Corrosion and Other Failures

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Purpose

• Brief overview of the types of corrosion and other deterioration mechanisms active in typical refinery processes

• Discussion of corrosion and other types of damage occurring at high and low temperature conditions

• Description of low and high temperature corrosion principles and the process conditions that drive them
Low Temperature Corrosion

- Below 500°F (260°C)
- Presence of water (even in very small amounts)
- Electrolyte in hydrocarbon stream
- Obeys electrochemical laws
- Stable films can reduce or prevent corrosion
- Vapor streams - at water condensation points
High Temperature Corrosion

- Above 500°F (260°C)
- No water present
- Result of a reaction between metal and process ions (such as oxygen, sulfur, etc.)
Causes of Deterioration

- Normal operation, upset, startup/shutdown conditions
- Refineries contain over (15) different process units
- Material/Environment condition interactions
- Many combinations of corrosive process streams and temperature/pressure conditions
- In the absence of corrosion, mechanical and metallurgical deterioration can occur
Types of Damage

- General loss due to general or localized corrosion
- Stress Corrosion Cracking
- High Temperature Hydrogen Attack (HTHA)
- Metallurgical Changes
- Mechanical Failures
- Other Failures

Damage types occur with specific combinations of materials and environmental/operating conditions
Corrosion Principles

- Corrosion rate is measured as **weight loss per unit area** and is expressed in mils per year (mpy)
- Rates can be affected by:
  - Passivity forming protective surface films (including corrosion inhibitors, paints and coatings)
  - Oxygen content
  - Flow velocity/rates
  - Temperature
  - Acidic conditions
Process Corrosion
Low Temperature Conditions

- Not caused by hydrocarbons
- Caused by inorganic compounds such as water, hydrogen sulfide, hydrogen chloride, sulfuric acid, etc.
- Crude oil contaminants
- Process chemicals
Process Corrosion
High Temperature Conditions

- Important due to serious consequences
- High temperatures usually involve high pressures
- Dependent on the nature of the scale formed
  - general thinning
  - localized thinning (pitting)
  - intergranular attack
  - mixed phase flow
- Corrosion due to sulfur compounds most common and well documented
# Corrosives Found in Refining Processes

<table>
<thead>
<tr>
<th>Corrosive</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>Present in raw crude. It causes high-temperature sulfidation of metals, and it combines with other elements to form aggressive compounds, such as various sulfides and sulfates, sulfuric, polythionic, and sulfuric acids.</td>
</tr>
<tr>
<td>Naphthenic Acid</td>
<td>A collective name for organic acids found primarily in crude oils from western United States, certain Texas and Gulf Coast and a few Mid-East oils.</td>
</tr>
<tr>
<td>Polythionic Acid</td>
<td>Sulfurous acids formed by the interaction of sulfides, moisture, and oxygen, an occurring when equipment is shutdown.</td>
</tr>
<tr>
<td>Chlorides</td>
<td>Present in the form of salts (such as magnesium chloride and calcium chloride) originating from crude oil, catalysts, and cooling water.</td>
</tr>
</tbody>
</table>
## Corrosives Found in Refining Processes

<table>
<thead>
<tr>
<th>Substance</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>Occurs in steam reforming of hydrocarbon in hydrogen plants, and to some extent in catalytic cracking. CO₂ combines with moisture to form carbonic acid.</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Nitrogen in feedstocks combines with hydrogen to form ammonia - or ammonia is used for neutralization - which in turn may combine with other elements to form corrosive compounds, such as ammonium chloride.</td>
</tr>
<tr>
<td>Cyanides</td>
<td>Usually generated in the cracking of high-nitrogen feedstocks. When present, corrosion rates are likely to increase.</td>
</tr>
</tbody>
</table>
# Corrosives Found in Refining Processes

<table>
<thead>
<tr>
<th>Corrosive</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrogen Chloride</strong></td>
<td>Formed through hydrolysis of magnesium chloride and calcium chloride, it is found in many overhead (vapor) streams. On condensation, it forms highly aggressive hydrochloric acid.</td>
</tr>
<tr>
<td><strong>Sulfuric Acid</strong></td>
<td>Used as a catalyst in alkylation plants and is formed in some process steams containing sulfur trioxide, water and oxygen.</td>
</tr>
<tr>
<td><strong>Hydrogen</strong></td>
<td>In itself not corrosive but can lead to blistering and embrittlement of steel. Also, it readily combines with other elements to produce corrosive compounds.</td>
</tr>
</tbody>
</table>
# Corrosives Found in Refining Processes

<table>
<thead>
<tr>
<th>Phenols</th>
<th>Found primarily in sour water strippers.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>Originates in crude, aerated water, or packing gland leaks. Oxygen in the air used with fuel in furnace combustion and FCC regeneration results in high-temperature environments which cause oxidation and scaling of metal surfaces of under-alloyed materials.</td>
</tr>
<tr>
<td>Carbon</td>
<td>Not corrosive but at high temperature results in carburization that causes embrittlement or reduced corrosion resistance in some alloys.</td>
</tr>
</tbody>
</table>
Metal Loss
General and/or Localized

- Galvanic corrosion
- Pitting
- Crevice corrosion
- Intergranular attack
- Erosion corrosion
- Hydrogen chloride
- Ammonia bisulfide
- Carbon dioxide
- Process chemicals
- Organic chlorides
- Aluminum chloride

- Sulfuric acid
- Hydrofluoric acid
- Phosphoric acid
- Phenol (carbolic acid)
- Amine
- Atmospheric corrosion
- Corrosion under insulation
- Oxidation
- High temperature sulfidation
- Naphthenic acid

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Galvanic Corrosion

Corroded End - Anodic - More Active
- Magnesium
- Magnesium alloys
- Zinc
- Aluminum
- Aluminum alloys
- Steel
- Cast iron
- Type 410 stainless steel (active state)
- Ni-Resist
- Type 304 stainless steel (active state)
- Type 316 stainless steel (active state)
- Lead
- Tin
- Nickel (active state)

Protected End - Cathodic - Less Active
- Brass
- Copper
- Bronze
- Copper-Nickel
- Monel
- Nickel (passive state)
- Type 410 stainless steel (passive state)
- Type 304 stainless steel (passive state)
- Type 316 stainless steel (passive state)
- Titanium
- Graphite
- Gold
- Platinum

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## Oxidation

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperature, °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Steel</td>
<td>1,050</td>
</tr>
<tr>
<td>Carbon - 1/2 Mo</td>
<td>1,050</td>
</tr>
<tr>
<td>1 1/4 Cr-1/2 Mo</td>
<td>1,100</td>
</tr>
<tr>
<td>2 1/4 Cr-1Mo</td>
<td>1,175</td>
</tr>
<tr>
<td>5 Cr-1/2 Mo</td>
<td>1,200</td>
</tr>
<tr>
<td>7 Cr-1/2 Mo</td>
<td>1,250</td>
</tr>
<tr>
<td>9 Cr-1Mo</td>
<td>1,300</td>
</tr>
<tr>
<td>Type 410 stainless steel</td>
<td>1,500</td>
</tr>
<tr>
<td>Types 304, 321, and 347 stainless steel</td>
<td>1,600</td>
</tr>
</tbody>
</table>
## Oxidation (continued)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperature (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Types 316 and 317 stainless steel</td>
<td>1,600</td>
</tr>
<tr>
<td>Type 309 stainless steel</td>
<td>2,000</td>
</tr>
<tr>
<td>Type 310 stainless steel</td>
<td>2,100</td>
</tr>
<tr>
<td>Monel 400</td>
<td>1,000</td>
</tr>
<tr>
<td>Inconel 625</td>
<td>2,000</td>
</tr>
<tr>
<td>Incoloy 825</td>
<td>2,000</td>
</tr>
<tr>
<td>Hastelloy B-2</td>
<td>1,400</td>
</tr>
<tr>
<td>Hastelloy C-4 and C-276</td>
<td>1,800</td>
</tr>
</tbody>
</table>

*Source: NACE Corrosion in the Oil Refining Industry*
Sulfuric Acid
$H_2S/H_2$ McConomy

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Carbon Steel Sulfidation
Cooper-Gorman
H$_2$S/H$_2$ Material Corrosion
Stress Corrosion Cracking

- Chloride stress corrosion cracking
- Caustic stress cracking
- Polythionic acid stress corrosion cracking
- Ammonia stress corrosion cracking
- Hydrogen effects (in steels)
- Sulfide stress corrosion cracking, hydrogen induced cracking, stress oriented hydrogen induced cracking
- Hydrogen cyanide
# Stress Corrosion Cracking

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Base</td>
<td>Air</td>
</tr>
<tr>
<td></td>
<td>Sea Water</td>
</tr>
<tr>
<td></td>
<td>Salt and chemical combinations</td>
</tr>
<tr>
<td>Magnesium Base</td>
<td>Nitric acid</td>
</tr>
<tr>
<td></td>
<td>Caustic</td>
</tr>
<tr>
<td></td>
<td>HF solutions</td>
</tr>
<tr>
<td></td>
<td>Salts</td>
</tr>
<tr>
<td></td>
<td>Coastal atmospheres</td>
</tr>
<tr>
<td>Copper Base</td>
<td>Primarily ammonia and ammonium hydroxide</td>
</tr>
<tr>
<td></td>
<td>Amines</td>
</tr>
<tr>
<td></td>
<td>Mercury</td>
</tr>
</tbody>
</table>

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## Stress Corrosion Cracking

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Steel</td>
<td>Caustic</td>
</tr>
<tr>
<td></td>
<td>Anhydrous ammonia</td>
</tr>
<tr>
<td></td>
<td>Nitrate solutions</td>
</tr>
<tr>
<td>Martensitic and Precipitation Hardening</td>
<td>Sea water</td>
</tr>
<tr>
<td>Stainless Steels</td>
<td>Chlorides</td>
</tr>
<tr>
<td></td>
<td>$H_2S$ solutions</td>
</tr>
<tr>
<td>Austenitic Stainless Steels</td>
<td>Chlorides - inorganic and organic</td>
</tr>
<tr>
<td></td>
<td>Caustic solutions</td>
</tr>
<tr>
<td></td>
<td>Sulfurous and polythionic acids</td>
</tr>
</tbody>
</table>

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# Stress Corrosion Cracking

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Base</td>
<td>Caustic above 600°F (315°C)</td>
</tr>
<tr>
<td></td>
<td>Fused caustic</td>
</tr>
<tr>
<td></td>
<td>Hydrofluoric acid</td>
</tr>
<tr>
<td>Titanium</td>
<td>Sea water</td>
</tr>
<tr>
<td></td>
<td>Salt atmospheres</td>
</tr>
<tr>
<td></td>
<td>Fused salt</td>
</tr>
</tbody>
</table>

Wet $H_2S$ Cracking

- Hydrogen from corrosion reaction
- $Fe + H_2S \Rightarrow FeS + 2H$
- $2H \Rightarrow H_2$
- Leads to various types of damage in steels
  - Blistering
  - Sulfide Stress Corrosion Cracking (SSC)
  - Hydrogen Induced Cracking (HIC)
  - Stress Oriented Hydrogen Induced Cracking (SOHIC)
Wet H$_2$S Cracking

SOHIC in soft base metal extending from the tip of SSC in a hard HAZ of a repair weld in the shell of a primary absorber (de-ethanizer) column in a FCC gas plant. The A 212-B steel shell was PWHT’d at original fabrication, but the repair weld was not. (Nital etch)
This micrograph shows the cross-sectional view of a representative crack. The depth is approximately 0.021”. The blistering effect can be seen as the metal above the crack appears to have been bulged out toward the surface.
Magnification: 30x   Etch: 3% Nital
This is micrograph of the crack tip observed in the previous figure. Note that crack propagation took place at the grain boundaries, characteristic of hydrogen induced cracking.
Magnification: 150x   Etch: 3% Nital
Hydrogen Induced Cracking
Micrograph of boat sample (longitudinal cut) taken from HSC 3055
Magnification: 50x  Etch: 3% Nital

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Photo of Wet Fluorescent Magnetic Particle indications. Note the number of indications spread throughout the surface. This indicates the phenomena is not localized to a single area. The light blue areas are paint marks used for identification, and the dark blue areas are paint marks found on the as received plate.
Photo of Wet Fluorescent Magnetic Particle surface indications found. The crescent shape indicates hydrogen blistering as the possible damage mechanism. The bluish circle around the indication is just a paint marking used to help identify crack sites. This indication is approximately 3/32” in length.
High Temperature Hydrogen Attack (HTHA)

- Carbon and low alloys steels exposed to hydrogen above 430°F (221°C)
- Partial pressure above 200 psi (1378 kPa)
- Dissociation of molecular hydrogen to atomic hydrogen
- Atomic hydrogen permeation into the steel
- Reaction of atomic hydrogen with carbon in steel
- Formation of methane at discontinuities
- API 941 recommended for new installation

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Operating Limits for Steels in Hydrogen Service
Longitudinal Weld

Magnification: 50x   Etch:  2% Nital
Longitudinal Weld

Magnification: 500x    Etch: 2% Nital
Replica micrograph from Exchanger 3083 shell ‘hot’ area depicting HA fissures and decarburization.

Magnification: 100x    Etch: 3% Nital
Enlarged micrograph of previous figure. Notice decarburization.
Magnification: 500x    Etch: 3% Nital
Metallurgical and Environmental Failures

- Grain growth
- Graphitization
- Hardening
- Sensitization
- Sigma phase
- $885^\circ$F Embrittlement
- Temper embrittlement
- Liquid metal embrittlement
- Carburization
- Metal dusting
- Decarburization
- Selective leaching
Mechanical Failures

- Incorrect or defective materials
- Mechanical fatigue
- Corrosion fatigue
- Cavitation damage
- Mechanical damage
- Overloading

- Over pressurization
- Brittle fracture
- Creep
- Stress rupture
- Thermal shock
- Thermal fatigue
Conclusions

• There are many causes of equipment failures in the refining industry
• Many are common and well documented
• Other, less common deterioration mechanisms are not well documented
• Deterioration is the results of metal and environment/operating conditions combinations
• These combinations vary somewhat in different process units
• Focus of the Corrosion in the Oil Refining Industry Conference