Challenges of Processing Heavy Canadian Crudes
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- Single & Two [2] Stage Desalting
  - Consequences of leaving salt in crude
- Solids in Canadian Crudes
  - Impact of solids
- Stream TAN’s
  - Why are they different?
- Corrosion Control Methods
  - Dilution
  - Chemicals
  - Metallurgy
- Processing Canadian Crude
  - Point of View
  - ID Effected Circuits
  - Requirements for TAN Corrosion
- Understanding 2\textsuperscript{nd} & 3\textsuperscript{rd} Order Effects
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Simplified Single Stage Desalters

90% Salt removal per stage. Therefore, a typical crude at 40 ptb would desalt to \( (0.1) \times 40 = 4 \text{ ptb} \) in the 1st Stage.
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What does two Stage Desalting look like?

90% Salt removal per stage. Therefore, a typical crude at 40 pb would desalt to \( (0.9) \times 40 = 4 \) pb in the 1\textsuperscript{st} Stage, and \( (0.9) \times (0.9) \times 40 = 0.4 \) pb at the end of the 2\textsuperscript{nd} stage.
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Results of leaving salt in the desalted crude?

- Crude preheat train fouling
- Crude heater fouling
- Vacuum heater fouling
- Duty requirement to vaporize water in the desalted crude
- Caustic usage or increased overhead chlorides/corrosion
- Overhead neutralizer usage
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Results of leaving salt in the desalted crude?

- Coker impact
- Deactivation of Coker Naphtha HDS due to Si
- Chemical/silicone usage
- Units downstream of crude – HCl corrosion issues
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Impact of solids in the desalted crude and solids going to the WWTP

- Negative impact on dehydration
- Crude preheat train fouling
- Crude heater fouling
- Vacuum heater fouling
Impact of solids in the desalted crude and solids going to the WWTP

- Negative impact on downstream Hydrotreating reactors:
  - Increasing reactor pressure drop
  - Poisoning of reactor catalyst bed
- Stabilize emulsions and increase chemical demand
- Difficult to process solids after they are removed from the water
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- TAN stands for Total Acid Number
- TAN represent the amount of KOH in mg required to neutralize the acids in one gram of oil.
- ASTM D664 is the most common method for measuring TAN
  - Potentiometric titration in nonaqueous solution
  - The oil is dissolved in a special solvent mixture consisting of toluene and propanol containing enough water so that the pH electrode can measure a potential.
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What is Naphthenic Acid?

- Naphthenic acid represents a mixture of several cyclopentyl and cyclohexyl carboxylic acids.

- Presence in crude oil and are a major contaminant in the oil derived from tar sands.
- Crude oils with a high naphthenic acid content are referred to as “high TAN” crudes.
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Not All Streams are Created Equal

- Insight into corrosivity versus TAN for fractions and whole crudes is very difficult at best
- Many studies have been undertaken and are underway to characterize the content, structure and corrosivity of high acid crudes and fractions
- Efforts to characterize the content, chemical structure and corrosivity of acids in crudes and their fractions are challenged by:
  - Complexity of the acid mixtures
  - Scarcity of suitable analytical means
Another complication is determining the distribution of naphthenic acids in the different fractions:

- Typically done by analyzing the various fractions from the completed assay.
- Distillation conditions may expose the naphthenic acid in the higher boiling fractions to longer resident times at higher temperatures than what would be seen in the actual unit.
- Because of thermal decomposition, this can lead to lower acid numbers which can lead to underestimating the risk of corrosion.
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Corrosion Control Methods

➢ Dilution is the solution
  • Blending of lower TAN crudes with higher TAN crudes to meet the desired crude TAN
  • Relatively inexpensive
  • Can cause fouling and desalter problems
  • Not an option for refiner with a single source of crude
  • Blending to a “safe” TAN is an uncertain method of control. i.e. tank heel management

➢ Chemicals
  • Can reduce corrosion rates by as much as 90%
  • All major chemical companies have naphthenic acid corrosion inhibitors [Sulfur or phosphorous]
  • Expensive – Low capital expense, significant operating costs. Can be used as a gap closer to get system to material upgrade
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Corrosion Control Methods

Metallurgy
- Most effective long term solution to reducing corrosion rates
- Expensive – Large capital expense
- Unlikely the complete unit would be able to be completed at one time. Phased approach must likely
  - Material availability
  - Shut-down windows are short
  - Complexity
- Can pick the correct alloy for the desired circuit

Other Methods
- Decarboxylation
  - Expensive – significant operating costs
  - Low capital required
  - Generates CO/CO₂ which can lead to additional corrosion issues
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- TAN Originates in Crude
- Destroyed in either:
  - Hydrotreater
  - Desulfurizer
  - Coke Drums
  - FCCU
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Streams to Build TAN Capability = Stream with Temp > 450F

- #1/2 Fuel Oil
- LGO
- Crude/Vacuum
- LVGO/HVGO
- VTB
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- **Point Of View [POV]** - A brief, but detailed description [TAN, Sulfur, Solids, Salt and Gravity] of the charge for each crude unit.

- Limits of operation [TAN, Sulfur] for each circuit [i.e. Whole Crude, Fuel Oils, Heavy & Light Gas Oils, Vacuum Tower Bottoms] that will see TAN and which operates at > 450 °F.
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Listing of all equipment which operates at > 450 °F

- Drums
- Towers
- Separators
- Exchangers
- Piping [include control valves]
- Pumps
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Information needed to determine expected life and corrosion rates

- Line or equipment number
- Description
- Service
- Material of construction
- Maximum operating temperatures
- % sulfur range
- Expected TAN range
- Minimum recorded thickness
- Last Inspection date
- Expected corrosion rates
- Remaining Life of existing material
## Challenges of Processing Heavy Canadian Crudes

<table>
<thead>
<tr>
<th>Line #</th>
<th>Description</th>
<th>Service</th>
<th>Material</th>
<th>Max. Operating Temp. °F</th>
<th>Sulfur (wt%)</th>
<th>Expected TAN @ 2</th>
<th>TAN Range @ 2</th>
<th>Corr. Rate [MPY] @ 2 TAN</th>
<th>Min. T Recorded</th>
<th>Min. T Required Trigger</th>
<th>Last Insp. Date</th>
<th>Lab Data Corr. Rate [MPY]</th>
<th>Rep. Corr. Rate [MPY]</th>
<th>Remaining Life Years Prior to Cond.</th>
<th>TML Retirement Date @ 2.0 TAN</th>
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<td>250-22 A/B inc 29022 EC</td>
<td>YTB</td>
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<td>642</td>
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<td>14.4</td>
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<td>28124 A</td>
<td>259-4 to 259-7</td>
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<td>575</td>
<td>2.50%</td>
<td>0.7 - 2.3</td>
<td>0.7 - 4.9</td>
<td>45</td>
<td>50</td>
<td>5.320</td>
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<td>0.7 - 4.9</td>
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<td>50</td>
<td>5.220</td>
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</tbody>
</table>
Challenges of Processing Heavy Canadian Crudes

Understanding 2\textsuperscript{nd} and 3\textsuperscript{rd} Order Effects

- TAN comes with the crude and is only destroyed at certain locations:
  - Hydrotreater/ desulfurizer reactors
  - FCCU reactors
  - Coker reactors

- The same system that was used for the front end of the refinery [i.e. crude/vacuum units] must now be completed for each unit:
  - Process streams that will see temperatures $>450^\circ F$
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Questions