API RP 571 Overview: Damage Mechanisms in the Refining Industry

AFPM Maintenance and Reliability Conference

by

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# Schedule

- Introduction
- Damage Mechanisms - General
- API 571 Overview
- The Crude / Vacuum Unit
- Sulfidation (Sulfidic Corrosion)
- Naphthenic Acid Corrosion (NAC)
- Ammonium Chloride Corrosion
- Hydroprocessing Units
- Ammonium Bisulfide Corrosion
- HTHA
- DMs and Current Initiatives
Refineries constructed out of a wide variety of materials:
- Carbon steel
- Alloy steels (e.g., 1.25Cr-0.5Mo, 9Cr-1Mo)
- Stainless steels (e.g., 300 series and 400 series, duplex)
- Nickel based (e.g. Alloy 625, Alloy 400 or Alloy C276)
- Titanium (e.g. Grade 2 or Grade 12)
- Copper based (e.g. Admiralty brass)

Each material subjected to some form of damage during service exposure
In-Service Damage Types

- General Corrosion
- Localized Corrosion
- Pitting, Crevice, Grooving Corrosion
- Planar Cracks
- Branched Cracks
- Metallurgical Changes & Hydrogen Effects
- Distortion
In-Service Damage Types

General Corrosion

Note uniform thinning
In-Service Damage Types

General Corrosion

• Moderate variability over a large area: +/- 25 mils (0.025 inch / 0.64 mm).
  - High Temperature Sulfur Corrosion
  - H₂ / H₂S Corrosion
  - Oxidation
  - Atmospheric Corrosion

• Usually can address thickness at corrosion monitoring locations (CMLs) with either ultrasonics (UT) or radiography (RT).
In-Service Damage Types

Localized Corrosion
In-Service Damage Types

Localized Corrosion

- High variability of corrosion rate or damage only present in small region.
  - Corrosion Under Insulation (CUI)
  - Sour Water (NH$_4$HS)
  - Naphthenic Acid Corrosion
  - Galvanic Corrosion
  - Erosion/Corrosion
  - Injection Point and Dead-leg Corrosion

- Difficult to handle with CMLs (requires grid, scanning UT, RT, and global methods).
In-Service Damage Types

Pitting Corrosion
In-Service Damage Types
*Pitting, Crevice, and Grooving Corrosion*

- Damage present with a high depth to area ratio.
  - Water services
  - Under deposit corrosion, e.g., amine salts
  - Weld knifeline attack
- Difficult to detect with UT, RT normally required.
In-Service Damage Types

*Planar Cracks*
In-Service Damage Types

Planar Cracks

- Straight, unbranched cracks that normally initiate at a weld.
  - Mechanical fatigue, e.g., cracking at attachments
  - Thermal fatigue
- If the cracks are on the outside surface, NDE typically:
  - MT – Magnetic particle testing
  - PT – Liquid penetrant testing
  - ACFM – Alternating current field measurement
- If the cracks are on the inside surface, NDE typically:
  - UT shearwave, however it is difficult to know where to look.
  - Acoustic emission (AE) may be an option.
In-Service Damage Types

Branched Cracks
In-Service Damage Types

Branched Cracks

- Web-like network of cracks often present in base metal.
  - Chloride or Polythionic Stress Corrosion Cracking (SCC)
  - Amine, Ammonia, Caustic, or Carbonate SCC
  - Liquid Metal Cracking (Hg/Al, Zn/SS)
- If the cracks are on the outside surface NDE typically:
  - MT, PT, and ACFM.
- If the cracks are on the inside surface,
  - UT shearwave, but it is difficult to know where to look.
  - Acoustic Emission (AE) may be an option.
In-Service Damage Types
Metallurgical Changes & Hydrogen Effects
In-Service Damage Types

Metallurgical Changes & Hydrogen Effects

- Hydrogen Induced Cracking (HIC)
- Embrittlement (885°F (475°C), Sigma, Temper Embrittlement)
- Creep
- High Temperature Hydrogen Attack (HTHA)

A combination of the following methods can be used:
- Field Metallography/Replication (FMR)
- Mechanical testing, e.g., hardness testing, impact testing
- NDE, e.g., Ultrasonic Testing (UT), WFMT
In-Service Damage Types

Distortion
In-Service Damage Types

Distortion

- Blistering – damage associated with corrosion product (atomic) hydrogen charging into steel and forming molecular hydrogen at imperfections in the plate.
- Bulging – typically from local hot spots and applied pressure loading.
- Creep – time dependent strain accumulation associated with applied stress at elevated temperatures.
Assessing Damage

- Material - chemistry, heat treatment, strength level, etc.
- Morphology of damage.
- Service exposure - normal (operating conditions, corrosives, concentration) and upset (carryover, fouling, leaking valves).
- How quickly did damage occur?
- Mitigating factors - coking, residual stresses, coatings, chemical additives, water wash.
- Any stream monitoring or other warning systems data (e.g., probes).
- Human factors
- Previous inspections and their effectiveness at targeting the particular mechanisms.
Sources of Damage Information

- API Publications
- National Association of Corrosion Engineers (NACE)
- Welding Research Council (WRC)
- General Publications (e.g., AICHE, Hydrocarbon Processing, Oil & Gas Journal, etc.)
American Petroleum Institute (API)

- API Publications
  - API 571 - Damage Mechanisms
  - API 572 - Inspection of Pressure Vessels
  - API 574 - Inspection Practices for Piping System Components
  - API 575 - Inspection of Atmospheric & Low Pressure Storage Tanks
  - API 579 - FFS, Appendix G
  - API 581 - RBI Technology
  - API 932-B – REAC
  - API 934 A/B/C/D/E – Heavy Wall CrMo
  - API 938-C – Duplex SS
  - API 939-A - Wet H₂S Cracking
  - API 939-B – Repair Strategies for Equipment in Wet H₂S Service
  - API 939-C – Guidelines for Avoiding Sulfidation Corrosion
  - API 939 D & E - Ethanol SCC
  - API 941 - Hydrogen Attack
  - API 945 - Environmental Cracking in Amine Units
NACE International Standards and Publications

- Publication 34105: Effect of Nonextractable Chlorides on Refinery Corrosion and Fouling
- Publication 34109: Crude Distillation Unit – Distillation Tower Overhead System Corrosion
- Publication 34108: Review and Survey of Alkaline Carbonate Stress Corrosion Cracking in Refinery Sour Waters
- Publication 34101: Refinery Injection and Process Mixing Points
- Standard Practice SP0472: Methods and Controls to Prevent In-Service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments
API RP 571 Overview: Damage Mechanisms in the Refining Industry
Overview of RP571

• Purpose of 571
  – To provide information on DM’s to inspection, mechanical and materials personnel
  – To support other existing and developing API inspection-related documents and activities including FFS, RBI
  – Study aid for API Inspector Certifications for 510, 570, 653, etc.

• Content of 571
  – Damage mechanism details
  – PFDs showing where damage occurs
More than 60 damage mechanisms common to the refining and petrochemical industry are included in API 571 – Second Edition April 2011

These can be grouped into five general categories:

1. Corrosion (general and localized)
2. Stress corrosion cracking (environmental)
3. Mechanical
4. Metallurgical
5. Other
## Damage Mechanism Description

**Corrosion**

<table>
<thead>
<tr>
<th>Corrosion Mechanisms</th>
<th>Environmental Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUI</td>
<td>Boiler water/condensate</td>
</tr>
<tr>
<td>Sulfidation</td>
<td>Hot flue gas</td>
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<tr>
<td>Naphthenic Acid</td>
<td>Flue gas dewpoint</td>
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<tr>
<td>High temperature H$_2$/H$_2$S</td>
<td>Galvanic</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>Graphitic corrosion of cast iron</td>
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<tr>
<td>HF</td>
<td>Soil</td>
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<tr>
<td>Amine</td>
<td>CO$_2$</td>
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<tr>
<td>Caustic</td>
<td>Cooling water</td>
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<tr>
<td>HCl</td>
<td>Atmospheric</td>
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<tr>
<td>Oxidation</td>
<td>Biological</td>
</tr>
<tr>
<td>Na/V</td>
<td>Aqueous Organic Acid</td>
</tr>
<tr>
<td>Ammonium Bisulfide</td>
<td></td>
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<tr>
<td>Ammonium Chloride</td>
<td></td>
</tr>
</tbody>
</table>
Damage Mechanism Description

Stress Corrosion Cracking

- Caustic
- Amine
- Carbonate
- Polythionic
- Chloride
- Sulfide
- Liquid Metal Cracking
- Ethanol
- Sulfate
Damage Mechanism Description

Mechanical Mechanisms

- Mechanical fatigue
- Thermal fatigue
- Brittle fracture
- Creep and stress rupture
Damage Mechanism Description

Metallurgical Mechanisms

- Sigma Phase embrittlement
- 885 Embrittlement
- Graphitization
- Spheroidization
- Temper embrittlement
Damage Mechanism Description

Other Mechanisms

- Hydriding
- HIC/SOHIC
- Corrosion fatigue (deaerators)
- **High Temperature Hydrogen Attack (HTHA)**
- Dealloying
- Cavitation
- Erosion
- Reheat Cracking
- Carburization
- Metal dusting
- Nitriding
- Gaseous Oxygen Enhanced Ignition & Combustion
Organization of 571

- Description of Damage
- Affected Materials
- Critical Factors
- Affected Units or Equipment
- Appearance or Morphology of Damage
- Prevention/Mitigation
- Inspection & Monitoring
- Related Mechanisms
- References
2.4.1 Sulfidation

2.4.1.1 Description of Damage
Corrosion of carbon steel and other alloys resulting from their reaction with sulfur compounds in high temperature environments. The presence of hydrogen accelerates corrosion.

2.4.1.2 Affected Materials
a) All iron based materials including carbon steel and low alloy steels, 300 Series SS, and 400 Series SS.
b) Nickel base alloys are also affected to varying degrees depending on composition, especially chromium content.
c) Copper base alloys form sulfide at lower temperatures than carbon steel.

2.4.1.3 Critical Factors
a) Major factors affecting sulfidation are alloy composition, temperature, and concentration of corrosive sulfur compounds.
b) Susceptibility of an alloy to sulfidation is determined by its ability to form protective sulfide scales.
c) Sulfidation of iron-based alloys usually begins at metal temperatures above 500°F (260°C). The typical effects of increasing temperature, chromium content, and sulfur content on metal loss are shown in Figure 2.4.2.1 and Figure 2.4.2.2.
d) In general, the resistance of iron and nickel base alloys is determined by the chromium content of the material. Increasing the chromium content significantly increases resistance to sulfidation. 300 Series SS, such as Types 304, 316, 321, and 347, are highly resistant in most refining process environments. Nickel base alloys are similar to stainless steels in that similar levels of chromium provide similar resistance to sulfidation.
2.4.1.4 Appearance or Morphology of Damage

a) Depending on service conditions, corrosion is most often in the form of uniform thinning but can also occur as localized corrosion or high velocity erosion-corrosion damage.

b) A sulfide scale will usually cover the surface of components. Deposits may be thick or thin depending on the alloy, corrosiveness of the stream, fluid velocities, and presence of contaminants. (See Figure 2.4.2.3.)

2.4.1.5 Prevention / Mitigation

a) Resistance to sulfidation is generally achieved by upgrading to a higher chromium alloy.

b) Piping and equipment constructed from solid or clad 300 Series SS or 400 Series SS can provide significant resistance to corrosion.

c) Aluminum diffusion treatment of low alloy steel components is sometimes used to reduce sulfidation rates and minimize scale formation, however, it may not offer complete protection. 300 Series SS catalyst support screens in hydroprocessing reactors can also be treated to prolong life.

2.4.1.6 Inspection and Monitoring

a) Process conditions should be monitored for increasing temperatures and/or changing sulfur levels.

b) Temperatures can be monitored through the use of tubeskin thermocouples and/or infrared thermography.

c) Evidence of thinning can be detected using external ultrasonic thickness measurements and profile radiography.
2.4.1.7 Related Mechanisms

Sulfidation is also known as sulfidic corrosion. High temperature sulfidation in the presence of hydrogen is covered in High Temp H\textsubscript{2}/H\textsubscript{2}S Corrosion (Section 3.1.1.5).

2.4.1.8 References


Process Descriptions

- Simplified Process Flow Diagrams (PFDs) with primary damage mechanism locations:
  - Crude Unit / Vacuum
  - Delayed Coker
  - Fluid Catalytic Cracking
  - FCC Light Ends Recovery
  - Catalytic Reforming – CCR
  - Catalytic Reforming – Fixed Bed
  - Hydroprocessing Units – Hydrotreating, Hydrocracking
  - Sulfuric Acid Alkylation
  - HF Alkylation
  - Amine Treating
  - Sulfur Recovery
  - Sour Water Stripper
  - Hydrogen Reforming
  - Isomerization
  - Visbreaker
  - Caustic Treating
API RP 571 Overview: Damage Mechanisms in the Refining Industry

The Crude/Vacuum Unit
In the Crude/Vacuum Unit preheated crude oil is treated to remove salts and then further heated to facilitate separation of the hydrocarbon (crude oil) in a distillation tower.
- Different fractions (cuts/product streams) are drawn off after condensing.
- Each of these streams is subsequently processed in downstream units.

Note: the final distillation steps are performed under vacuum conditions to maximize liquid recovery.
Crude Unit Feed and Products

- Feed Stream:
  - Crude Oil

- Products:
  - LPG (Liquefied Petroleum Gas), e.g. propane and butane
  - Naphtha
  - Kerosene/Jet Fuel
  - Diesel/Atmospheric Gas Oil
  - Crude Tower Bottoms (Atmospheric Resid)
  - Vacuum Gas Oils (e.g., LVGO, MVGO, HVGO)
  - Vacuum Tower Bottoms (Vacuum Resid)
## Other Primary Streams

- Desalter wash water
- Caustic (optional)
- Chemical treatments
  - Filming amines
  - Neutralizers
  - Demulsifiers
- Tower overhead wash water (optional)
Contaminants

- S - promotes sulfidation.
- Naphthenic acid (organic acids) - causes corrosion.
- Chlorides - forms HCl, ammonium chloride, amine hydrochloride.
- NaOH (caustic) - poisons FCC catalyst and can lead to coking.
- Nitrogen - contributes to ammonia formation.
<table>
<thead>
<tr>
<th>Some Process Parameters Affecting Damage</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Metal temperature (sulfidation).</td>
</tr>
<tr>
<td>- Velocity (naphthenic acid).</td>
</tr>
<tr>
<td>- Desalter efficiency (chloride removal)</td>
</tr>
<tr>
<td>- Desalter wash water pH (NH₃ in crude).</td>
</tr>
<tr>
<td>- pH in crude tower reflux drum (HCl formation).</td>
</tr>
<tr>
<td>- Reflux temperature (shock condensation)</td>
</tr>
</tbody>
</table>
### Materials of Construction

- CS
- Low alloy steels (5Cr, 9Cr)
- High alloy (12Cr) stainless steels, e.g., 410, 405, 410S
- Austenitic stainless steels, e.g., 304, 316, 317
- Nickel copper/nickel moly alloys, e.g., Alloy 400, Alloy C-276
- Titanium
Primary Damage Mechanisms

- Sulfidation
- Naphthenic Acid Corrosion (NAC)
- HCl Corrosion
- Ammonium Chloride Corrosion
- 885°F Embrittlement
API RP 571 Overview: Damage Mechanisms in the Refining Industry

Sulfdation (Sulfidic Corrosion)
Sulfidation refers to the corrosion of CS and other metallic materials resulting from their reaction with sulfur compounds in high temperature (hydrogen free) environments.

Note: The presence of hydrogen accelerates corrosion and creates a different corrosion mechanism ($H_2/H_2S$) than addressed in this discussion.
Affected Materials

- Carbon steel
- Low alloy steels
- 300 Series SS
- 400 Series SS
- Nickel base alloys
Sulfidation Failure of NPS 8 CS Pipe

Note uniform thinning
Critical Factors

- Major factors are alloy composition, temperature and concentration of corrosive sulfur compounds as shown in the Modified McConomy curves.
  - Increasing Cr content improves corrosion resistance.
  - Corrosion increases at temperatures >500°F (260°C).
  - While crude oils contain many different sulfur compounds, sulfidation is primarily caused by H₂S and other reactive sulfur species as a result of the thermal decomposition of sulfur compounds at high temperatures.
- It can be misleading to predict corrosion rates based on total (weight %) sulfur alone since some compounds react more readily to form H₂S. However, the Modified McConomy curves are based on total sulfur.
Critical Factors

- Susceptibility of an alloy is determined by its ability to form protective sulfide scales.

- Sulfide scales offer varying degrees of protection depending on the alloy and the severity of the process stream.
  - The 400 series (e.g., 405, 410, 410S) and especially the 300 series SS (e.g., 304, 316, 321, 347) are highly resistant.

- Carbon steel with <0.10% Si (e.g., A53 piping) is susceptible to higher rates of corrosion than steels with >0.10% Si (e.g., A106 piping).
FCC Bottoms Piping – Failure of Low Si Component at ~650°F (340°C)
Actual Failure Shown in Previous Slide
API 939-C Sulfidation Impact of Si

Figure C.1—Corrosion Rate vs Si Content for FCC Slurry Carbon Steel Piping Failure (Shown in Figure 3 and Figure 4), (Operating Conditions: 150 psig and 650 °F to 700 °F)
Affected Units or Equipment

- Piping and equipment in high temperature environments where sulfur-containing streams are processed.
- Common areas of concern are the crude/vacuum, FCC, coker, visbreaker and feed system of hydroprocessing units.
- Heaters fired with oil, gas, coke and most other sources of fuel may be affected depending on sulfur levels in the fuel.
- Boilers and high temperature equipment exposed to sulfur-containing gases can be affected.
Appearance or Morphology of Damage

- Most often in the form of uniform thinning, but also occurs as localized corrosion or high velocity erosion-corrosion damage.
- A sulfide scale will usually cover the surface. Deposits may be thick or thin depending on the alloy, corrosiveness of the stream, and fluid velocities.
Prevention/Mitigation

- Resistance to sulfidation is generally achieved by upgrading to a higher chromium alloy.
  - Upgrading to 300 Series SS or 400 Series SS can provide significant resistance to corrosion.

- Aluminum diffusion treatment of low alloy steel components is sometimes used to reduce sulfidation rates and minimize scale formation. However, it may not offer complete protection.
Inspection and Monitoring

- Inspection
  - Conduct thickness surveys
  - Proactive and retroactive PMI recommended to check for alloy mix-ups

- Operations
  - Monitor process conditions for increasing temperature or changes in sulfur content
Key References

- NACE Publication 34103 – Overview of Sulfidic Corrosion in Petroleum Refining
- API RP 939-C – Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries
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Naphthenic Acid Corrosion (NAC)
Description of Damage

- Naphthenic acid corrosion is a form of high temperature corrosion that occurs primarily in crude and vacuum units.
  - Also noted in downstream units that process certain fractions or cuts that contain naphthenic acids, e.g., hydrotreating and lubes processing.
## Affected Materials

- Carbon steel
- Low alloy steels
- 400 Series SS
- 300 Series SS
- Nickel base alloys
### Critical Factors

- **NAC** is a function of the specific naphthenic acids present (molecular weight), temperature, sulfur content, velocity and alloy composition.

- **Naphthenic acid content**: Reported as Neutralization Number (Neut Number) or Total Acid Number (TAN). These are measures of the acidity (organic acid content) as determined by ASTM test methods, e.g. ASTM D-664.

- **Temperature**: Normally occurs in streams above 425°F (218°C) but has been reported down to 350°F (177°C). Severity increases with temp up to about 750°F (399°C).

- **Sulfur Content**: Promotes iron sulfide formation and can have an inhibiting effect on NAC.
Critical Factors

- **Velocity**: Corrosion is most severe in two phase (liquid and vapor) flow, in areas of high velocity or turbulence and in distillation towers where hot vapors condense to form liquid phase droplets, e.g., at the underside of trays. Note: Recent JIP laboratory studies have highlighted the importance of wall shear stress vs velocity.

- **Alloy Composition**: Increasing amounts of molybdenum show improved resistance. A minimum of 2% to 2.5% is required depending on the aggressiveness (TAN?) of the whole crude and its side cuts, i.e., 316SS (2-3% Mo) or 317SS (3-4% Mo).
<table>
<thead>
<tr>
<th>Alloys Listed In Approximate Order of Increasing Resistance to NAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS</td>
</tr>
<tr>
<td>5Cr-0.5Mo, 12Cr</td>
</tr>
<tr>
<td>9Cr-1Mo, 304L SS, 321SS, 347 SS</td>
</tr>
<tr>
<td>316 SS</td>
</tr>
<tr>
<td>317 SS</td>
</tr>
<tr>
<td>6% Mo Alloys</td>
</tr>
<tr>
<td>Alloy 625, Alloy 276</td>
</tr>
</tbody>
</table>
Critical Factors

- The TAN of the crude may be misleading because this family of acids has a range of boiling points and tends to concentrate in various cuts. Important to measure TAN in cuts of interest.

- No widely available prediction methods (other than industry JIP) have been developed to correlate corrosion rate with the various factors influencing it.

- Severity of corrosion often (but not always) increases with increasing TAN of the hydrocarbon phase.
  - The various acids which comprise the naphthenic acid family can have distinctly different corrosivity.

- Historically, TAN values <0.5 were not considered corrosive. However, NAC can be a problem with low sulfur crudes (<0.5 wt% S) with TANs as low as 0.10.
Critical Factors

- NAC is associated with hot liquid hydrocarbon streams. Normally not seen in all vapor phase.
- Naphthenic acids remove protective iron sulfide scales on the surface of metals – forms iron naphthenate.
- Naphthenic acids are destroyed in FCCU units.
- Data suggests that all austenitic stainless steels are unaffected after the point of hydrogen injection in hydroprocessing units.
NAC in Vacuum Heater 5 Cr Outlet Elbow
NAC of 12 Cr Bubble Caps and Trays in HVGO Section of Vacuum Tower
Affected Units or Equipment

- Crude Unit, VGO Hydrotreaters (e.g., CFHU), Lube Unit - extract circuit.
- Crude & vacuum heater tubes, transfer lines, vacuum btms piping, AGO circuits, HVGO circuits (sometimes LVGO), pump internals.
- Piping systems, e.g., valves, elbows, tees and reducers as well as areas of flow disturbance such as weld beads and thermowells.
- Crude and vacuum tower may also be corroded in the flash zones, along with packing and internals where high acid streams condense or high velocity droplets impinge.
Appearance or Morphology of Damage

NAC is characterized by:

- Localized corrosion.
- Pitting, especially in low velocity condensing systems.
- Flow induced grooving in high velocity areas, e.g., bear claws.
Prevention/Mitigation

- For units and/or components which have not been designed for NAC, the options are:
  - Reduce NAC by blending crude to reduce the TAN and/or increase the sulfur content.
  - Use NAC chemical inhibitor. Especially useful for intermittent processing of high TAN crudes; inhibitor effectiveness needs to be monitored carefully.
  - For severe conditions, Type 317L stainless steel or other alloys with higher molybdenum content may be required.
Inspection and Monitoring

**Inspection:**
- Localized damage is difficult to find so RT should be the primary detection method followed by UT thickness measurement.
- Use electrical resistance corrosion probes and corrosion coupon racks.
- Hydrogen flux probes have also been used to detect hydrogen activity which may be indicative of NAC.

**Operations:**
- Monitor TAN and sulfur content of the crude charge and side streams to determine the distribution of acids in the various cuts.
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Ammonium Chloride Corrosion
Ammonium chloride corrosion is typically a localized damage mechanism that occurs under salt deposits of ammonium chlorides. It results in pitting and frequently occurs in the absence of a water phase.

Note: Amine salts can form from over-injection of amine based inhibitors and can also contribute to under deposit pitting.
Affected Materials

In order of increasing resistance:

- Carbon steel and low alloy steels
- 300 Series SS and 400 Series SS
- Alloy 825
- Alloy 625 and C276
- Titanium

Note: Duplex SS (i.e., 2205) can be no better than CS
Critical Factors

- Concentration of NH₃ and chlorides.
- Temperature:
  - Can deposit well above the water dewpoint – up to about 400°F (204°C).
  - Corrosion rates increase with increasing temperature.
- Availability of moisture - the salt is hygroscopic and will readily absorb water producing corrosion rates >100 mpy (>2.5mm/yr).
- Salts are highly water soluble and can be flushed away by a water wash.
Affected Units

- Crude tower overheads.
- FCCU and Coker fractionator overheads and top pumparound.
- Catalytic reforming effluent streams and overheads from light ends towers.
- Hydroprocessing reactor effluent streams, e.g., naphtha and kero hydrotreaters.
Appearance or Morphology of Damage

- Salts may have been removed during clearing operations prior to opening equipment, and hence are not always seen.

- When present, salts are typically white or brown. Often a voluminous FeS / FeCl₂ scale is observed.

- Corrosion is typically evident as localized pitting.
Prevention/Mitigation

- Select alloys with adequate resistance to corrosion.
- Use water washing if possible.
- Consider use of filming amines.
- Limit the volume of chlorides in the unit through treatment of the feeds, e.g., desalting in crude units, chloride traps in reforming hydrogen feed to hydroprocessing.
Inspection and Monitoring

- **Inspection:**
  - Inspection is difficult due to localized nature of deposits, consequently, RT often more suitable than UT.

- **Operations:**
  - Steward wash water injection sites to ensure adequate water flow.
  - Monitor for delta P buildup as an indicator of salting. Carbon steel exchanger bundles may be packed solid with FeS / FeCl₂ scale resulting from corrosion.
  - Work with chemical vendor to develop ionic model to establish salt deposition temperatures for monitoring.
API RP 571 Overview: Damage Mechanisms in the Refining Industry

Hydroprocessing Units
Hydroprocessing involves a reaction between hydrocarbon feed and hydrogen over a catalyst at elevated temperatures:

- Removes sulfur and nitrogen to produce a clean product.
- Cracks the feed into higher value fractions (hydrocracking).
Hydroprocessing Feed and Products

- **Feed Streams:**
  - Naphtha
  - Diesel
  - Vacuum Gas Oils (e.g., LVGO, MVGO, HVGO)
  - Crude Tower Bottoms (Atmospheric Residue)
  - Vacuum Tower Bottoms (Vacuum Residue)

- **Products:**
  - Low sulfur hydrocarbons (desulfurization)
  - Low nitrogen hydrocarbons (de-nitrification)
  - Cracked products (via Hydrocracking) and light ends
PFD

Hydroprocessing Units - Hydrotreating, Hydrocracking

Key to Damage Mechanisms

1. Sulfidation
2. Wet H2S Damage (Blistering/HIC/304MC/SSC)
3. Creep / Stress Rupture
4. High Temp H2/H2S Corrosion
5. Polythionic Acid Cracking
6. Naphthenic Acid Corrosion
7. Ammonium Bisulfide
8. Ammonium Chloride Corrosion
9. HCl Corrosion
10. High Temperature Hydrogen Attack
11. Temper Embrittlement
12. Erosion / Erosion-Corrosion
13. Amine Corrosion
14. Chloride Stress Corrosion Cracking
15. Hydrogen Embrittlement
16. Short Term Overheating - Stress Rupture
17. Brittle Fracture
18. Sigma Phase/ Chi Embrittlement
19. Rehct Crocking
20. Amine Corrosion
21. Corrosion Under Insulation (CUI)
Contaminants

- S - contributes to sulfidation prior to the reactor.
- H$_2$S - combines with ammonia to form ammonium bisulfide.
- Nitrogen - forms ammonia and combines with H$_2$S to form ammonium bisulfide or with chlorides to form ammonium chloride.
- Chlorides (organic and inorganic) - forms HCl and ammonium chloride.
Some Process Parameters Affecting Damage

- $H_2$ partial pressure
- Temperature
- Wash water quality
- Recycle hydrogen purity (chloride content, $H_2S$ content)
- $H_2S$ and $NH_3$ content
Guidelines on wash water quality found in API RP932-B, e.g.,:

- $\text{O}_2 < 50 \text{ ppb}$
- $\text{Fe} < 1 \text{ ppm}$
- $\text{Cl}^- < 100 \text{ ppm}$
Materials of Construction

- CS
- 1.25Cr-0.5Mo
- 2.25Cr-1Mo
- Enhanced CrMo’s e.g., 3%Cr
- Austenitic stainless steels, e.g., 304, 304L, 321, 347
- Duplex SS
- Ferritic Stainless Steels, e.g., 410S, 405
Primary Damage Mechanisms

- HTHA
- H₂/H₂S Corrosion
- Wet H₂S Corrosion (HIC / SOHIC)
- Ammonium Bisulfide
- Ammonium Chloride
- Temper Embrittlement
- Polythionic Acid Stress Corrosion Cracking (PASCC)
- Chloride SCC
- Wash Water Injection Point Corrosion
API RP 571 Overview: Damage Mechanisms in the Refining Industry

Ammonium Bisulfide (NH₄HS) Sour Water Corrosion
Description of Damage

- Sour water corrosion refers to aggressive localized corrosion in cooler portions of hydroprocessing reactor effluent streams and in units handling alkaline waters containing H$_2$S.
  - Nitrogen in the process stream is converted to ammonia and reacts with H$_2$S to form NH$_4$HS.
  - NH$_4$HS sublimes out of the gas phase at temps below about 250° F (121° C). The actual temperature is dependant on the concentration of NH$_3$ and H$_2$S.
  - May cause fouling/plugging unless flushed away with wash water or condensed process water.
Affected Materials

- CS - most commonly used in this service due to low operating temperatures.
- 300 Series SS.
- Duplex SS.
- Alloy 825, Alloy 625 and other high nickel alloys - very resistant.
Critical Factors

- Critical factors include NH₄HS concentration, velocity and/or localized turbulence /wall shear stress, temperature, and flow distribution.

- NH₄HS Concentration: Historical “rules of thumb” -- Corrosion increases with increasing NH₄HS concentration and increasing velocity.
  - At < 2 wt%, solutions are not generally corrosive. CS typical.
  - Above 2 wt%, solutions are increasingly corrosive. Velocity controls with CS important.
  - Above 8 wt %, corrosion of CS expected to be severe. Alloys normally required.
Critical Factors

- **Velocity:** Limit flow in CS piping to 20 fps (6 mps) maximum.

- **Temperature:** Deposits occur below the NH₄Cl deposition temperature. If below the water dewpoint, salts are typically flushed away by condensed process water so solid salt deposits may not be observed.

- **Wash water flow distribution:** Uniform distribution critical to ensure adequate dilution and flushing of salts.
Affected Units or Equipment

- Hydroprocessing Units - Critical areas include:
  - Inlet and outlet piping of air coolers (REAC) and condensers.
  - Air cooler header boxes and tubes (also S&T HX).
  - Sour water draw piping from reactor effluent separators; flashing may cause severe erosion-corrosion downstream of control valves.
  - Vapor line from the high pressure separators (if water condenses prior to desired point).
  - HC lines from reactor effluent separators due to entrained sour water.
  - Stripper Column overhead.
Affected Units and Equipment

- FCC Units: NH$_4$HS concentrations are usually less than 2 wt % in fractionator overhead and downstream light ends, but high velocities and/or the presence of cyanides can remove protective iron sulfide scales.

- Sour Water Strippers (SWS): High concentrations of NH$_4$HS in stripper overhead affects piping, condensers, accumulator and reflux circuit. Note possible presence of cyanides.

- Amine Units: High concentrations of NH$_4$HS may be found in regenerator overheads. Extent of corrosion may resemble SWS depending on unit operation.

- Delayed Coker: High concentrations of NH$_4$HS may be found in the gas concentration plant downstream of the fractionator tower.
Appearance or Morphology of Damage

- General loss in thickness of CS with the potential for extremely high localized rates of wall loss at changes in direction or turbulent flow areas with >2 wt % concentration.
- Localized under-deposit corrosion if insufficient water is available to dissolve the NH$_4$HS salts.
- Heat exchangers may show plugging or loss of duty from fouling.
2” CS Elbow in Sour Water Line from Cold HPS in HDS Unit
Piping Section of 2” CS Sour Water Line from Cold HPS in HDS Unit
Prevention/Mitigation

- Good design practice with symmetrical and hydraulically balanced flow in and out of air coolers.
- Monitor for change in process conditions, e.g., flow velocities, particularly as the NH$_4$HS concentration exceeds 2 wt% for CS and begins to approach 8 wt%.
- Maintain velocities within industry guideline of 20 fps (6 mps) maximum for CS. CS may be susceptible to high corrosion rates at higher velocities.
Prevention/Mitigation

- Use resistant materials of construction (e.g. Alloy 825, Alloy 625) at velocities > 20 fps (6 mps) depending on NH₄HS concentration.
  - Titanium and Alloy C276 have been used in overhead condensers in SWS units.
  - Aluminum also used in some SWS. Exchanger tubes are extremely susceptible to erosion-corrosion damage.

- Properly design wash water distribution system.
  - Symmetrical HX design important.
  - Use injection spray nozzles, flow control and appropriate metallurgy.
  - Maintain water wash injection with low O₂ content.
  - Provide excess water to ensure adequate dilution. Target for 25% excess water.
Inspection and Monitoring

**Inspection:**
- Plans should include input from process and materials/corrosion engineers to determine specific areas of vulnerability.
- UT scanning and/or RT profile thickness of high velocity areas.
- UT / RT downstream of control valves at high NH$_4$HS concentrations.
- IRIS, RFEC and flux leakage inspection of CS finfan tubes.
- Eddy Current (EC) inspect non-magnetic finfan tubes.

**Operations:**
- Determine NH$_4$HS content through sampling and/or calculation.
- Monitor water injection facilities and flow meters to ensure proper operation.
Key References

API RP 571 Overview: Damage Mechanisms in the Refining Industry

High Temperature Hydrogen Attack (HTHA)
Description of Damage

- HTHA refers to decarburization, fissuring and cracking resulting from exposure to hydrogen at elevated temperatures and pressures.
  - H reacts with carbides in steel to form methane, CH$_4$, which cannot diffuse out of the steel.
  - The loss of carbide causes an overall loss in strength and methane causes internal stress (very similar to creep).
  - Methane pressure builds up, forming bubbles or cavities, microfissures and finally fissures that combine to form cracks.
  - Failure occurs when the cracks reduce the load carrying ability of the component.
Affected Materials

- CS
- C-0.5Mo, Mn-0.5Mo
- 1Cr, 1.25Cr
- 2.25Cr
Critical Factors

- For specific material, HTHA f (temperature/hydrogen partial pressure/time/stress).
  - Higher temperatures generally more severe.
  - A temperature/hydrogen partial pressure safe operating envelope for carbon and low alloy steels based on experience is found in ARI RP 941. These are referred to as the “Nelson Curves”.
  - Service exposure time is cumulative.
  - Attack typically slow, appears to have incubation period before properties are affected. May vary from hours to many years depending on operating conditions.
  - Typically, both base metals and HAZ are affected.
- 300 Series SS, as well as 5, 9, and 12 Cr alloys, are not susceptible to HTHA at conditions normally seen in refinery units.
What is Partial Pressure?

- **Partial Pressure** = that part of the total pressure exerted by each component in a gaseous mixture. The effective partial pressure depends on the amount of the component (e.g., H₂ gas) in the mixture.
Affected Units or Equipment

- Hydroprocessing units, such as hydrotreaters (desulfurizers) and hydrocrackers.
- Catalytic reformers.
- Hydrogen plants/pressure swing absorption units.
Appearance or Morphology of Damage

- Damage moves from ID through the wall.
- Surface decarburization often observed.
- Early stages of damage (bubbles / voids) can be detected with scanning electron microscopy (SEM) 15,000X. May resemble creep damage.
- Advanced stages (fissuring and cracking) can be found by metallography. The damage is typically intergranular.
- In rare cases, blisters are observed.
A Normal Carbon Steel Microstructure Showing Ferrite and Pearlite
A CS Pipe Section Showing Decarburization Along Pipe ID Surface
A C-0.5Mo Steel Illustrating Decarburization, Fissures & Cracks

Pearlite – alternating layers of ferrite and carbide
Localized Damage (Decarb and Cracking) Adjacent to Weld Heat Affected Zone
Prevention/Mitigation

- Use alloy steels with higher levels of Cr and Mo to increase carbide stability.
  - Note C-0.5 Mo design curve was eliminated in 1990 4th Edition of API 941 and should not be used for new equipment.

- Add a safety factor of 25-50°F (14-28°C) to temperature during design.

- 300 Series SS overlay and/or roll bond clad material will reduce the pp H₂; not used in design, but for inspection/FFS.
**Inspection and Monitoring**

### Inspection

- Advanced stages of damage in many cases appear to be localized, challenging the ability of inspection.
- Ultrasonic techniques (AUBT) consisting of a combination of backscatter, velocity ratio, and spectral analysis have been the most successful in finding fissuring and/or serious cracking.
- FMR can only detect fissuring and decarburization near the surface. Most equipment has decarburized surfaces due to the various heat treatments used during fabrication. Selective sample removal may be an option.
- VT for blisters on ID may indicate potential HTHA, but HTHA does not require blisters.

### Operations:

- Be aware of process creep that can result in higher operating temperatures.
Miniature Sample for HTHA Analysis
Key References

- API RP 941 – Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants
API RP 571 Overview: Damage Mechanisms in the Refining Industry

Influence of Damage Mechanisms on Current Initiatives
Current Initiatives

- Risk Based Inspection (RBI)
- Integrity Operating Windows (IOWs)
- Fitness for Service (FFS)
- Fixed Equipment Mechanical Integrity (FEMI)
Risk Based Inspection (RBI)

- Evaluate equipment’s ability to resist relevant damage mechanisms over a specified interval
- Risk determined based on assumptions of future operation
- RBI used to develop effective inspection plans to mitigate risk to an acceptable level
RBI/Damage Mechanisms

• Crude/Vacuum Unit
  – Sulﬁdation: Damage uniform. Enables prediction of remaining life through measured or estimated corrosion rates.
  – Naphthenic acid: Damage localized. Assessment is subjective with reliance on experience.
  – Ammonium chloride: Damage localized. Assessment is subjective with reliance on experience.
RBI/Damage Mechanisms

- Hydroprocessing
  - Ammonium Bisulfide: Damage localized. Assessment is subjective with reliance on experience
  - HTHA: Damage localized. RBI best suited for high level screening rather than typical assessment. Will likely require detailed engineering review outside of the RBI study to better quantify damage potential
Integrity Operating Windows (IOWs)

- API 584 Integrity Operating Windows, First Edition May 2014
- IOWs intended to place limits on those variables that directly influence corrosion
- Knowledge of existing damage mechanisms critical in setting limits
  - Limits influenced by materials of construction
  - Unit operations
- Feeds into overall mechanical integrity program for vessels and piping
Integrity Operating Windows (IOWs)

- Note: If they are already established at the time of RBI implementation, IOWs can be used to:
  - Protect the integrity of the RBI analysis by ensuring that assumptions, e.g. temperature and sulfur content, remain valid
  - Alert FE stakeholders if the RBI premise has been violated which might require changes to the inspection plan
IOWs/Damage Mechanisms

- Crude/Vacuum Unit - typical IOW controls include:
  - Sulfidation
    - Feed and stream sulfur levels
    - Operating temperatures
  - Naphthenic Acid
    - TAN in feed and relevant bottoms and side streams
    - Sulfur in feed and relevant bottoms and side streams
  - Ammonium Chloride
    - Salt deposition temperature
    - Wash water injection rates
IOWs/Damage Mechanisms

- Hydroprocessing – typical IOW controls include:
  - Ammonium Bisulfide
    - Concentration of $\text{NH}_4\text{HS}$
    - Velocity (wall shear stress)
    - Wash water injection rates
  - HTHA
    - Operating temperature
    - Hydrogen partial pressure
Fitness for Service (FFS)

- FFS provides methodology to evaluate existing damage to determine if component is suitable for continued service.
- Must understand the damage mechanism that created the problem and how damage will progress.
- Assessments address various DM including general thinning, localized thinning, pitting, brittle fracture, blistering, etc.
Fitness for Service/Damage Mechanisms

- **Crude/Vacuum Unit**
  - Sulfidation: general thinning
  - Naphthenic acid: local thinning
  - Ammonium chloride: pitting

- **Hydroprocessing**
  - Ammonium Bisulfide: local thinning
  - HTHA: not well addressed by current technology, but methodologies being developed
Fixed Equipment Incident Investigation

- API 585 – Pressure Equipment Integrity Incident Investigation, First Edition April 2014
- Must understand damage mechanisms to:
  - Identify factors contributing to failure,
  - Recommend effective solutions,
  - Modify inspection plans.
Summary

- Industry documents and practices dealing with mechanical integrity of refining equipment (e.g., IOWs, RBI, FFS) place heavy reliance on understanding damage mechanisms.
- API 571 provides guidance on the DM influencing refining equipment and directly supports the FEMI initiative.