Lets just jump right into it...

Todays CCQTA Project Focus deals with two topics

1. H2S in Crude Oil update
   (a Transport Canada Initiative)

2. Condensate Quality
# PROJECTS LIST

## Participant Funded

1. Condensate Quality (Closed)
2. Organic Chlorides (Suspended)
3. Phosphorus (Suspended)
4. TAN
5. Emulsion Characterization
6. Pipeline Corrosion
7. Pipeline Sour Service

## CCQTA Sponsored

1. Bitumen Volumetric Correction
2. Bitumen Blend Viscosity
3. TVP/RVP
4. \( \text{H}_2\text{S} \) PVT
5. Crude Oil Flammability
6. Crude Compatibility Method
7. VLE Method Development
8. Toluene Insoluble Organic Material (TIOM)
9. Properties of Thermally Processed Material
10. Organic Chlorides in Distillate

## Sub-Committees

1. Condensate Quality (new)
2. Education (pending)
H₂S IN CRUDE OIL
H$_2$S in Crude Oil

In late 2016 Transport Canada began moving forward with the intend to delineate between Crude Classifications. Currently in comment “gazette” stage of legislation…

- **UN 1267** Petroleum Crude Oil
  - <10 ppm H2S in the liquid phase

- **UN 3494** Petroleum Sour Crude Oil
  - >10ppm H2S in the liquid phase
H2S in Crude Oil

Rail Transportation Requirements

• UN1267 Crude Oil
  – CPC-1232 non-jacketed and jacketed rail car until eliminated as per current phase-out schedule.
    – TC-117

• UN 3494 Sour Crude Oil
  – TC-117 Only
H$_2$S in Crude Oil

Highway Transportation Requirements

- **UN1267 Crude Oil**
  - No changes

- **UN 3494 Sour Crude Oil**
  - Currently TC 407 (40 psi)
  - Proposed change to TC 407 (25 psi) regardless of packing group.
H₂S in Crude Oil

Technical Review of new TC Proposal

CCQTA Specific Concerns

1. No specified sampling method
2. No specified test methods listed with threshold
3. Reporting units are vague
4. No consideration of test method MDL and precision (±)
5. Excessive scavenger use to reach threshold
6. Amine contamination in crude oil and the effect on refining

(Submitted to Transport Canada Regulatory Affairs Branch Feb 21, 2017)
H$_2$S in Crude Oil

Technical Review

1. No specified sampling method
   - Define “Live” or “Dead” crude oil using API/ASTM published definitions
   - Measured vapor pressure via D7975 or D6377 will determine state
   - Definition will determine appropriate sampling method
     - D4057 (Dead)
     - D8009 (Live – low pressure)
     - D3700 (Live – high pressure)
2. No specified test methods listed with threshold

- **Available test methods**
  - D5705, D5623, D7621 and UOP 163
  - Crude oil is not listed in the scope of any of these
  - Which method should be used? Referee method?

- **Methods do not measure the same phase**
  - D5623 and UOP 163 are direct liquid phase measurements.
  - D7621 measures the vapor phase but calculates on liquid basis
  - D5705 measures the vapor phase only

- **CCQTA H2S in Crude Method in Development**
  - Prototype available in September 2017
H₂S in Crude Oil

Technical Review

3. Reporting units are vague — ppm?
   - D5623, D7621 and UOP 163 report in mg/kg (ppmw)
   - D5705 reports in mole/volume ppm (ppmv)

4. No consideration of test method MDL and precision (±)
   - UOP 163 (10ppmw) – no precision listed.
   - ASTM D5623 (0.1ppmw) – precision listed.
   - ASTM D5705 (5 ppmv) – precision listed.
   - ASTM D7621 (0-10ppmw) – precision listed.
H$_2$S in Crude Oil

Technical Review

• **Example of Reproducibility at 10 ppm threshold**
  – UOP 163 — no reproducibility listed
  – ASTM D5623 — 10 ppm ± 5 ppm
  – ASTM D5705 — 10 ppm ± 18 ppm
  – ASTM D7621 — 10 ppm ± 2 ppm
H₂S in Crude Oil

Technical Review

5. Excessive scavenger use to reach threshold

- Terminal operators report up to 1000 ppm of scavenger to treat 40-50 ppm H₂S
- Both MEA Triazine and MMA Triazine are being reported.
- Reacted Triazine leaves MEA or MMA tails in the crude for processing.
6. Amine contamination in crude oil and the effect on refining

- Triazine reaction products
  - MEA and/or MMA
- Unreacted Triazine decompose in the crude tower to form MEA or MMA
- Amines react with hydrolyzed salt
  - to form corrosive amine hydrochloride
- At 1000 ppm these are significant potential contaminants
H$_2$S in Crude Oil

CCQTA Experience (1100+ results)

28.8% between 10 ppm & 100 ppm
H₂S in Crude Oil

CCQTA Experience (1100+ results)
CONDENSATE QUALITY
Condensate Quality

Condensate Quality Project Summary

• **Initiated in 2008**
  – Imperial Oil identified high solids and dark condensate in CRW samples causing operability issues
  – 2009 Cenovus, Connacher and Devon reported similar operability issue

• **Initial Conclusions**
  – Many condensate samples >1000 ppmw solids
  – Both toluene soluble and insoluble components
  – Insoluble components included:
    • Inorganics (salt, sand, clays and corrosion products)
    • Toluene Insoluble Organic Materials (TIOM)
Condensate Quality

Condensate Quality Project Summary

• **Test Method work**
  – In 2010 the CCQTA Modified ASTM D4807 for filterable solids (toluene insoluble) was added to CRW specification
  – In 2012 the CCQTA Particulates test method was developed to differentiate asphaltenic solids from toluene insoluble solids
    • Test Method was not added to CRW spec
    • Since the density specification change from 815 to 775 kg/m$^3$ had resulted in reduced asphaltene related plant operability issues.
Condensate Quality

Condensate Quality Project Summary

- **Project closed in December 2016**
  - Formation of Condensate Quality Sub-Committee
  - Condensate Quality project members are default SC members
  - Forum for members to:
    - Participate
    - Get updates
    - Provide feedback on multiple related projects
  - Related Projects including:
    - TIOM
    - TVP/RVP
    - H2S PVT
    - Phosphorus
    - Organic Chlorides
Condensate Quality

Condensate Quality Project Summary

• Toluene Insoluble Organic Material (TIOM) Work
  – Began prior to this project
  – Two projects established the role of TIOM in fouling
    • NGL Contamination (2005-2009)
    • Iron Fouling (2006-2010)
  – Condensates were viewed as the common factor in both projects
  – In 2012 the Deposit Analysis Protocol (DAP) was launched in an attempt to characterize the TIOM and potential source(s)
Condensate Quality

Condensate Quality Project Summary

• TIOM Work
  – TIOM composition from DAP
    • Carbon based
    • No measurable functional chemistry
    • Similar characteristics to Drag Reducing Agent (DRA)
  – Due to the number of locations within the industry that TIOM’s appeared the TIOM Project was separated as a stand alone CCQTA sponsored project.
TIOM Solids Characterization

Unidentified Solid Material

- Hot Toluene Extraction
  - Toluene Soluble
  - Toluene Insoluble

- Thermal Gravimetric Analysis (TGA)
  - Inorganic
  - Organic

ICP/XRD/EDS

XRD/EDS High carbon %
Recent Experience

• Applying testing protocol since 2014

• In early 2015 approached to assist with solid characterization based on existing data
  – No conclusion but predominately carbon

• Problem persisted in additional wells in the same formation
Recent Experience

• Feb 2016 immediately following well completion showed similar solids
  – No identified source

• Solids appear for limited period after well completion so sample collection is difficult

• May 2016 immediately following well completion showed similar solids again
  – More detailed testing indicated ~4% TIOM material
  – Recommended further investigation into completion chemicals with vendor
Testing Results – Lab Created Solids

• October 2016 testing on well completion friction reducer in contact with formation water and condensate at elevated temperatures (50°C) resulted in black precipitate similar to what had been observed in the field.
Testing Results – Lab Created Solids

(Interesting to note that the same experiment with fresh water did not produce the precipitate.)

-75% Toluene Insoluble
-25% Toluene Soluble*
* May be residual condensate included.
## Testing Results – Lab Created Solids

<table>
<thead>
<tr>
<th></th>
<th>Raw Sample Hot Toluene Filtration – Mass %</th>
<th>Raw Sample (TGA – Mass %)</th>
<th>Normalized – Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene Soluble</td>
<td>24.6</td>
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<tr>
<td>Toluene Insoluble</td>
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<td>Combustible</td>
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<td>TIOM</td>
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<td>35.3</td>
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<tr>
<td>Inorganic</td>
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<table>
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<th>Normalized – Mass % w/o Inorganics</th>
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<tbody>
<tr>
<td>Toluene Soluble</td>
<td>41.1</td>
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<tr>
<td>TIOM</td>
<td>58.9</td>
</tr>
</tbody>
</table>
Testing Results – Field Collected Solids (400 bbl Tank) – Sample 1

- **August 2016** — 400 bbl production tank sample submitted with similar solids
  - Similar material as found in condensate separator at gas plant
- **Solids isolated from water**

*13% Toluene Soluble
87% Toluene Insoluble*
Testing Results – Field Collected Solids – Sample 1

- Sub-sample of sludge stable in toluene over 3 days
# Testing Results – Field Collected Solids – Sample 1

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<tr>
<td>Toluene Soluble</td>
<td>43.8</td>
</tr>
<tr>
<td>TIOM</td>
<td>56.2</td>
</tr>
</tbody>
</table>
Testing Results – Field Collected Solids (400 bbl Tank) – Sample 2

- Dean stark extracted solids
- Extracted @ ~110°C for 96 hours

Sludge in bottle with water decanted

Extracted Toluene Insoluble Solids

28.4% Toluene Soluble
71.6% Toluene Insoluble
# Testing Results – Field Collected Solids – Sample 2

<table>
<thead>
<tr>
<th></th>
<th>Raw Sample Deans Stark (96 hr) – Mass %*</th>
<th>DS Solids (TGA – Mass %)</th>
<th>Normalized – Mass %</th>
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<tr>
<td>TolueneSoluble</td>
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<td>TolueneInsoluble</td>
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</table>

*DS data renormalized with water removed

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</table>
## Testing Results – Comparison

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<tbody>
<tr>
<td>Toluene Soluble</td>
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<td>43.8</td>
<td>64.8</td>
<td>52.0</td>
<td>85.4</td>
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<tr>
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<td>58.9</td>
<td>56.2</td>
<td>35.2</td>
<td>48.0</td>
<td>14.6</td>
</tr>
</tbody>
</table>

Normalized – Mass % w/o Inorganics

Duplicate Sample

Fresh Sample

Residue
TIOM Source Hypothesis

• Polyacrylamide monomer (PAM) based or other types of polymers used in gas well drilling, completions, fracking, etc…
  – undergo decomposition at formation temperatures and are returned to the surface with early production

• The decomposed PAM has no functional chemistry and would appear as a long chain high molecular weight molecule similar to DRA
Testing Results

Preliminary Conclusions

– Similar TIOM material appears throughout industry
  • Production
  • Processing & Fractionation
  • Blending
  • Pipeline?
  • Refining?

– Source material may be PAM based or other polymer type

– Cumulative type fouling effect on equipment
  • Low PPM levels slowing fouling over time
Testing Results

Preliminary Conclusions (continued)

- May be part of BS&W but would be atypical of the solids operators expect as BS&W (salt, sand, asphaltene…)
  - BS&W spec would not be sufficient to prevent
- Limited effectiveness by solvent wash or backflush cycles
- Other solids could be trapped in matrix (asphaltene, inorganic) compounding the problems
Brief CRW Committee Update

New Microcarbon (MCR) spec

Industry now added a new MCR limit of 0.5wt% max to partially manage resid containing feeders and subsequent issues with desalters/SAGD treaters

(see Enbridge website)
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