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

Project# 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
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
– 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

- 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 $\Delta P$ increase$^1$
- ExxonMobil field trial suggests hydrate deposits caused majority of $\Delta P$ 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
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

- Pressure
- Temperature
- Temperature
- Composition
- Pressure
- Composition

Sloan & Koh, CRC Press, 2007; Slb.com
Project Organization and Milestones

**Phase I: Lab Scale Testing**
- Milestone A: Flowloop upgrades

**Phase II: Sub-Scale Testing in Simulated Field Conditions**
- Milestone B: Field Experimental Plan
- Milestone C: Demonstrate In-situ application

**Phase III: Field Scale Testing**
- Milestone D: Identify Field Trial Partner/Site
- Milestone E: Verify material longevity

**Industry Support:**
- Chevron
- ExxonMobil
- Shell
- TOTAL

**Dissemination to CHR Industry Consortium:**
- ExxonMobil
- Schlumberger
PROGRESS & CURRENT STATUS OF PROJECT
Optimized Omniphobic Coating for Commercialization

Corrosion Resistance
- Untreated
- Treated

Hydro- & Oleophobicity
- Untreated w/ Water
- Untreated w/ Oil
- Treated w/ Water
- Treated w/ Oil

Chemical Resistance
- Jet Fuel (JP8)
  - Initial
  - 120 Days
- Kerosene
  - Initial
  - 120 Days
- Xylene
  - Initial
  - 120 Days

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

Water-Dispersible, Low Viscosity, Nano-Structured Polymer Topcoat Capable of In-Situ Application to Existing Materials
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)
Hydrate-Phobic Coatings Tests in Deposition Loop

Flowloop Extension Construction & Installation Complete
Hydrate Deposition Mitigated in Oil-Dominated Systems

50% LL, 25% WC, 535 psig, 600 kg/hr, $T_{\text{subcooling}} = \sim 6^\circ C$

- Plugged, 8x, $\varnothing_{\text{hyd}} \approx 90\%$
- Flowing, 3x, $\varnothing_{\text{hyd}} \approx 55\%$
- Uncoated
- Coated
- Sloughing Events
- Coated, Long Shut-In
- Baseline

Time After Restart (min)
Hydrate Deposition Mitigated in Oil/Gas-Dominated Systems

Deposition loop: hydrate formation delayed with coating

<table>
<thead>
<tr>
<th>System</th>
<th>Surface Treatment</th>
<th>Induction Time [h]</th>
<th>$T_{\text{subcool}}$ [°C]</th>
<th>Experimental Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil-Dominated</td>
<td>N</td>
<td>10</td>
<td>~9</td>
<td>50% LL, 25% WC, 600 kg/hr, 540 psia, Continuous: Film Growth</td>
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<tr>
<td></td>
<td>Y</td>
<td>&gt;110</td>
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<tr>
<td></td>
<td>Y</td>
<td>&gt;236</td>
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<tr>
<td>Gas-Dominated</td>
<td>N</td>
<td>5</td>
<td>~10</td>
<td>30% LL, 100% WC, 564 psia, Continuous: Film Growth</td>
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<td></td>
<td>Y</td>
<td>&gt;120</td>
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<td></td>
<td>Y</td>
<td>&gt;168</td>
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</table>
Asphaltene Deposition Mitigated in Oil-Dominated Systems

No Deposit

Asphaltene Deposit

Testing Section: pipe 20” length, 0.25” OD
Pipe OD = 0.5”
Mobile tops

flow

<table>
<thead>
<tr>
<th>Deposited Amounts (mg)</th>
<th>Uncoated</th>
<th>Coated</th>
<th>Pristine</th>
<th>Corroded</th>
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<tbody>
<tr>
<td>Total Deposit</td>
<td>5.78</td>
<td>2.77</td>
<td>1.63</td>
<td>4.5</td>
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<tr>
<td>Extracted Asphaltenes</td>
<td>1.23</td>
<td>1.23</td>
<td>1.63</td>
<td>4.5</td>
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<td>Total Deposit</td>
<td>11.9</td>
<td>1.7</td>
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</table>
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 $\Rightarrow$ 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

3.2 km, 4” OD, 1200 psia

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)
Project Organization for Deployment of Coatings

Project Initiation

Phase I: Lab Scale Testing
- Technical Development
- NETL Evaluation
- Industry Input

Phase II: Sub-Scale Testing in Simulated Field Conditions
- Technical Development
- NETL Evaluation
- Industry Input

Phase III: Field Scale Testing
- Technical Development
- NETL Evaluation
- Industry Input
- Field Trial

Industry Support: Chevron, ExxonMobil, Shell, TOTAL

Dissemination to CHR Industry Consortium: Chevron, ExxonMobil, multi-chem, HALLIBURTON, Schlumberger
### Gantt Chart

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<td>Q2</td>
<td>Q3</td>
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<td>Deposition Experiments</td>
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<td>Evaluation of Coating Performance</td>
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<td>Shut-In/Startup Testing</td>
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<td>Adhesion Measurements using Waxes/Asphaltenes</td>
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<td>Development of Quality Control Parameters</td>
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<td>Multiphase Modeling of Field Site</td>
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<td>Loop Scale Testing of Simulated Field Conditions</td>
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<td>Multi-Component Flowloop Experiments</td>
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<td>Extended Service Guidelines and Durability</td>
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<td>Compatibility with In-line Tools</td>
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<td>E</td>
<td>Verify Long Term Coating Durability</td>
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<td>13.0</td>
<td>Initialize Planning for Field Testing</td>
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<td>F</td>
<td>Field Trial Partner/Site Identified</td>
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<td>14.0</td>
<td>Documentation and Reporting</td>
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</tbody>
</table>

- **Current Progress**: Green square
- **Proposed Timeline**: Blue square
Bibliography


• Abstract & papers: OTC conference (May 2019 (1), May 2020 (2)), NACE 2020, ICGH10 (June 2020)
BACKUP SLIDES
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™ Treatment

DragX™ 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

<table>
<thead>
<tr>
<th>JP8 - Compound</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8-C9 aliphatic hydrocarbons</td>
<td>9%</td>
</tr>
<tr>
<td>C10-C14 aliphatic hydrocarbons</td>
<td>65%</td>
</tr>
<tr>
<td>C15-C17 aliphatic hydrocarbons</td>
<td>7%</td>
</tr>
<tr>
<td>aromatics</td>
<td>18%</td>
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# Technical Data

## Typical Uncured Physical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Clear/White/Blue</td>
</tr>
<tr>
<td><strong>Specific Gravity</strong></td>
<td>1.1 g/cm³</td>
</tr>
<tr>
<td><strong>Application Methods</strong></td>
<td>Spray, Dip, or Flood and Drain</td>
</tr>
<tr>
<td><strong>Viscosity</strong></td>
<td>100 – 5000 c.p. (Tunable)</td>
</tr>
<tr>
<td><strong>Base</strong></td>
<td>Water</td>
</tr>
<tr>
<td><strong>VOC Content</strong></td>
<td>None</td>
</tr>
<tr>
<td><strong>Shelf Life</strong> (stored between 50°-80°F in unopened state)</td>
<td>&gt;6 months</td>
</tr>
</tbody>
</table>

## Typical Application Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td><strong>Mixing Time</strong></td>
<td>Approximately 15 minutes prior to application</td>
</tr>
<tr>
<td><strong>Time Between Coats</strong></td>
<td>Recommended 60 minutes between coats.</td>
</tr>
<tr>
<td><strong>Coating Window</strong></td>
<td>Additional recoats can be applied for up to 72 hours from first application/mixing of Part A and Part B</td>
</tr>
<tr>
<td><strong>Full Cure Time</strong></td>
<td>Less than two hours</td>
</tr>
<tr>
<td><strong>Coating Thickness</strong></td>
<td>1-4 mils recommended</td>
</tr>
<tr>
<td><strong>Applicable Surfaces</strong></td>
<td>Metals, concrete, composites, etc.</td>
</tr>
</tbody>
</table>

## DragX Treatment

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td><strong>Appearance of Coating Film</strong></td>
<td>Clear/White/Blue</td>
</tr>
<tr>
<td><strong>Maximum Usable Temperature</strong></td>
<td>400°F</td>
</tr>
<tr>
<td><strong>Adhesion Test</strong></td>
<td>5A after 48 hours</td>
</tr>
<tr>
<td><strong>Flow Assurance</strong></td>
<td>Up to 10-fold reduction in Hydrate Formation/Adhesion</td>
</tr>
<tr>
<td><strong>Salt Fog Corrosion Resistance + Scribing (ASTM B117 + ASTM D1654)</strong></td>
<td>1000 + hr</td>
</tr>
<tr>
<td><strong>Erosion Resistance (ASTM G76)</strong></td>
<td>&lt; 5% Mass Loss at sand particle impact of 70 m/s</td>
</tr>
<tr>
<td><strong>Wear Resistance (ASTM D4060)</strong></td>
<td>50mg / 1000 cycles / 1 kg</td>
</tr>
</tbody>
</table>
| **Chemical Compatibility Tested (No Reactivity)** | Acidic Conditions (pH < 2)  
Alkaline Conditions (pH >11)  
Acid Gas ( > 1000 ppm CO₂)  
Sour Gas ( > 4 ppm H₂S) |
| **Surface Roughness After Application** | 60-120 μinch |
New deposition section for asphaltene loop

Former deposition section

Testing Section: 43”, 0.12” ID

New deposition section

Testing Section: pipe 20” length, 0.25” OD

Pipe OD = 0.5”

Mobile tops

0-10 inH₂O DP Transmitter

Testing Section: 43”, 0.12” ID

Peristaltic Pump @ 50-200 mL/min

Tygon Tubing

Crude C v/ Hexane 3.2 g/mL

Clean

After deposition