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

Project# DE-FE0031578 – Program Manager: Bill Fincham

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Colorado School of Mines

Vinod Veedu, Erika Brown, *Oceanit*

U.S. Department of Energy

National Energy Technology Laboratory

Oil & Natural Gas

2020 Integrated Review Webinar

Presentation Outline

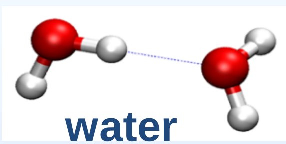
- Project Overview & Background & Scope
- Technical Progress & Status
  - Robust Coatings for Deepwater Operations
    - Mitigating Gas Hydrate & Other FA Solids Deposition
- Accomplishments to Date
- Lessons Learned & Synergies
- Project Summary

Project Overview

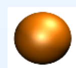
- Funding: DOE: $1,497,543 , Costshare: $374,386
- Overall Project Performance Dates: 3/2018 - 3/2022
- Project Participants
  - CSM: Carolyn Koh, Marshall Pickarts, Jose Delgado, Hao Qin
  - Oceanit: Vinod Veedu, Erika Brown
- Overall Project Objectives
  - Develop for ***field & commercial deployment*** 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

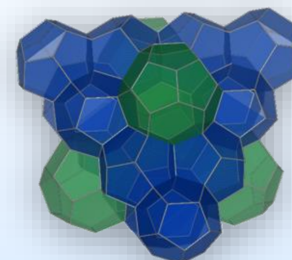
Hydrates Cause Major Economic & Safety Risks During Energy Production & Transportation



+ gas



+ High *P* Low *T* →



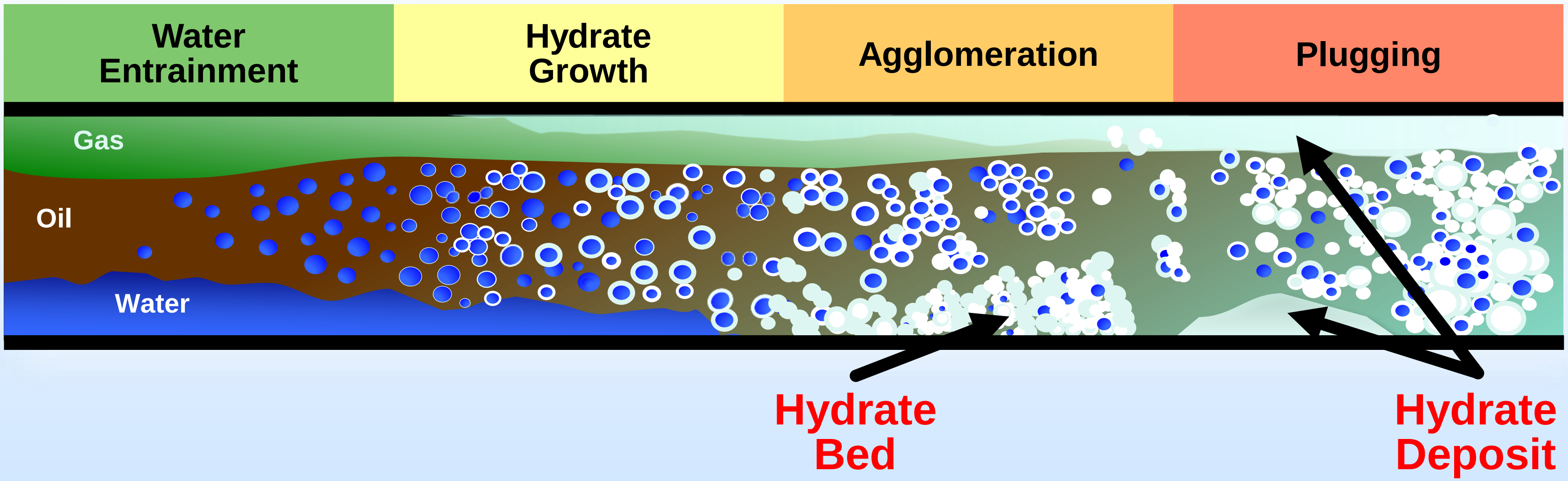
Hydrate crystal

- **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

Motivation for Hydrate Deposition

A Major Outstanding & Critical Flow Assurance Problem



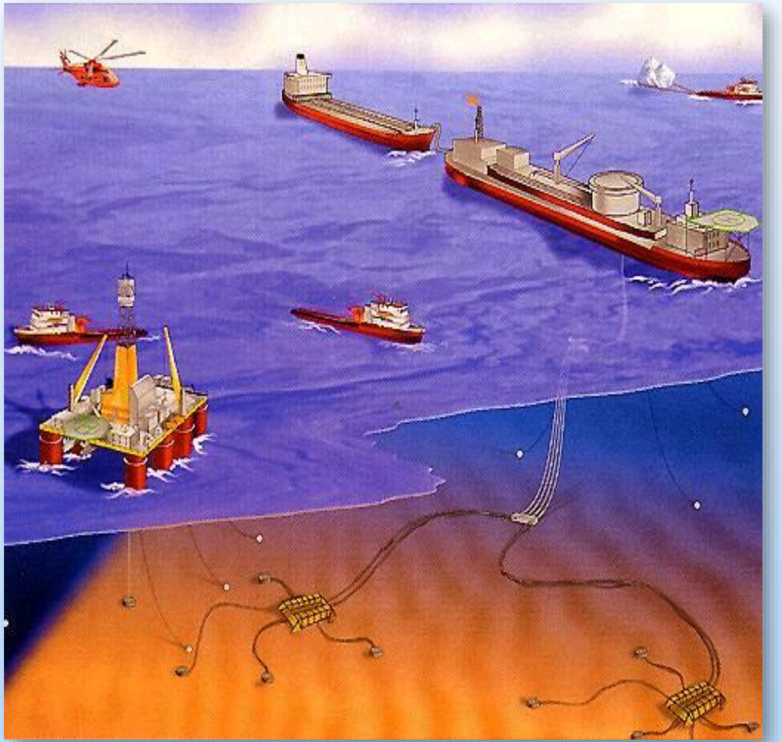
- Flowloop tests show agglomeration alone cannot account for large ΔP increase[1]
- ExxonMobil field trial suggests hydrate deposits caused **majority** of ΔP increases[2]

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 to 8,000 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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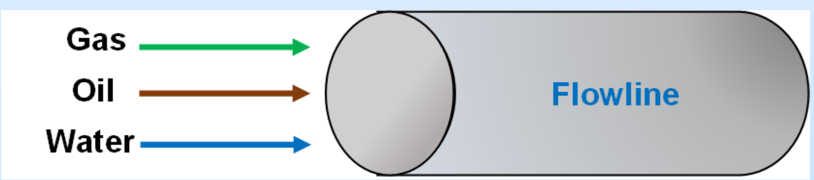
Project Scope: Flow Assurance Solids – Hydrates/Wax/Asphaltenes

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

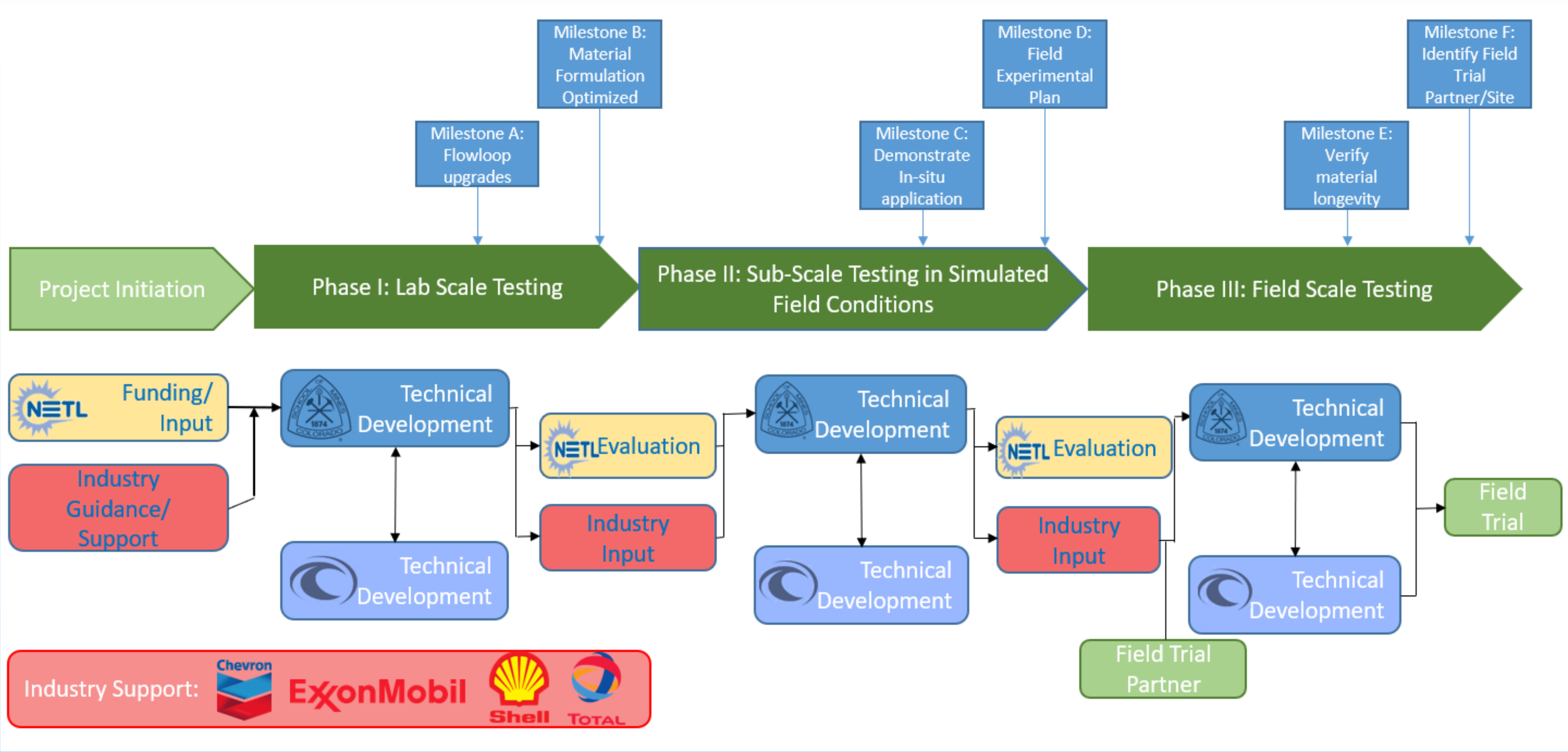
- **Temperature**
- **Composition**


Asphaltenes

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

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

Project Organization and Milestones

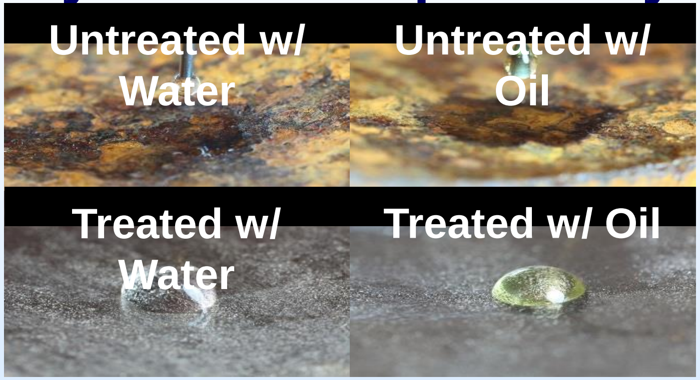


PROGRESS & CURRENT STATUS OF PROJECT

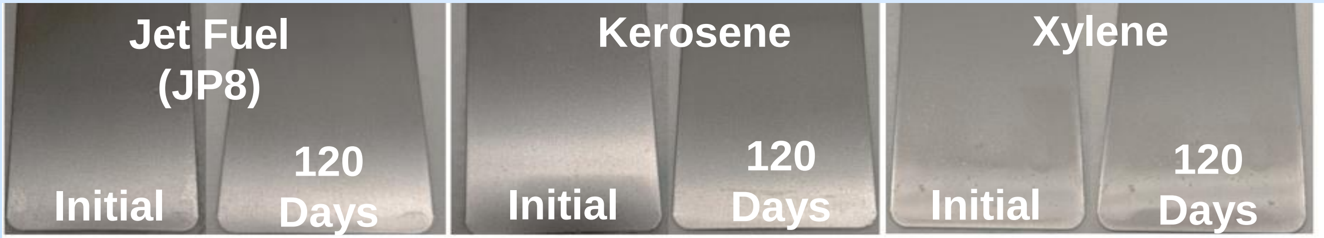
Optimized Omniphobic Coating for Commercialization

Corrosion Resistance

Hydro- & Oleophobicity



Chemical Resistance



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

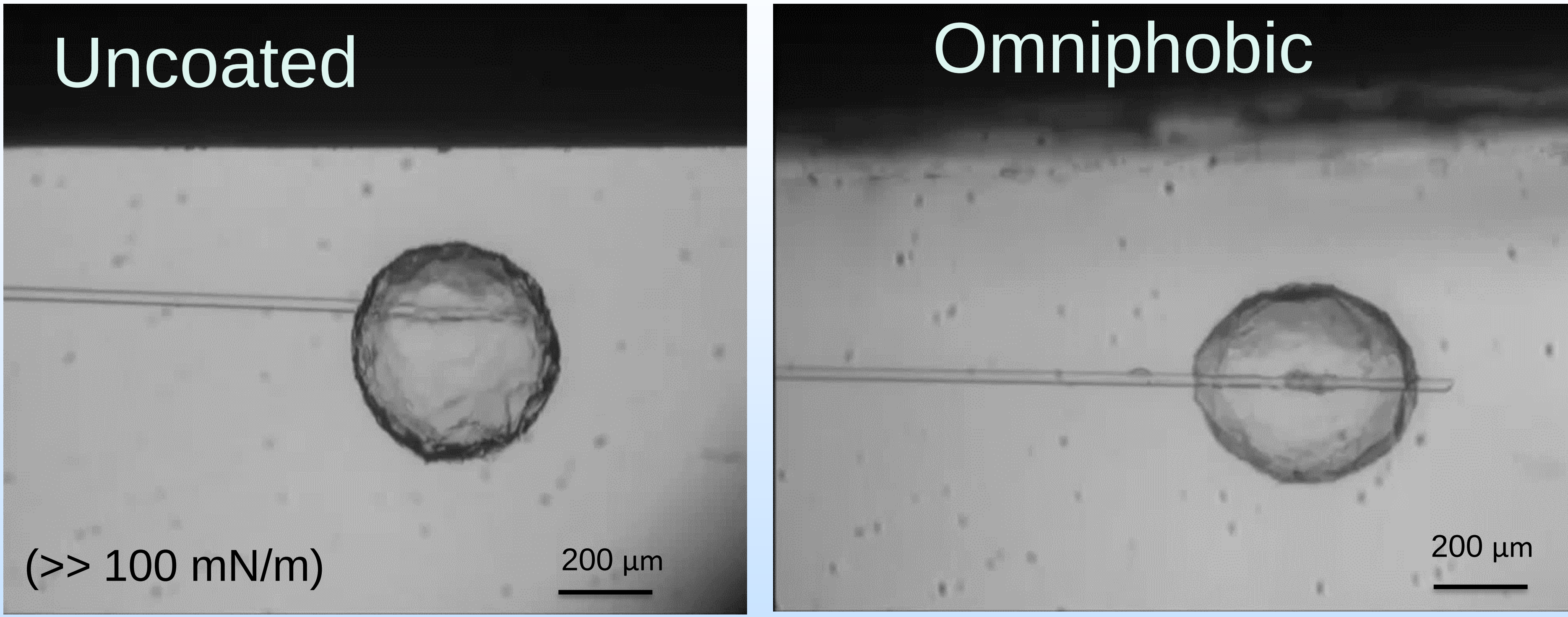
Coating Details

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

Application Properties

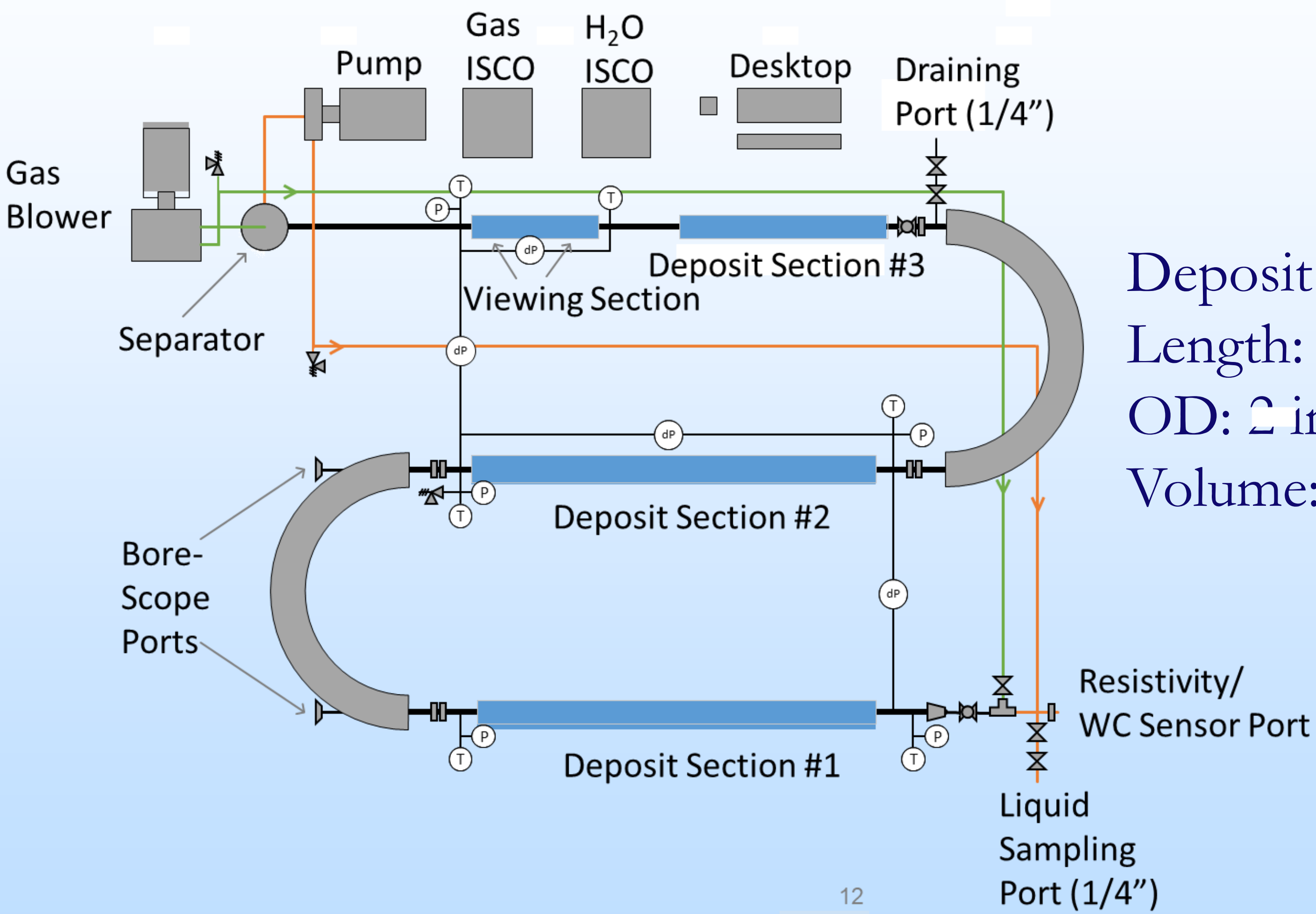
Method: Spray, Dip, Flood & Drain
Surface: Metals, Concretes, Composites
Thickness: ~100 μm

Corroded Pipe Surface Coating Reduces Adhesion Forces



Hydrate-phobic coatings can reduce adhesion/deposition

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)

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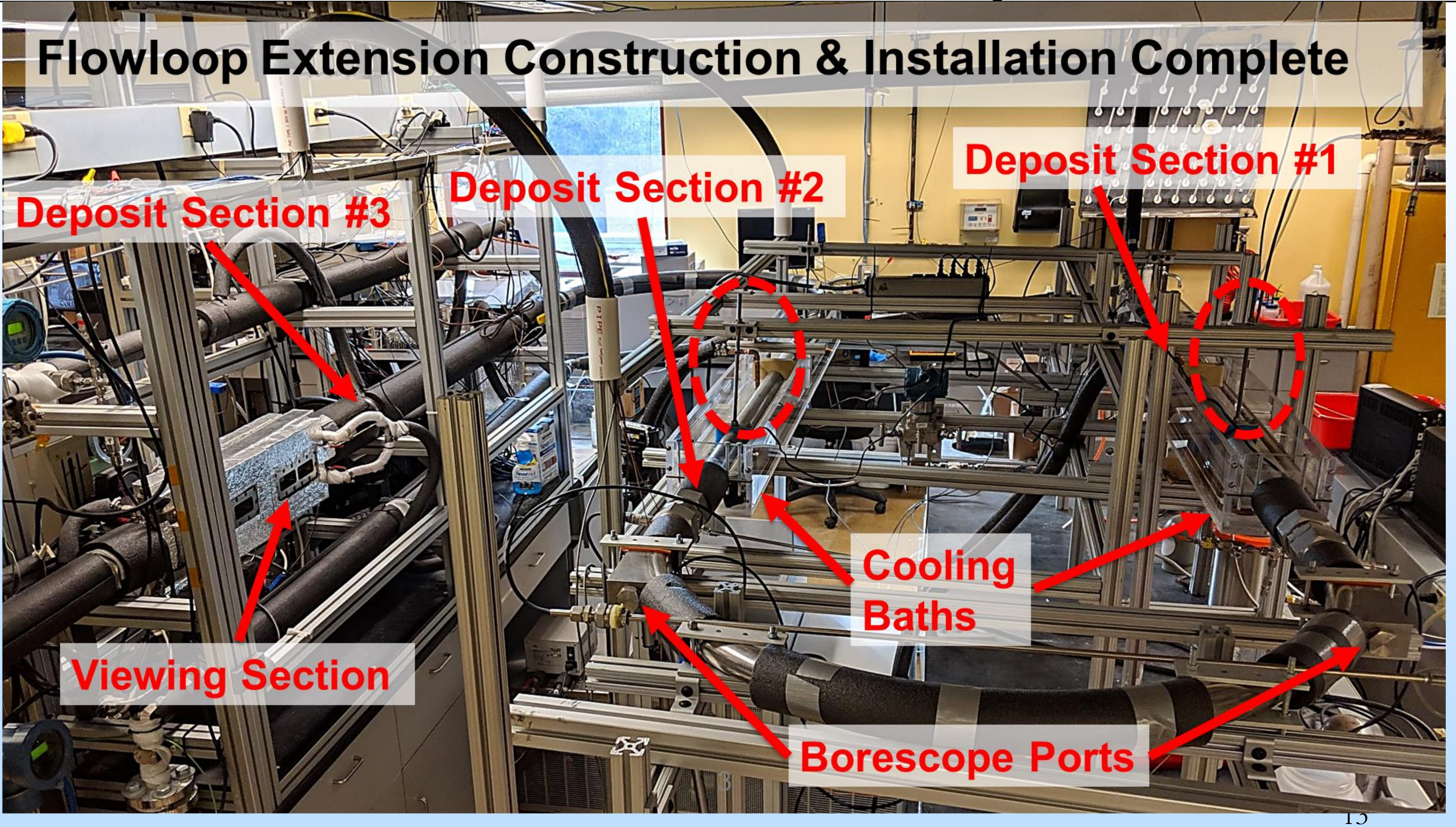
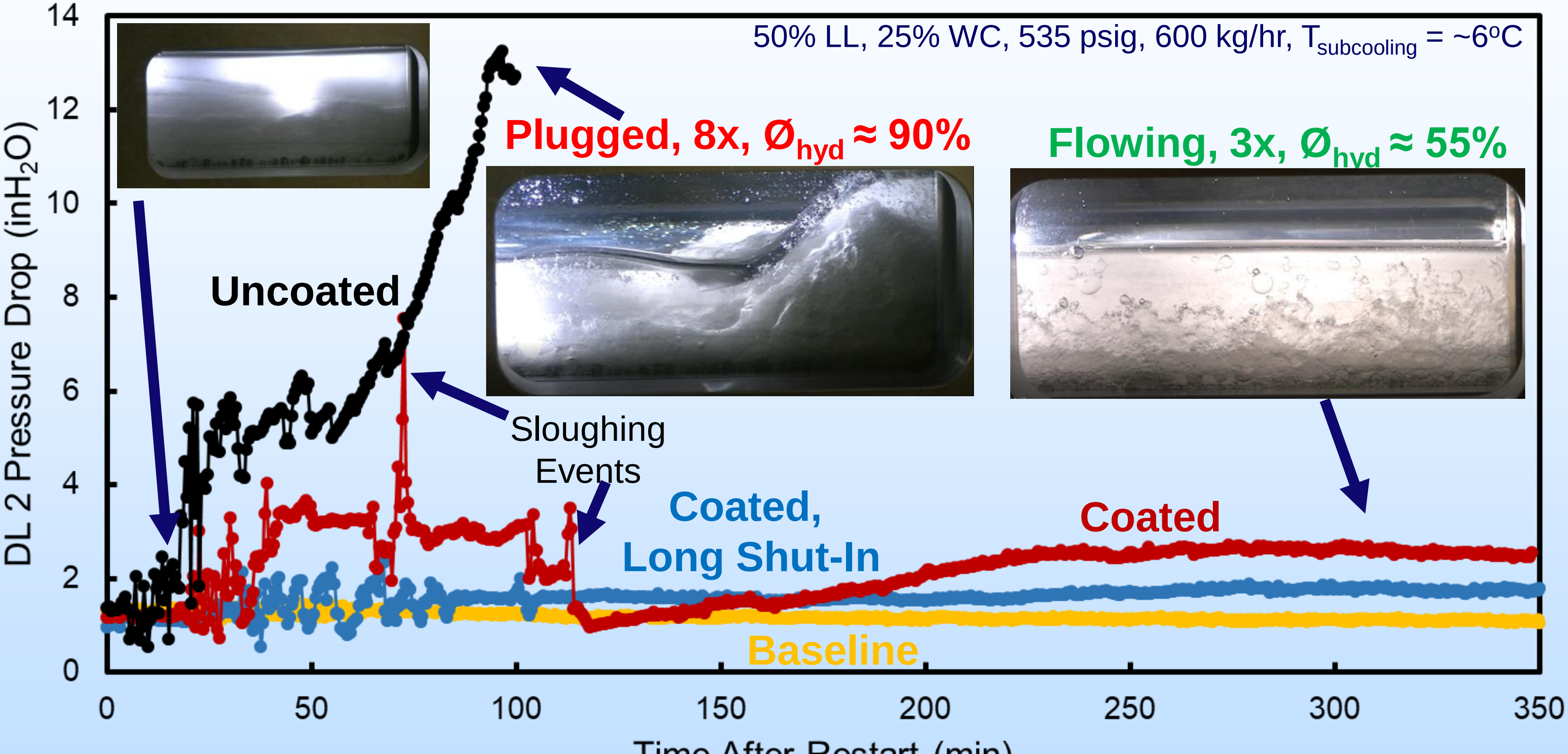
Hydrate-Phobic Coatings Tests in Deposition Loop



Hydrate Deposition Mitigated in Oil-Dominated Systems



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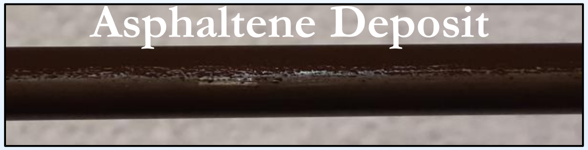
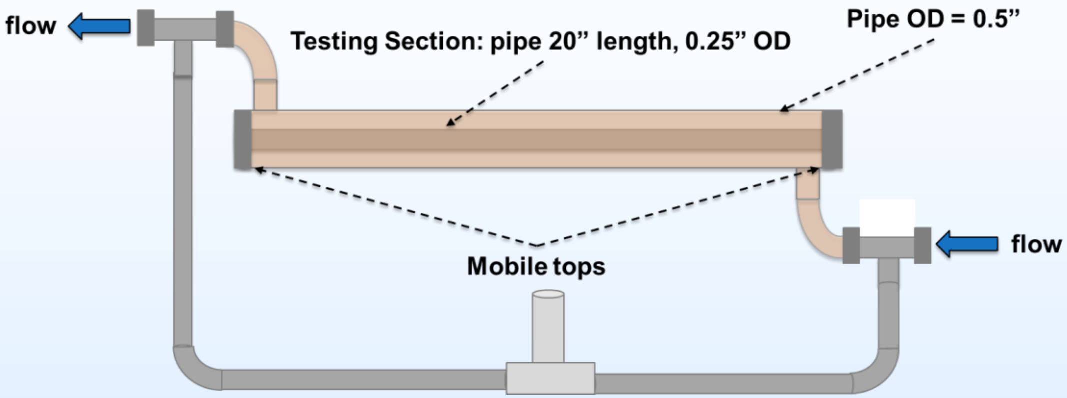
Hydrate Deposition Mitigated in Oil/Gas-Dominated Systems

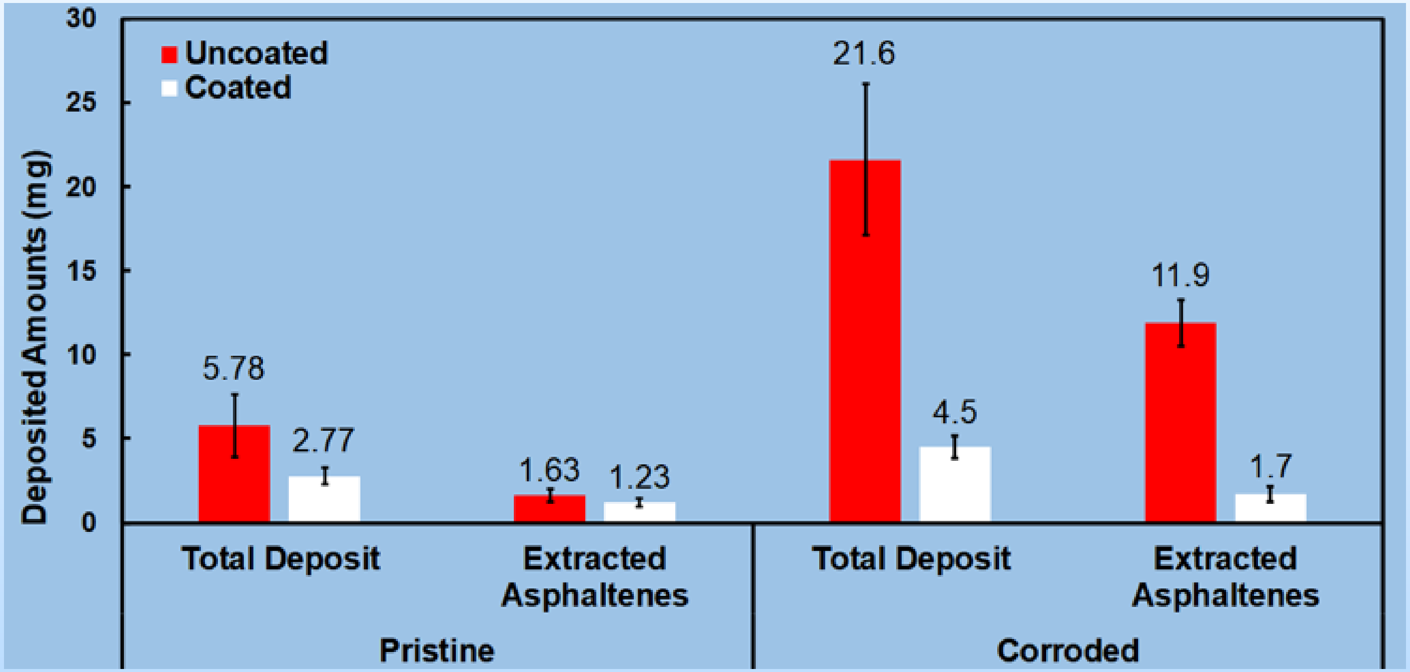
Deposition loop: hydrate formation delayed with coating

System	Surface Treatment	Induction Time [h]	$T_{subcool}$ [^oC]	Experimental Details
Oil-Dominated	N	10	~9	50% LL, 25% WC, 600 kg/hr, 540 psia, Continuous: Film Growth
		24		
	Y	>110		
		>236		
Gas-Dominated	N	5	~10	30% LL, 100% WC, 564 psia, Continuous: Film Growth
		12		
	Y	>120		
		>168		

Asphaltene Deposition Mitigated in Oil-Dominated Systems

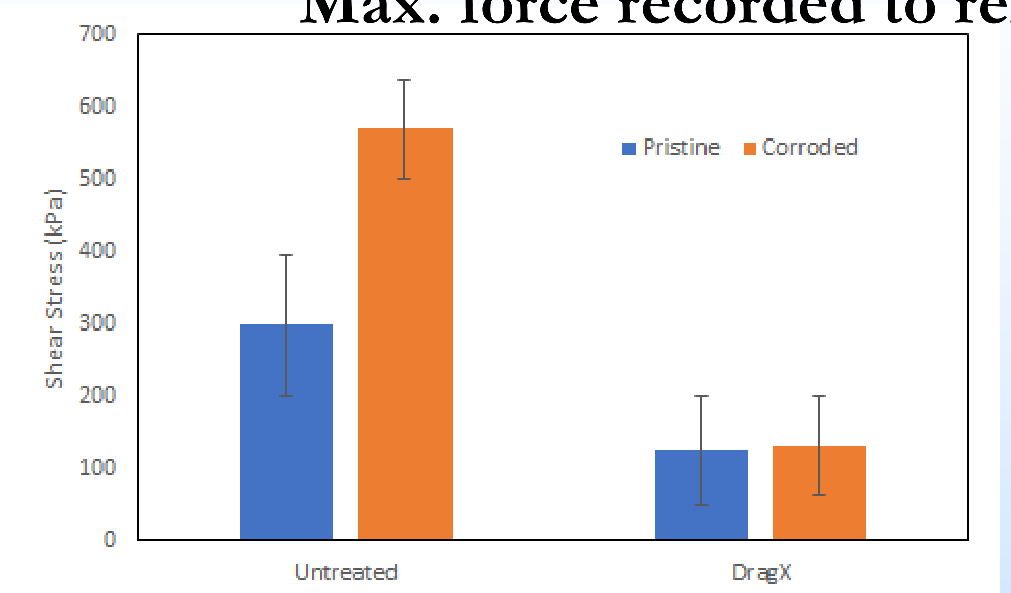


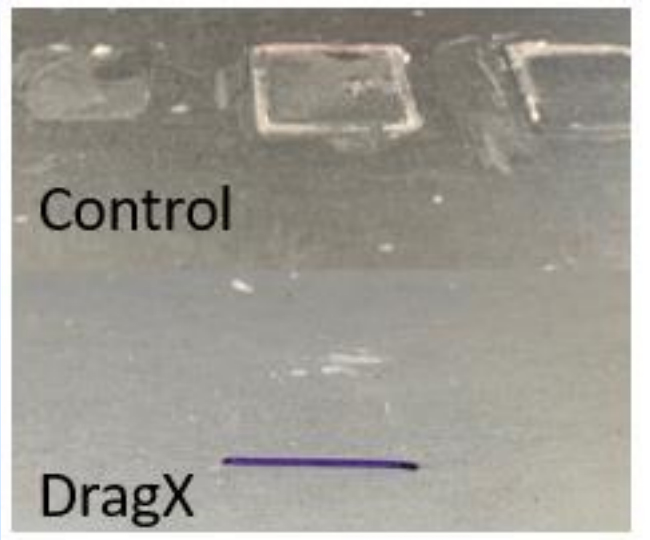




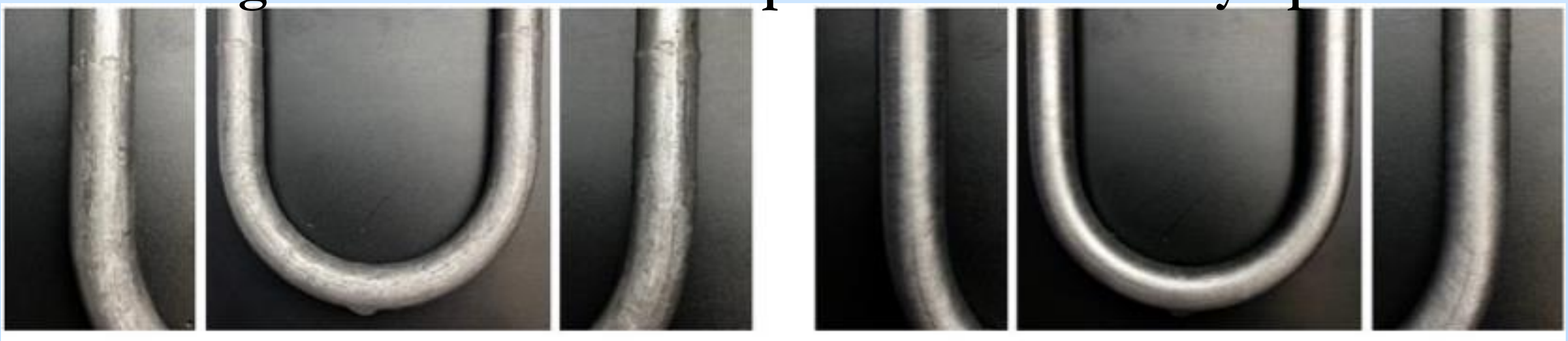
Wax Deposition Mitigated in Oil-Dominated Systems

Max. force recorded to remove cuvette/wax





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



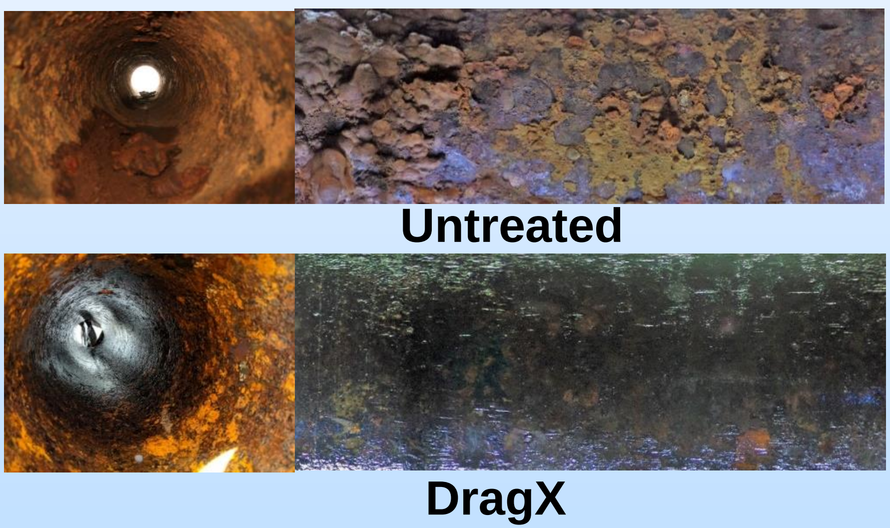
Long-Term Coating Durability

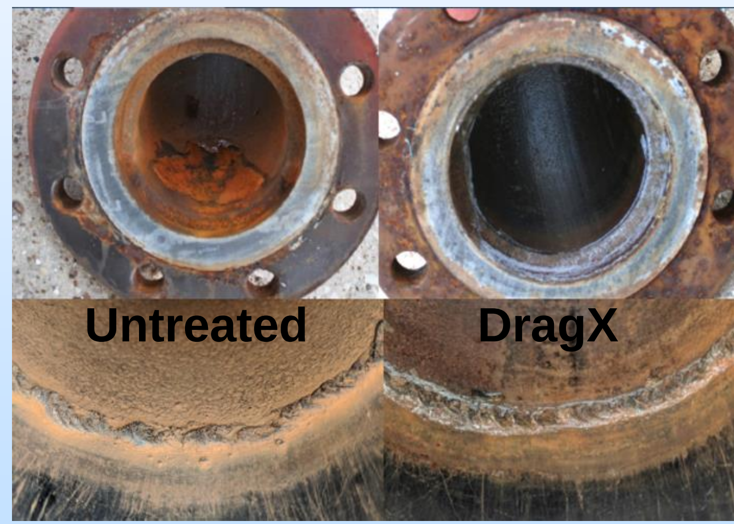
- 6+ Months High Pressure Testing
  - ~3300 Operating Hours
  - Solid Particle/Fluid Flow
  - Pressure Cycles

No corrosion → No delamination

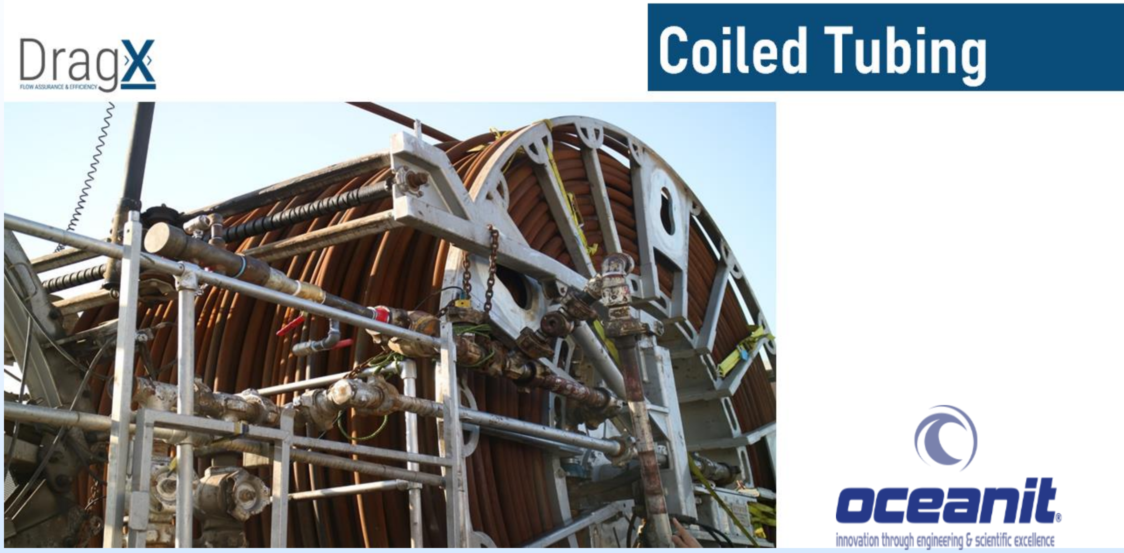
In-Situ Application Development

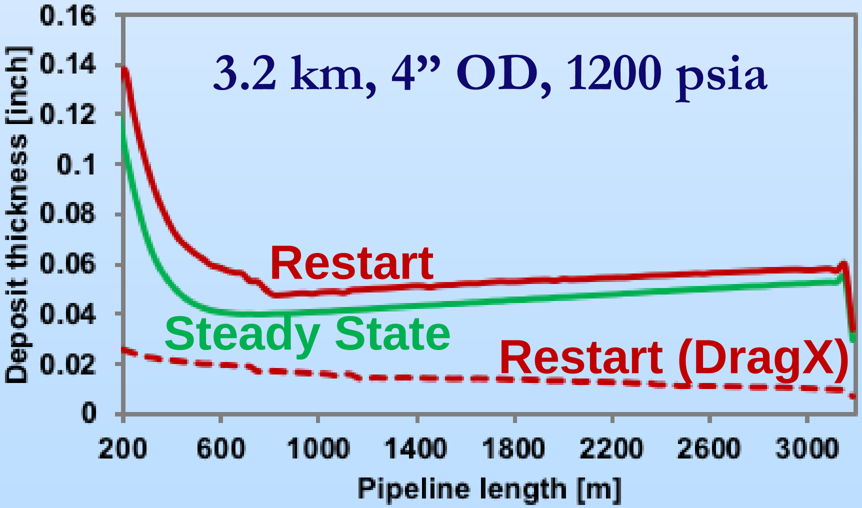
- DragX can be applied in-situ to production lines via pigging
- Can also be applied to new pipes by spray, flush, or paint





Focused Towards Field Deployment





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

Project Summary

- Hydrate film growth/deposition is a major problem in deepwater operations leading to major economic, environmental & safety risks
- Hydrate-phobic coatings can be applied to corroded pipe surfaces to mitigate hydrate deposition
  - Coatings reduce formation & deposition of hydrates, waxes, and asphaltenes in oil/gas lines under simulated field conditions
  - Hydrate & other FA solids multi-resistant coatings for deepwater operations development/testing & field test plan underway

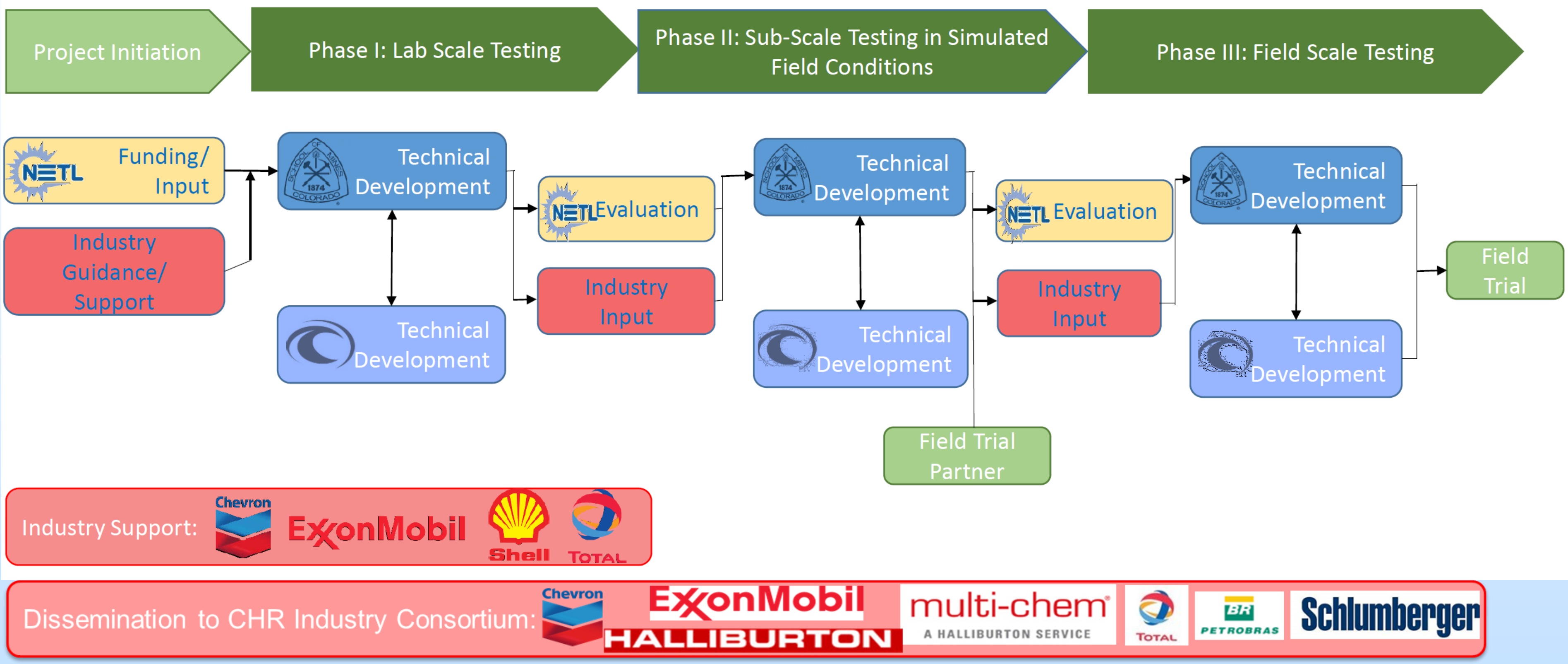
Acknowledgements

- 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 (ExxonMobil), and Daniel Crosby (Shell)

Appendix

Project Organization for Deployment of Coatings



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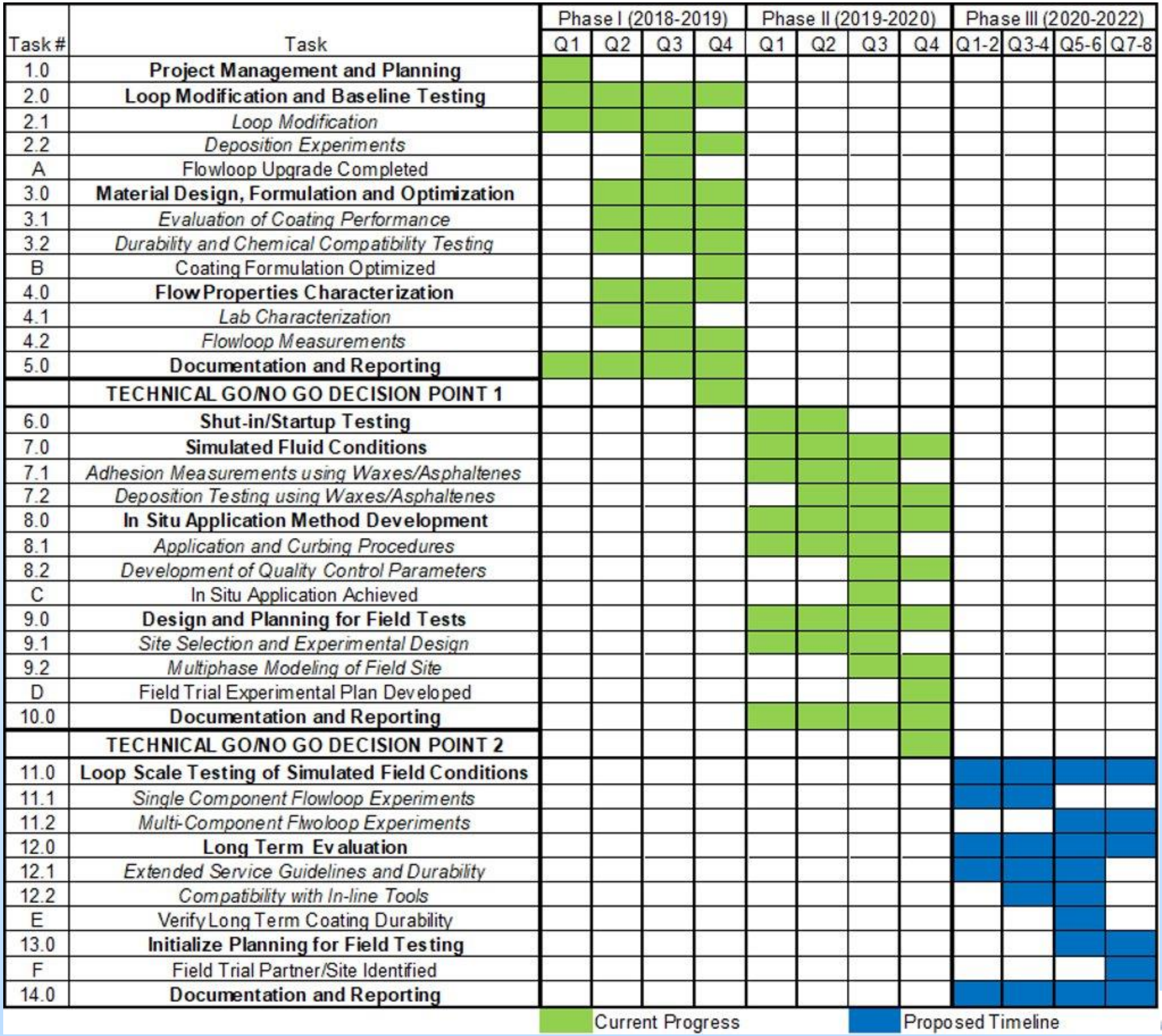
Gantt Chart



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- 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)

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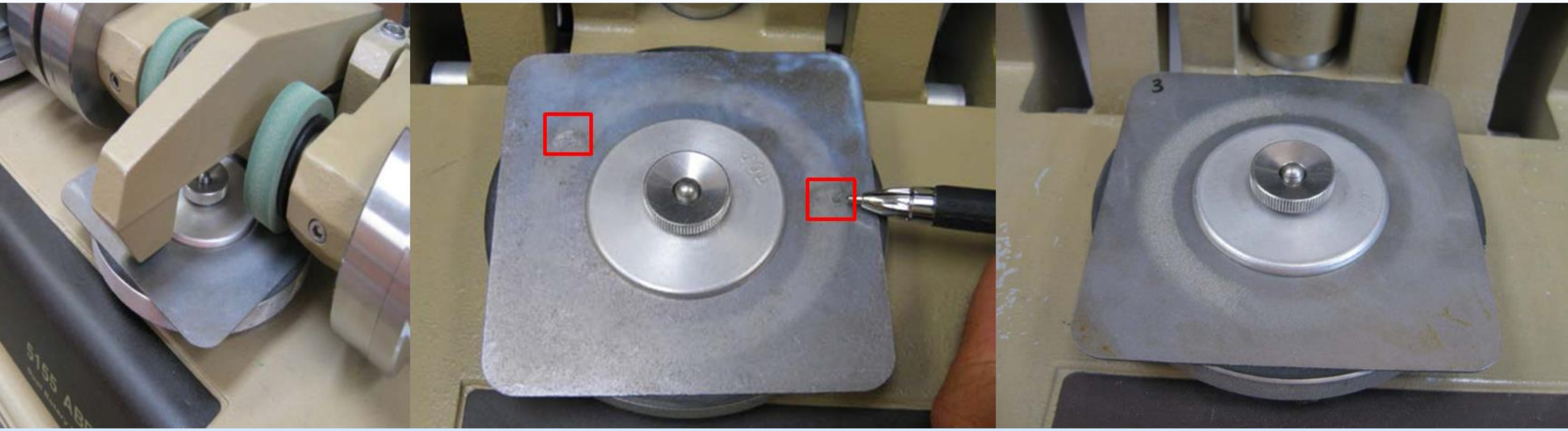
BACKUP SLIDES

Coating Abrasion Resistance

Taber Abrader Testing (ASTM D4060)



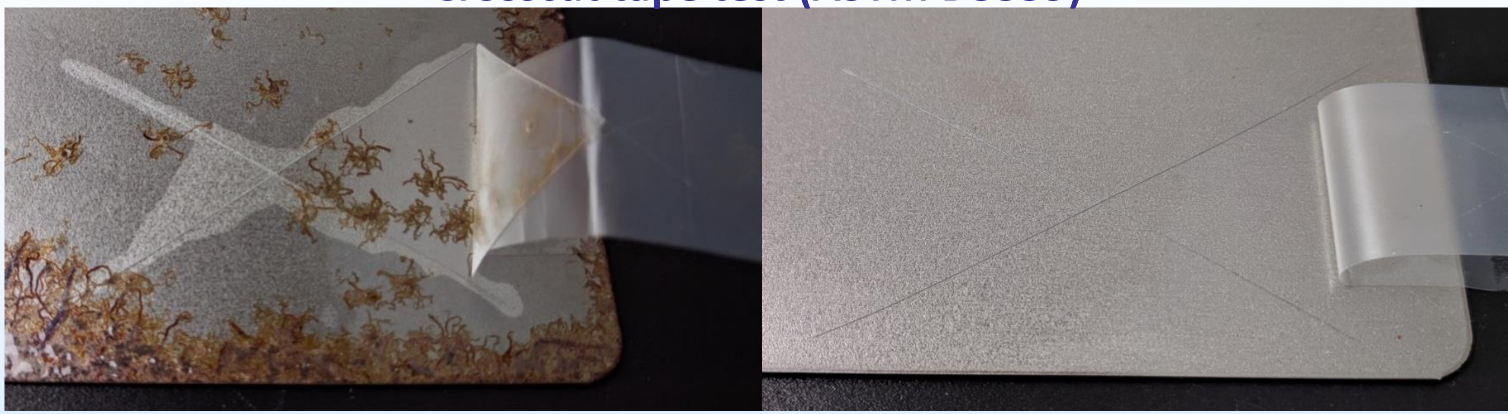
Poorly Adhered Coating
(Mass Loss ~ 100mg/1000 cycles)

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

Optimized DragX^{TM} 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)



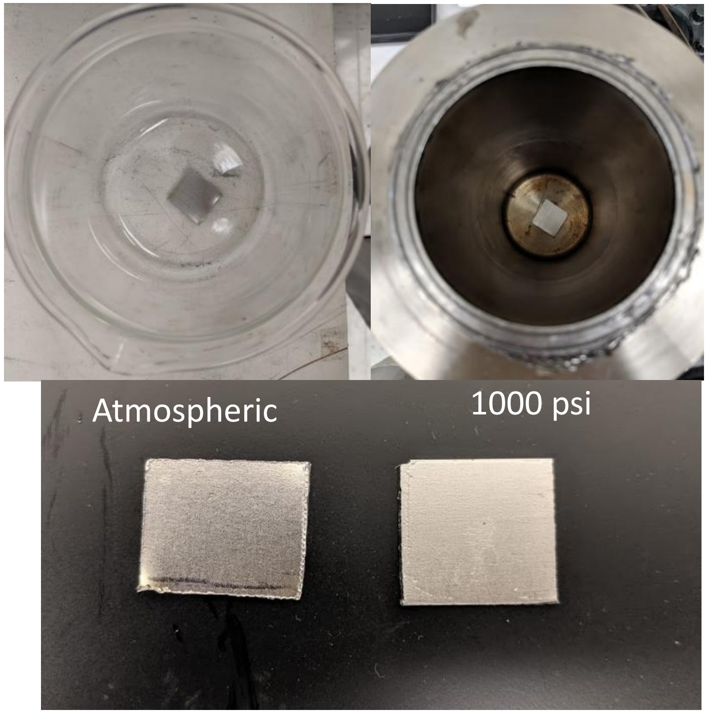
Knife adhesion test (ASTM D6677)

Novolac Epoxy Coated | DragX^{TM} Treatment

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

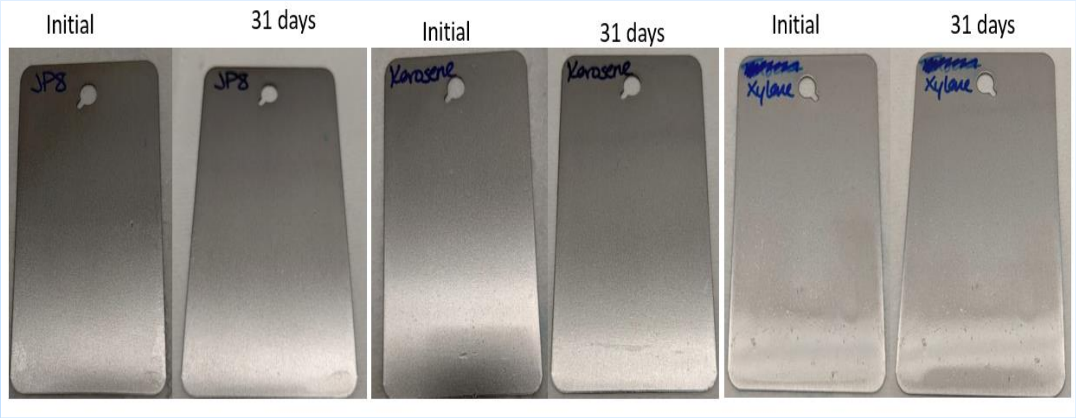
In-Situ Application Method Development

- 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



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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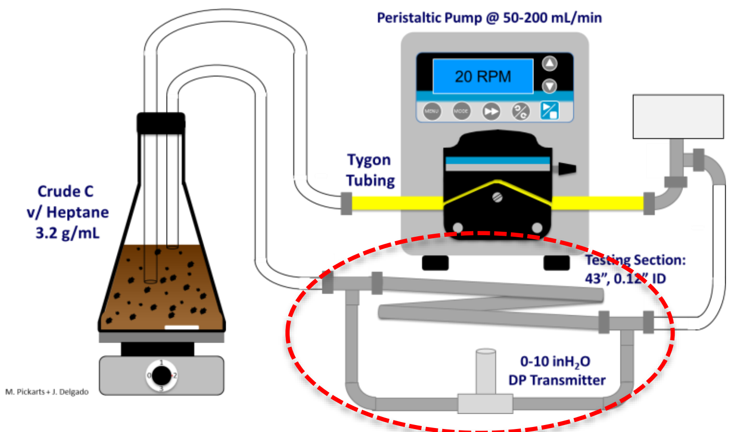
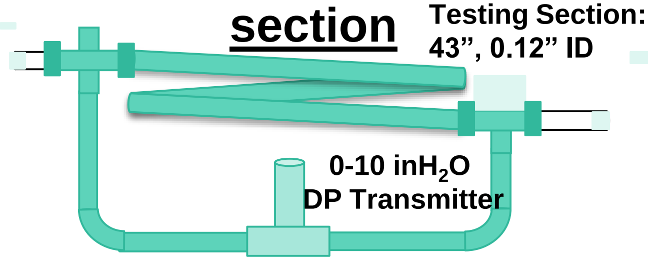
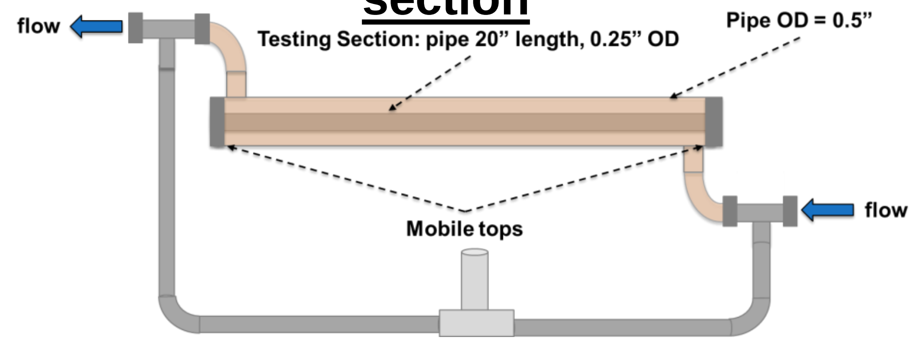
New deposition section for asphaltene loop



Former deposition section



New deposition section



Clean

After deposition

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