Primer on Organic Chlorides and Their Control

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Organic Chloride OR Undesaltable Chloride?

• High Chlorides have been reported on….
  – Crude Unit Atmospheric Distillation Overheads
  – Vacuum Unit Overheads
  – Naphtha Hydrotreaters Feed/Effluent Exchangers
  – Hydrotreater Stripper Overheads
  – Catalytic Reformers (De Butanizer Overheads)
  – Hydrocracker Overheads

*Typified by no “apparent” increase in salt in desalted Crude*
Problematic crudes

- Urals Tallyn & Ventspills
- Illinois Basin Crude (analysed 135 ppm 1,1,1,Trichloroethane)
- Equadorian Oriente Crude (analyzed 20-50 ppm Organic Chloride)
- Cabinda
- Rabi

- Didon
- Ashtart
- Arab medium/Heavy
- Ratawi
- Palanca
- Russian Export Pipeline
- CPC (Tengiz)

*REFIN* COR / Internal Search
What are Organic Chlorides?

- Organic Molecules with C-Cl Bond
  - Chloroform \( \text{CH}_3 - \text{Cl} \)
  - Carbon Tetrachloride \( \text{C} - \text{Cl}_4 \)
  - Tetrachloroethylene \( \text{C-Cl}_2 = \text{C- Cl}_2 \)
  - Vinyl Chloride \( \text{C}_2\text{H}_3\text{Cl} \)
  - ChloroBenzene \( \text{C}_6\text{H}_5\text{-Cl} \)
  - “Freon” 113 \( \text{C}_2\text{Cl}_3 \)
  - Chloroprene \( \text{CH}_2=\text{CClICH}=\text{CH}_2 \)
  - Propylene Di Chloride \( \text{C}_3\text{H}_6\text{Cl}_2 \)
  - Dichloro methane \( \text{CH}_2 \text{Cl}_2 \)
  - Trichloro ethylene \( \text{CHCl}=\text{CCl}_2 \)
What are Undesalttable Chlorides?

- Inorganic Molecules with M-Cl Bond
  - Normally Desalttable
    - Sodium Chloride Na - Cl (Relatively stable)
    - Calcium Chloride Ca - Cl2 (Hydrolyzable)
    - Magnesium Chloride Mg - Cl2 (Easily hydrolyzable)
    - Others Ba, Sr, (minimal effect)
  - Why Undesalttable?
    - Not removed by desalter
    - Crystalline salts
    - Bound up in a complex ashphaltene complex
    - Hydrolyses under furnace conditions

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## Properties Of Some Organic Chlorides

<table>
<thead>
<tr>
<th>Material</th>
<th>Molecular Weight</th>
<th>Vapour Pressure kPa @20°C</th>
<th>Boiling Point °C</th>
<th>Relative Density (water = 1)</th>
<th>Solubility in Water @20°C g/100ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>119</td>
<td>21</td>
<td>62</td>
<td>1.48</td>
<td>0.80</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>154</td>
<td>12</td>
<td>77</td>
<td>1.59</td>
<td>0.10</td>
</tr>
<tr>
<td>TetraChloroethylene</td>
<td>166</td>
<td>2</td>
<td>121</td>
<td>1.60</td>
<td>0.02</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>62</td>
<td>337</td>
<td>-13</td>
<td>0.90</td>
<td>0.27</td>
</tr>
<tr>
<td>Chloro Benzene</td>
<td>113</td>
<td>1</td>
<td>132</td>
<td>1.11</td>
<td>0.02</td>
</tr>
<tr>
<td>Chloroprene</td>
<td>88</td>
<td>23</td>
<td>59</td>
<td>0.96</td>
<td>0.03</td>
</tr>
<tr>
<td>FREON 113</td>
<td>187</td>
<td>36</td>
<td>48</td>
<td>1.56</td>
<td>0.02</td>
</tr>
<tr>
<td>Propylene dichloride</td>
<td>113</td>
<td>28</td>
<td>96</td>
<td>1.16</td>
<td>0.26</td>
</tr>
<tr>
<td>Dichloro methane</td>
<td>85</td>
<td>47</td>
<td>40</td>
<td>1.13</td>
<td>1.30</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>131</td>
<td>8</td>
<td>87</td>
<td>1.50</td>
<td>0.10</td>
</tr>
</tbody>
</table>
# Common AKA’s for some Organic Chlorides

<table>
<thead>
<tr>
<th>Material</th>
<th>Common AKA's</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>Trichloromethane, Methanetrichloride, Formyltrichloride</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>Tetrachloromethane, Tetrachlorocarbon</td>
</tr>
<tr>
<td>TetraChloroethylene</td>
<td>Perchloroethylene, Tetrachlorethene</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>Monochloroethylene, Monochloroethene, Chloroethene</td>
</tr>
<tr>
<td>Chloro Benzene</td>
<td>Benzene Chloride, Chlorobenzol, MCB, Phenyl Chloride</td>
</tr>
<tr>
<td>Chloroprene</td>
<td>2Chloro-1,3butadiene, 2Chlorobutadiene, Beta-Chloroprene</td>
</tr>
<tr>
<td>FREON 113</td>
<td>1,1,2-trichloro, 1,2,2trifluoroethane</td>
</tr>
<tr>
<td>Propylene dichloride</td>
<td></td>
</tr>
<tr>
<td>Dichloro methane</td>
<td>Methylene Chloride, DCM</td>
</tr>
</tbody>
</table>
## General Uses of Some Organic Chlorides

<table>
<thead>
<tr>
<th>Material</th>
<th>Common Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>For production of dichlorodifluoromethane - refrigerant; Solvent intermediate in dyes and pesticides</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>Chlorinated rubber manufacture, semiconductor manufacture; Metal recovery</td>
</tr>
<tr>
<td>TetraChloroethylene</td>
<td>Dry Cleaning, Degreasing, textile, printing, soap, and paint remover</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>Monomer for PVC</td>
</tr>
<tr>
<td>Chloro Benzene</td>
<td>Tar and Grease Remover, Surface Coatings remover</td>
</tr>
<tr>
<td>Chloroprene</td>
<td>Monomer for Polychloroprene used as wire and cable cover, gaskets and automotive components</td>
</tr>
<tr>
<td>FREON 113</td>
<td>Degreasers, Refrigerants</td>
</tr>
<tr>
<td>Propylene dichloride</td>
<td>Dry Cleaning, Paint removals</td>
</tr>
<tr>
<td>Dichloro methane</td>
<td>Paint and Varnish Removers (phasing out)</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>Industrial Cleaner, Solvent in paint and glue manufacture</td>
</tr>
</tbody>
</table>
Sources Of Organic Chlorides

- Generally NOT naturally occurring
- Used to be used extensively in the oil field - Wax dissolver
- Generally banned on environmental grounds

- Primary sources now believed to be contamination
- Unscrupulous dumping into transportation pipelines
- Contamination of tankers and barges
- Refinery Slop (workshop metal cleaning fluids)
Detection Of Organic Chlorides

- ASTM D4929 (Distillation and Combustion
  - Sodium Biphenyl Reduction & Potentiometry
  - Combustion and Microcoulometry

- X RAY FLUORESCENCE (UOP)

- ION CHROMATOGRAPHY
Crude Unit/Vacuum Unit Overheads Overheads
Crude and Vacuum Overheads
- Where the Problems Appear

- High Chlorides
- High Iron
- Low pH

- Overheads
- Crude Preheat
- Atmospheric Column
- Hot Well
- Desalter Vacuum Preheat
- Vac Furnace

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Corrosion Control
(Crude Unit Overheads)

• Improving Desalter Operation
  – Maintain High temperatures (> 250°F/120°C)
  – Maintain water wash at ~5%
  – Optimize mix valve dP
  – Wash water quality
    • If recycling overheads water, organic acids will concentrate in
      the wash water and potentially re-partition into the crude oil
    • Lower pH generally favorable as destabilizes emulsions
  – Demulsifier selection
Control of Corrosion in Crude Unit Overheads

- Water Wash
- Filmer Neutralizer
- Atmospheric Column
- Overheads
- Caustic
- Desalter
- Vacuum Preheat
- Vac Furnace
- To Vac Column

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Hydroprocessing Corrosion
Organic Chlorides Usually Present Problems On Naphtha Hydrotreaters
Areas Of Corrosive Attack

To Recycle Hydrogen & Fuel Gas Treating

To Fuel Gas Treating

H2O Wash

Steam

Light’ Products

Heavy’ Products

Feed/ Effluent HX

Feed

Reactor

H2

Heater

Fin Fan

To SWS

LP Sep

HP Sep

Stripper

SWS

‘Light’ Products

‘Heavy’ Products

To Fuel Gas Treating

Fin Fan

To SWS

H2
Factors Affecting Corrosivity in HDS Units

• H$_2$S and NH$_3$ levels are high: 0.5% to more than 8%
  – Pitting attack and iron sulfide fouling
• Ammonium chloride fouling and corrosion also an issue
  – Underdeposit salt acid corrosion and accelerated bisulfide corrosion
• Units operate “almost dry”
  – Localized high concentrations of corrosives
Factors Affecting Corrosivity in HDS Units

• Corrosion often starts in the feed/effluent exchangers
  – Point of water condensation
• Corrosion may continue downstream
  – Other areas may concentrate corrosives
# Source of Corrosives

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{S}$</td>
<td>Sulfur in the Feed - normally low in naphtha hydrotreaters</td>
</tr>
</tbody>
</table>
| $\text{NH}_3$ | Nitrogen Compounds in the Feed  
Natural Nitrogen Dominates  
Additives (Filmers / Neutralizers) May Add A Trace |
| $\text{HCl}$ | Reformer Hydrogen  
Salt Contamination  
*Organic Chlorides* |
### When Is Corrosion Likely

<table>
<thead>
<tr>
<th>NH₄Cl</th>
<th>Salt Deposition</th>
<th>Salt fouling drives HCl corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dissolved salt</td>
<td>Chlorides accelerate NH₄HS⁻ corrosion</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NH₄HS⁻</th>
<th>Salt Deposition</th>
<th>Salt deposition is unlikely, but possible</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dissolved salt</td>
<td>Concentration above 2% is often corrosive</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Concentration above 8% to be avoided</td>
</tr>
</tbody>
</table>
HDS Design Issues

• Piping dead-legs; Exchanger dead-zones
  – Stagnant areas promote corrosion

• Vapor velocity to limit corrosion
  – Vapor flow rate of less than 20 ft/sec (6.2 m/sec) for carbon steel
  – Vapor flow rate of less than 30 ft/sec (10 m/sec) for alloy

• Design for condensed water and/or water wash
  – Good water removal and water wash capabilities help
  – Limit fouling and corrosion
HDS Design Issues

• Numerous variations of header design
• Liquid and vapor flow impacts corrosion
Monitoring

- Feed for Organic Chlorides
- HP Separator Water Boots
- LP Separator Water Boots
- Rerun Column/Stripper Overhead Accumulator Boots

What to test for:
- pH
- Chloride
- Ammonia
- Hydrogen Sulfide
- Iron
- Organic acids and Sox species
- Corrosion Probe/ Datalogger/UT/RT
Corrosion Control - Prevention

- Avoid excess chloride in reformer catalyst regeneration
- Install chloride guard beds in reformer
- Wash salt out of imported feed
- Eliminate in-house sources of salt
- Eliminate organic chloride feed sources
- Eliminate in-house sources of organic chlorides (slops)
- Minimize nitrogen in feed (slops)
Corrosion Control

• **Water Wash**
  - Typical wash is 3-5% based on feed rate
    - Wash target is 25% minimum free water by calculation
    - Goal is to wash away NH₄Cl salts and/or dilute NH₄HS
  - Water source is oxygen free boiler feed water or stripped sour water
  - Water wash must be well designed
    - Water wash may require single or multiple wash points
    - Addition point is upstream of the first fouled or corroded exchangers
    - An injection quill (inserted pipe) is required
    - Spray nozzles (full cone) are recommended
Water Wash - Full Cone Spray Distributor
Corrosion Control

- **Filming Corrosion Inhibitor**
  - Hydrocarbon soluble filmer is recommended
  - Use of hydrocarbon slipstream is advised for good surface coverage
  - Good design of injection system required to match the unit design

- **Salt Dispersant**
  - Use of hydrocarbon slipstream is advised for good surface coverage
  - Good design of injection system required to match the unit design

- **Neutralizer**
  - Often not needed due to high NH3 levels
  - Use of slipstream is advised for good distribution
  - Good design of injection system required to match the unit design
Chemical Treatment Strategy

- Feed/Feed/Effluent HX
- …
- To Recycle Hydrogen & Fuel Gas Treating
- To Fuel Gas Treating
- To SWS
- H2
- HP Sep
- LP Sep
- Fin Fan
- Reactor
- Heater
- Feed/Effluent HX
- H2
- H2O Wash
- Stripper
- Salt Dispersant/Filmer/Neutralizer
- ‘Light’ Products
- ‘Heavy’ Products
- Steam
- ‘Heavy’ Products
Summary

- Undesalttable and organic chloride exist
- Can pose problems on CDU’s & VDU’s
- Major concern - downstream HDS units
  - Naphtha hydrotreaters
- Organic chlorides due to contamination
- Use is diminishing
Summary

- Effects can be catastrophic
- HCl generation
- NH₄Cl salt deposition
- Control
  - Water wash
  - Filming corrosion inhibitor
  - Neutralising amine
  - Salt dispersant