WEBINAR INFORMATION WHILE YOU ARE WAITING

- Welcome!
- All participants will be muted
- Please check your computer audio settings before the meeting to **BE SURE YOUR MICROPHONE IS MUTED** to avoid background noise
- Call in number: 1 (213) 929-4212 with Access Code: 784-454-804
- Questions will be answered at the end of the presentation
- Use the question chat box or the “raise your hand” feature and we will unmute you
- If you are experiencing any difficulty during the webinar, send a message via chat
- Presentation and recording will be available on the AFPM website
- Please join Slido Live Polling on your phone or computer before we begin:
CRUDE FEEDSTOCK

OILFIELD PRODUCTION CHEMICALS IMPLICATIONS ON THE REFINING PROCESSES

OCTOBER 29, 2020
WHAT IS THE AFPM WEBINAR SERIES?

• AFPM has been doing various webinars for years, primarily safety related topics

• As we continue developing The Summit, Excellence in Plant Performance, there will be more opportunity for member engagement

• Deliver educational content and knowledge sharing opportunities throughout the year

• Previous Summit Webinars are Available on the AFPM Summit Website
  February - Safeguarding the FCCU during Transient Operations
  March - Shutdown Best Practices for Reactor Systems
  April - Reboiler Circuits For Trayed Columns
  May – Learning Teams Part 1 & 2
  June – Highlights of the Proposed Changes to API RP 751 Rev 5
  July - Digital Transformation: Positioning for What’s Next
  September – FCC Key Equipment Reliability
John Hazlewood
Technology Manager - Technical Services
John.Hazlewood@Halliburton.com
YOU’RE NOT JUST RESPONSIBLE FOR WHERE YOU ARE, BUT ALSO FOR WHERE YOU’VE BEEN.

That’s particularly important when you’re working at heights. In addition to taking precautions while you’re working, you must be mindful of how you leave the worksite.

Items blown by the wind or jarred loose can cause damage to property and people. Make sure no loose objects are left behind after you’ve completed your work. Check your area before you check out.

At Halliburton, Priority No. 1 is safety.
SLIDO QUESTIONS 1-2

• To access the poll, use your phone to scan the QR code or visit the link and type in the meeting code
• Live results will be displayed in the presentation
• Note: responses are anonymous

Join at slido.com #Crude
PRODUCTION METHODS
Production Methods

- Conventional
  - Offshore
    - Mars, Poseidon, Bonito Sour, Cascade
  - Enhanced Oil Recovery
    - CO\textsubscript{2} Flooding
    - Chemical Flooding
    - SAGD
      - Suncor OSH, Kearl Lake, Borealis Heavy, Access Western Blend
- Unconventional
  - Eagle Ford, Bakken, light tight oil (LTO)
Technical Challenges – Gulf of Mexico

- Higher Temperature and Pressures
- Speed of oil and water separations (low residence times)
- Water Quality Specifications (29 ppm O/G)
- Sub-Sea tiebacks for new production
- Shut In
- Treatment issues
  - Hydrates
  - Water Soluble Organics
  - Foam
Gulf of Mexico Issues
Hydrates, Water Soluble Organics, Foaming

- Hydrates
  - Hydrate remediation
    - Methanol – causes WWTP issues
    - MEG – causes WWTP issues
    - LDHI (Anti Agglomerates) – oil soluble, surfactancy issues

- Water Soluble Organics (WSO)
  - WSO remediation
    - Buffered acids
    - Weak acids - drives WSO’s into oil phase, alters pH and emulsion tendencies

- Foam
  - Foam remediation
    - Silicone based defoamers widely used
    - Separation issues, catalyst fouling
Heavy Canadian Bitumen

Bitumen Production

- Conventional
  - Condensate (Diluent)
  - Bitumen
  - Heavy Bitumen
  - Bitumen
  - Light Synthetic Crude
  - Heavy Synthetic Crude

- In-Situ
  - Mining
  - Upgraders

- By Rail
  - DilBit
  - SynBit
  - Heavy Bitumen

- By Rail
  - Conventional
    - Bitumen
    - Heavy Bitumen
    - Light Synthetic Crude
    - Heavy Synthetic Crude

- SynBit

- Long Lake Heavy
- Surmont Heavy Blend
- CNRL Light Sweet Synthetic
- Husky Synthetic Blend
- Long Lake Light Synthetic
- Premium Albian Synthetic
- Shell Synthetic Light
- Suncor Synthetic
- Syncrude Synthetic
- Albion Heavy Synthetic

- Lloyd Blend
- Lloyd Kerrobert
- Cold Lake
- Peace River Heavy
- Seal Heavy
- Smiley-Coleville
- Wabasca Heavy
- Western Canadian Select

- Bow River
- Fosterton
Heavy Canadian Bitumen

- **Bitumen Characteristics**
  - Large fraction of complex, long-chained hydrocarbons (asphaltenes, 10-20%)
  - Heavy metals, corrosive salts, and sulfur
  - BS&W up to 2% (not pipeline spec)
  - Upgraded (40%) or diluted (60%) to meet pipeline spec

- **Technical Challenges**
  - High demand for separations chemicals
    - Emulsion Breakers – 200 to 500 ppm
    - Reverse Breakers – 50 to 200 ppm
  - Blending with lighter crudes at refineries
    - Asphaltene precipitation

- **Impact to downstream operations**
  - Entrained chemicals from upstream treatment
  - Blended crudes hide difficult species that affect downstream operations
Unconventional Light Tight Oil, Eagle Ford, Bakken

- Sources
  - Oil Sands - mining
  - Light Tight Oil - Fracturing
  - Oil Shale – fracturing

- Crude Characteristics
  - Light / Sweet - API (35 +) / low sulfur
  - Paraffinic / Waxy
  - Low Metals
  - Solids

- Technical challenges
  - Tank Farm - wax precipitation
  - Compatibility - changing compatibility
  - Solids stabilized emulsions

Photo Credit: Champion Technologies 2010
Upstream Chemical Applications

FLOW ASSURANCE
- Asphaltenes
- Hydrates
- Paraffin
- Scale

ASSET INTEGRITY
- Corrosion
- Microbiology
- Gas Conditioning

PHASE SEPARATION
- Emulsion
- Water Quality
- Foaming

STIMULATION
- Water Treating
- Reservoir Sourcing
- H₂S and Iron Sulfide in Frac Pits
- Low Initial Production
Flow Assurance Chemicals

- **Scale Inhibitors**
  - Phosphonates, polyacrylates

- **Paraffin Control**
  - Amine oxides, polyacrylates, sulfonates

- **Asphaltene Control**
  - Alkyl phenol resins, sulfonates, quaternary amine salts

- **Hydrate Inhibitors**
  - Ethylene glycol, methanol, quaternary amine salts, LDHI-AA

*Photo Credit: Champion Technologies 2010*
Asset Integrity Chemicals

- Corrosion Inhibitors
  - Fatty amines
  - Amides
  - Phosphate ester
  - Quaternary amine salts

- Biocides
  - Glutaraldehyde
  - THPS
  - Quaternary amine salts

Photo Credit: Champion Technologies 2010
Phase Separation Chemicals

- **Emulsion Breakers**
  - Sulfonates
  - Surfactants
  - Alkyl phenol resins

- **Defoamers**
  - Polydimethylsiloxane (PDMS)
  - Polyether alcohols
  - Fluorosilicones

*Photo Credit: Champion Technologies 2010*
Phase separation / Scavengers

- Water Clarifiers
  - Metal salts
  - Polymers
  - Polyacrylates

- H$_2$S Scavengers
  - MEA/MA triazines
  - Aldehydes
  - Glyoxal

Photo Credit: Champion Technologies 2010
Stimulation Chemicals

- Friction Reducers
  - Polyacrylamides
  - Guar

- Surfactants
  - Sulfonates
  - Ethoxylated alcohols

- Clay Stabilizers
  - Quaternary amine salts
THANK YOU
SPEAKERS

Harold Eggert
Chief Global Technical Advisor
Harold.Eggert@Halliburton.com
DOWNSTREAM IMPACTS

Refinery Impact
SLIDO QUESTION 3

• To access the poll, use your phone to scan the QR code or visit the link and type in the meeting code
• Live results will be displayed in the presentation
• Note: responses are anonymous
Absence of chemicals can also be a problem.
## “The Usual Suspects”

<table>
<thead>
<tr>
<th>Functional Chemistry</th>
<th>Potential Impact</th>
<th>Water/Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Chlorides (Carbon Tet)</td>
<td>Banned in 1994 Boil</td>
<td>Oil</td>
</tr>
<tr>
<td>Quaternary amine salts</td>
<td>Corrosion and Fouling</td>
<td>Water</td>
</tr>
<tr>
<td>Mineral Acids</td>
<td>Corrosion in Crude Unit</td>
<td>Water</td>
</tr>
<tr>
<td>Triazines</td>
<td>Crude Tower Fouling/Corrosion Waste Water</td>
<td>Both</td>
</tr>
<tr>
<td>Carboxylic Acid</td>
<td>Crude Unit Corrosion</td>
<td>Water</td>
</tr>
<tr>
<td>Calcium Stearate</td>
<td>Crude Unit Fouling</td>
<td>Both</td>
</tr>
<tr>
<td>Alkyl Phenol resins</td>
<td>Desalter Emulsion Stability</td>
<td>Oil</td>
</tr>
<tr>
<td>Fatty amines/amides</td>
<td>Desalter Emulsion Stability</td>
<td>Oil</td>
</tr>
<tr>
<td>Polymers</td>
<td>Desalter Emulsion Stability</td>
<td>Both</td>
</tr>
<tr>
<td>Sulfonates</td>
<td>Desalter Emulsion Stability</td>
<td>Both</td>
</tr>
<tr>
<td>Surfactants</td>
<td>Desalter Emulsion Stability</td>
<td>Both</td>
</tr>
<tr>
<td>Metal Salts</td>
<td>Desalter Emulsion Stability / Downstream Poison</td>
<td>Water</td>
</tr>
<tr>
<td>Polycrylates</td>
<td>Fouling and Emulsion Stability</td>
<td>Water</td>
</tr>
<tr>
<td>Phosphate Esters</td>
<td>Fouling In Crude Tower</td>
<td>Oil</td>
</tr>
<tr>
<td>Phosphonates</td>
<td>Fouling In Crude Tower</td>
<td>Water</td>
</tr>
<tr>
<td>Vinyl acetate copolymers</td>
<td>Fouling Potential</td>
<td>Oil</td>
</tr>
<tr>
<td>Solvents</td>
<td>Phase Separation Potential Fouling</td>
<td>Both</td>
</tr>
<tr>
<td>Fluorosilicones</td>
<td>Silicone Poisoning of Catalyst</td>
<td>Oil</td>
</tr>
<tr>
<td>Polydimethylsiloxane</td>
<td>Silicone Poisoning of Catalyst</td>
<td>Oil</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>Waste Water Plant</td>
<td>Water</td>
</tr>
<tr>
<td>Gluteraldehyde</td>
<td>Waste Water Plant</td>
<td>Water</td>
</tr>
<tr>
<td>Methanol</td>
<td>Waste Water Plant</td>
<td>Water</td>
</tr>
<tr>
<td>Polyether alcohols</td>
<td>Waste Water Plant</td>
<td>Water</td>
</tr>
<tr>
<td>THPS</td>
<td>Waste Water Plant</td>
<td>Water</td>
</tr>
</tbody>
</table>
Crude Unit

Raw Crude Storage
- ~ 65 °F

Tank De-Watering
- ~ 250 °F
- 5% Fresh H₂O

Wastewater Treatment Plant

Crude Preheat
- ~ 250 °F

Desalter

Furnace
- ~ 475 °F
- ~ 675 °F

Crude Fractionator
- ~ 300 °F
- ~ 400 °F
- ~ 500 °F
- ~ 600 °F
- ~ 650 °F
- ~ 65 °F

Mechanical and Biological Treatment

Other Process Units Waste H₂O

Typical Specifications
- < 1.0 PTB Salt
- < 25 PTB Solids
- < 0.2% H₂O

Brine H₂O

Typical Specifications
- < 500 PPM O&G

Downstream Processing Units
Wastewater Treatment Plant

Mechanical and Biological Treatment

Crude Unit – Solvent Package Alone

- Solvents and co-solvents
  - Ethylene Glycol
  - Butanol
  - Octanol
  - Methanol
  - Ethanol
  - Iso-Propanol

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude Charge</td>
<td>100,000  BPD</td>
</tr>
<tr>
<td>Production Chemical in raw crude</td>
<td>70  ppm</td>
</tr>
<tr>
<td>70% Solvent (Methanol) in raw crude</td>
<td>50  ppm</td>
</tr>
<tr>
<td>Wash Water (5%)</td>
<td>5,000  BPD</td>
</tr>
<tr>
<td>Cycle up</td>
<td>20  times</td>
</tr>
<tr>
<td>Solvent (Methanol) in Eff Water</td>
<td>1000  ppm</td>
</tr>
</tbody>
</table>

Creates High COD/TOC
Desalter & Emulsion Stability

- Increased O&G in desalter brine
  - Increased organic loading to WWTP
  - Chemical spend
  - Recovered oil reprocessing cost

- Growing and stabilized emulsion
  - Erratic amps and volts
  - Increased caustic demand to desalted crude
  - Water Carryover
  - High OH Chlorides

<table>
<thead>
<tr>
<th>Chemistries</th>
<th>Oil/Water</th>
<th>Potential Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl Phenol Resins</td>
<td>Oil</td>
<td>Desalter Emulsion Stability</td>
</tr>
<tr>
<td>Fatty Amines/Amides</td>
<td>Oil</td>
<td>Desalter Emulsion Stability</td>
</tr>
<tr>
<td>Polymers</td>
<td>Both</td>
<td>Desalter Emulsion Stability</td>
</tr>
<tr>
<td>Sulfonates</td>
<td>Both</td>
<td>Desalter Emulsion Stability</td>
</tr>
<tr>
<td>Surfactants</td>
<td>Both</td>
<td>Desalter Emulsion Stability</td>
</tr>
<tr>
<td>Metal Salts</td>
<td>Water</td>
<td>Desalter Emulsion Stability</td>
</tr>
<tr>
<td>Polyacrylates</td>
<td>Water</td>
<td>Desalter Emulsion Stability</td>
</tr>
<tr>
<td>Solvents</td>
<td>Both</td>
<td>Phase Separation</td>
</tr>
</tbody>
</table>
Complex Emulsions from Surfactants

Water Continuous Emulsion

Oil Continuous Emulsion
Brine Quality - Polyacrylates

Heptane remains clear and oil free

Small amount of oil extracted from brine into Toluene

Some “Polymer” and oil flocked at interface

Water is Mostly Oil Free
Brine Quality - Polyacrylates

- Insoluble in crude and water
- Highly polar
- Insoluble in Heptane and Toluene
- Soluble in polar solvents
  - Acetone
  - IPA

Microscope picture of polymer

Polymer and Asphaltenes

Potential Source
1. Drag Reducer
2. Water Clarifier

Analysis indicates polyacrylamide
Corrosion and Fouling

- Phosphorus fouling
  - Hydrolyzes to form phosphoric acid
  - Fouling typical in 400 – 475 degF
- MEA hydrochloride salts
  - Liquid salts
  - Significant impact on iDP corrosion

---

<table>
<thead>
<tr>
<th>Chemistries</th>
<th>Oil/Water</th>
<th>Potential Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Chlorides (Carbon Tet)</td>
<td>Oil</td>
<td>Banned in 1994 - Don't hydrolyze</td>
</tr>
<tr>
<td>Quaternary Amine Salts</td>
<td>Water</td>
<td>Corrosion and Fouling - High OH Cl-</td>
</tr>
<tr>
<td>Mineral Acids</td>
<td>Water</td>
<td>Corrosion</td>
</tr>
<tr>
<td>Triazines</td>
<td>Both</td>
<td>Corrosion and Fouling</td>
</tr>
<tr>
<td>Carboxylic Acid</td>
<td>Water</td>
<td>Corrosion</td>
</tr>
<tr>
<td>Calcium Stearate</td>
<td>Both</td>
<td>Fouling</td>
</tr>
<tr>
<td>Phosphate Esters</td>
<td>Water</td>
<td>Fouling</td>
</tr>
<tr>
<td>Phosphonates</td>
<td>Both</td>
<td>Fouling</td>
</tr>
<tr>
<td>Vinyl Acetate Copolymers</td>
<td>Oil</td>
<td>Fouling</td>
</tr>
</tbody>
</table>
Downstream Catalyst & WWTP

- Increased organic load to WWTP
  - Increased food = increased bacteria production
  - Increased food = Settling issues
  - Increased food = Increased $O_2$ demand

- Solvent Packages
  - Glycols
  - Alcohols

- Biocides
  - Bug Kill

<table>
<thead>
<tr>
<th>Chemistries</th>
<th>Oil/Water</th>
<th>Potential Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorosilicones</td>
<td>Water</td>
<td>Catalyst poisoning</td>
</tr>
<tr>
<td>Polydimethylsiloxane</td>
<td>Oil</td>
<td>Catalyst poisoning</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>Water</td>
<td>WWTP</td>
</tr>
<tr>
<td>Glutaraldehyde</td>
<td>Water</td>
<td>WWTP</td>
</tr>
<tr>
<td>Methanol</td>
<td>Water</td>
<td>WWTP</td>
</tr>
<tr>
<td>Polyether Alcohols</td>
<td>Water</td>
<td>WWTP</td>
</tr>
<tr>
<td>THPS</td>
<td>Water</td>
<td>WWTP</td>
</tr>
</tbody>
</table>
H₂S Scavengers

- Production & Midstream
  - Off Spec Propane
  - Fouling
  - Lost Production

- Tankage
  - Poor dehydration
  - Oil in Effluent
  - Poor Salt Removal
  - High Salt Removal Cost

- Desalters
  - Tower Fouling
  - Tower Corrosion
  - Unplanned Shut Down
  - Low Production Rates
  - Low Operating Temperature
  - Unfavorable Operating Economics
  - Catastrophic Failure (Explosions)
  - Exposure of hot oil to atmosphere
  - Environmental Exposure
  - Safety Exposure
  - Exposure to community
  - Mechanical Integrity

- Crude/Vac
  - Fouling from Corrosion Byproducts
  - Fouling From NH₃ Salts
  - Corrosion from NH₃ Salts

- Sat Gas Plant
  - HDS/Reformer
  - Lost Production
  - Corrosion from NH₃ Salts
  - Basic Nitrogen Poisoning
  - Higher Gas Make
  - Higher Coke Make
  - Lower Conversion
  - Compressor Limited
  - Blower Limited

- FCCU
  - Purchased Feed
  - High Ammonia in Outfall
  - High TOC & COD
  - Bug Kills
  - Out of Compliance
  - Fines and Citations

- WWTP
  - High Chemical Cost
  - Poor Dehydration
  - Oil in Effluent
  - Poor Salt Removal
  - High Chemical Cost

- Coker
  - Catastrophic Failure (Explosions)
  - Exposure of hot oil to atmosphere
  - Environmental Exposure
  - Safety Exposure
  - Exposure to community
  - Mechanical Integrity
Triazines

Monoethanol amine triazine

Monomethylamine triazine

MEA Triazine

MA Triazine
Reaction Steps - MEA Triazine

MEA Triazine

1. Reaction with H₂S
2. Localization of corrosion
3. Formation of Dithiazine
4. Transformation into Trithiane

Localized Corrosion > 1000 mpy in HSR 90°

Step 3. Most Prevalent In Crude Oil at Refinery

Can create solid polymer

As HS⁻ salt

Dithiazine

Thiadiazine
Low Dosage Hydrate Inhibitors

- 10% will partition to water in deleter
- >500 ppm can be toxic at WWTP
- LDHI is expected to decompose in crude distillation unit
- Decomposition products have boiling point at jet fuel and diesel (375 – 600 °F)
- Analysis can be confused with corrosion inhibitors (filmers)
- Commodityhydrate inhibitors are glycols and alcohols
“Tailgate Testing”
Quick Tests for Potential Issues

- Water retention of crude oil
  - Mix 10 mls water with 90 mls raw crude
  - Shake well
  - Let settle to determine water retention

- Asphaltene stabilized emulsion
  - Take two 100 ml samples of desalter brine or emulsion
  - Add 20 mls heptane to one and 20 mls toluene to other
  - Compare oil content in hydrocarbon phase of two samples
  - If toluene is darker than heptane, potential asphaltenes

- Is TOC in brine from methanol or glycol
  - Measure TOC of water
  - Extract water with activated charcoal
  - Difference in value is from glycols

- High scavenger or acid content in crude
  - Monitor pH in:
    - Desalter wash water
    - Desalter Brine Water
  - Observe Delta of two values

- Micro-Emulsion in Crude Oil < 10-micron droplet size
  - Run one sample with knock out drops
  - Run 2nd sample without knock out drops
  - Delta in water value from micro-emulsion
THANK YOU
UPCOMING WEBINARS – SEE AFPM EVENTS PAGE FOR MORE DETAILS AND 2021 DATES

“Mobile Worker OpCo Panel Discussion”
November 18, 2020
2:00 PM Eastern
Register Here

Description
Sponsored by the AFPM Maintenance Committee, this moderated panel will focus on the justification, infrastructure and use cases for mobile worker technology at facilities.

Participants
• Hardy Kemp, FlintHills Resources
• Jim Irwin, CHS
• Jimmy Jernigan, LyondellBasell
• Paul Simmons, Phillips 66
• Bruce Taylor, Sinclair Oil

“Getting the Most From Your Hydrogen Plant in Challenging Times”
December 3, 2020
2:00 PM Eastern
Register Here

Description
Sponsored by AFPM's Hydroprocessing Group, this webinar will focus on getting the most from your hydrogen plant in challenging times. Operational advice, industry advancement and guidance for hydrogen plant operations will be discussed.

Participants
• Thor Gallardo, Haldor Topsoe
• Ken Chlapik, Johnson Matthey
• Marco Márquez, Matheson Gas

“Walk the Line and Energy Isolation”
December 8, 2020
2:00 PM Eastern
Register Here

Description
This webinar will review newly published practice sharing documents. A company case study will be presented, focusing on engaging Maintenance in WTL.

Intended Audience
Maintenance, Operations, Safety

Participants
• Amir Anderson, AmSty
• Tjokro Hermanto, AmSty
• Wesley Farrell, LyondellBasell
• Michael Vopatek, LyondellBasell
REQUEST FOR FEEDBACK

Join at slido.com #Crude
THANK YOU FOR YOUR PARTICIPATION