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

Project Number: DE-FE0031578 – Program Manager: Bill Fincham

Carolyn Koh, Marshall Pickarts, Jose Delgado, Hao Qin

Colorado School of Mines

Vinod Veedu, Erika Brown, *Oceanit*

U.S. Department of Energy

National Energy Technology Laboratory

Addressing the Nation's Energy Needs Through Technology Innovation – 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting

August 26-30, 2019

Presentation Outline

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

TECHNICAL STATUS

Hydrates in Flow Assurance

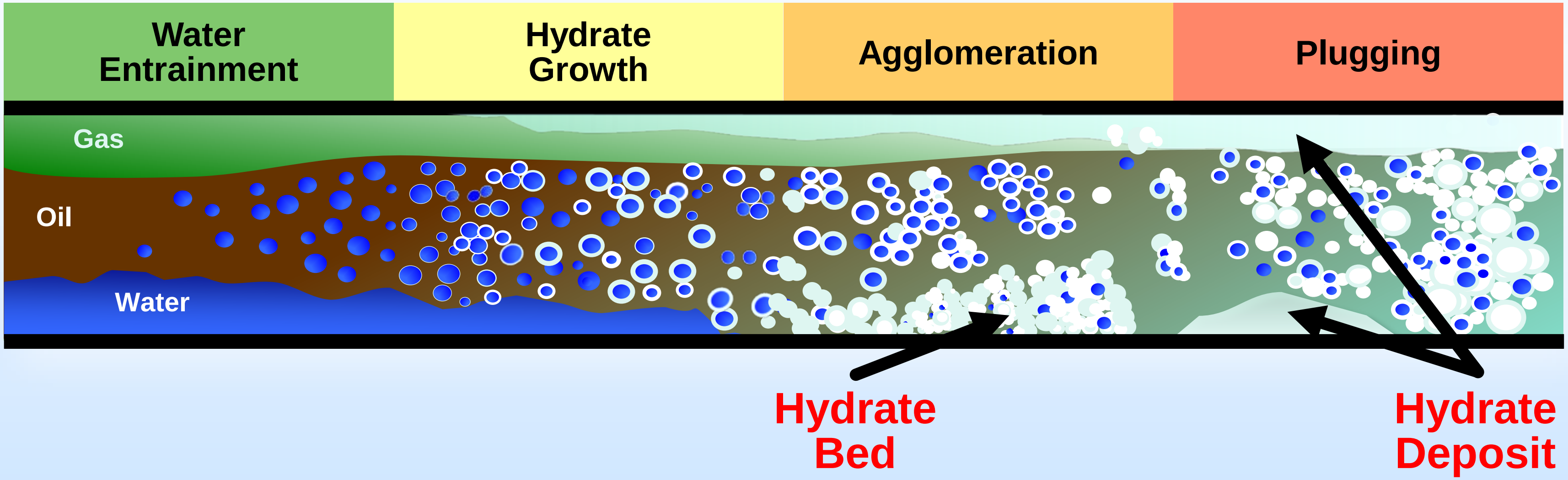
Hydrates Cause Major Economic & Safety Risks During Energy Production & Transportation

- **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

Motivation for Hydrate Deposition

A Major Outstanding & Critical Flow Assurance Problem



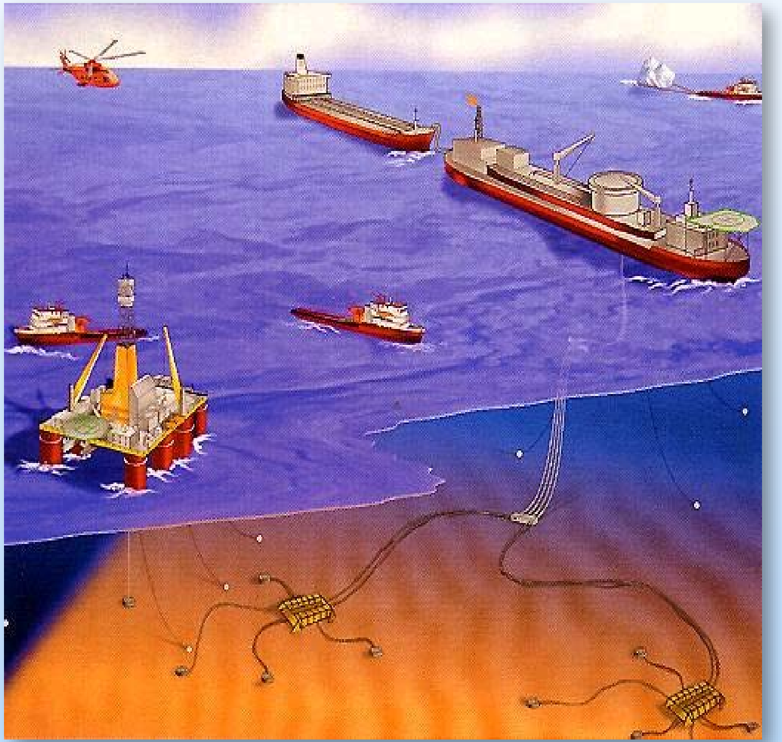
- Flowloop tests show agglomeration alone cannot account for large ΔP increase[1]
- ExxonMobil field trial suggests hydrate deposits caused **majority** of ΔP increases[2]

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
- Multiphase deposition flowloop evaluations in simulated field conditions
- Investigations under simulated field conditions & field test plans



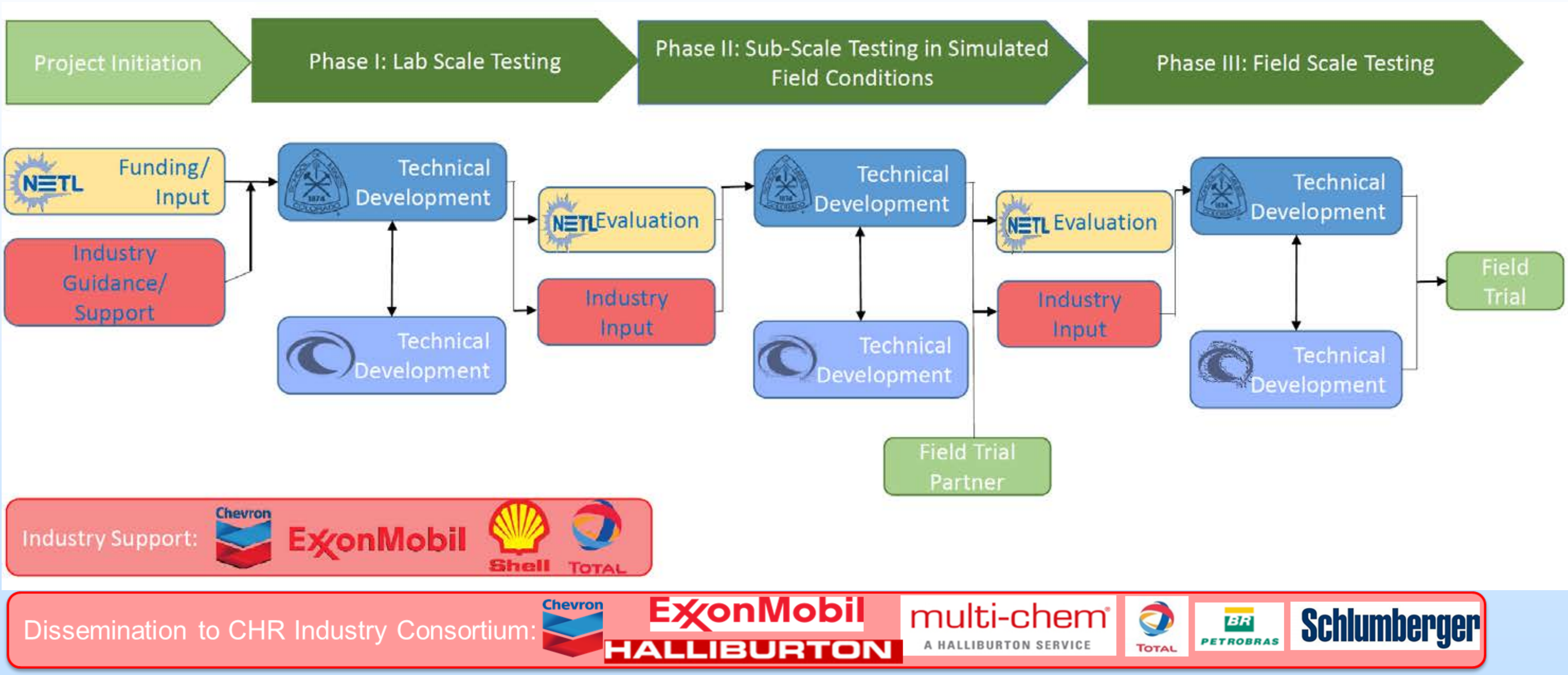
Sloan & Koh, Clathrate Hydrates of Natural Gases, CRC Press, 2007

FOR HYDRATE RESEARCH CENTER

COLORADO SCHOOL OF MINES
EARTH • ENERGY • ENVIRONMENT

oceanit
innovation through engineering & scientific excellence

Project Organization for Deployment of Coatings



Functional Coatings to Reduce Adhesion

Salt Fog Exposure (ASTM B117) – 500 hr duration

Uncoated   DragX Treated

Water and Oil Repellency

Uncoated

Coated

Water   Oil

Uncoated

Coated

FOR RESEARCH CENTER HYDRATE

COLORADO SCHOOL OF MINES

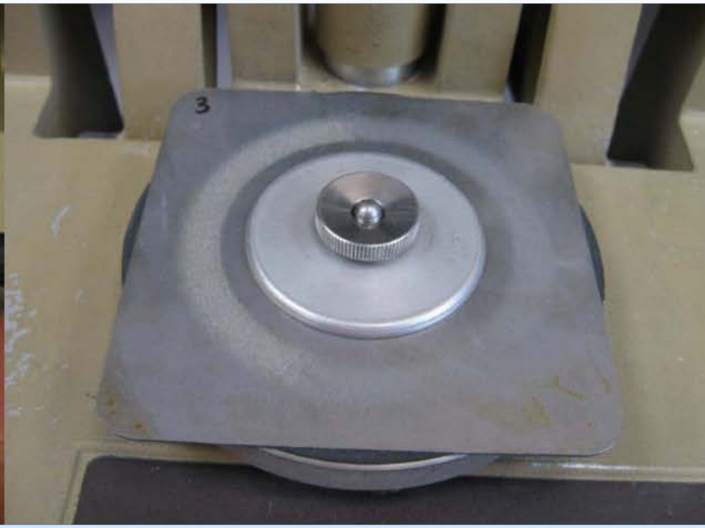
oceanit

innovation through engineering & scientific excellence

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

oceanit
innovation through engineering & scientific excellence

Corroded Pipe Surface Coating Reduces Adhesion Forces

Hydrate-phobic coatings can reduce adhesion/deposition

Corroded Pipe Surface Coating Reduces Adhesion Forces

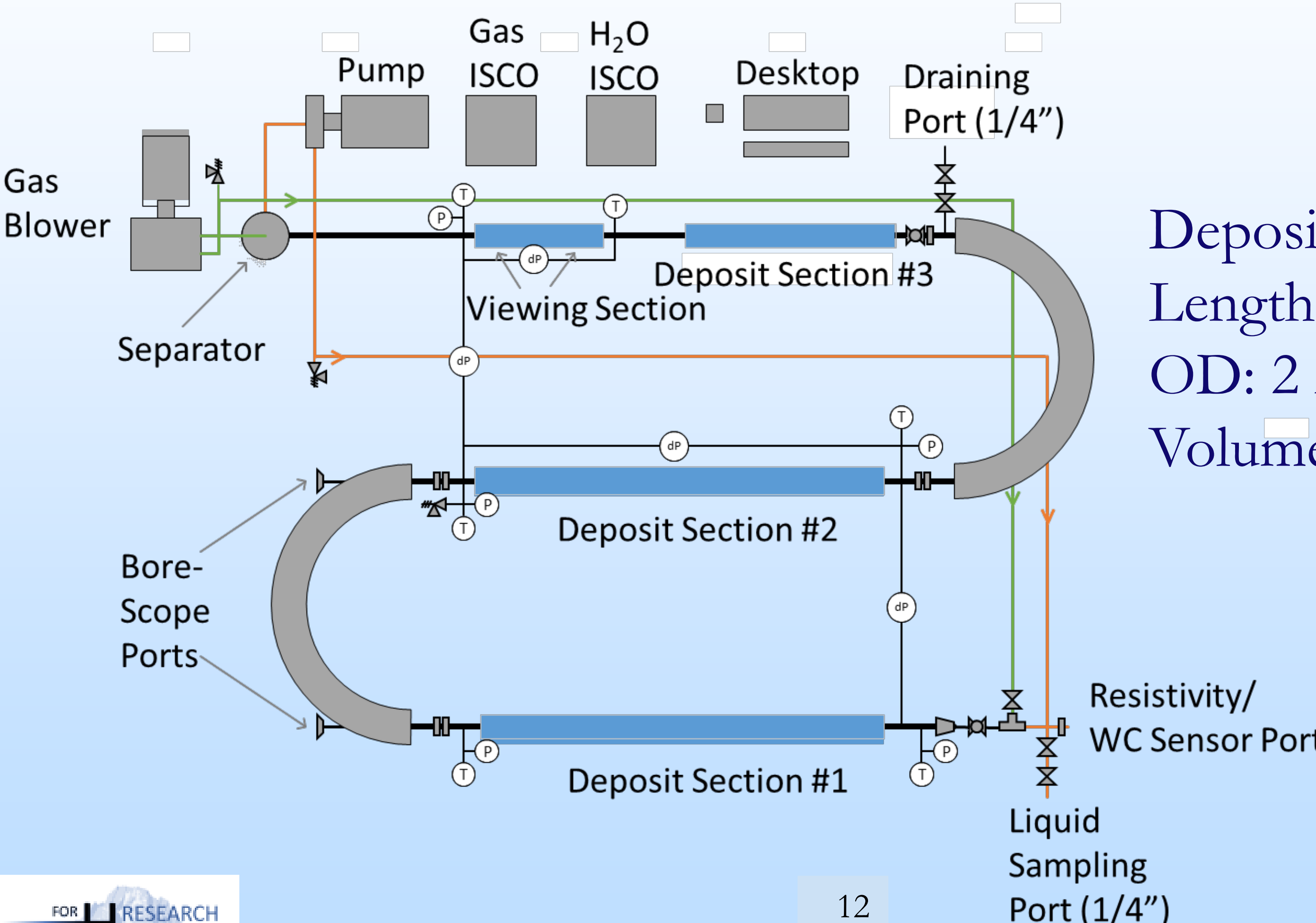
Hydrate deposit formed

No hydrate deposit

Hydrate-phobic coatings resist deposition for 72+ hrs

Coupon Coated		Induction Times [hr]	$T_{subcooling}$ [°C]	Comments
Cell 1	N	7	~13	Cell 2 No Nucleation
Cell 2, 3	Y	>147.5, 67		

Hydrate-Phobic Coatings Tests in Deposition Loop



Deposit Section:

Length: 225 in (5.72 m)

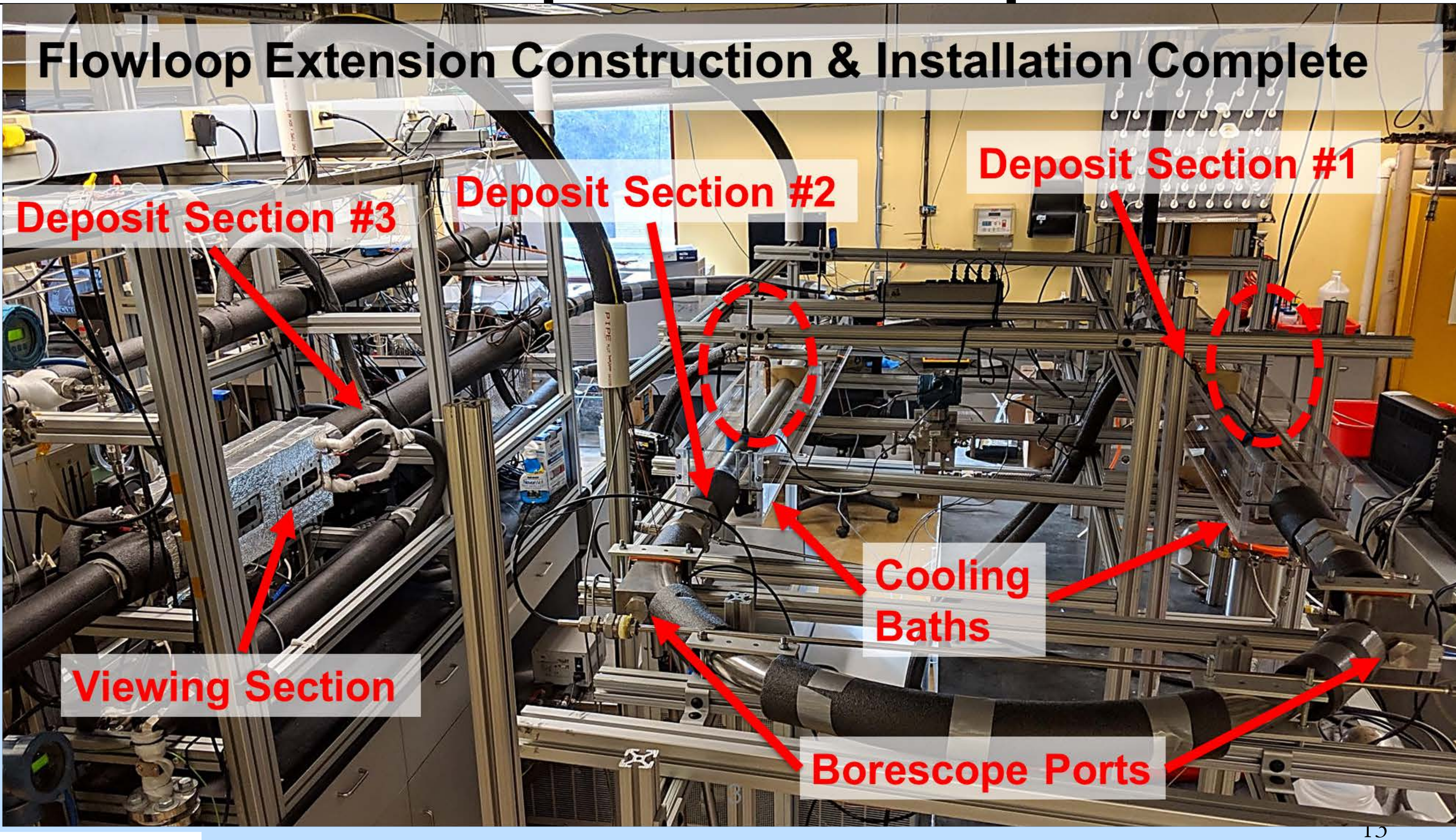
OD: 2 in (5.08 cm)

Volume: 2.68 gal (10.14 L)

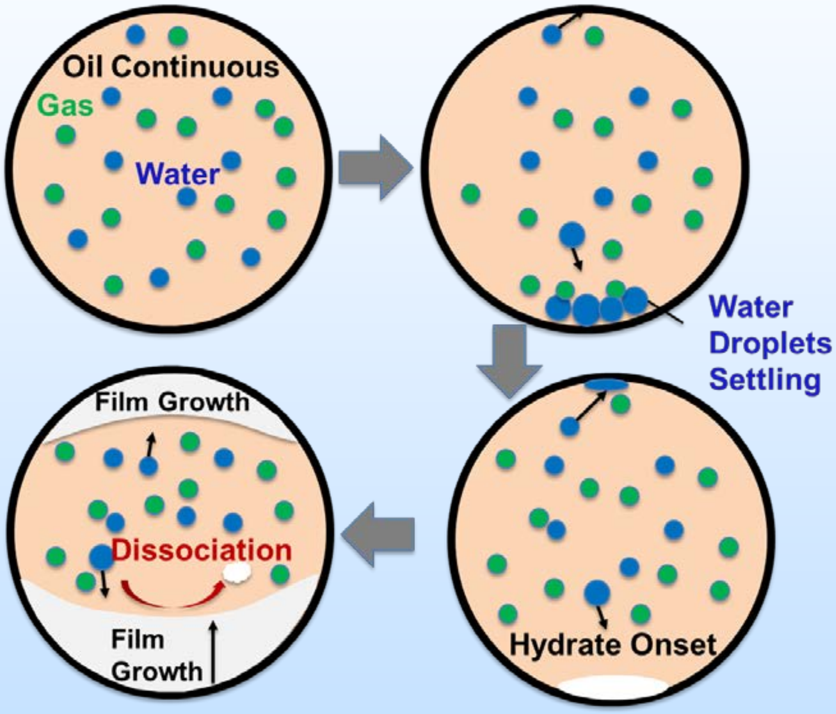
CENTER FOR HYDRATE RESEARCH

COLORADO SCHOOL OF MINES

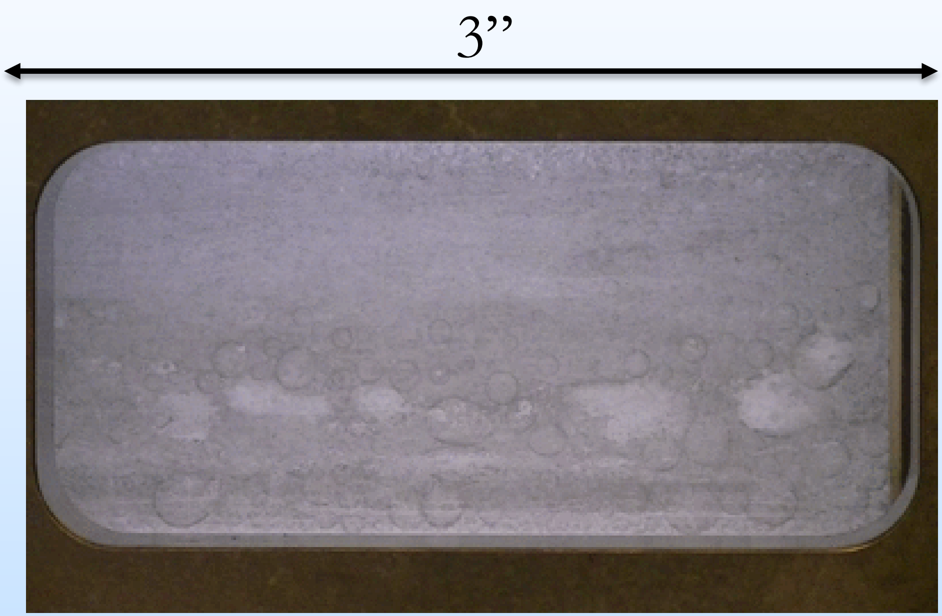
Hydrate-Phobic Coatings Tests in Deposition Loop



Hydrate Deposit Formation in Oil-Dominated Systems



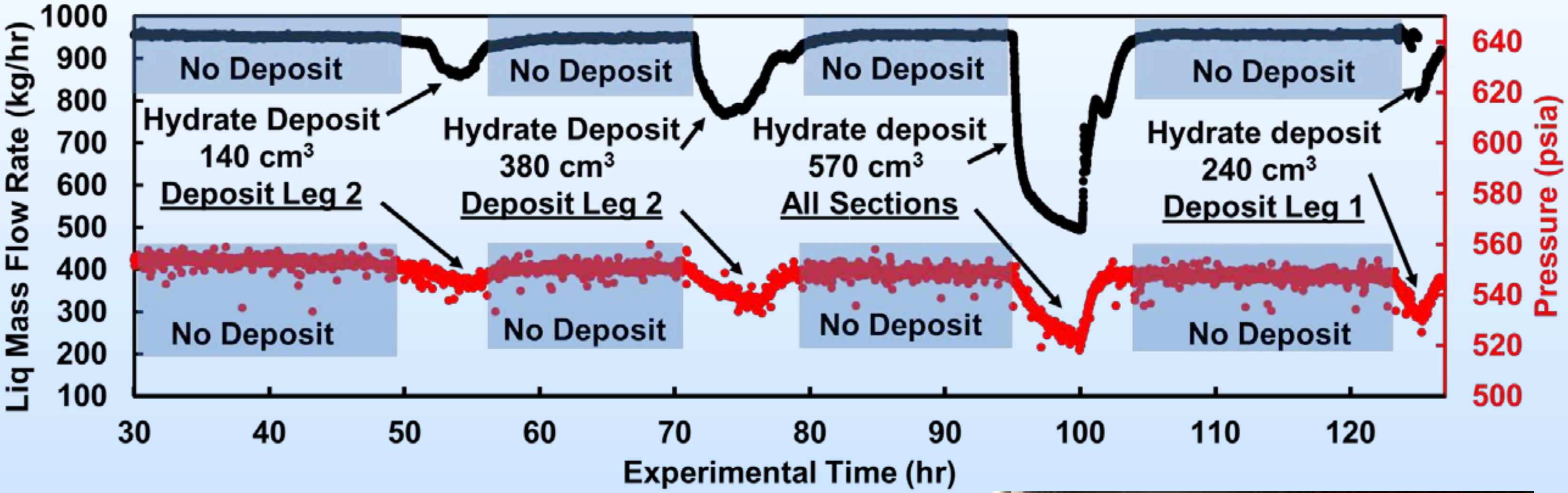
H. Qin, M. Pickarts, C. Koh et al., OTC 2018



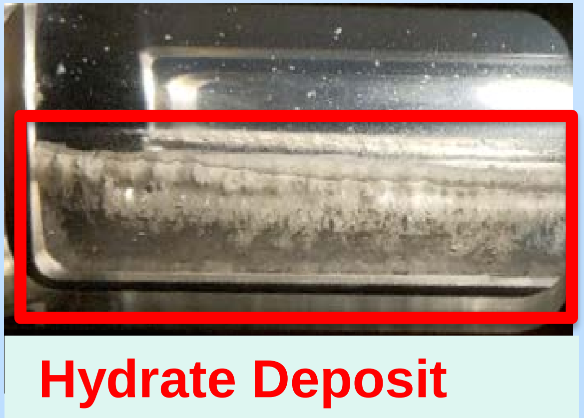
10% WC, 100% LL, 550 psi, V_{SL}=2.8 ft/s T_{bulk}=48°F, T_{hyd}-$T_{surface}$=18°F

Hydrate Deposit Formation in Oil-Dominated Systems

- Deposition flowloop data capturing hydrate deposit formation from mass flow (black), loop pressure (red), video imaging.



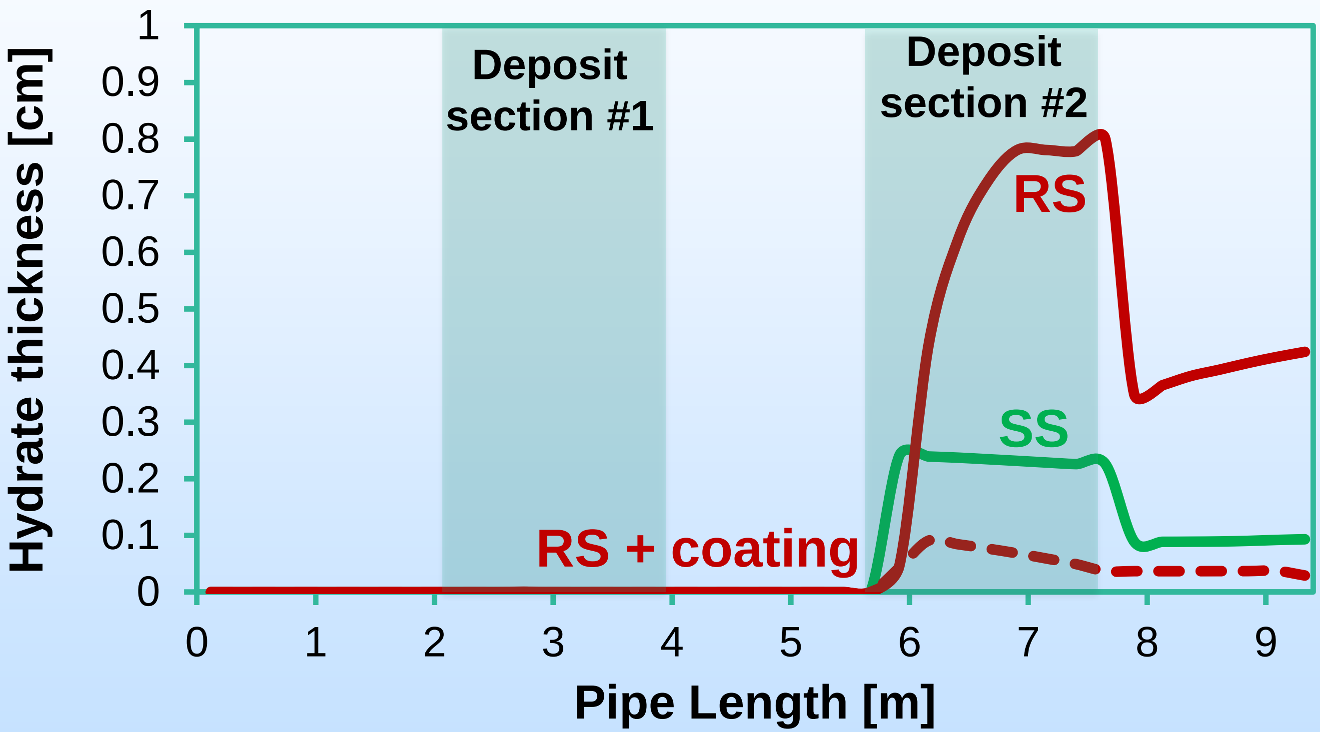
100% WC, 30% LL, C1/C2 gas, 550 psia, V_{SL}=0.5 ft/s T_{bulk}= 53°F, T_{hyd}-$T_{surface}$= 11,16, 20 °F



M. Pickarts, C. Koh et al., OTC 2019

CENTER FOR HYDRATE RESEARCH
COLORADO SCHOOL OF MINES

Hydrate Deposit Resistance under Simulated Transient Conditions



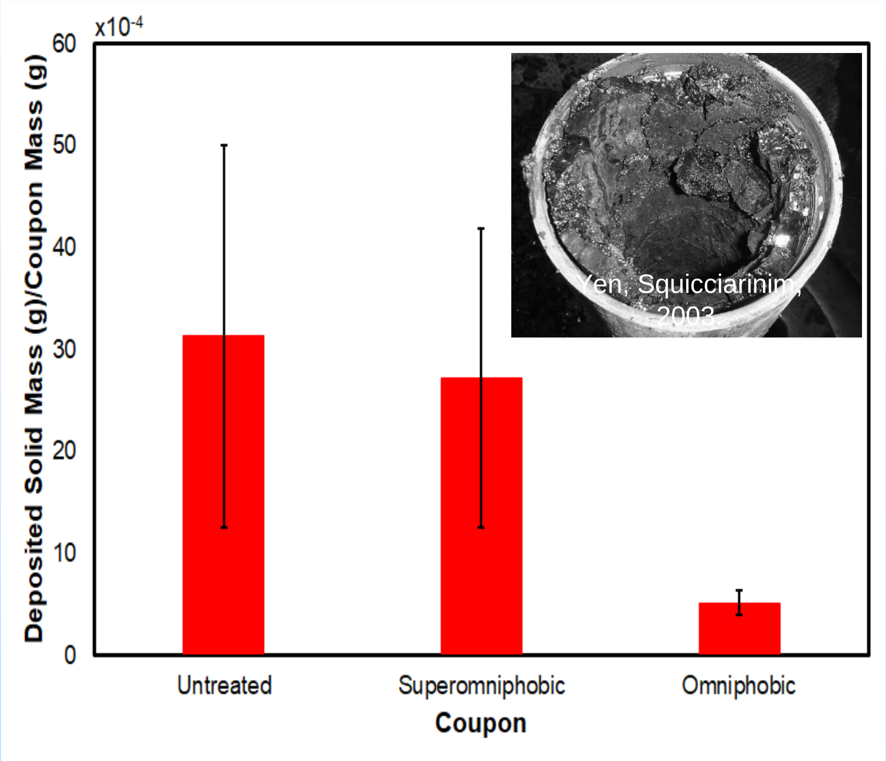
Section #2 < Teq (hydrate)

Contact angle:
Coated surface > Uncoated surface

30% WC, ~100% LL, MO 70T, 24 hr shut-in

Corroded Pipe Surface Coating Reduces Adhesion Forces

Coatings also reduce asphaltene deposition - a critical FA problem, causing production deferment/losses



Accomplishments to Date

- Developed larger-scale deposition flowloop to test materials performance under simulated field conditions
  - Loop modification and baseline testing (Milestone A, Task 2)
- Developed coating formulation to mitigate hydrate deposition
  - Material design, formulation and optimization (Milestone B, Task 3)
- Flow properties characterization (Task 4)
- Gas Hydrate Deposition under Transient Shut-in/Restart Simulated Lab-Scale Conditions (Task 6)
  - Shut-in/restart simulated operations in the deposition loop show higher plugging risks compared to steady-state operations
- Asphaltene and Wax Deposition Testing under Simulated Lab-Scale Conditions (Task 7)

Project Summary

- Hydrate film growth/deposition is a major problem in deepwater operations leading to major economic, environmental & safety risks
- Hydrate-phobic coatings could be applied to corroded pipe surfaces to mitigate hydrate deposition
  - Hydrate-phobic coatings can reduce deposition of hydrates and asphaltenes
  - Large-scale, multiphase flow tests development completed
  - Hydrate & other FA solids resistant coatings for deepwater operations development/testing at transient conditions underway

Lessons Learned

- Omniphobic surface treatments can resist flow assurance solids deposition, while protecting pipe surfaces from corrosion
- Lower surface roughness combined with surface functionality can resist a variety of species, including gas hydrates and asphaltenes

Synergy Opportunities

- Hydrate multiphase flow deposition data over range of Deepwater operating conditions could be used for "NETL's Big Data Technologies for Offshore Spill Prevention" (Kelly Rose, NETL-RIC)

Acknowledgements

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

- Industry Advisors: Douglas Estanga (Chevron), Mayela Rivero (Total), Doug Turner (ExxonMobil), and Gaurav Bhatnagar (Shell)

APPENDIX

Benefit to the Program

- The research project is developing and investigating for deployment robust pipeline coatings to mitigate gas hydrate & other FA solids deposition in deepwater oil flowlines, which will be critical in offshore leak and spill prevention. In-situ application is being developed for a range of pipeline conditions, with scale-up to simulated field conditions and multiphase field modeling to prepare for field testing.

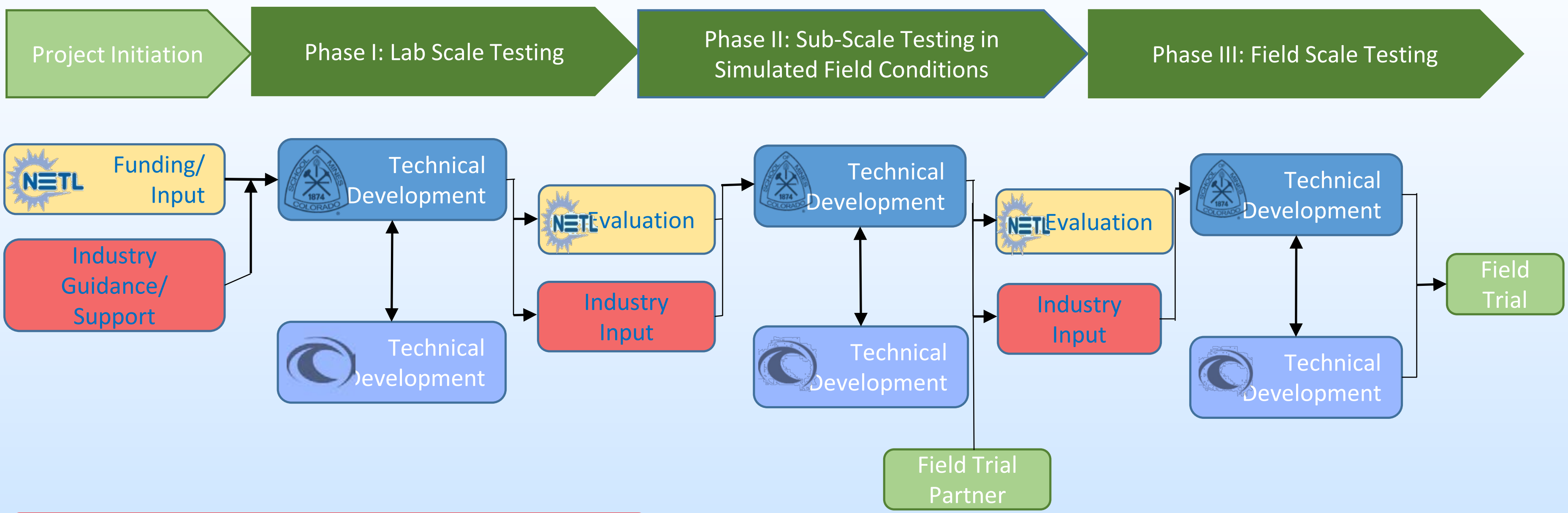
- The technology, when successfully demonstrated, will provide mitigation strategies for hydrates & other solids deposition, which are current $multi-million challenges that can lead to production losses/deferment. This technology contributes to the Offshore leak and spill prevention program.

Project Overview

Goals and Objectives

- Hydrate-phobic coating system applied in-situ to existing pipelines
  - Durability testing (high P, high T, chemical exposure, abrasive conditions) & flow characterization
- Multiphase deposition flowloop evaluations in simulated field conditions for transient shut-in and restart conditions (highest risks to the industry)
- Investigations under simulated field conditions & field trial test plans

Project Organization Chart for Deployment of Coatings



Industry Support: Chevron ExxonMobil Shell Total

Dissemination to CHR Industry Consortium: Chevron ExxonMobil Halliburton multi-chem A Halliburton Service Total Petrobras Schlumberger

Gant Chart

		Phase I (2018-2019)				Phase II (2019-2020)				Phase III (2020-2021)			
Task #	Task	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
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

oceanit
innovation through engineering & scientific excellence

CENTER FOR HYDRATE RESEARCH

COLORADO SCHOOL OF MINES
EARTH • ENERGY • ENVIRONMENT

Bibliography

- 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.

CENTER FOR HYDRATE RESEARCH

COLORADO SCHOOL OF MINES
EARTH • ENERGY • ENVIRONMENT

oceanit
innovation through engineering & scientific excellence

Coating Durability and Adhesion

Crosscut tape test (ASTM D3359)

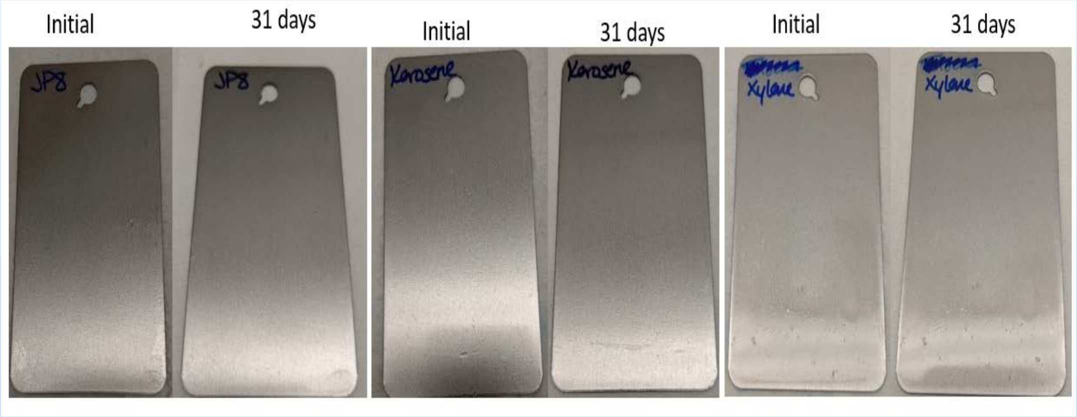
Knife adhesion test (ASTM D6677)

Novolac Epoxy Coated | DragX^{TM} Treatment

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

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%

oceanit
innovation through engineering & scientific excellence

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

oceanit
innovation through engineering & scientific excellence