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#Crude

2020 AFPM
SUMMIT
Excellence in Plant Performance

CRUDE FEEDSTOCK OILFIELD PRODUCTION CHEMICALS IMPLICATIONS ON THE REFINING PROCESSES

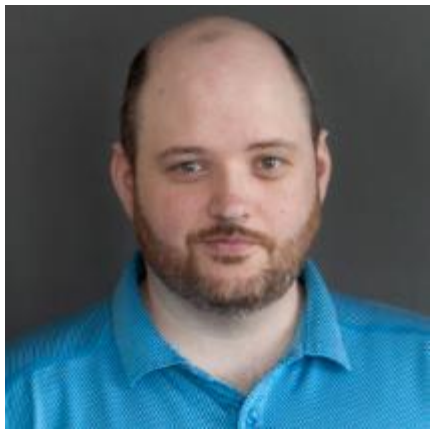
OCTOBER 29, 2020

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

SPEAKERS

HALLIBURTON



John Hazlewood
Technology Manager - Technical Services
John.Hazlewood@Halliburton.com

2020 AFPM SUMMIT
Excellence in Plant Performance

DID YOU KNOW

YOU'RE NOT JUST RESPONSIBLE FOR WHERE YOU ARE, BUT ALSO FOR WHERE YOU'VE BEEN.

HEALTH & SAFETY
SAFETY MOMENT
ENVIRONMENT

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.

The Halliburton *10 to Zero Life Rules* are a compilation of basic rules that all Halliburton employees know and live by. These are key components for identifying and managing the hazards in our business.

HALLIBURTON

SLIDO QUESTIONS 1-2

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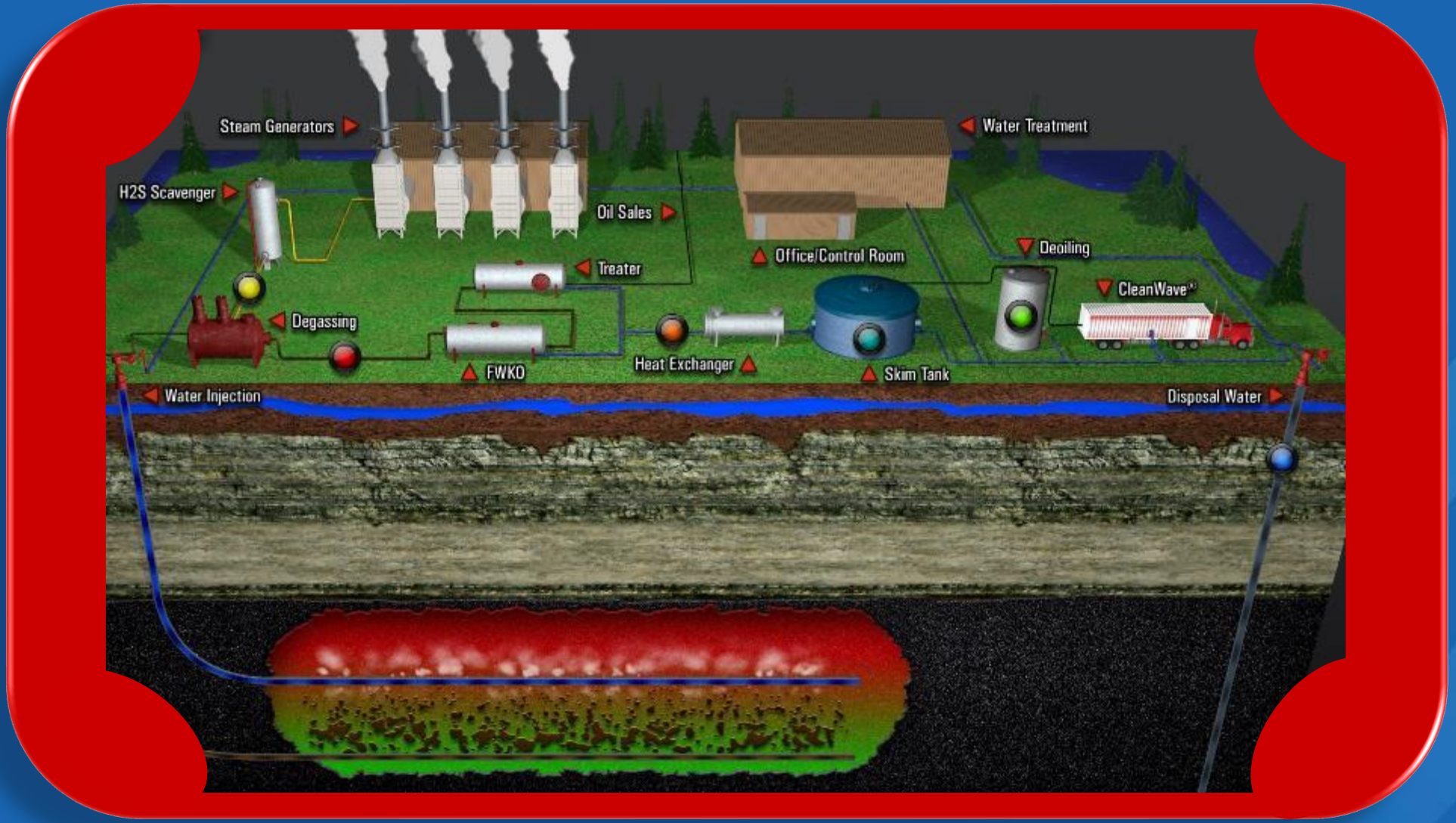
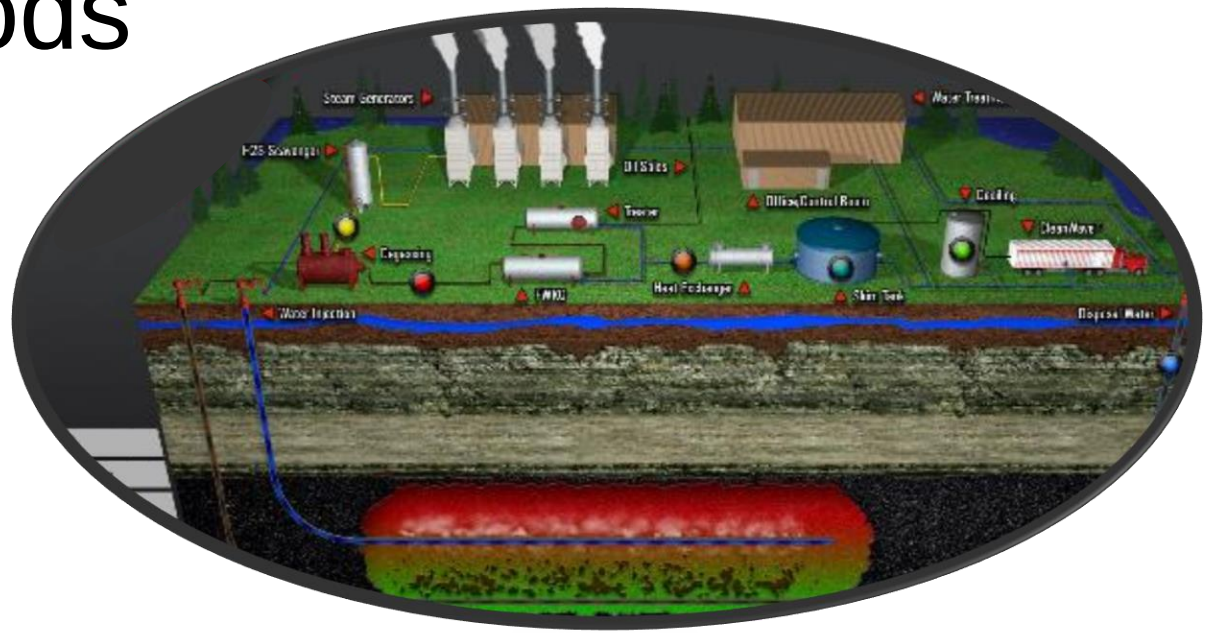
American
Fuel & Petrochemical
Manufacturers

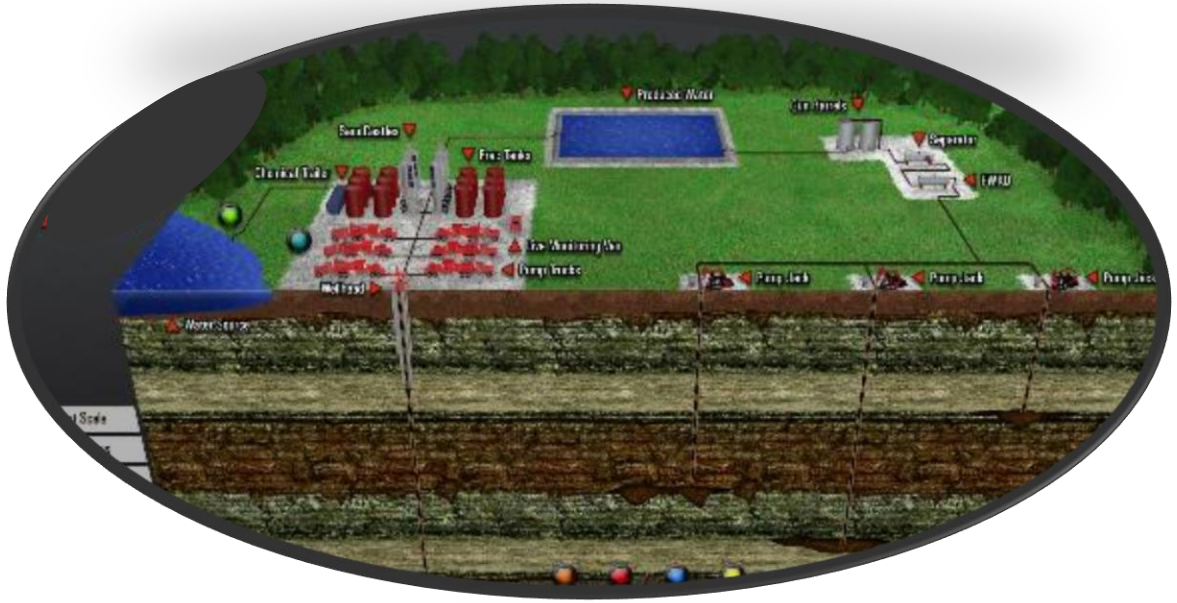
PRODUCTION METHODS



Production Methods

- Conventional
  - Offshore
    - Mars, Poseidon, Bonito Sour, Cascade
  - Enhanced Oil Recovery
    - CO_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

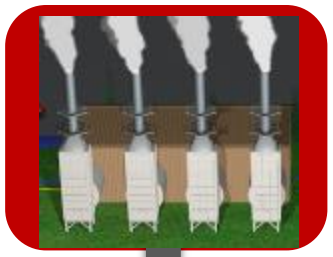
- Higher Temperature and Pressures
- Speed of oil and water separations (low residence times)
- Water Quality Specifications (29 ppm O/G)
- Sub-Sea tiebacks for new production
- Shut In
- Treatment issues
  - Hydrates
  - Water Soluble Organics
  - Foam

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



In-Situ

Mining

Bitumen Production

Condensate (Diluent)

Bitumen

Conventional

- Bow River
- Fosterton
- Lloyd Blend
- Lloyd Kerrobert

DilBit

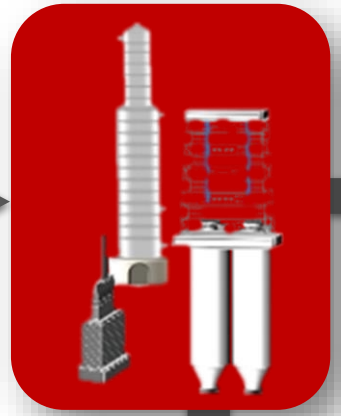
- Cold Lake
- Peace River Heavy
- Seal Heavy
- Smiley-Coleville
- Wabasca Heavy
- Western Canadian Select

Heavy Bitumen By Rail

Bitumen

SynBit

- Long Lake Heavy
- Surmont Heavy Blend



Upgraders

Light Synthetic Crude

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

Heavy Synthetic Crude

- Albian Heavy Synthetic

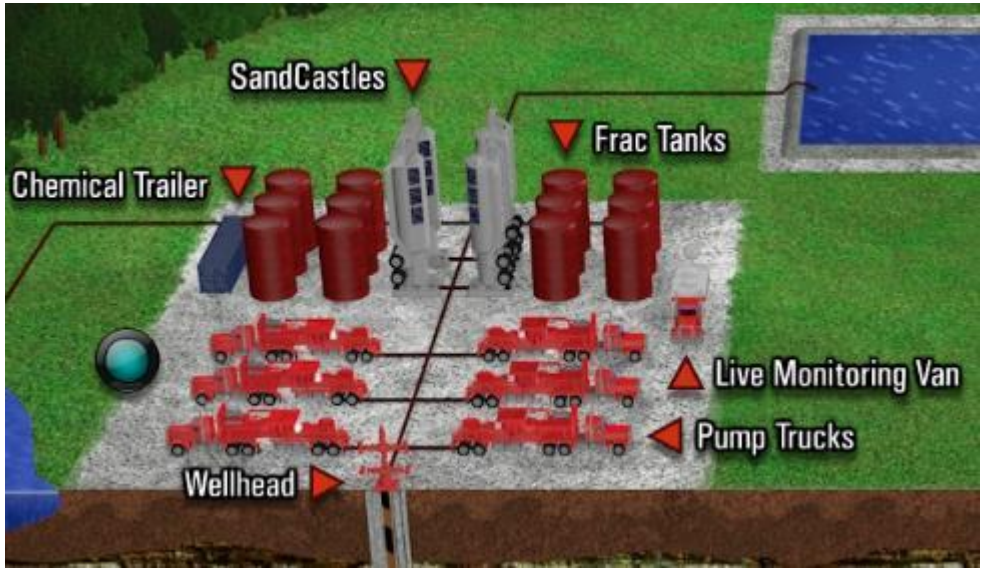
Heavy Canadian Bitumen

- 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



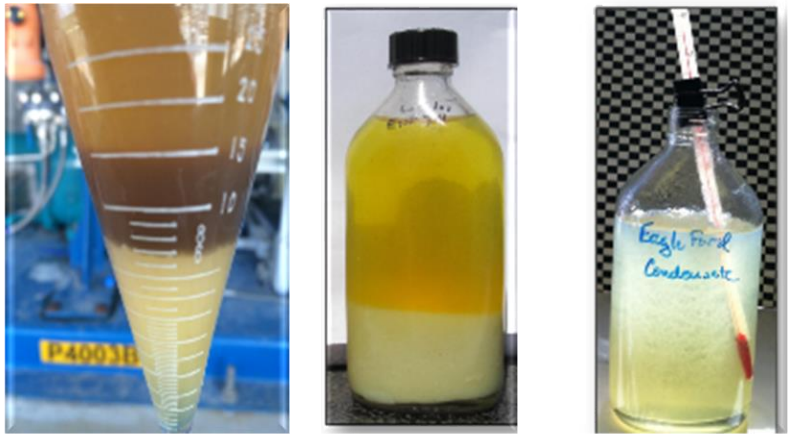


Photo Credit: Champion Technologies 2010

UPSTREAM CHEMICALS

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 Souring
- H_2S 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

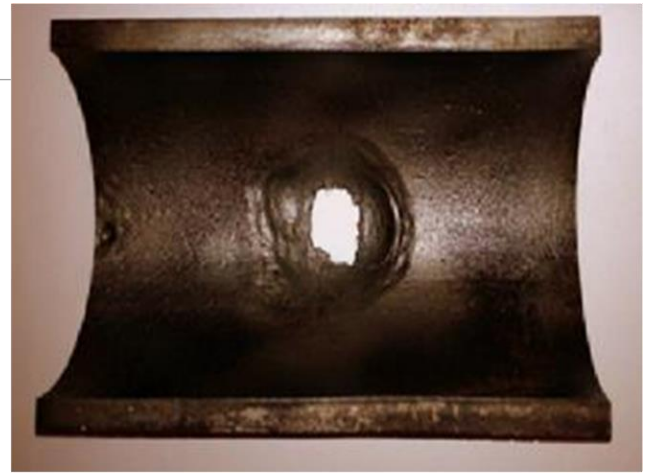
- Hydrate Inhibitors
  - Ethylene glycol, methanol, quaternary amine salts, LDHI-AA

Photo Credit: Champion Technologies 2010

Asset Integrity Chemicals

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

- Biocides
  - Glutaraldehyde
  - THPS
  - Quaternary amine salts



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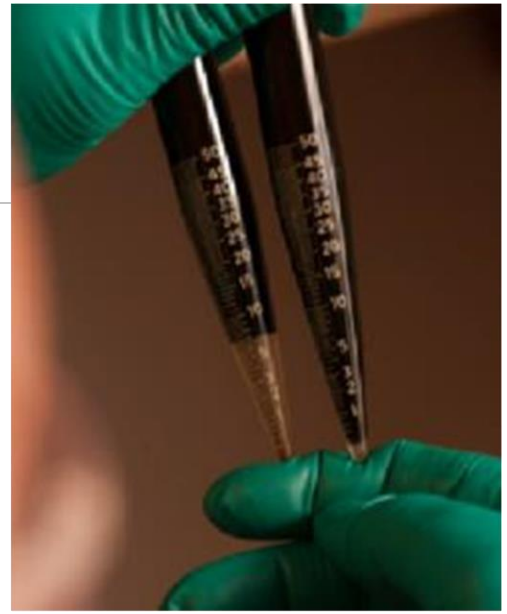
Phase Separation Chemicals

- Emulsion Breakers
  - Sulfonates
  - Surfactants
  - Alkyl phenol resins



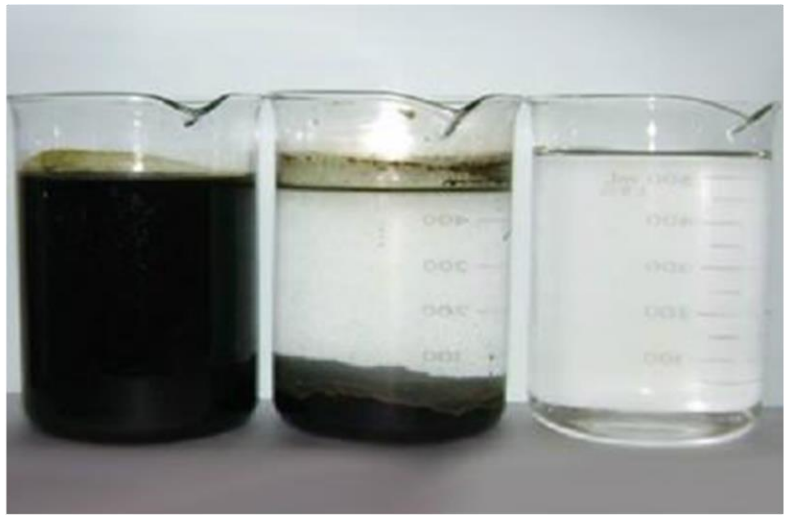
- Defoamers
  - Polydimethylsiloxane (PDMS)
  - Polyether alcohols
  - Fluorosilicones

Photo Credit: Champion Technologies 2010

Phase separation / Scavengers

- Water Clarifiers
  - Metal salts
  - Polymers
  - Polyacrylates

- H_2S Scavengers
  - MEA/MA triazines
  - Aldehydes
  - Glyoxal



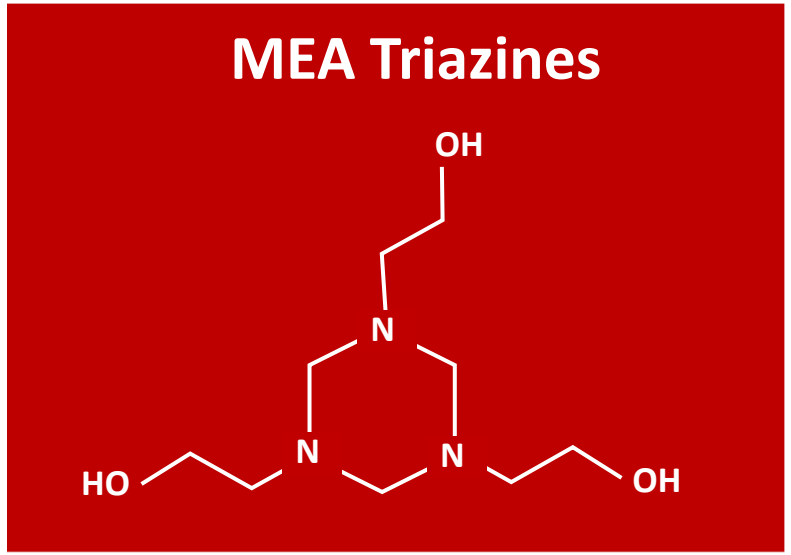


Photo Credit: Champion Technologies 2010

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

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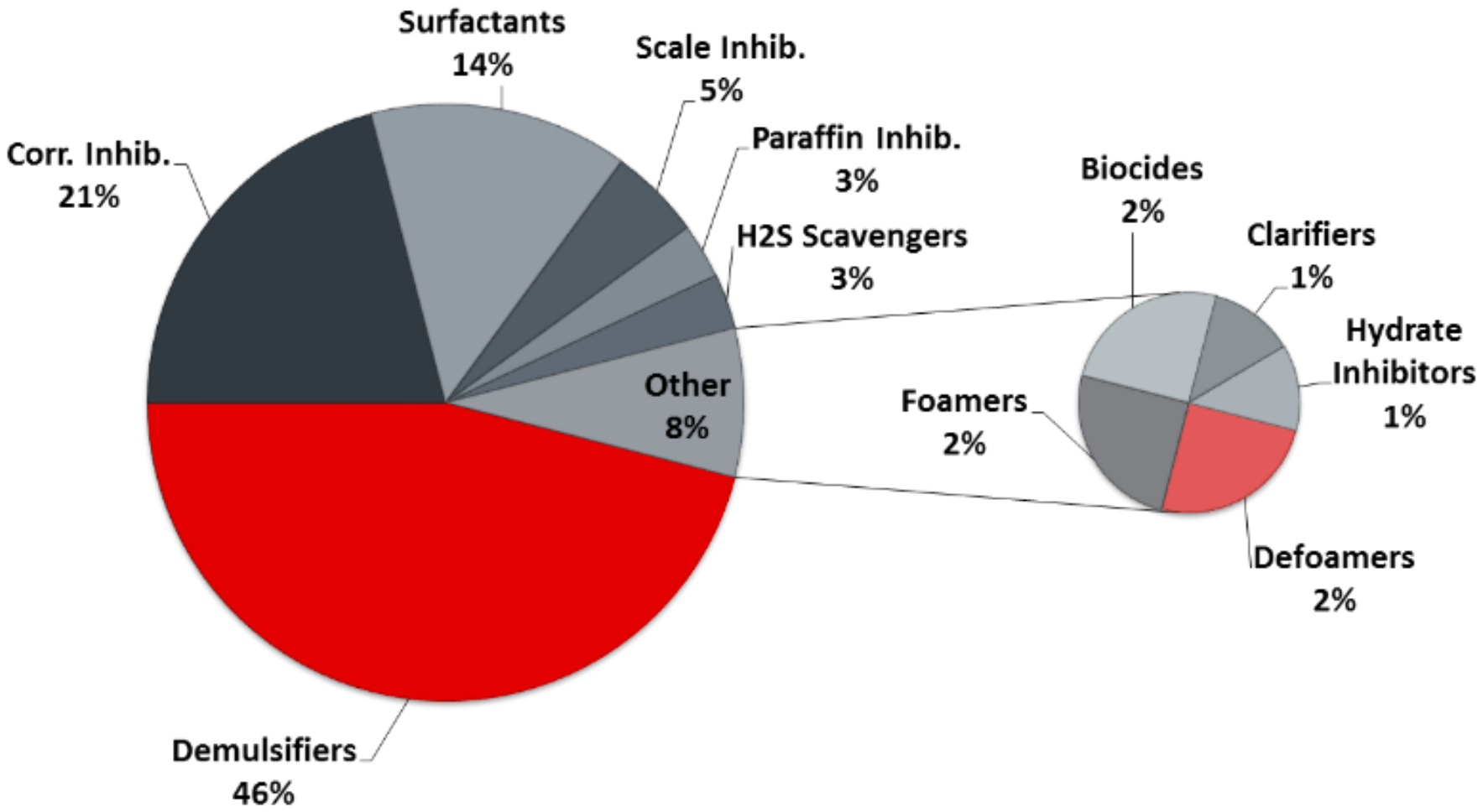
Production Chemical Breakdown



Absence of chemicals can also be a problem.

“The Usual Suspects”

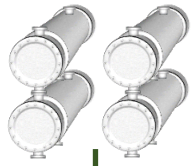
Functional Chemistry	Potential Impact	Water/Oil
Organic Chlorides (Carbon Tet)	Banned in 1994 Boil	Oil
Quaternary amine salts	Corrosion and Fouling	Water
Mineral Acids	Corrosion in Crude Unit	Water
Triazines	Crude Tower Fouling/Corrosion Waste Water	Both
Carboxylic Acid	Crude Unit Corrosion	Water
Calcium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

Crude Unit

~ 65 °F

Raw Crude Storage

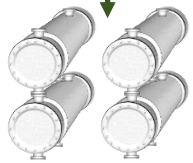
Tank
De-Watering



Typical
Specifications

< 1.0 PTB Salt
< 25 PTB Solids
< 0.2% H_2O

Crude Preheat



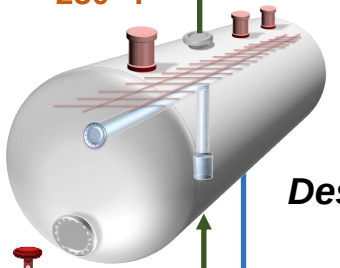
~ 475 °F

~ 675 °F

Furnace

~ 250 °F

5% Fresh
H_2O



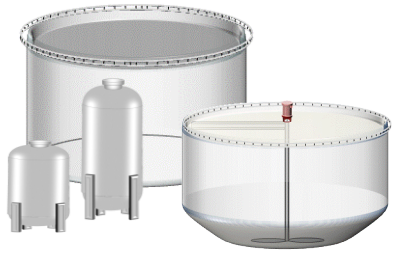
Desalter

Brine H_2O

Typical
Specifications

< 500 PPM O&G

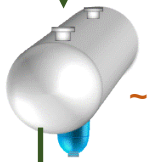
Wastewater
Treatment Plant



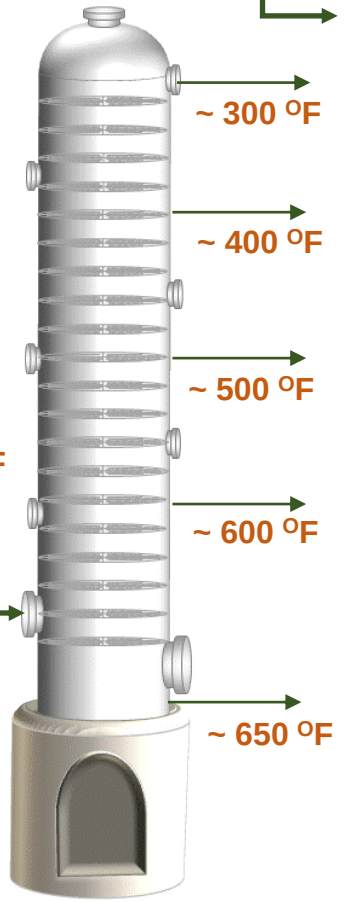
Mechanical and Biological
Treatment

Other Process Units Waste H_2O

~ 250 °F



~ 100 °F



~ 300 °F

~ 400 °F

~ 500 °F

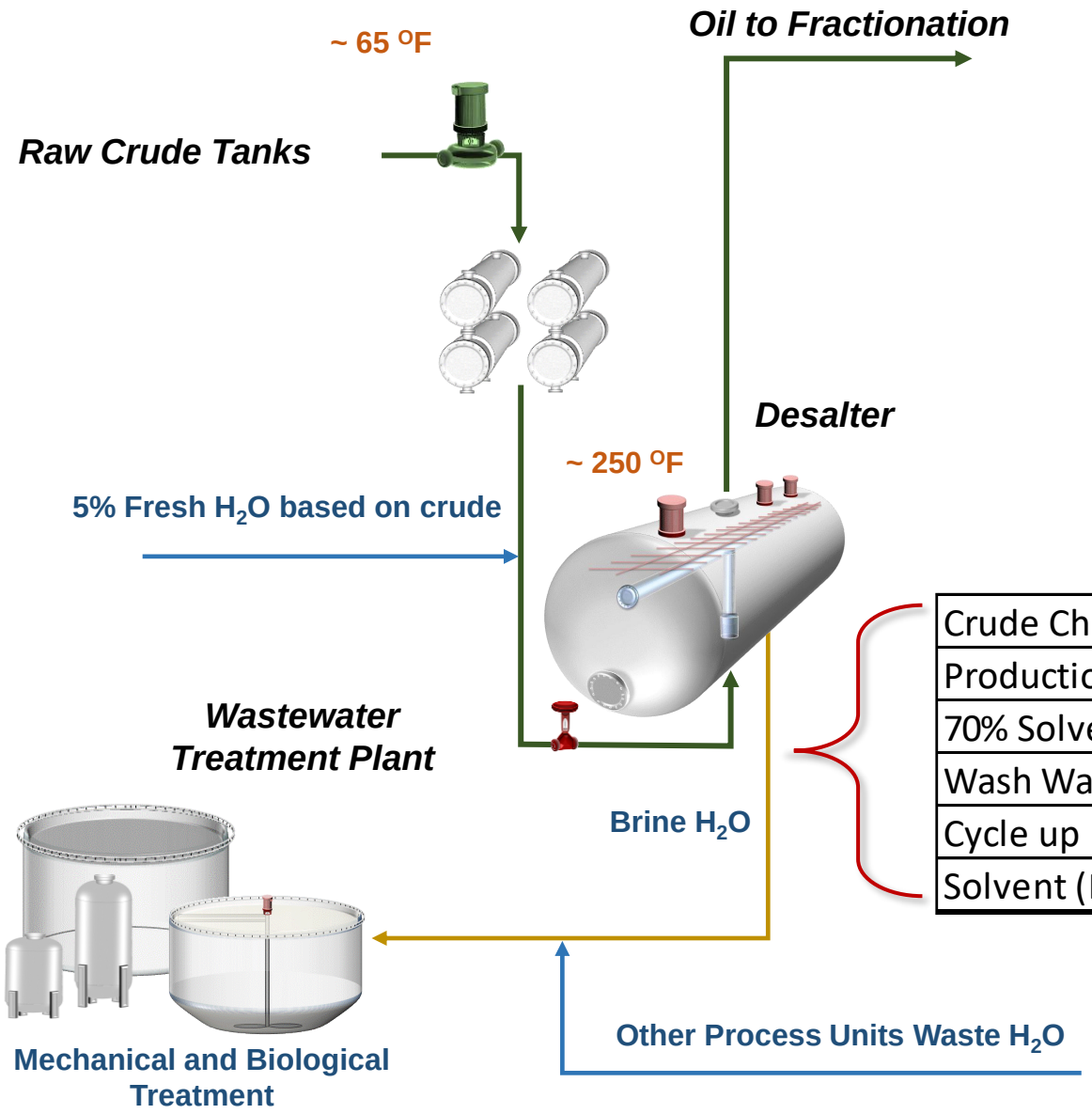
~ 600 °F

~ 650 °F

Crude
Fractionator

Downstream Processing Units

Crude Unit – Solvent Package Alone



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

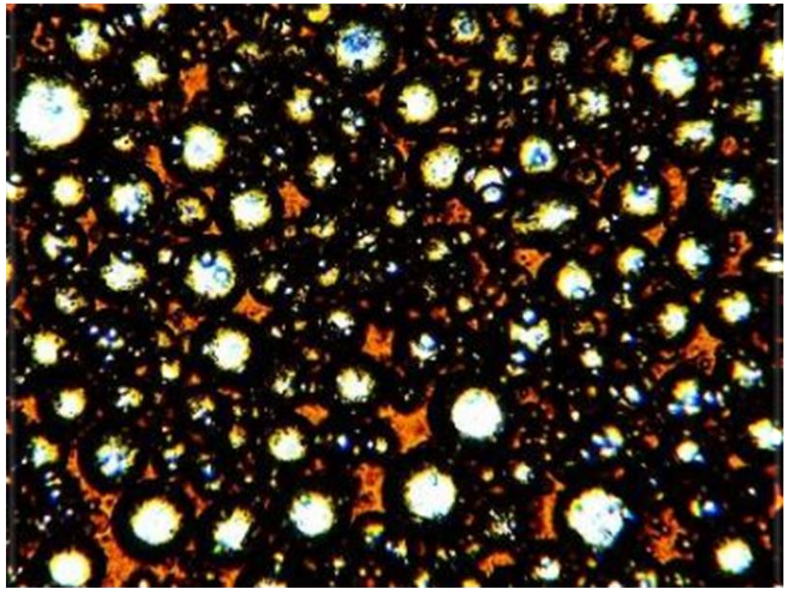
Crude Charge	100,000	*BPD*
Production Chemical in raw crude	70	*ppm*
70% Solvent (Methanol) in raw crude	50	*ppm*
Wash Water (5%)	5,000	*BPD*
Cycle up	20	*times*
Solvent (Methanol) in Eff Water	1000	*ppm*

Creates High COD/TOC

Desalter & Emulsion Stability

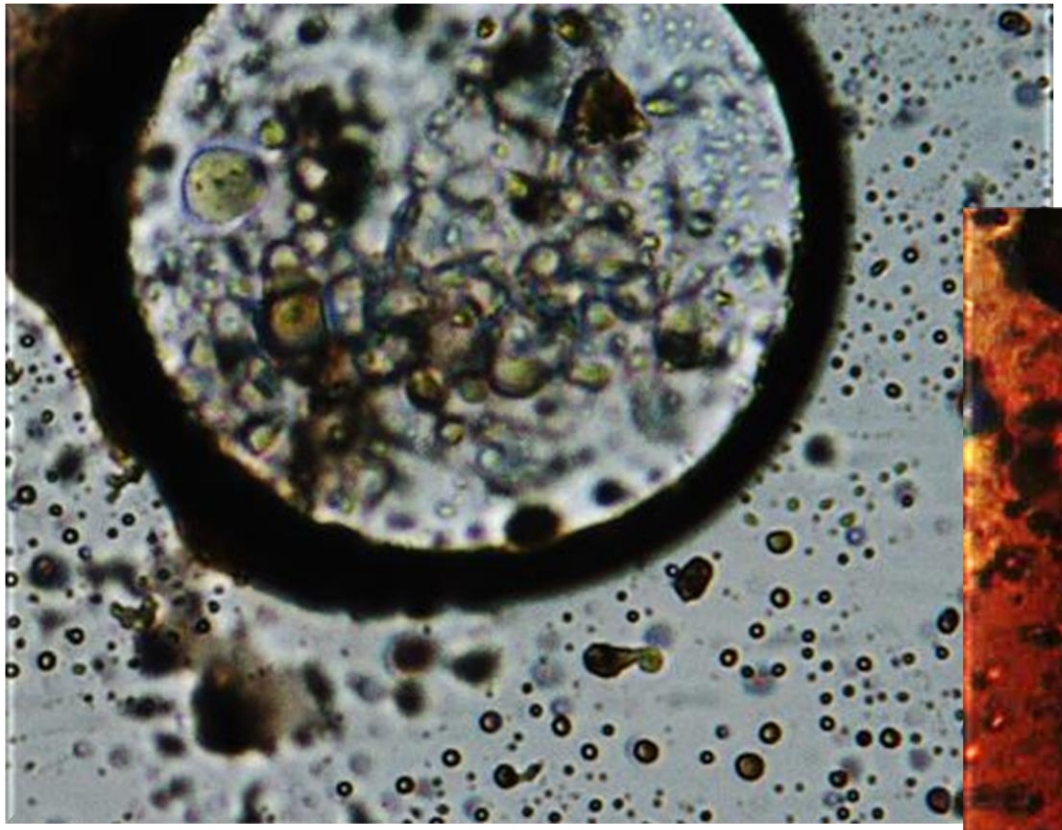
Chemistries	Oil/Water	Potential Impact
Alkyl Phenol Resins	Oil	Desalter Emulsion Stability
Fatty Amines/Amides	Oil	Desalter Emulsion Stability
Polymers	Both	Desalter Emulsion Stability
Sulfonates	Both	Desalter Emulsion Stability
Surfactants	Both	Desalter Emulsion Stability
Metal Salts	Water	Desalter Emulsion Stability
Polyacrylates	Water	Desalter Emulsion Stability
Solvents	Both	Phase Separation

- 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

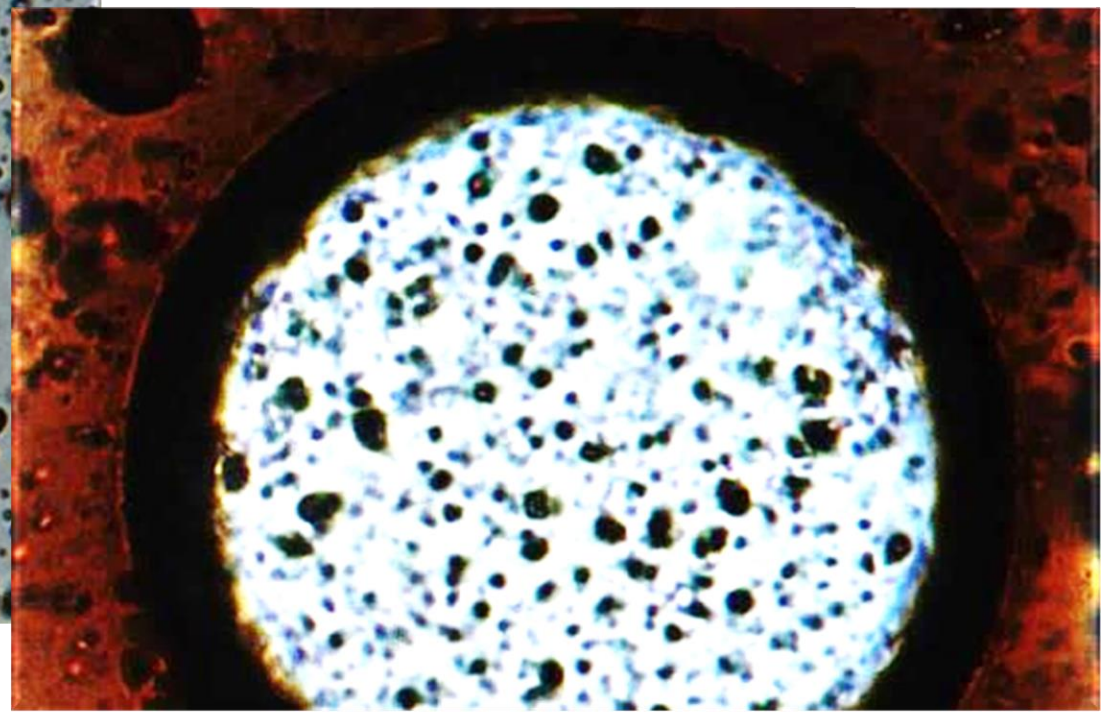


Complex Emulsions from Surfactants

Water Continuous Emulsion

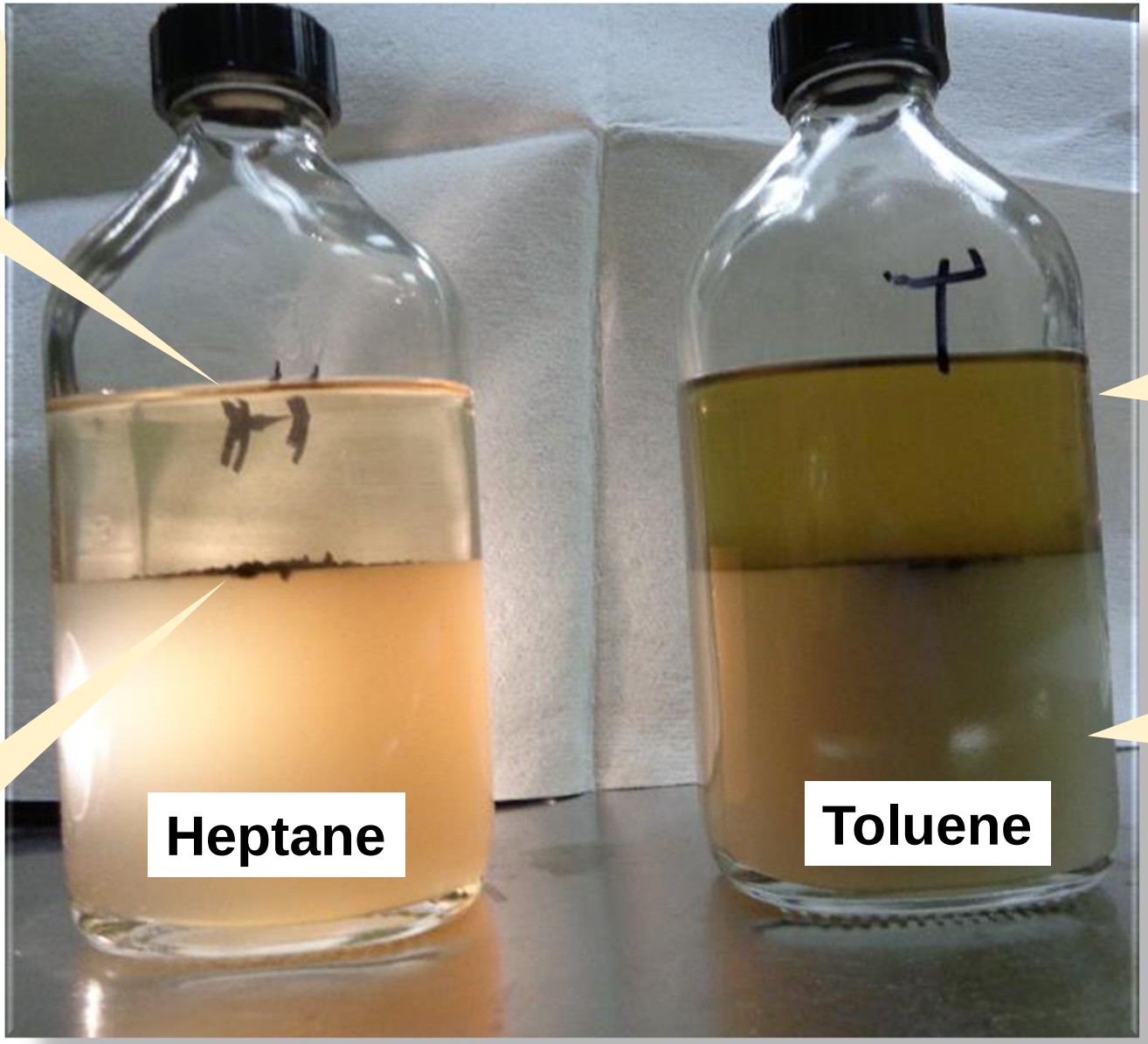


Oil Continuous Emulsion



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

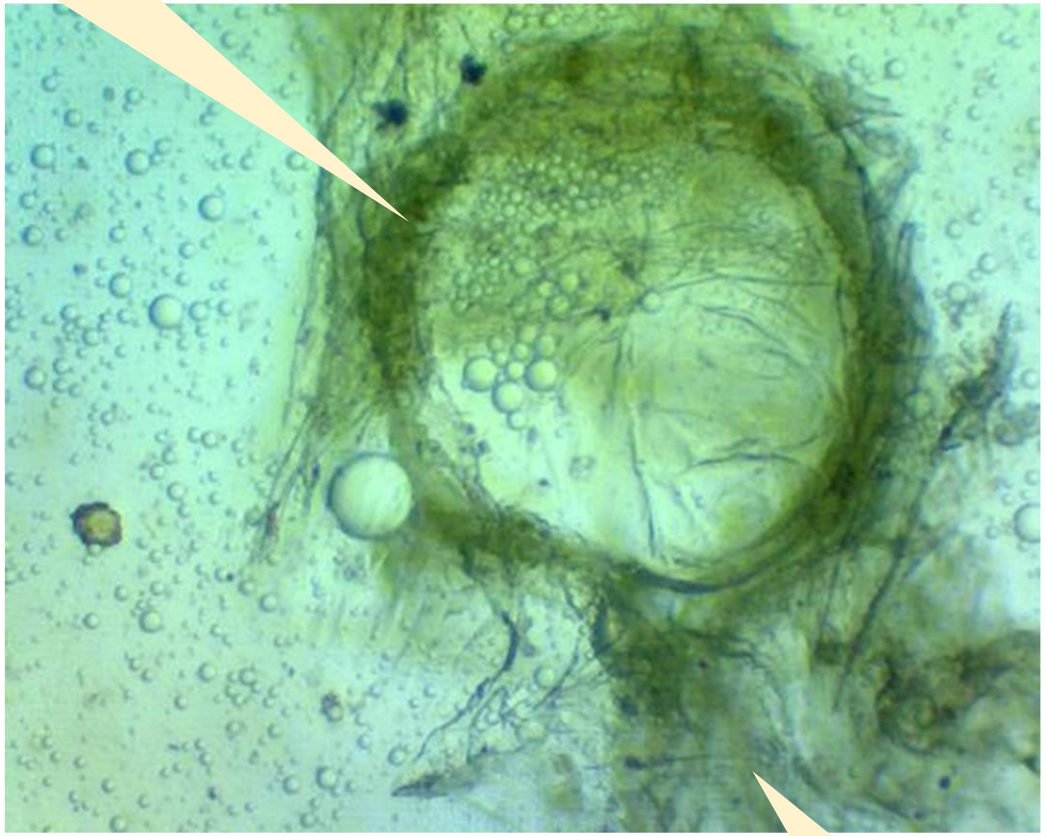
Water is Mostly Oil Free

Brine Quality - Polyacrylates

Polymer and Asphaltenes

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

Microscope picture of polymer



Potential Source

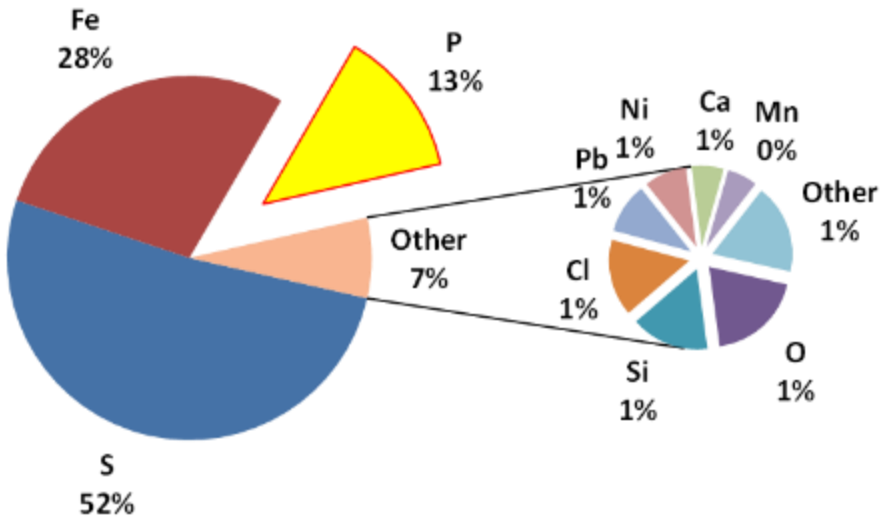
1. **Drag Reducer**
2. **Water Clarifier**

Analysis indicates polyacrylamide

Corrosion and Fouling

Chemistries	Oil/Water	Potential Impact
Organic Chlorides (Carbon Tet)	Oil	Banned in 1994 - Don't hydrolyze
Quaternary Amine Salts	Water	Corrosion and Fouling - High OH Cl-
Mineral Acids	Water	Corrosion
Triazines	Both	Corrosion and Fouling
Carboxylic Acid	Water	Corrosion
Calcium Stearate	Both	Fouling
Phosphate Esters	Water	Fouling
Phosphonates	Both	Fouling
Vinyl Acetate Copolymers	Oil	Fouling

Tray 12 Deposit



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

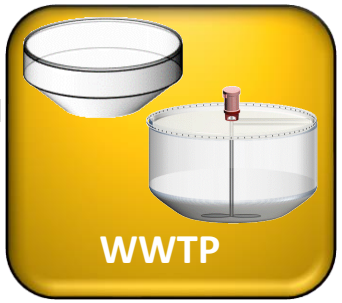
Downstream Catalyst & WWTP

Chemistries	Oil/Water	Potential Impact
Fluorosilicones	Water	Catalyst poisoning
Polydimethylsiloxane	Oil	Catalyst poisoning
Ethylene Glycol	Water	WWTP
Glutaraldehyde	Water	WWTP
Methanol	Water	WWTP
Polyether Alcohols	Water	WWTP
THPS	Water	WWTP

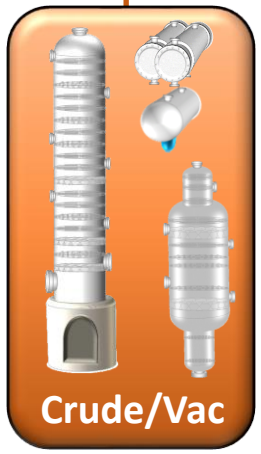
- Increased organic load to WWTP
  - Increased food = increased bacteria production
  - Increased food = Settling issues
  - Increased food = Increased O_2 demand
- Solvent Packages
  - Glycols
  - Alcohols
- Biocides
  - Bug Kill

H_2S Scavengers

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

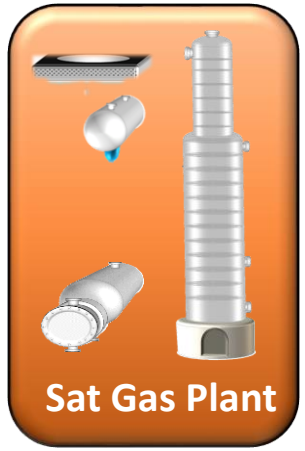


- Poor dehydration
- Oil in Effluent
- Poor Salt Removal
- High Chemical Cost



- 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

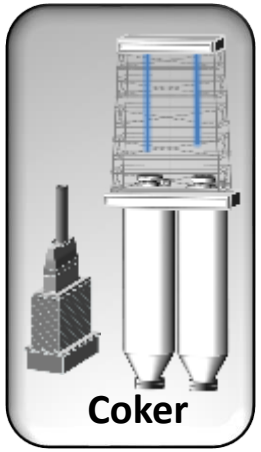
- Off Spec Propane
- Fouling
- Lost Production



- Fouling from Corrosion Byproducts
- Fouling From NH_3 Salts
- Corrosion from NH_3 Salts

- Lost Production
- Corrosion from NH3 Salts
- Basic Nitrogen Poisoning
  - Higher Gas Make
  - Higher Coke Make
  - Lower Conversion
  - Compressor Limited
  - Blower Limited

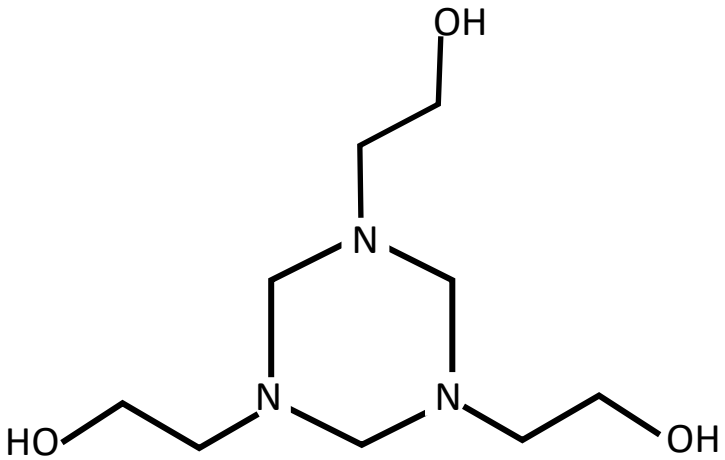
Purchased Feed



Triazines

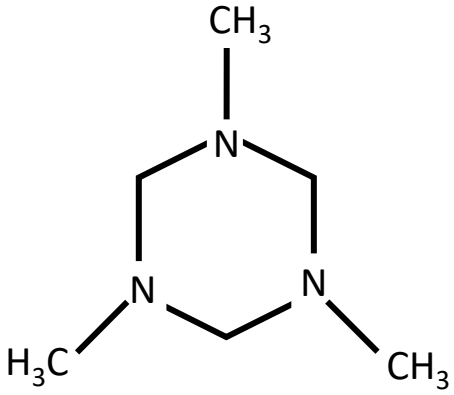
Monoethanol amine triazine

MEA Triazine

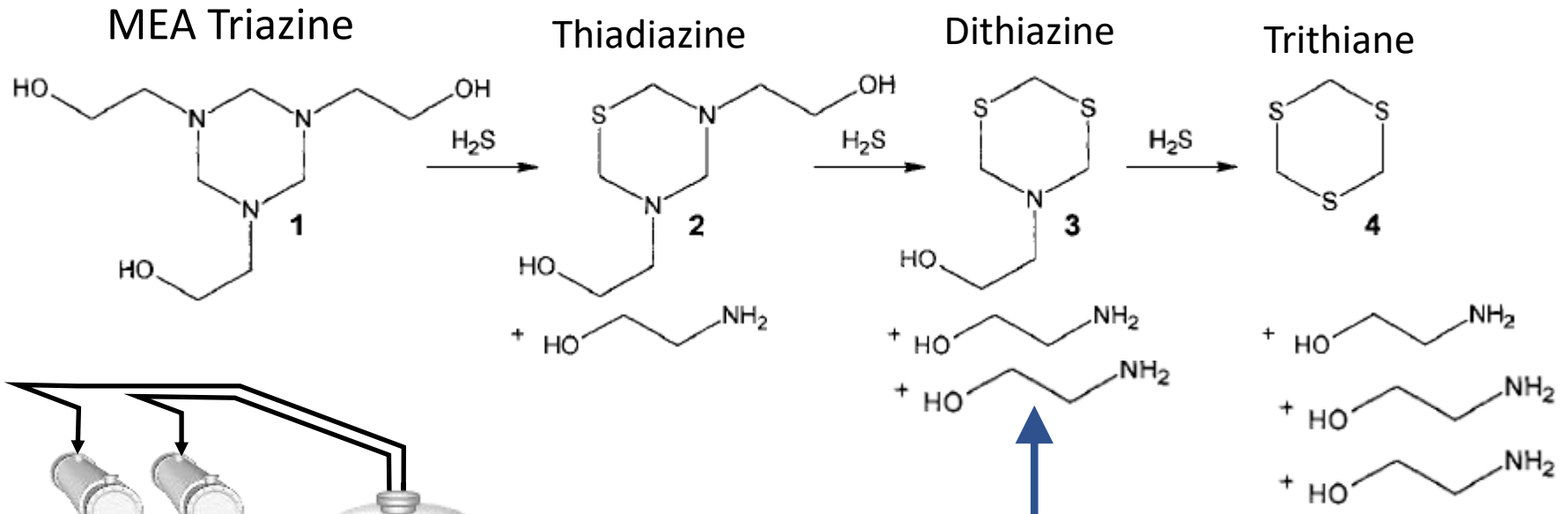


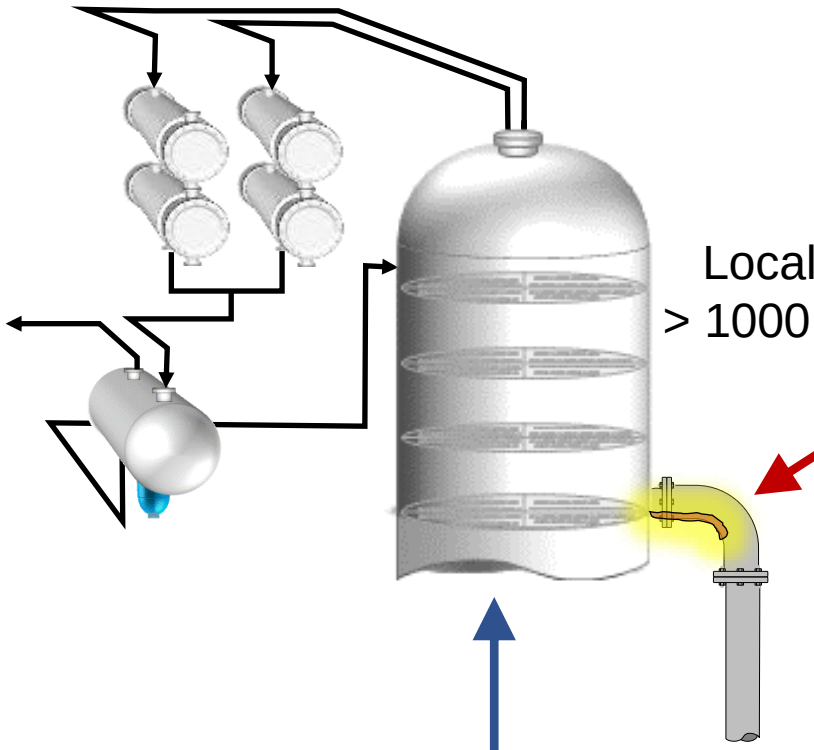
Monomethylamine triazine

MA Triazine



Reaction Steps - MEA Triazine

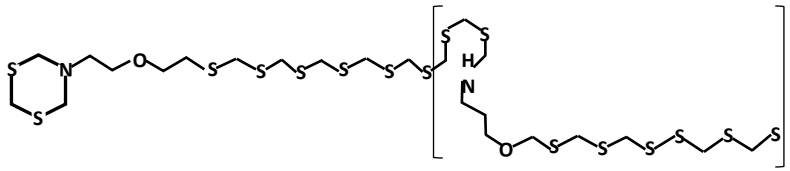




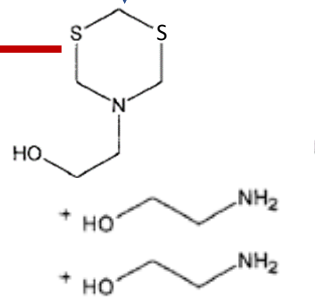
Localized Corrosion
> 1000 mpy in HSR 90º

Step 3. Most Prevalent
In Crude Oil at Refinery

Dithiazine

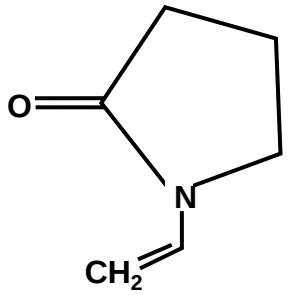


Can create solid polymer

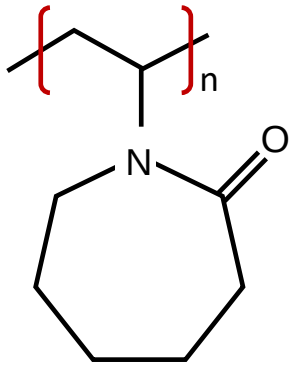


As HS^- salt

Low Dosage Hydrate Inhibitors



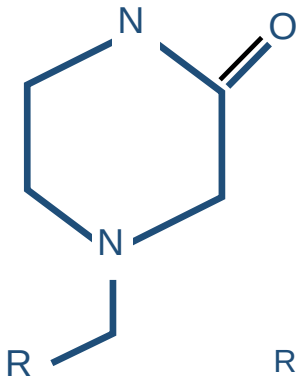
Vinylpyrrolidone



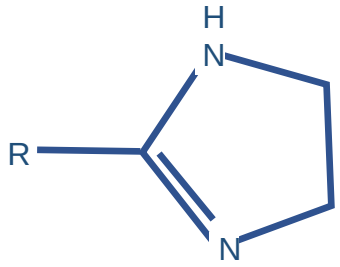
Polyvinylcaprolactam

Typical Refinery Corrosion Inhibitor

Pyrimidine



Imidazoline



- 10% will partition to water in dealter
- >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)
- Commodity hydrate 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

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THANK YOU FOR YOUR PARTICIPATION