, J. Tylczak, M. Ziomek-Moroz "Corrosion Evaluation of CoCrFeMnNi High-Entropy Alloys (HEAs) for Corrosion Protection of Natural Gas Transmission Pipelines," NACE/ CORROSION 2018, Paper No. 11174
- 5- R.F. Wright, E. R. Brand, M. Ziomek-Moroz, J. H. Tylczak, P. R. Ohodnicki Jr Effect of HCO<sub>3</sub><sup>-</sup> on Electrochemical Kinetics of Carbon Steel Corrosion in CO<sub>2</sub>-saturated Brines," Electrochimica Acta, 2018 (290): pp. 626-638
- 6- A. Rodriguez, J. Tylczak, M. Ziomek-Moroz, T.D. Hall, J. Xu, S. H. Vijapur, "Characterization and corrosion behavior of electrodeposited binary and ternary nickel alloys in a CO<sub>2</sub>-saturated NaCl solution, NACE/ CORROSION 2019, Paper No. C2019-13381

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- 8- C. Koerner, D. Hopkinson, M. Ziomek-Moroz, F. Xiang, “Environmentally Friendly Tannic Acid Multilayer Coating for Carbon Steel Corrosion Prevention,” Industrial & Engineering Chemistry Research 2021(60) 243-250
- 9- M. Ziomek-Moroz, A. Rodriguez,” High Entropy Alloys-Aqueous Corrosion, Encyclopedia of Materials: Metals and Alloys-in press
- 10- Z. Belarbi, J. Tylczak, M. Ziomek-Moroz,” Investigations of Corrosion Protection of Natural Gas Pipeline Steel by Al Sacrificial Corrosion Coatings Using Electrochemical Technique” AMPP/CORROSION 2021, Paper No. C2021-16689
- 11- L. Teeter, J. Tylczak, M. Ziomek-Moroz, G. Crawford, “ZnCr and ZnNb Thermal and Cold Spray Coatings” AMPP/ CORROSION 2021, Paper No. C2021-16977
- 12- F. Xiang, D. Hopkinson. “Environmentally Friendly Multilayer Coating for Carbon Steel Corrosion Prevention” presented at Materials Science & Technology 2019, Portland, OR, September 29-October 3, 2019

## **Patent Application**

- US2020/0283874 A1 “High performance corrosion-resistant high-entropy alloys” J. Hawk. P. Jablonski, M. Ziomek-Moroz, J. Tylczak, A. Rodriguez, M. Gao, published September10, 2020