In-Situ Applied Coatings for Mitigating Gas Hydrate Deposition in Deepwater Operations

Project# DE-FE0031578 – Program Manager: Bill Fincham

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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

- Project Overview & Background & Scope
- Technical Progress & Status
  - Robust Coatings for Deepwater Operations
    - Mitigating Gas Hydrate & Other FA Solids Deposition
- Accomplishments to Date
- Lessons Learned & Synergies
- Project Summary

Project Overview

- Funding: DOE: $1,497,543 , Costshare: $374,386
- Overall Project Performance Dates: 3/2018 - 3/2022
- Project Participants
  - CSM: Carolyn Koh, Marshall Pickarts, Jose Delgado
  - Oceanit: Vinod Veedu, Erika Brown, *Oceanit*
- Overall Project Objectives
  - Develop for ***field & commercial deployment*** robust pipeline coatings to mitigate hydrate & other solids deposition
    - Multiphase flowloop evaluations in simulated field conditions & field test plans

Technology Background: Hydrates in Flow Assurance

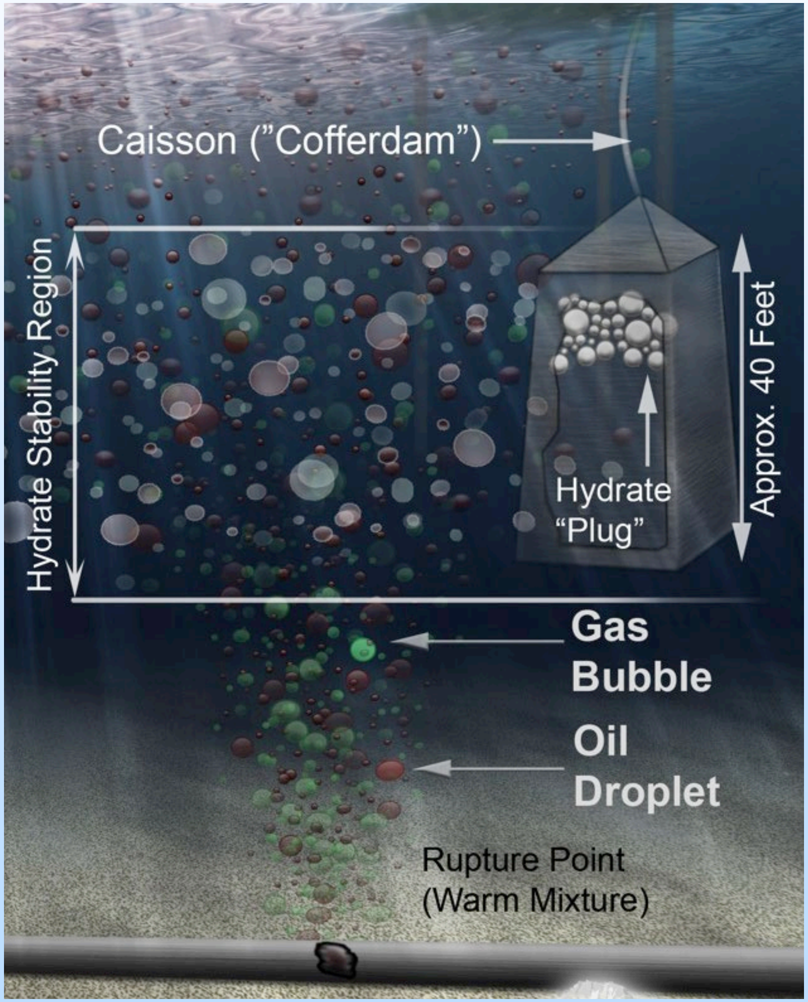
Hydrates Cause Major Economic & Safety Risks During Energy Production & Transportation

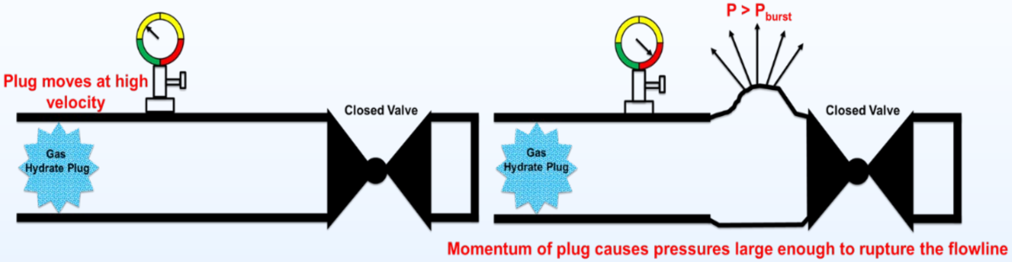
- **Hydrate formation in oil/gas flowlines**
- **#1 problem in flow assurance**
- **Costly to prevent**
  - $1M/mile of pipeline + $100M/year in THI chemicals
- **Costly to remove**
- **Safety concern** (pipe rupture, personnel fatalities/injuries, environmental hazards

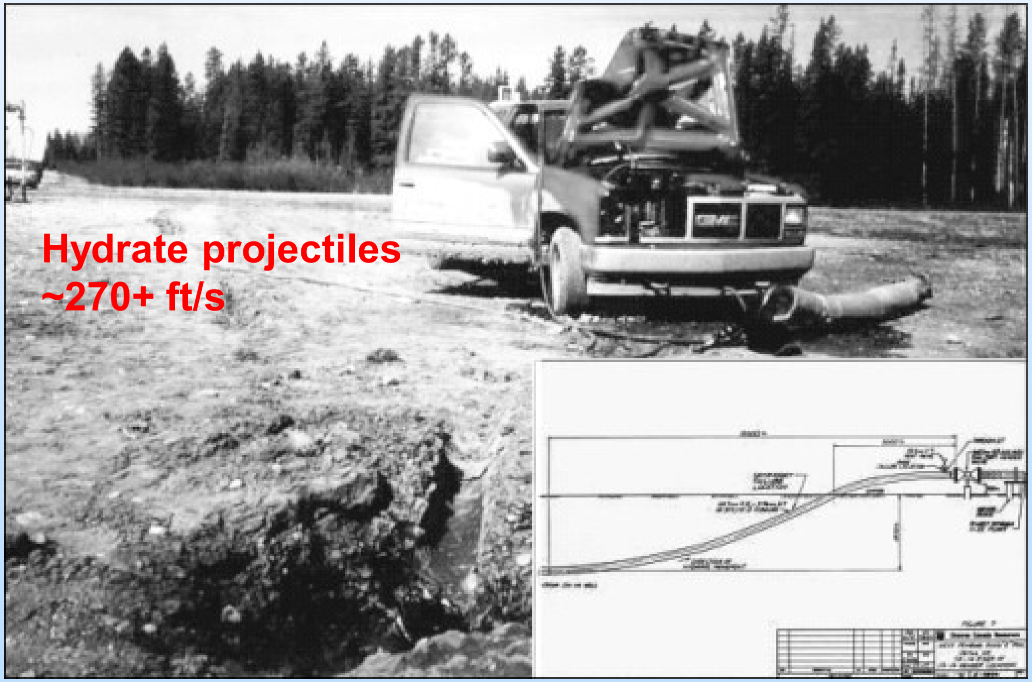
Koh et al., Annual Reviews, 2011

Safety & Environmental Risks Due to Hydrate Plugs
Fatalities & Injuries in the Field

Gas hydrates main cause for failed initial containment of Gulf oil spill



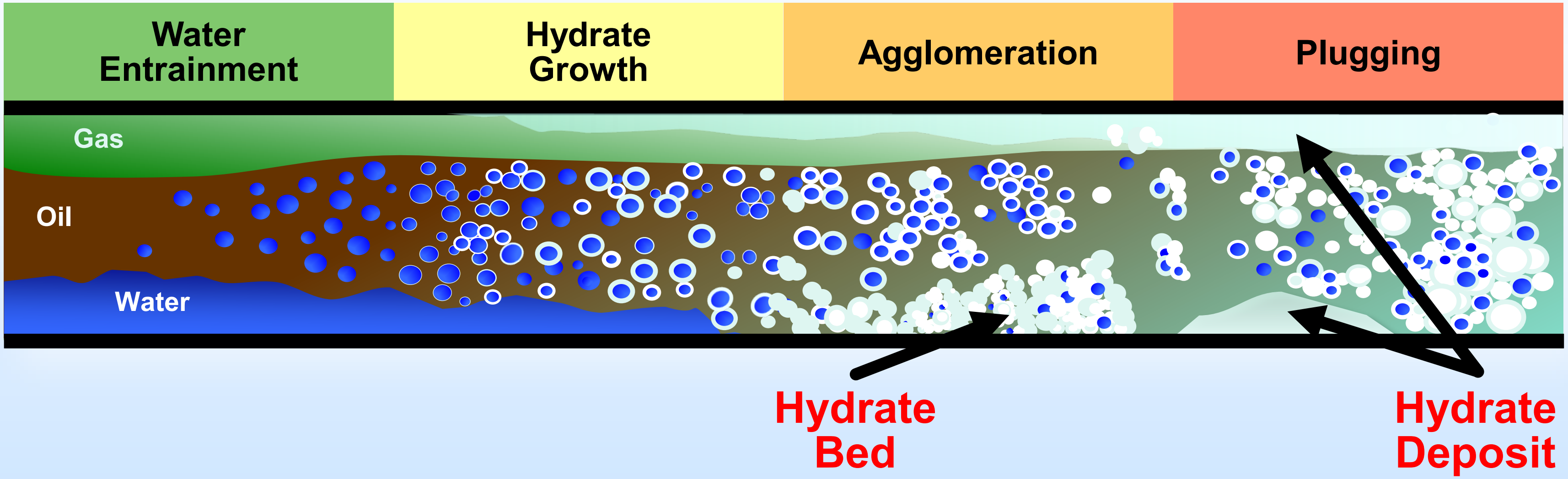




Koh, C. A. & J. Creek (2011)

Motivation for Hydrate Deposition

A Major Outstanding & Critical Flow Assurance Problem



- Flowloop tests show agglomeration alone cannot account for large ΔP increase[1]
- ExxonMobil field trial suggests hydrate deposits caused **majority** of ΔP increases[2]

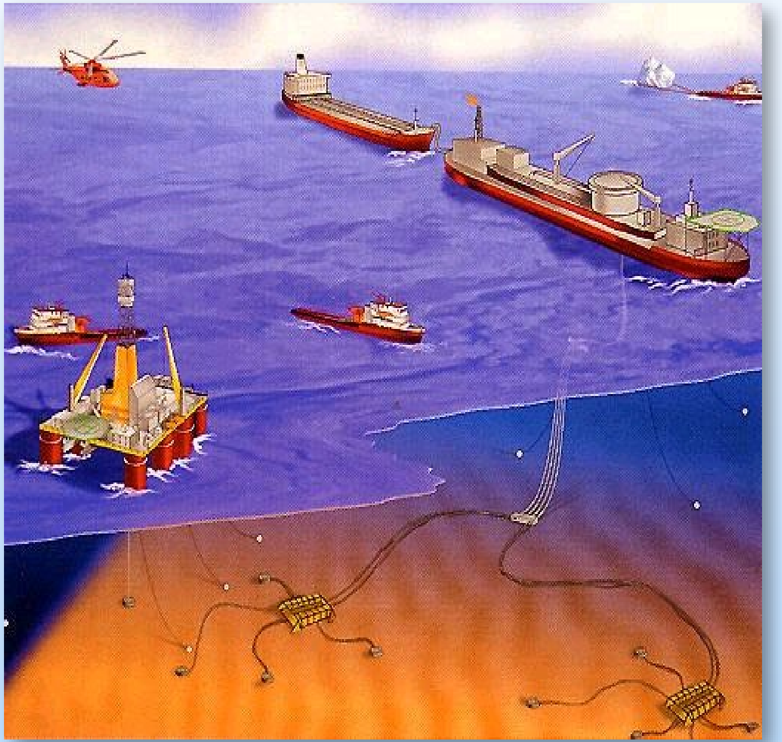
1. Majid, Koh et al., *OTC* 2017

2. Lachance et al., *Energy Fuels* 2012

Project Objectives to Address Key FA Technology Challenge

Develop for field & commercial deployment robust pipeline coatings to mitigate hydrate deposition in subsea oil flowlines

- Hydrate-phobic coating system applied in-situ to existing (corroded) pipelines
  - Tested up to 8000 psia, 400 F to -20 F
- Multiphase deposition flowloop evaluations in simulated field conditions
- Investigations under simulated field conditions & field test plans



Sloan & Koh, Clathrate Hydrates of Natural Gases, CRC Press, 2007

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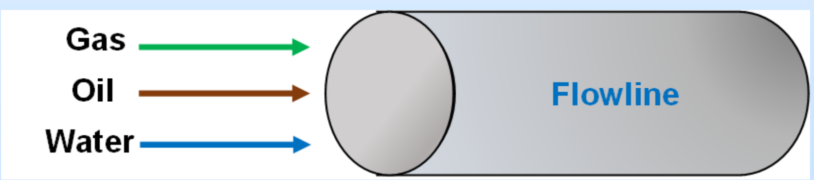
Project Scope: Flow Assurance Solids – Hydrates/Wax/Asphaltenes

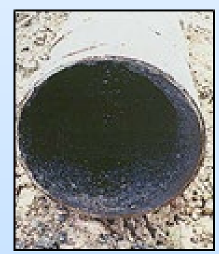
Flow assurance solids can occur in several steps in subsea oil & gas production leading to ***severe safety and economic risks***



Critical Parameters

Hydrates

- **Pressure**
- **Temperature**



Waxes

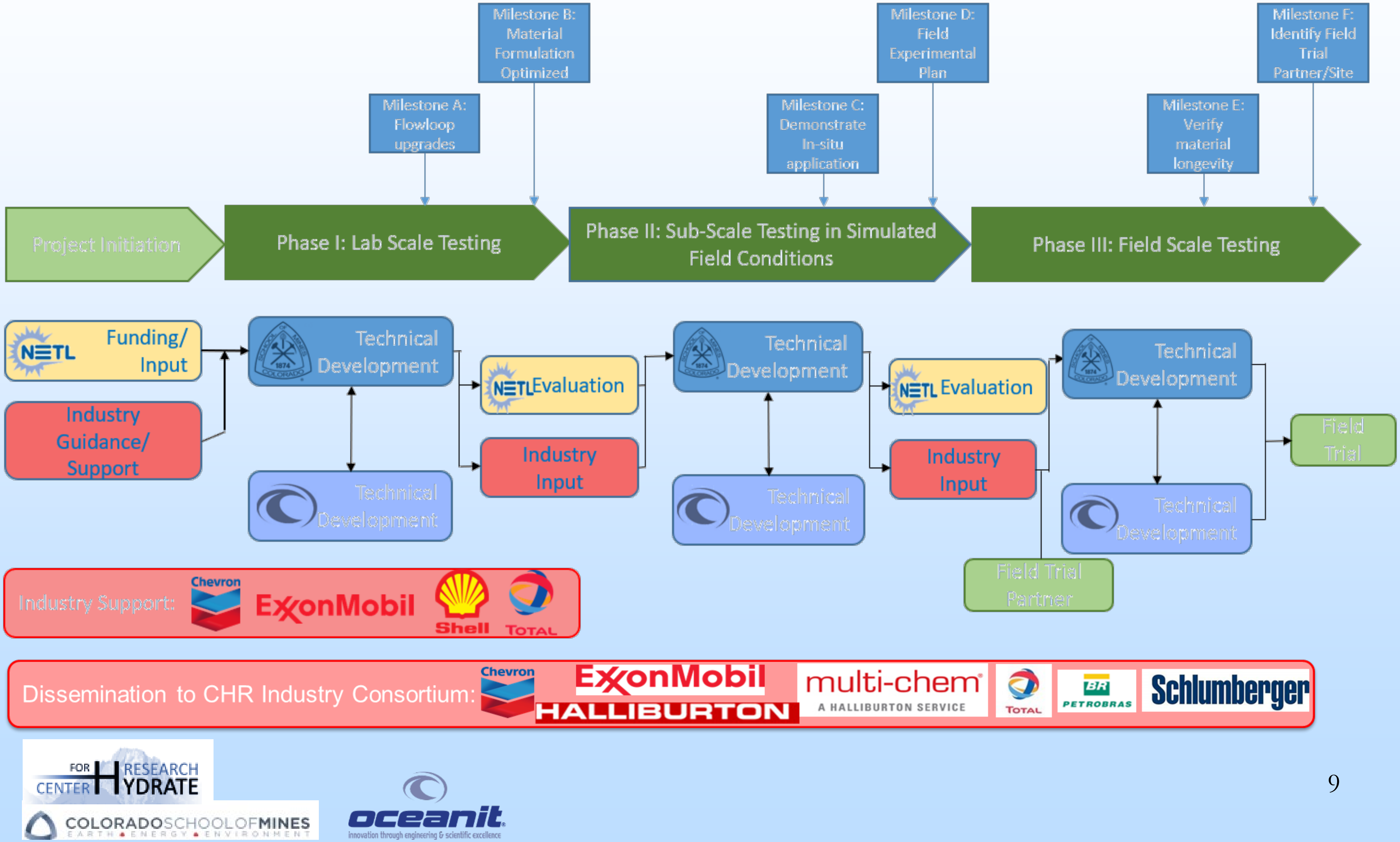
- **Temperature**
- **Composition**

Asphaltenes

- **Pressure**
- **Composition**

Sloan & Koh, CRC Press, 2007; Slb.com
Guozhong and Gand. 2010. J. Pet. Sci. Eng.

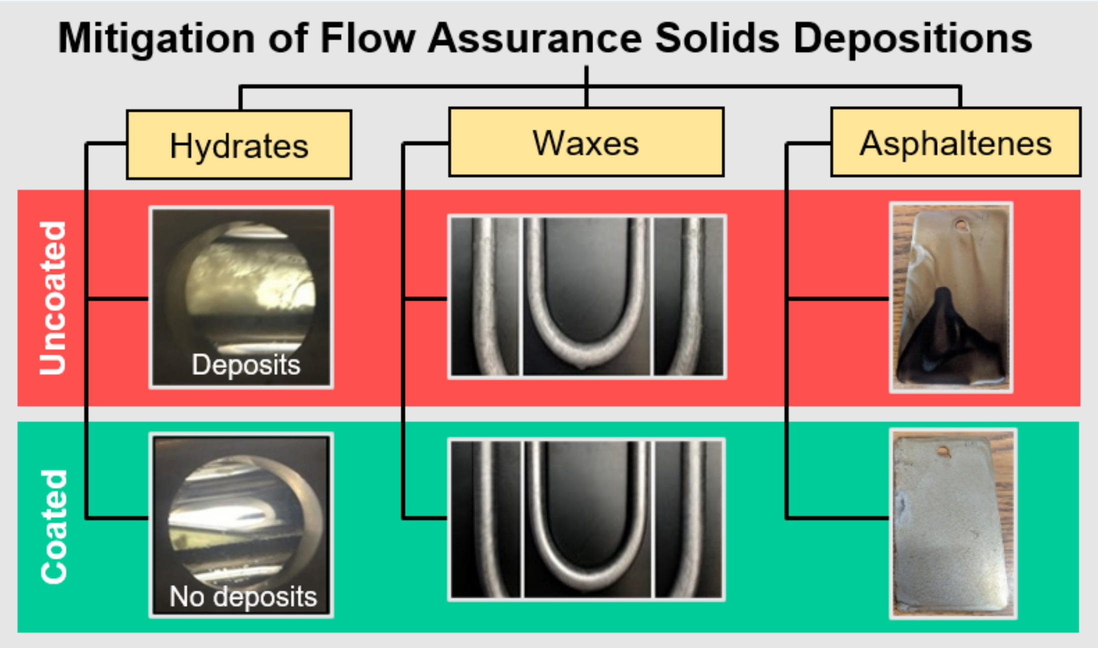
Project Organization and Milestones

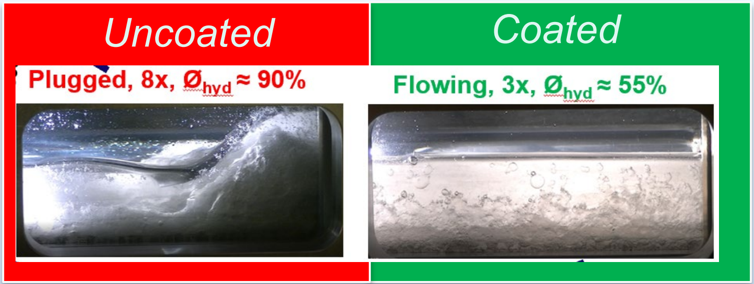


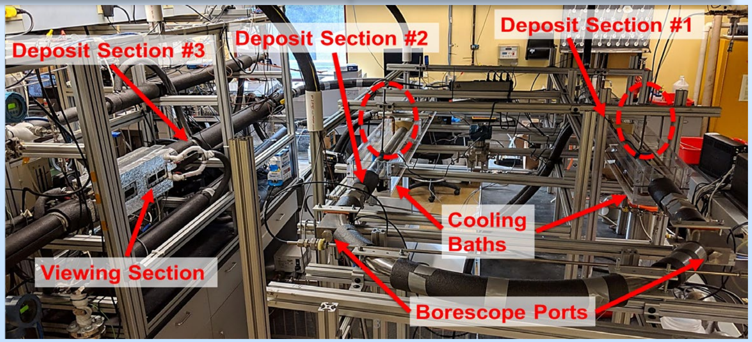
PROGRESS & CURRENT STATUS OF PROJECT

CURRENT STATUS OF PROJECT

Simulated field conditions







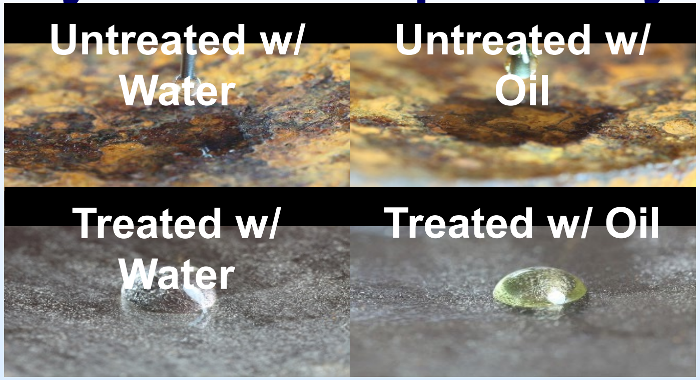
Rocking cells *Cold Finger/Coupon*
Coupon/Loop

Flowloop

Optimized Omniphobic Coating for Commercialization

Corrosion Resistance

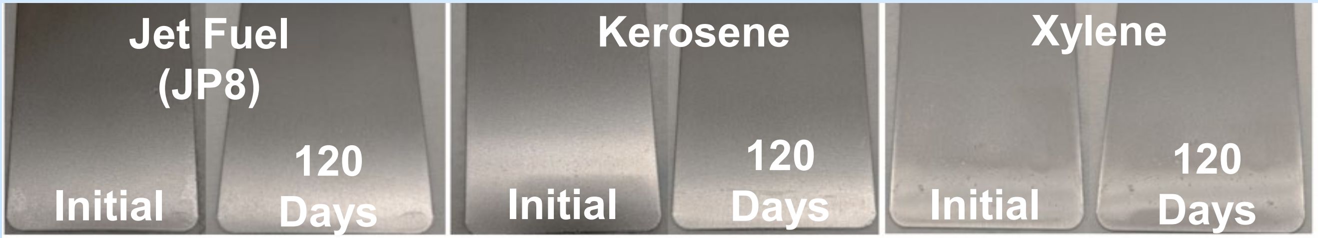
Hydro- & Oleophobicity



Coating Details

Erosion Resistance (ASTM G76)
Adhesion Test (ASTM D3359)
Wear Resistance (ASTM D4060)
Corrosion Resistance (ASTM B117 + D1654)

Chemical Resistance

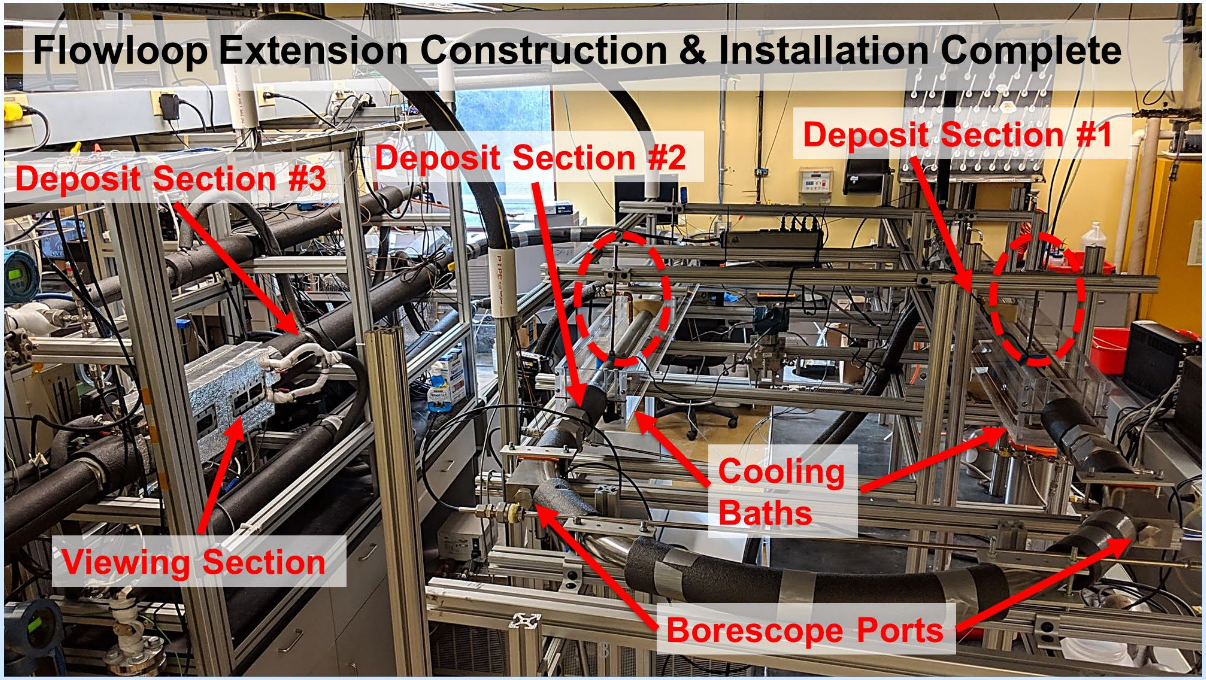


Application Properties

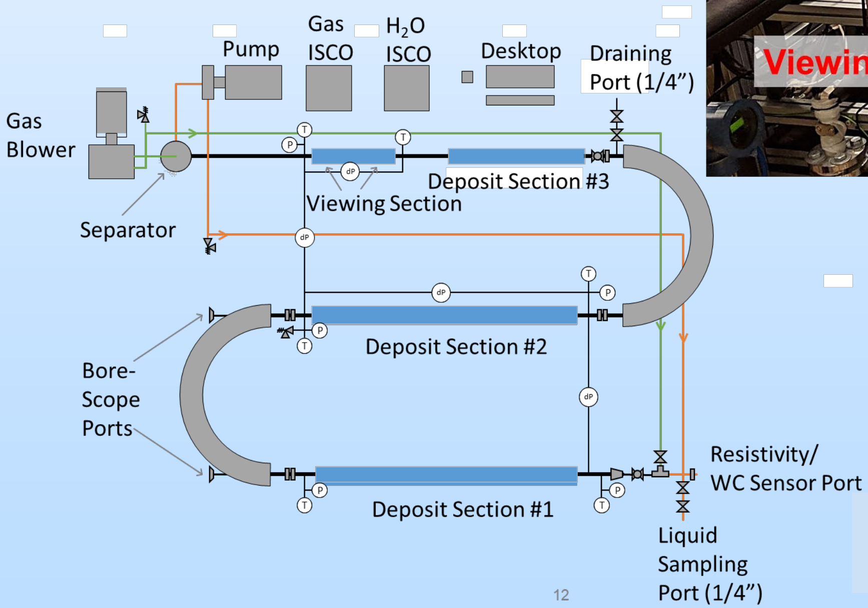
Method: Spray, Dip, Flood & Drain
Surface: Metals, Concretes, Composites
Thickness: ~100 μm

Water-Dispersible, Low Viscosity, Nano-Structured Polymer Topcoat Capable of In-Situ Application to Existing Materials

Hydrate-Phobic Coatings Tests in Deposition Loop

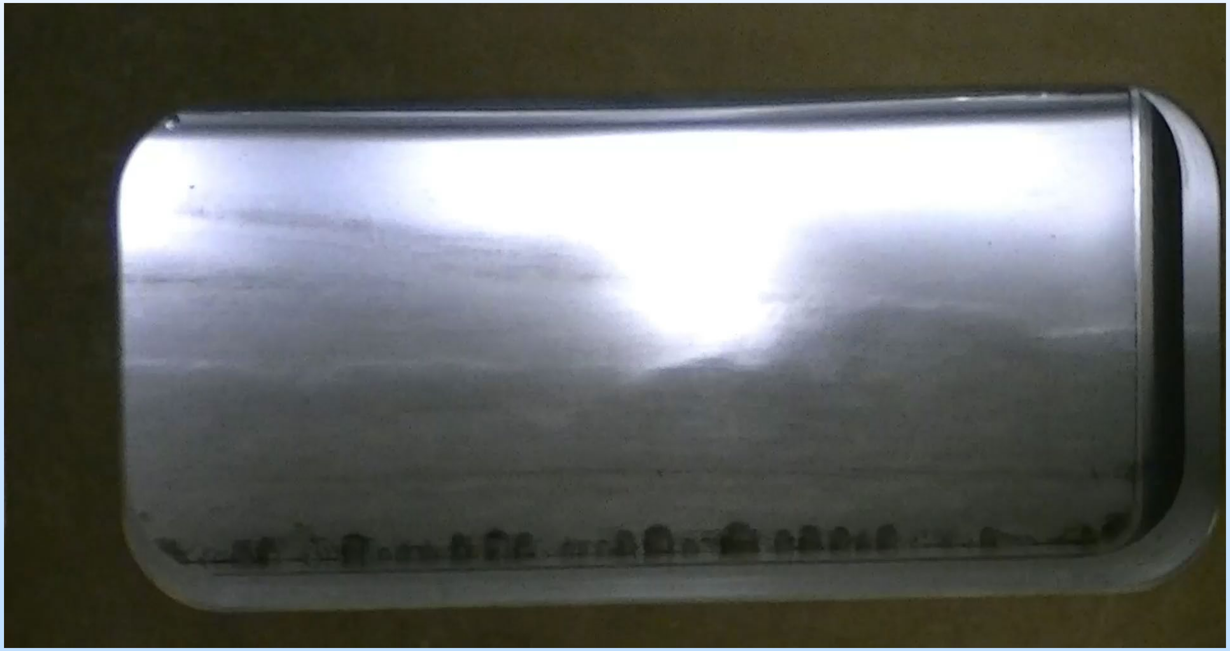


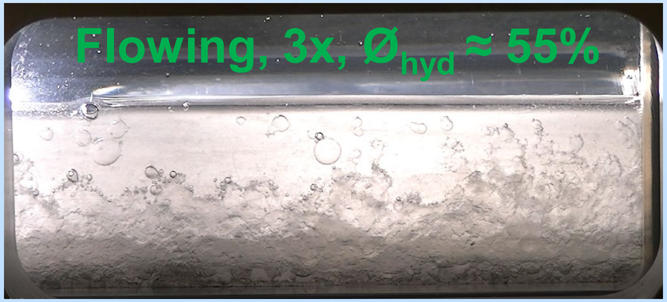
Deposit Section:
Length: 225 in (5.72 m)
OD: 2 in (5.08 cm)
Volume: 2.68 gal (10.14 L)



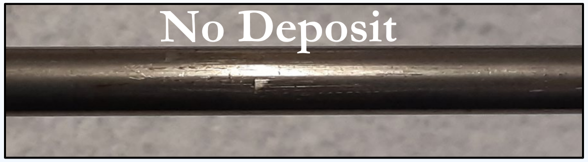
Hydrate Deposition Mitigated in Oil-Dominated Systems

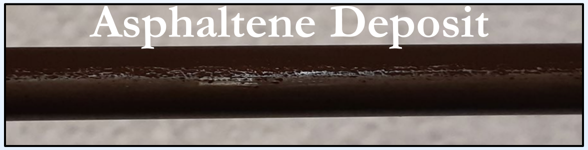
- Deposition Loop - Hydrate mitigation with surface treatment
  - SS & Transient tests show no plugs with coating (6+ mo)
  - Induction times delayed for oil/gas-dominated (up to 230+ h)
  - Growth reduced by ~60+%

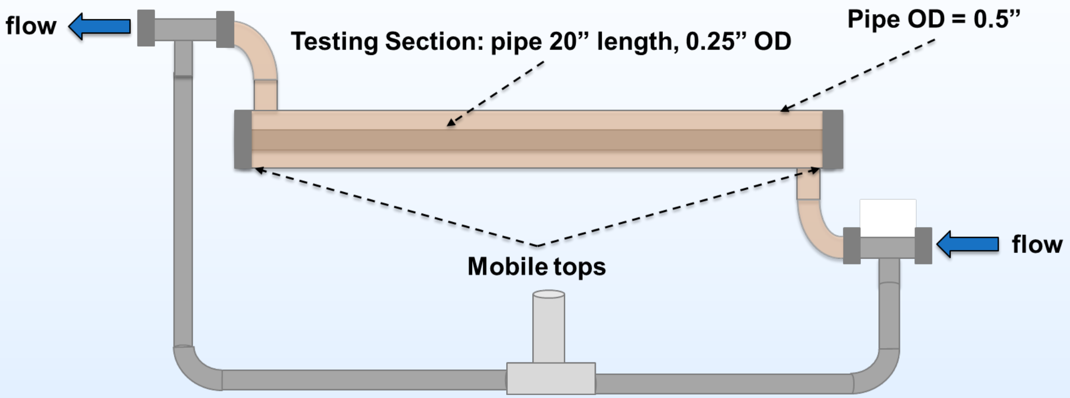


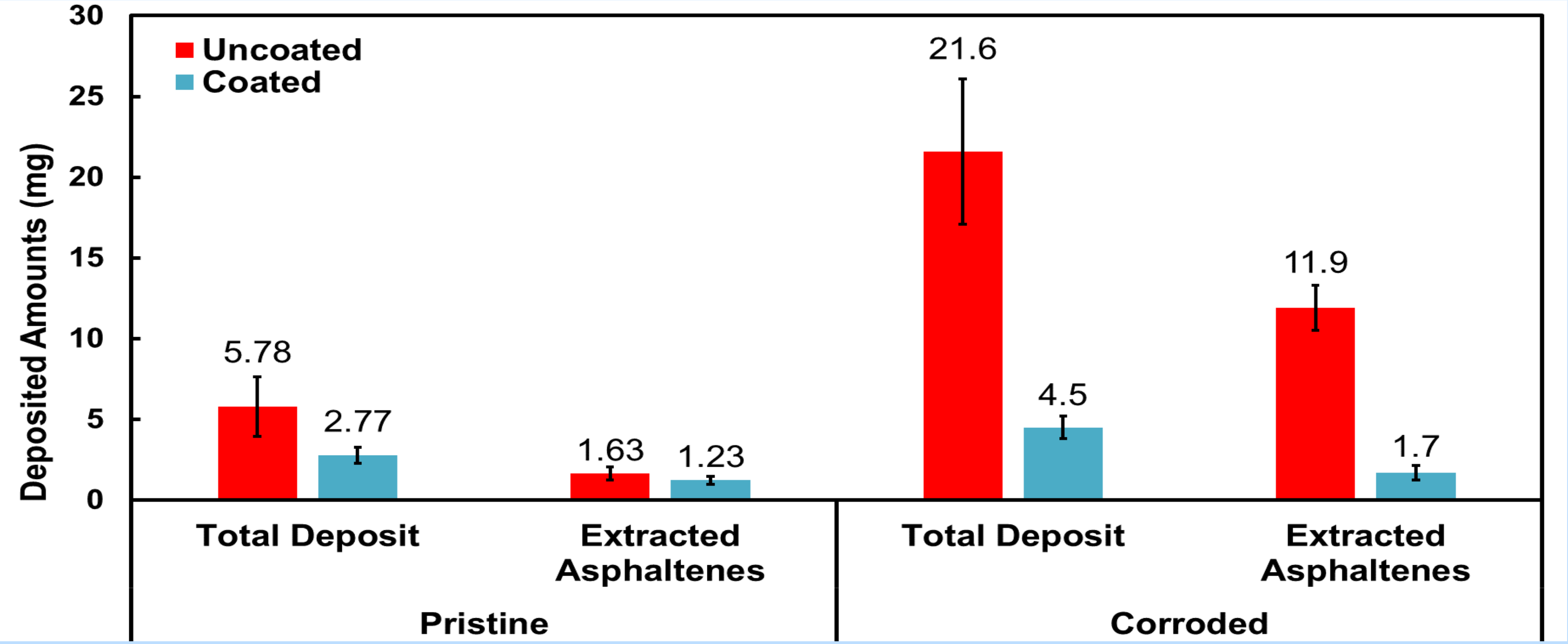


Asphaltene Deposition Mitigated in Oil-Dominated Systems



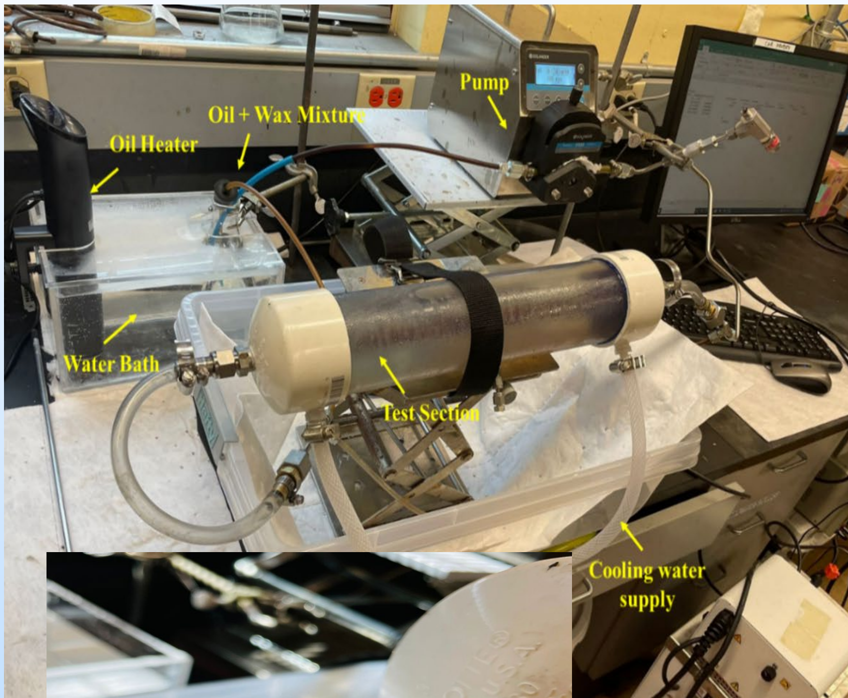


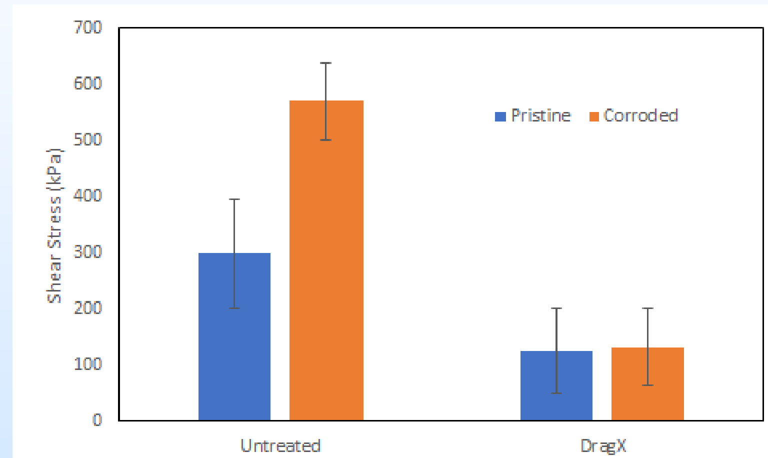


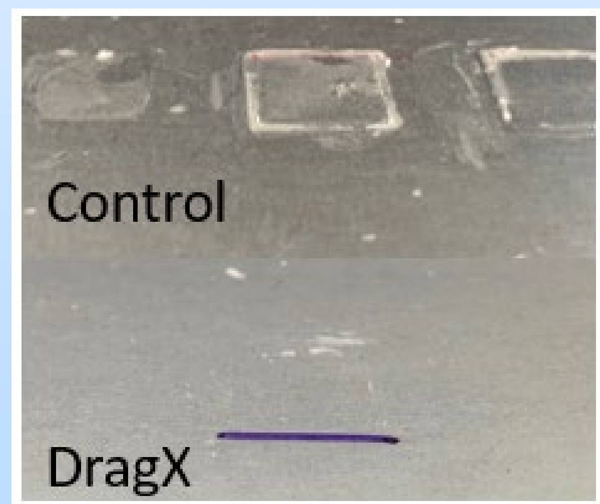


Wax Deposition Mitigation in Oil-Dominated Systems

Wax Deposition Loop Testing with Simulated GoM Wax Composition



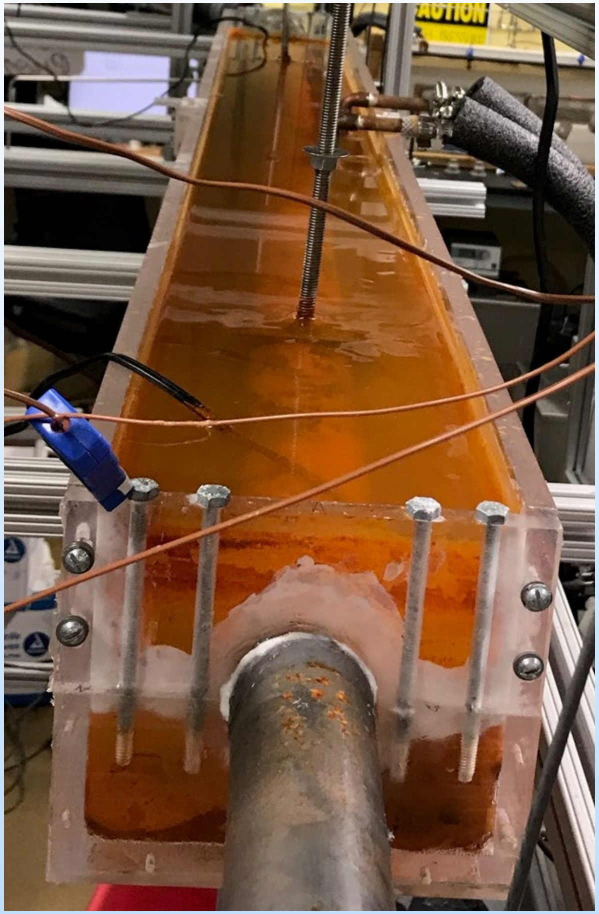




Long-Term Coating Durability

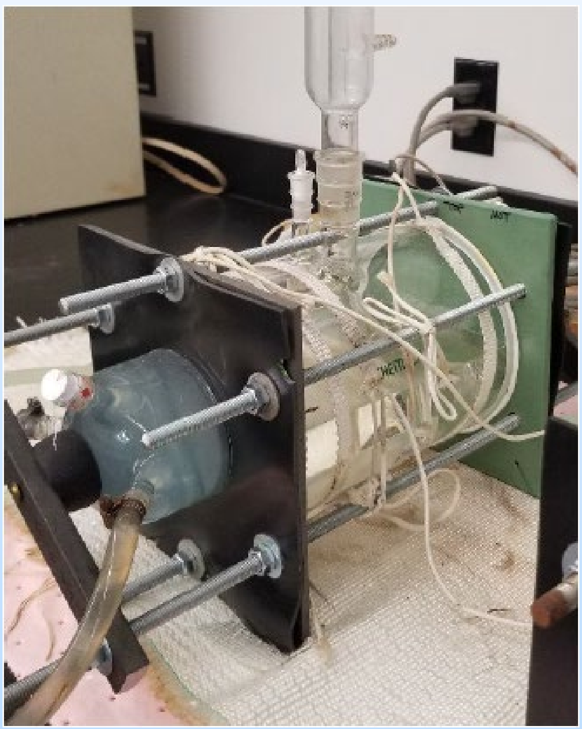
- 6+ Months High Pressure Testing
  - ~3300 Operating Hours
  - Solid Particle/Fluid Flow
  - Pressure Cycles

No corrosion → No delamination



Long-Term Coating Durability:
ASTM Cold Wall & Pressurized Tests

ASTM D6943-15 C, ASTM D6943-15 B2 (seawater, toluene/kerosene) – significant protection by DragX (7 days)

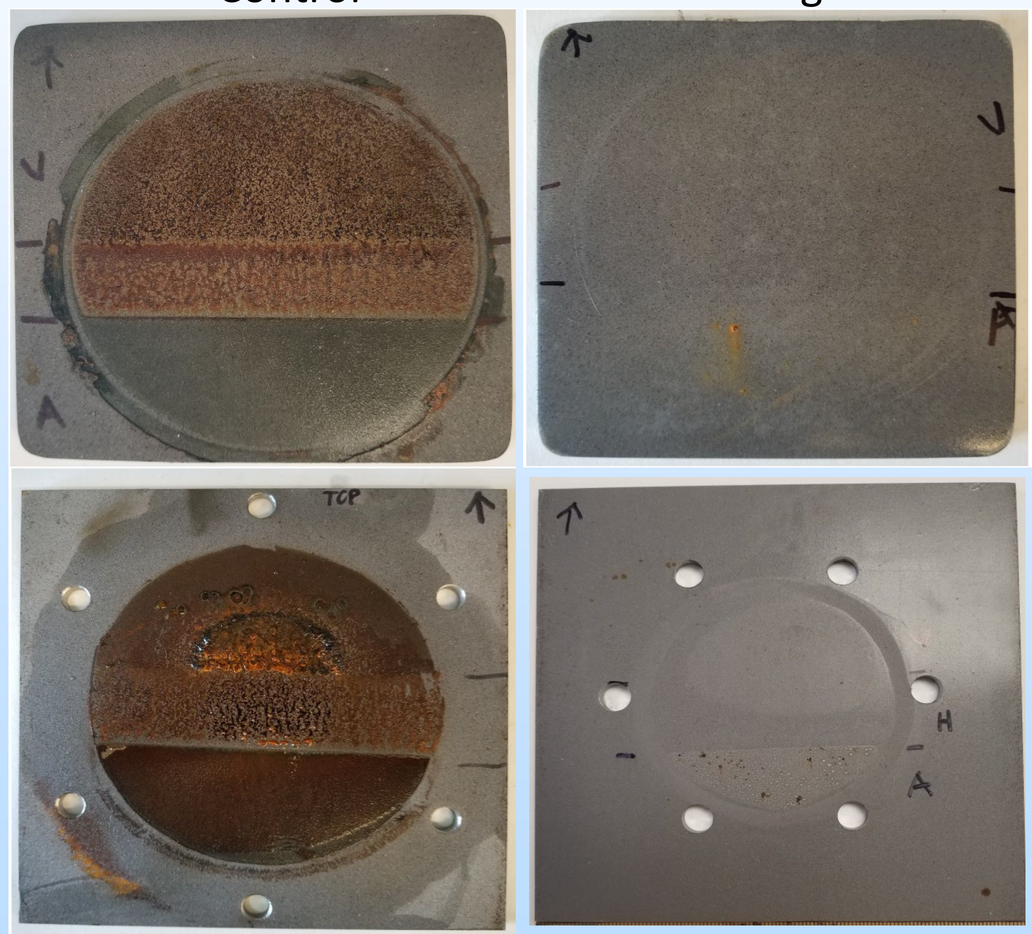


Pressurized

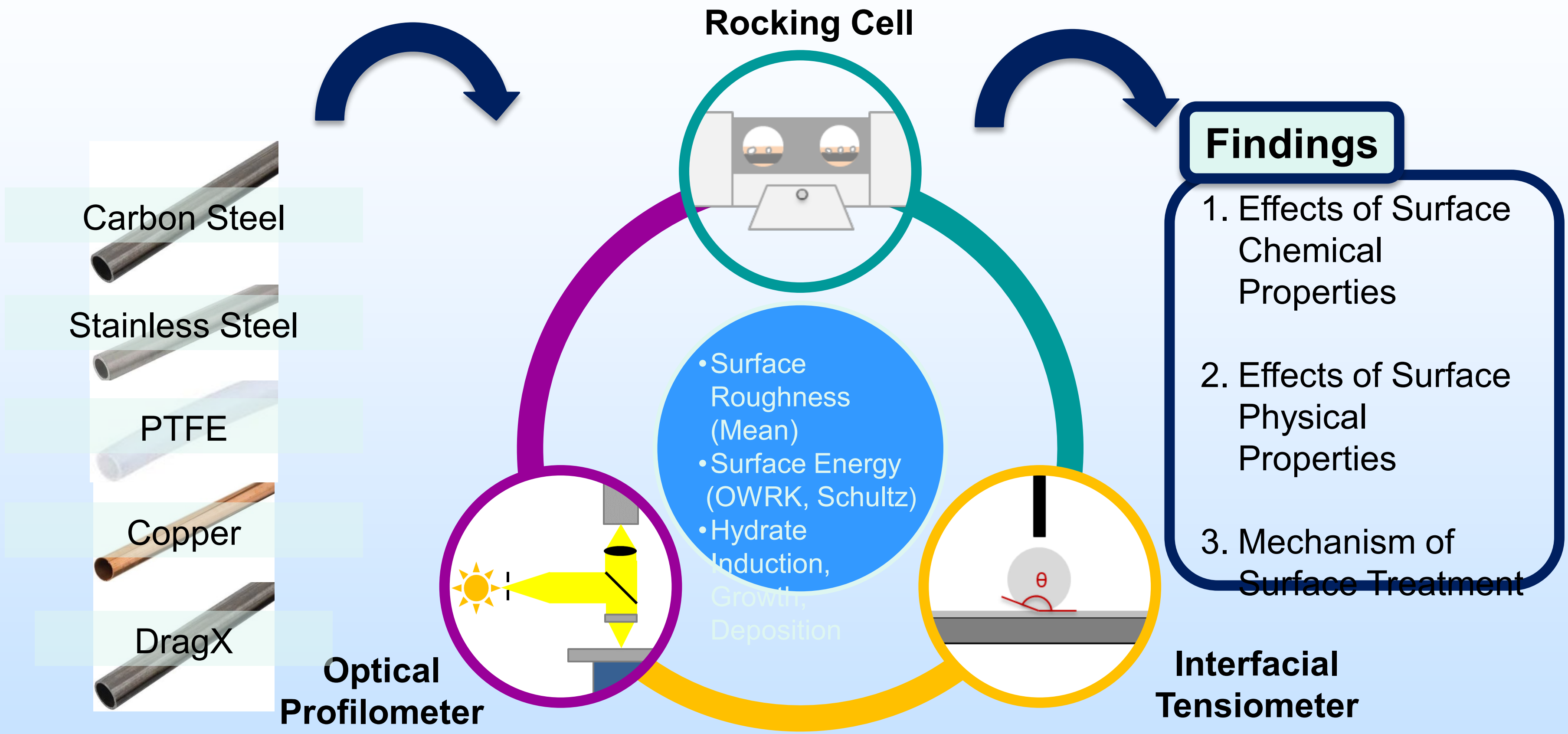
Cold Wall

Control

DragX



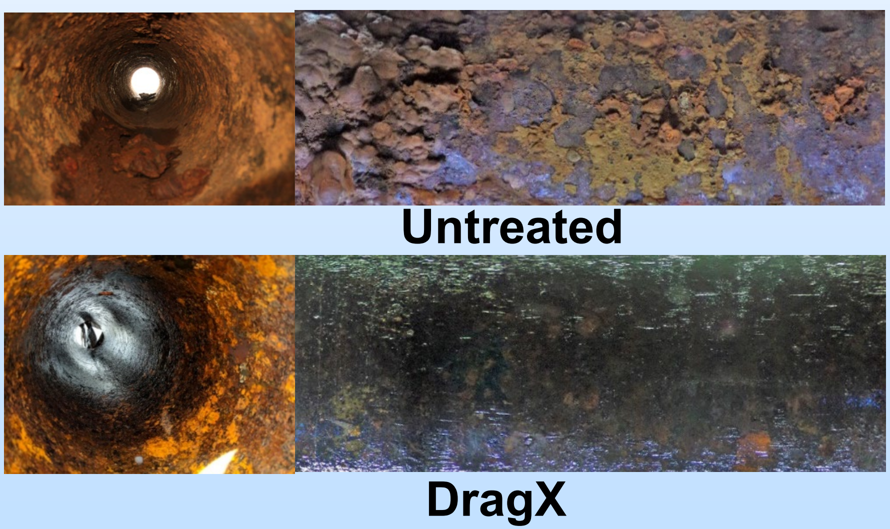
Surface Materials Properties & Mechanisms Contributing to Deposition & Mitigation

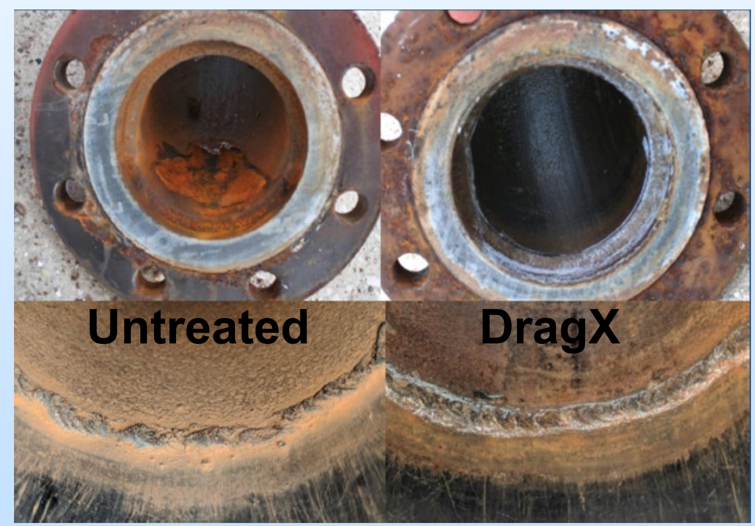


Surface	Dispersive Surface Energy [mJ/m2]	Polar Surface Energy [mJ/m2]	Total Surface Energy [mJ/m2]	Median Surface Roughness [µm]
Carbon Steel	137	1.8	139	0.82
Stainless Steel	82.2	0.41	82.6[1,2]	1.9
Copper	348	1.4	350[3]	0.1
PTFE	20.8	0.3	21.1[4]	0.1
DragX	15.4	0.5	16	0.27

In-Situ Application Development

- DragX can be applied in-situ to production lines via pigging
- Can also be applied to new pipes by spray, flush, or paint

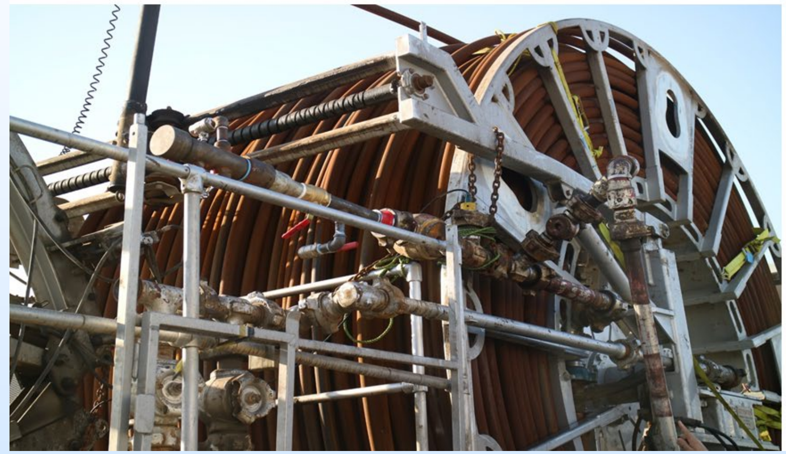




Focused Towards Field Deployment

DragX

Coiled Tubing



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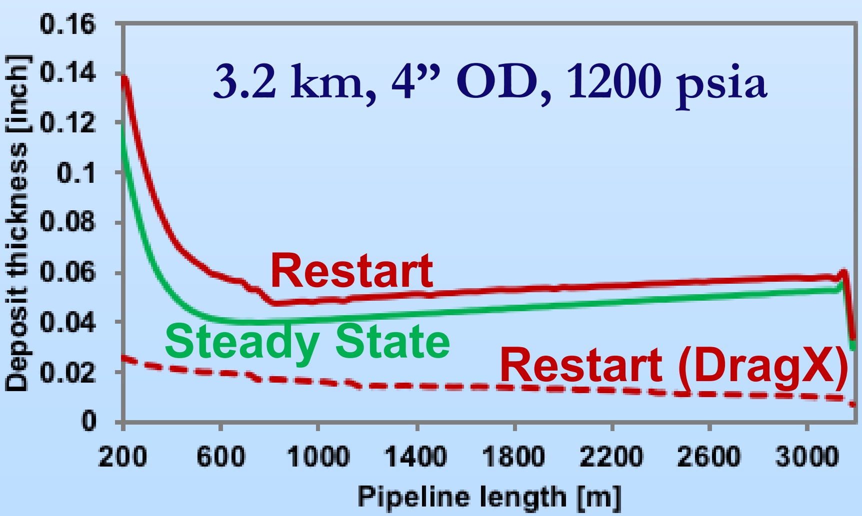


Field test plans – discussion with industry (May 5,6,18, June 2, 2021)

Simulated XoM field trial conditions to design **field test**

Project Summary

- Hydrates, waxes, and asphaltenes are top flow assurance challenges
  - Complex systems typically require site-specific solutions
  - Significant safety & economic consequences result from incorrect practice

- Low surface energy, omniphobic surface treatments shown to mitigate deposition of multiple flow assurance solids
  - Flowloop tests show deposition resistance in field-simulated conditions
  - Nucleation & growth delayed in hydrate-forming system
  - Application & survivability in field conditions show promise for lasting FA treatment & field test plan underway

Acknowledgements

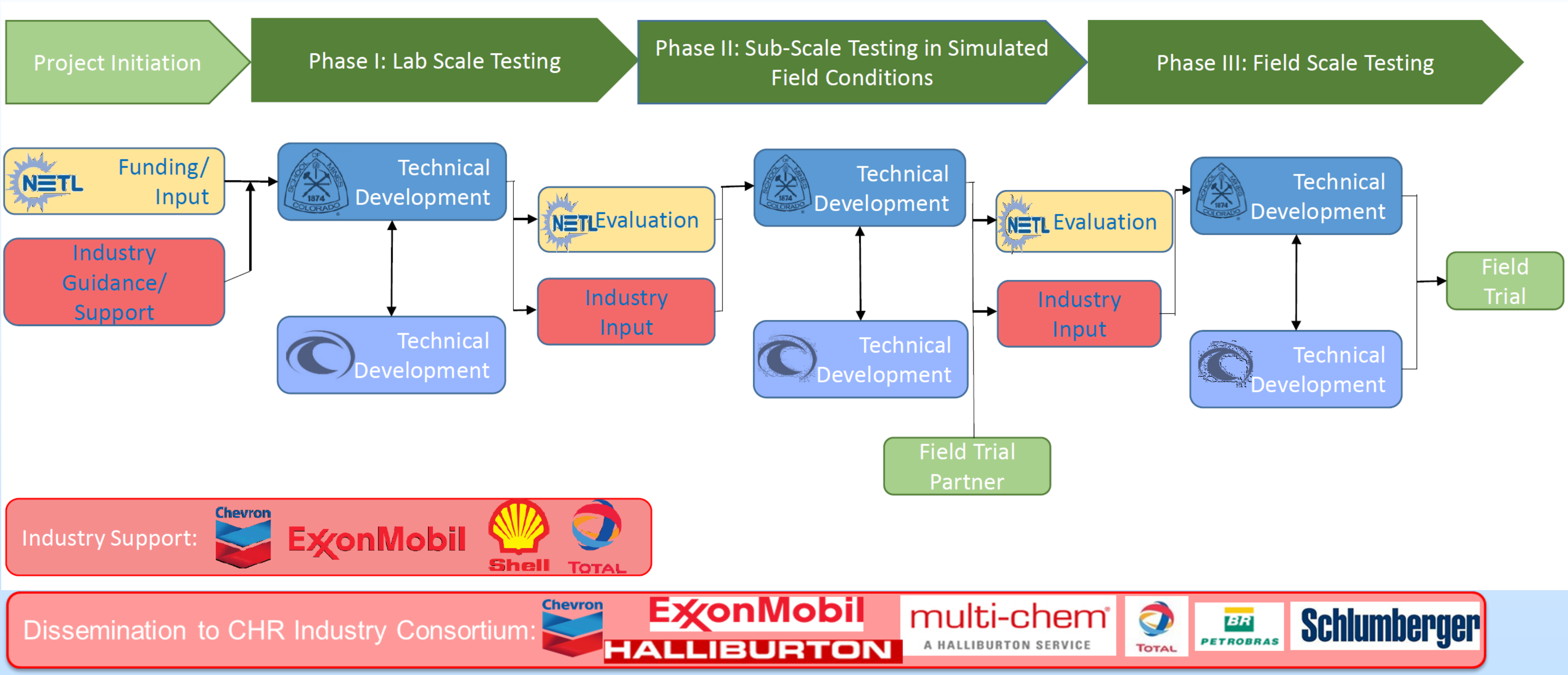
- U.S. Department of Energy / NETL for funding & Bill Fincham, Program Manager (Award no.: DE-FE0031578)

- Industry Advisors: Douglas Estanga (Chevron), Khalid Mateen (Total), Doug Turner, Giovanny Grasso (ExxonMobil), and Daniel Crosby (Shell)

Appendix

- These slides will not be discussed during the presentation, but are mandatory.

Project Organization for Deployment of Coatings



Gant Chart

Task #	Task	Phase I (2018-2019)				Phase II (2019-2020)				Phase III (2020-2022)			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1-2	Q3-4	Q5-6	Q7-8
1.0	**Project Management and Planning**												
2.0	**Loop Modification and Baseline Testing**												
2.1	*Loop Modification*												
2.2	*Deposition Experiments*												
A	Flowloop Upgrade Completed												
3.0	**Material Design, Formulation and Optimization**												
3.1	*Evaluation of Coating Performance*												
3.2	*Durability and Chemical Compatibility Testing*												
B	Coating Formulation Optimized												
4.0	**Flow Properties Characterization**												
4.1	*Lab Characterization*												
4.2	*Flowloop Measurements*												
5.0	**Documentation and Reporting**												
	TECHNICAL GO/NO GO DECISION POINT 1												
6.0	**Shut-in/Startup Testing**												
7.0	**Simulated Fluid Conditions**												
7.1	*Adhesion Measurements using Waxes/Asphaltenes*												
7.2	*Deposition Testing using Waxes/Asphaltenes*												
8.0	**In Situ Application Method Development**												
8.1	*Application and Curbing Procedures*												
8.2	*Development of Quality Control Parameters*												
C	In Situ Application Achieved												
9.0	**Design and Planning for Field Tests**												
9.1	*Site Selection and Experimental Design*												
9.2	*Multiphase Modeling of Field Site*												
D	Field Trial Experimental Plan Developed												
10.0	**Documentation and Reporting**												
	TECHNICAL GO/NO GO DECISION POINT 2												
11.0	**Loop Scale Testing of Simulated Field Conditions**												
11.1	*Single Component Flowloop Experiments*												
11.2	*Multi-Component Flwoloop Experiments*												
12.0	**Long Term Evaluation**												
12.1	*Extended Service Guidelines and Durability*												
12.2	*Compatibility with In-line Tools*												
E	Verify Long Term Coating Durability												
13.0	**Initialize Planning for Field Testing**												
F	Field Trial Partner/Site Identified												
14.0	**Documentation and Reporting**												

Current Progress Proposed Timeline

Bibliography

- Pickarts, M.A., Delgado-Linares, J., Brown, E., Veedu, V., Koh, C.A., 2020, *Evaluation of a Robust, In-Situ Surface Treatment for Pipeline Solids Deposition Mitigation in Flowing Systems*. Proceedings of the Offshore Technology Conference, OTC-30817-MS, Houston, TX, May 2020.
- Pickarts, M.A., Croce, D., Zerpa, L.E., Koh, C.A, 2020, *Gas Hydrate Formation & Transportability during Transient Shut-In/Restart Conditions*. Proceedings of the Offshore Technology Conference, OTC-30857-MS, Houston, TX, May 2020.
- Pickarts, M.A., Brown, E., Delgado-Linares, J., Blanchard, G., Veedu, V., and Koh, C.A., 2019, *Deposition Mitigation in Flowing Systems Using Coatings*. Proceedings of the Offshore Technology Conference, OTC-29380-MS, Houston, TX, May 2019. https://doi.org/10.4043/29380-MS.
- Abstract & papers: OTC conference (May 2019 (1), May 2020 (2)), NACE 2020, ICGH10 (June 2020)

BACKUP SLIDES

Project Overview

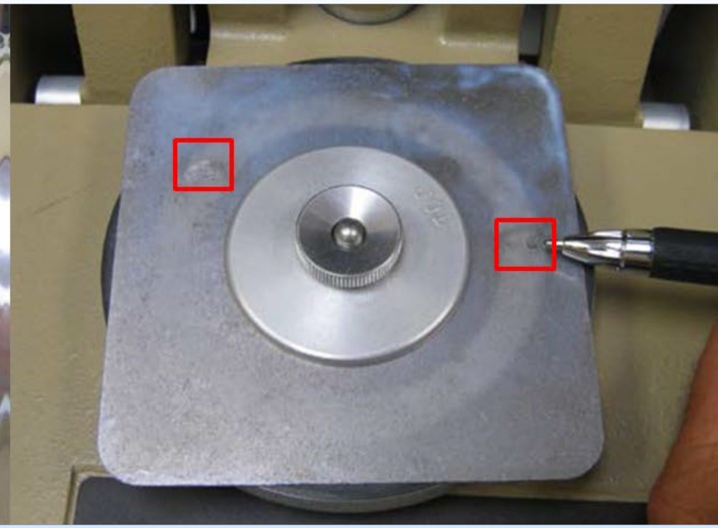
Goals and Objectives

<u>Develop for field & commercial deployment robust pipeline coatings to mitigate deposition in subsea flowlines</u>

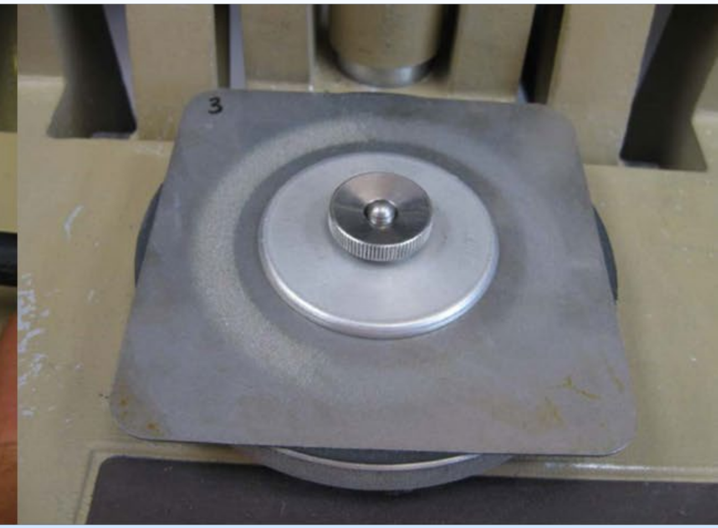
- Deposition-resistant coating system can be applied in-situ to existing (corroded) pipelines
- Larger-scale multiphase deposition flowloop evaluations in simulated field conditions
- Investigations under simulated field conditions & field test plans

Coating Abrasion Resistance

Taber Abrader Testing (ASTM D4060)



Poorly Adhered Coating
(Mass Loss ~ 100mg/1000 cycles)

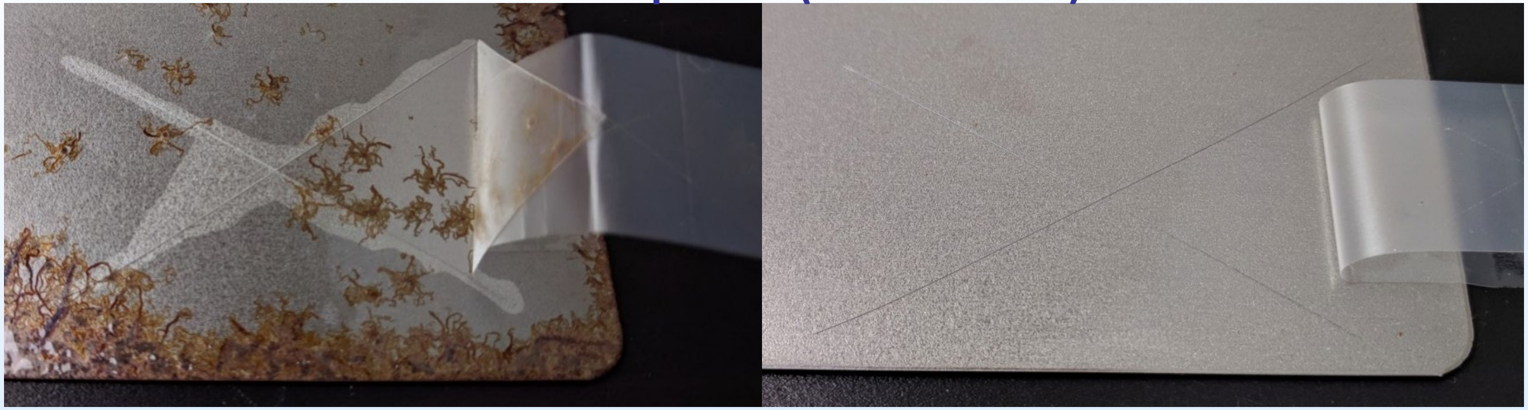


DragX™ Treatment
(Mass Loss ~ 50mg/1000 cycles)

Optimized DragX™ formulation passes abrasion testing standard for internal pipeline coating materials. Typical Epoxy 70-85 mg loss/1000 cycles

Coating Durability and Adhesion

Crosscut tape test (ASTM D3359)



Knife adhesion test (ASTM D6677)

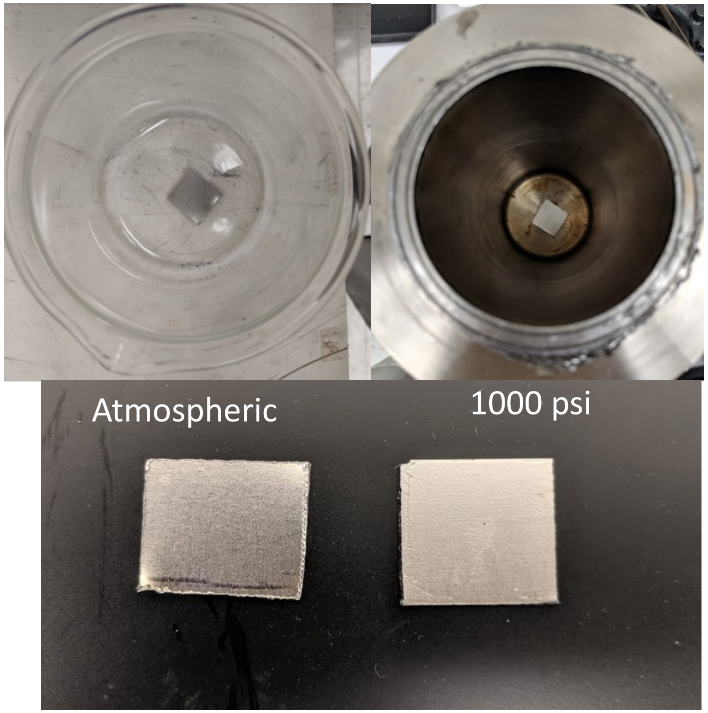
Novolac Epoxy Coated

DragX^{TM} Treatment

DragX^{TM} shows no peeling, delamination or bubbling, even when subjected to direct cutting

Task 8 – In-Situ Application Method Development

- Subsea lines present unique challenges in-situ
- Low temperature and high pressure compared to on shore conditions testing performed (Milestone C: In-situ Application)
  - Low temperature curing showed slightly longer cure times
  - Testing compared 1000 psi curing on a coupon to coupon cured at atmospheric
  - No change in appearance, contact angle, durability
  - Key is to measure dew point to determine cure



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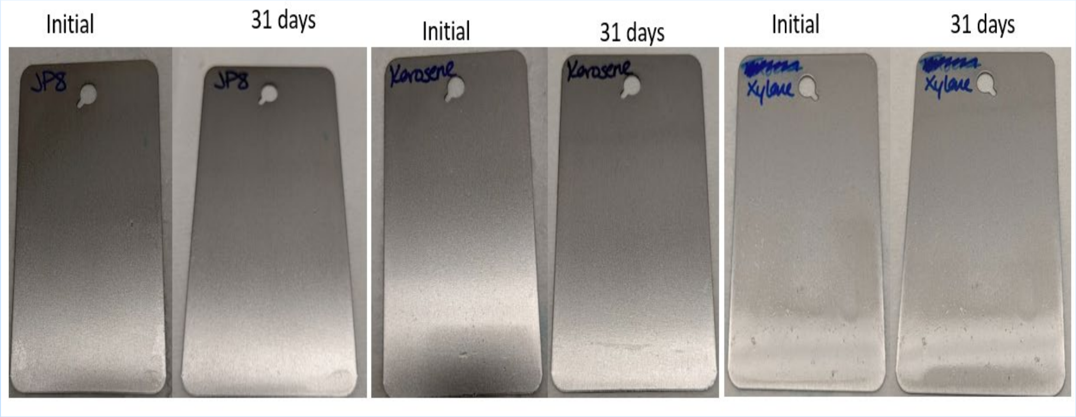
Pipeline Fluids, Chemicals & Solvent Compatibility of Coatings

- Flowline fluids: oil, water, brine, natural gas
- Chemicals/solvents: kerosene, xylene, JP8
- Compatibility testing up to 31 days



JP8 - Compound	Amount
C8-C9 aliphatic hydrocarbons	9%
C10-C14 aliphatic hydrocarbons	65%
C15-C17 aliphatic hydrocarbons	7%
aromatics	18%

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Technical Data

Typical Uncured Physical Properties	
Color	Clear/White/Blue
Specific Gravity	1.1 g/cm^3
Application Methods	Spray, Dip, or Flood and Drain
Viscosity	100 – 5000 c.p. (Tunable)
Base	Water
VOC Content	None
Shelf Life (Stored Between 50 - 80°F in unopened state)	>6 months
Typical Application Properties	
Mixing Time (Part A and Part B)	Approximately 15 minutes prior to application
Time Between Coats	Recommended 60 minutes between coats.
Coating Window	Additional recoats can be applied for up to 72 hours from first application/mixing of Part A and Part B
Full Cure Time	Less than two hours
Coating Thickness	1-4 mils recommended
Applicable Surfaces	Metals, concrete, composites, etc.

DragX Treatment	
Appearance of Coating Film	Clear/White/Blue
Maximum Usable Temperature	400°F
Adhesion Test (ASTM D3359)	5A after 48 hours
Flow Assurance* (As conducted by the Colorado School of Mines Center for Hydrates)	Up to 10-fold reduction in Hydrate Formation/Adhesion
Salt Fog Corrosion Resistance + Scribing (ASTM B117 + ASTM D1654)	1000 + hr
Erosion Resistance (ASTM G76)	< 5% Mass Loss at sand particle impact of 70 m/s
Wear Resistance (ASTM D4060)	50mg / 1000 cycles / 1 kg
Chemical Compatibility Tested (No Reactivity)	Acidic Conditions (pH < 2) Alkaline Conditions (pH >11) Acid Gas (> 1000 ppm CO_2) Sour Gas (> 4 ppm H_2S)
Surface Roughness After Application	60-120 µinch

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Transient Flowloop Experiments: Consortium Comments & Questions Addressed

	Comment/Question	Answer
Chevron	How is wall deposit porosity calculated?	Water Volume Balance $V_{input} = V_{flow} + V_{hydrate} + V_{deposit}$
	How does water wicking into deposit change with time?	Wicking decreases with penetration depth (time)*
	Is the decreasing flow a result of significant deposition on untreated surfaces?	Similar amounts of hydrate deposited in both cases, result of porous deposition
XOM	What happens when there are multiple attempts at restart?	Performed for transient tests, 2-3 attempts before permanent plugging
	Potential redistribution of hydrates is not captured	Possible, but difficult due to fluid warming in non-cooled sections
MultiChem	Have you performed repeats for uncoated/ coated trials?	Yes, 8x Uncoated, 3x Coated
	Try to dissociate and reform in loop to see if results are the same?	Procedure is to dissociate and reform
	May consider including brine into system (slower hydrate growth & corrosion)	Don't expect corrosion to occur, slow hydrate growth could be interesting

*Yang et al. 2019

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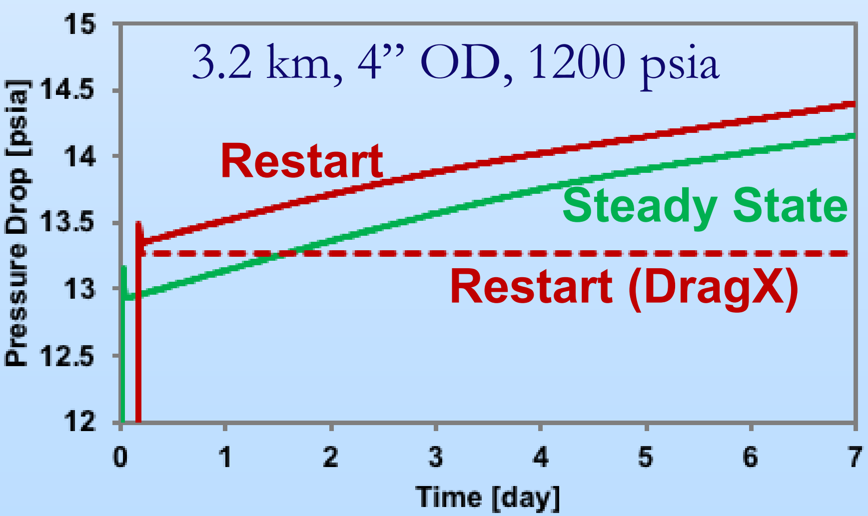
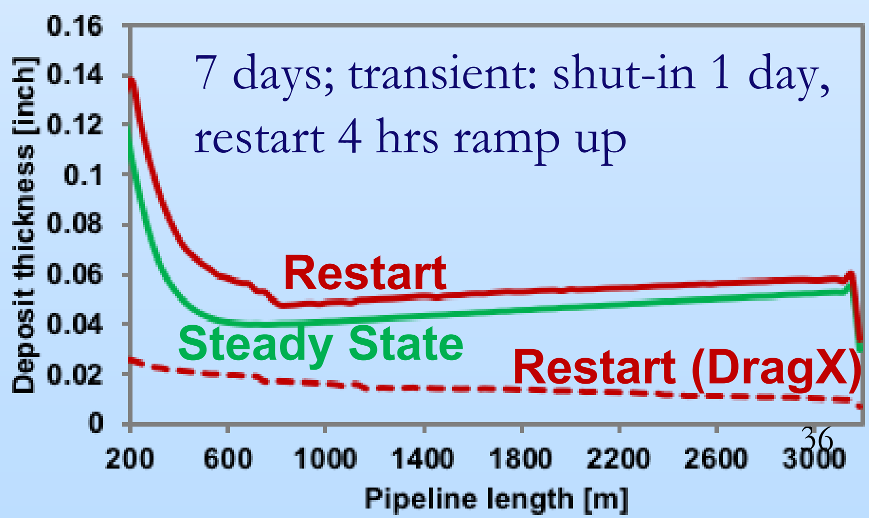
CENTER FOR HYDRATE RESEARCH

Focused Towards Field Deployment

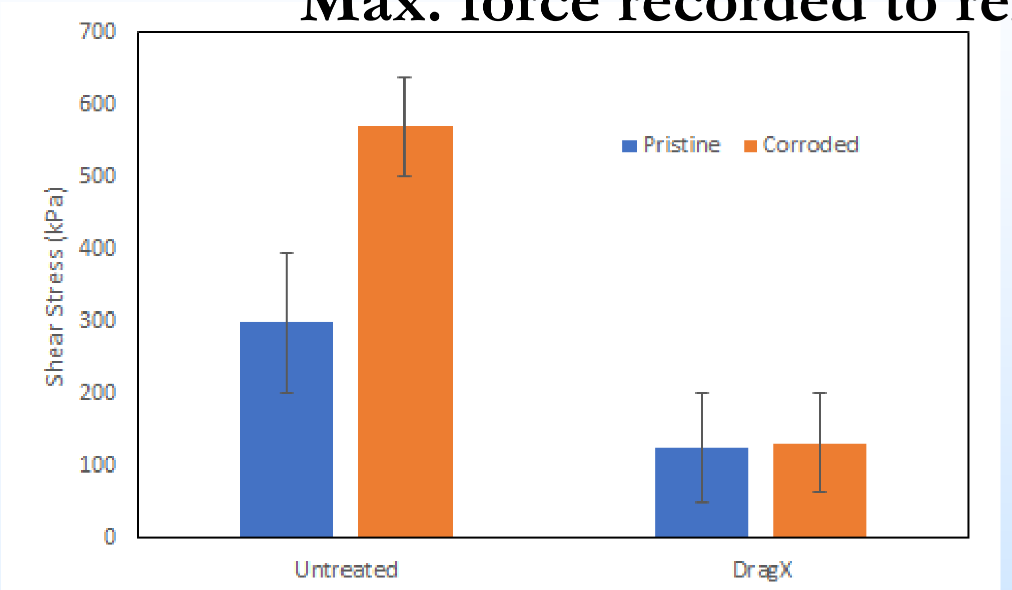
- Discussions held & will continue with Industry champions to assess site and costs for deployment
- Potential sites: North Sea (Shell, Chrysaor, Premier Oil etc), Gulf of Mexico
- Continue simulated XoM field trial pipe geometry and conditions to aid subsequent experimental design

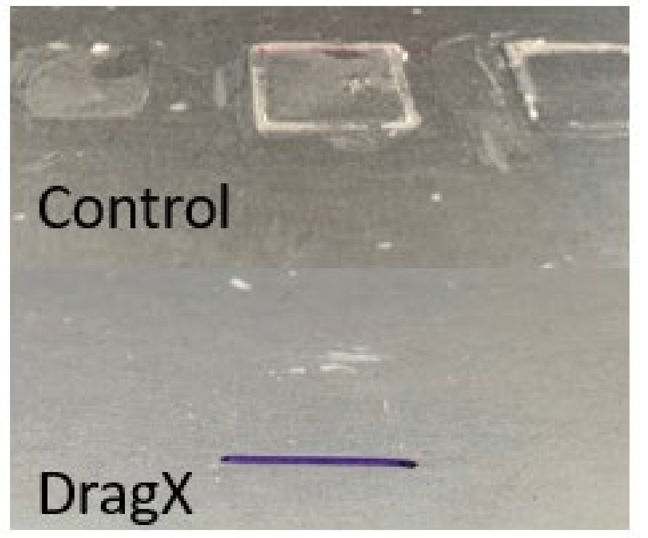




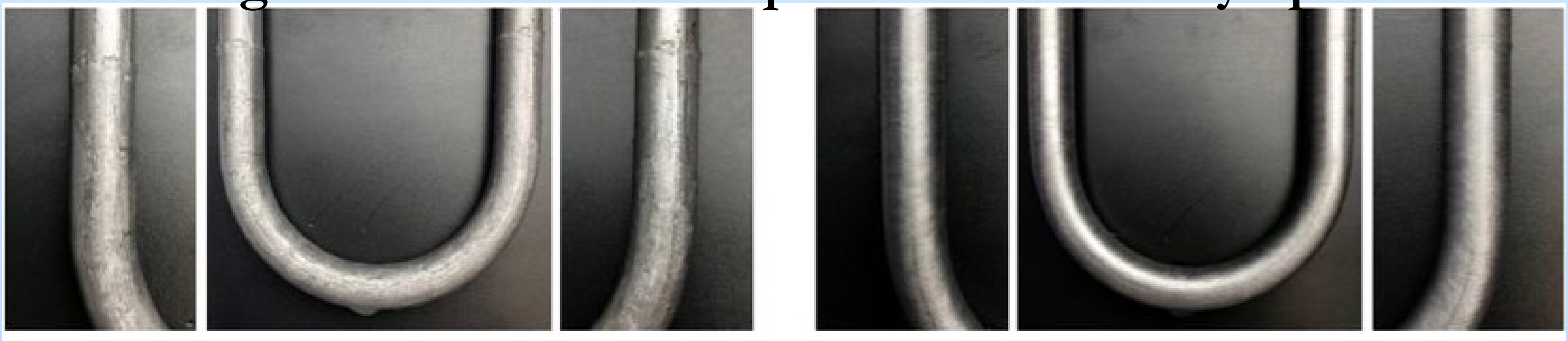
Wax Deposition Mitigated in Oil-Dominated Systems

Max. force recorded to remove cuvette/wax





Cold finger tests show wax deposition reduced by up to 55%



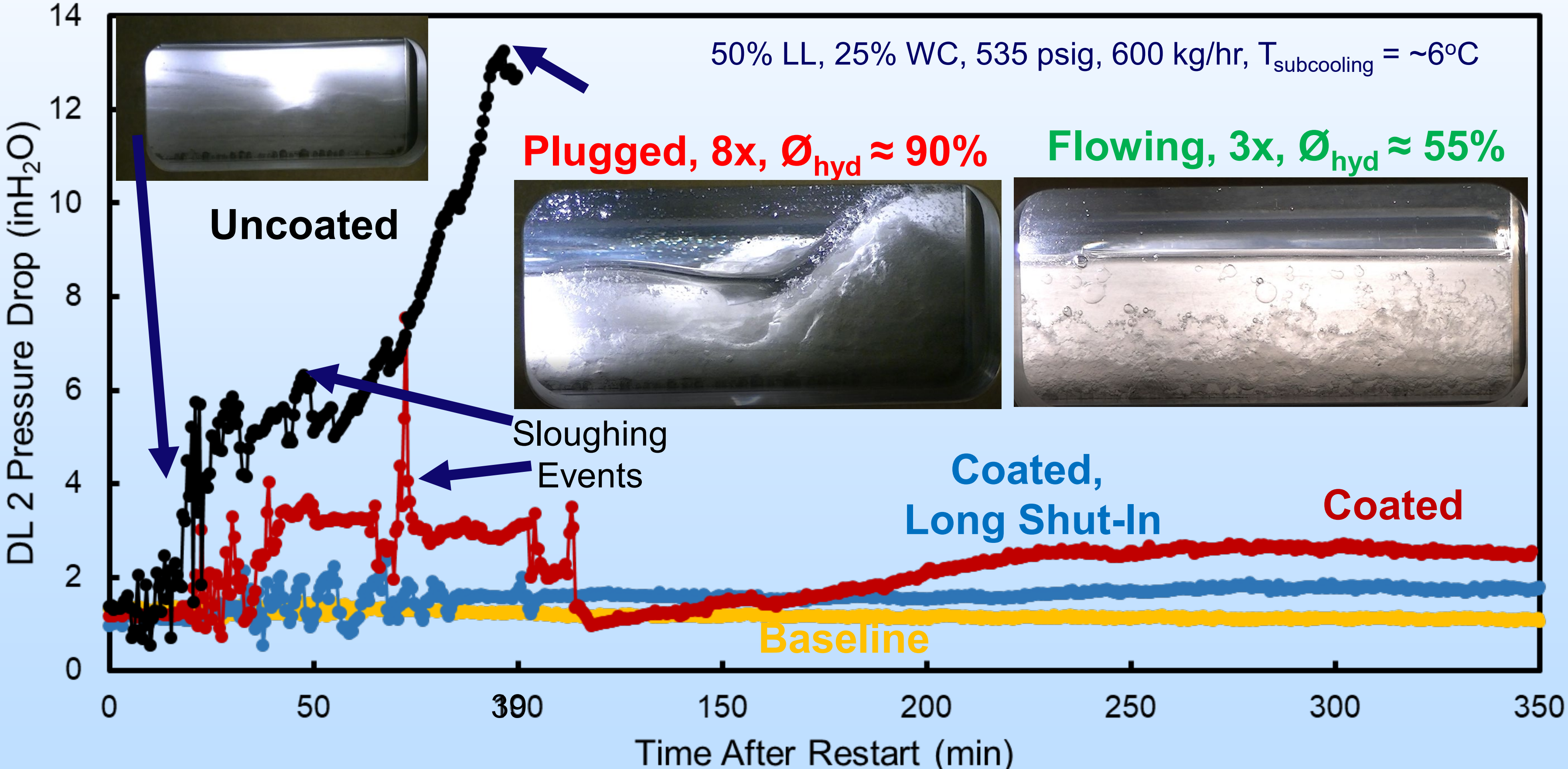
Surface Materials Properties & Characterization

Investigating surface energy & roughness effects on hydrate formation

Surface	Dispersive Surface Energy [mJ/m2]	Polar Surface Energy [mJ/m2]	Total Surface Energy [mJ/m2]	Median Surface Roughness [μm]
Carbon Steel	137	1.8	139	0.82
Stainless Steel	82.2	0.41	82.6[1,2]	1.9
Copper	348	1.4	350[3]	0.1
PTFE	20.8	0.3	21.1[4]	0.1
DragX	15.4	0.5	16	0.27

Hydrate Deposition Mitigated in Oil-Dominated Systems

Flowloop transient tests show no plugs with coating (6+ mo)



Hydrate Deposition Mitigated in Oil-Dominated Systems

- Deposition Loop: Induction times delayed for oil/gas-dominated (up to 230+ h); Growth reduced by ~60+%

System	Surface Treat-ment	Induction Time [h]	T_{sub} [°C]	Expt. Details
Oil-Dom.	N	10	~9	50% LL, 25% WC, 600 kg/hr, 540 psia
		24		
	Y	>110		
		>236		
Gas-Dom.	N	5	~10	30% LL, 100% WC, 564 psia
		12		
	Y	>120		
		>168