High Temperature Crude Oil Corrosivity: Where Sulfur & Naphthenic Acid Chemistry & Metallurgy Meet

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Organization

- Introduction
- Background – Corrosion Mechanisms
- Corrosion Prediction Methods
- Applications of Stainless Steels
  - Is 317L the “silver bullet” for Naphthenic Acid (Nap Acid) Corrosion?
- Service Experience
- Where Do We Stand on Alloy Selection?
There are few areas of industrial operation where corrosion assessment is more complex than high temperature refinery corrosion.

It is a kind of “chemical soup” of sorts.
- Many species and structures.
- They can decompose, interact and have varying impact on corrosion.
- They are actively distilled and concentrated along with the hydrocarbon fractions.
For decades the complexity and lack of fundamental understanding lead to:

- Focus on empirical findings (e.g. TAN > 1.5)
- Reliance on service experience
- Decisions based on limited knowledge from specific refineries, plant conditions, and crude oil types (e.g. SJV)
- Inability to accurately predict corrosion severity

Then, situation changed from long term contracts from existing crude sources to:

- New crude sources and types
- Short term, changing crude slates with “opportunity crudes”.
- Need for new & more accurate corrosion prediction methodologies.
Nap Acid vs. Sulfidic Corrosion

- Two dominant corrosion mechanisms
  - Naphthenic acid corrosion – soluble corrosion products
  - Sulfidic corrosion – film forming corrosion products under most cases.
- The two mechanisms can act independently with one dominating the corrosion behavior, but often they interact adding to the complexity.
- Both can interact with velocity, more accurately quantified as flow/turbulence induced wall shear stress (WSS).
Nap Acid Corrosion – 1

- Caused by a large class of organic acids:
  - Normally, containing 1 or more cycloaliphatic rings
  - In refining expanded further to include organic acids with thermal stability up to typical oil distillation temperatures.

- Dissolution of iron to form soluble iron naphthenates.

- Damages protective FeS scale. Exposes fresh metal surfaces; corrosion rate very sensitive to WSS

Examples of naphthenic acid structures:
(a) cyclopentane carboxylic acid,
(b) cyclohexane acetic acid
(c) bicyclic carboxylic acid, and
(d) tricyclic carboxylic acid.
Complexity of nap acid corrosion comes from several factors:

- Distillation behavior of different acid species varies.
- Leads to concentration of acids over specific temperatures and in oil fractions.
- Corrosive tendencies at specific TAN also varies with chemical structure of acids present.
Active sulfur species and organic acids can interact to produce ranges of varying corrosion severity.

In some cases, active sulfur can inhibit or promote corrosion (see Figure).
Sulfidic Corrosion – 1

- Occurs by the thermal activation of sulfur species (of which there are hundreds to thousands).
- Two general mechanisms considered involve H₂S as “active” sulfur formed by mercaptan catalysis or by thermal decomposition of organic sulfur species.
- Then, subsequent reaction of “active” sulfur species with materials of construction (normally 0 to 12Cr steels).
- Corrosion severity generally increases with temperature and amount of active sulfur present.
Guidelines for predicting sulfidic corrosion uses the McConomy Curves.

However, they are not representative of systems containing liquid where local turbulence, impingement produce WSS effects elevating corrosion.

This approach does not differentiate “active” sulfur from total sulfur.
Corrosion Prediction Models

- **Modified McConomy Curves:**
  - Show in previous slide; only useful in absence of nap acid and high WSS. Thus, mainly for gas streams and pure sulfidic attack.

- **API 581 Appendix G:**
  - Tables provide notional “corrosion rates” for assessment of corrosion risk and risk-based inspection. Utilizes McConomy for sulfidic baseline. Over simplified flow rate factor. In some cases, little or no data were available for the development of the tables.

- **Predict®-Crude Model:**
  - Software program and prediction model based on laboratory assessment of regimes of sulfidic, nap acid and combined corrosion at high temperature and with velocity. JIP data/model are benchmarked by testing of samples of actual crude fractions.

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Three models benchmarked to testing of crude VGO fraction:

- Mod. McConomy approach non-conservative; resulting from not including nap acid considerations.
- API 581 predictions overly conservative for all alloys; intended for risk assessment NOT material selection.
- Predict-Crude closely predicts corrosion of actual crude fraction based on input of crude and service parameters.

Comparison of laboratory corrosion rate data for VGO (TAN 3, 0.6 wt% S) and prediction methods from API 581, McConomy, and Predict-Crude
Application of 317L Stainless Steel

- Historically, considered the “magic bullet” resisting nap acid and sulfidic corrosion.
- Data generally shows low to negligible corrosion rates for 317L. But, any better than 316L?
- However, many new crude feedstocks including those derived from oil sands bitumen
- Many are high in nap acid and/or sulfur.
- What’s been the service experience? Anything of concern?

Comparison of laboratory corrosion rate data for VGO (TAN 3, 0.6 wt% S) and prediction methods from API 581, McConomy, and Predict-Crude
**Type α nap acid characteristics include:**
- Low molecular weight; ~125 - 425
- Moderate to high solubility in water, moderate to low solubility in oil
- Carboxyl group readily ionizes in aqueous solutions
- Neutralizes to form salts
- Iron naphthenates - highly soluble in oil
- True boiling point up to ~725°F (385°C)
- No protective film formation
- NAC follows classical model

**Type β nap acid characteristics include:**
- High molecular weight, ~325 - 900
- Low solubility in water, high solubility in oil
- Carboxyl group poorly ionizes in aqueous solutions
- Difficult to neutralize
- Iron naphthenates - difficult to form
- True boiling point ~675°F - 1500°F (357°C – 816°C) typically above average crude true boiling point
- Formation of protective and inhibitive film
- Does not follow classical NAC model
Differentiating between Type $\alpha$ and $\beta$ acids in crude oil feedstocks.

- Many classic feedstocks are defined by aggressive Type $\alpha$ acids.
- Several newer sources (e.g. oil sands bitumen) are defined by what appear to be less aggressive Type $\beta$ acids (and contain substantial “active” sulfur that reduces nap acid corrosion.
- This has lead to questioning: Is 317L necessary? Is 317L good enough?

By and large, the industry experience with 317L as been good, but some damage has been reported. Where?

- High flow turbulence and impingement (high WSS).
- High nap acid aggressivity and lack of “active” sulfur under process conditions.
Corrosion of California crude vacuum transfer line, heat exchanger and inside VDU @ TAN 6.1 and 600 F.
- Stream characteristics: aggressive (SJV Crude) with Type α nap acids, low “active sulfur”
- Alternative materials: 904L (4 Mo alloy) and 6XN (6 Mo alloy) performed well.

Other system replaced 317L vacuum transfer line with 317L (w/3.5% min. Mo) and welded with alloy 625 and 371LM (w/4% min. Mo) were successfully utilized in severe nap acid service.

North Sea crude resulted in good service from 317L for 10-15 yrs, but then experienced corrosion. Indicated organic salts/chlorides may be an issue.
Is 317L the “Silver Bullet” for Nap Acid Corrosion?

- **In some specific cases, “No”:**
  - Severe nap acid service in combination with aggressive nap acids, low “active sulfur” and severe turbulence (WSS) conditions may require higher Mo stainless and nickel alloys.
  - In the presence of organic chlorides.
  - Problems in oil sand upgrader in CDU and VDU operations lower alloys were upgraded to alloys 800, 825 and 317L. Failure prone location was return bends in heater tubes. Contribution to attack may be from high velocities combined with fine particulates in stream not found in normal refining operations.

- **In some cases, “Yes”:**
  - Venezuelan crude feedstock with high TAN that also have high sulfur. Alloys in the range 9Cr to 317L performed acceptably.
### 316/317 Failures in Nap Acid Service

<table>
<thead>
<tr>
<th>Location/Unit</th>
<th>Year</th>
<th>Equip/Piping Material &amp; Description</th>
<th>%Mo</th>
<th>Feed</th>
<th>TAN</th>
<th>Temp.</th>
<th>Condensing (Yes/No)</th>
<th>Velocity</th>
<th>Corrosion Rate</th>
<th>Corrosion Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA/Vacuum Flasher</td>
<td>316L</td>
<td>Vacuum transfer line</td>
<td></td>
<td>SJV</td>
<td>5.0</td>
<td>750F</td>
<td>Yes</td>
<td>100 ft/s</td>
<td>5 mpy</td>
<td></td>
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<tr>
<td>CA/Vacuum Flasher</td>
<td>316</td>
<td>Liner in Vacuum column</td>
<td></td>
<td>SJV</td>
<td>4.7</td>
<td>560F</td>
<td>Yes</td>
<td>&lt;10 ft/s</td>
<td>15-20 in liner, 30-40 in weld overlay with diluted Mo</td>
<td></td>
</tr>
<tr>
<td>CA/Vacuum Flasher</td>
<td>317</td>
<td>Liner in Vacuum column</td>
<td></td>
<td>SJV</td>
<td>4.7</td>
<td>560F</td>
<td>Yes</td>
<td>&lt;10 ft/s</td>
<td>Corroded</td>
<td>Used 904L</td>
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<tr>
<td>CA/Vacuum Flasher</td>
<td>316L</td>
<td>Hvy Flash Distillate</td>
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<td>SJV</td>
<td>4.7</td>
<td>560F</td>
<td></td>
<td>13 ft/s</td>
<td>5 mpy</td>
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<tr>
<td>CA/Lube Oil distilling</td>
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<td>Vacuum furnace outlet to column inlet reducer</td>
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<td>SJV</td>
<td>1.8</td>
<td>645F</td>
<td>Yes</td>
<td>180 ft/s</td>
<td>&gt; 30 mpy at welds</td>
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<tr>
<td>316 Vacuum transfer line</td>
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<td></td>
<td>3</td>
<td>400-500 ft/s</td>
<td>Failed</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>317L Mitered elbow vacuum transfer line</td>
<td></td>
<td></td>
<td>5-6</td>
<td>Failed in 4 months</td>
<td></td>
<td></td>
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<tr>
<td>316 vacuum transfer line</td>
<td>86</td>
<td></td>
<td>2.1</td>
<td>400-500 ft/s</td>
<td>Failed</td>
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<tr>
<td>317L vacuum transfer line</td>
<td>94</td>
<td></td>
<td>5-6</td>
<td>Failed in 4 months at elbow</td>
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<tr>
<td>Vacuum Unit</td>
<td>97</td>
<td>317 Column, transfer line, HE’s,</td>
<td>6.1</td>
<td>600F</td>
<td></td>
<td></td>
<td>Corrosion</td>
<td>Upgrade to ALSXN and 904L are working</td>
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</tr>
<tr>
<td>Vacuum Unit</td>
<td>06</td>
<td>317L vacuum bottoms pump</td>
<td>1.1-2.0</td>
<td>700F</td>
<td>No</td>
<td></td>
<td>Suffered fair corrosion in 6 years</td>
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</tr>
</tbody>
</table>

Gallo and Edmondson: NACE #08555
Conclusions – 1

- Common mechanisms of high temperature corrosion in refinery operations:
  - naphthenic acid corrosion,
  - sulfidic corrosion, and
  - interactions which can either accelerate or inhibit corrosion severity.

- Multiple corrosion prediction models are available with varying methodologies.
  - McConomy and API 581 are based on service experience and empirical data
  - Newer models (e.g. Predict®-Crude) is based on extensive data derived from corrosion testing under simulated process conditions.

- The service experience with AISI 317L suggests that it is resistant to corrosion under many conditions involving naphthenic acid corrosion
  - However, there are conditions where it can be subject to degradation.

- AISI 317L appears most susceptible to corrosion under conditions of:
  - high naphthenic acid aggressivity (Type A naphthenic acids), with
  - accompanying low levels of active sulfur in the process environment.
AISI 317L has shown to be less susceptible to corrosion for conditions of:
- high TAN involving less aggressive Type B naphthenic acids in combination with high levels of “active” sulfur
- These conditions are typically found in refining hydrocarbon feeds derived from bituminous oil sands.

Other conditions resulting in failures of 317L equipment used in refinery atmospheric and vacuum distillation service include:
- excessive salts and organic chlorides are present in the process environment, and
- where the process environment contained excessive particulates (sand and fines).

Some refinery applications involving naphthenic acid corrosion have required alloy upgrading to enhance corrosion resistance with higher alloy content (particularly in terms of Ni, Cr, Mo) beyond conventional AISI 317L. These alloys include:
- stainless alloys 904L and 6XN, and
- nickel-based alloys 825, 625 and C-276.