SECTION 5.0

REFINING INDUSTRY DAMAGE MECHANISMS

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5.1 General
Damage mechanisms found in the refining environment are discussed in the following sections. Section 5.2 includes process unit PFD’s. These PFD’s show the location in the unit where particular damage mechanisms are most likely to be found.

5.1.1 Uniform or Localized Loss in Thickness Phenomena

5.1.1.1 Amine Corrosion

5.1.1.1.1 Description of Damage

a) Amine corrosion refers to the general and/or localized corrosion that occurs principally on carbon steel in amine treating processes. Corrosion is not caused by the amine itself, but results from dissolved acid gases (CO₂ and H₂S), amine degradation products, Heat Stable Amine Salts (HSAS) and other contaminants.

b) Stress corrosion cracking of carbon steel in amine services is discussed in 5.1.2.2.

5.1.1.1.2 Affected Materials

Primarily carbon steel. 300 Series SS are highly resistant.

5.1.1.1.3 Critical Factors

c) Corrosion depends on design and operating practices, the type of amine, amine concentration, contaminants, temperature and velocity.

d) Amine corrosion is very closely tied to the operation of the unit. With a few exceptions, carbon steel is suitable for most components in a properly designed and operated unit. Most problems can be traced to faulty design, poor operating practices or solution contamination.

e) Corrosion is also dependent on the type of amine used. In general, alkanolamine systems can be rated in order of aggressiveness from most to least as follows: monoethanolamine (MEA), diglycolamine (DGA), diisopropylamine (DIPA), diethanolamine (DEA), and methyldiamine (MDEA).

f) Lean amine solutions are generally not corrosive because they have either low conductivity and or high pH. However, an excessive accumulation of heat stable amine salts (HSAS) above about 2%, depending on the amine, can significantly increase corrosion rates.

g) Lean amine solutions contain a small amount of H₂S which helps to maintain a stable iron sulfide film. Overstripped lean solutions can be corrosive if there is inadequate H₂S present to maintain the protective iron sulfide film.

h) Ammonia, H₂S and HCN accelerate corrosion in the regenerator overhead condenser and outlet piping as well as reflux piping, valves and pumps.

i) Corrosion rates increase with increasing temperature, particularly in rich amine service. Temperatures above about 220°F (104°C) can result in acid gas flashing and severe localized corrosion due to 2-phase flow, if the pressure drop is high enough.

j) Process stream velocity will influence the amine corrosion rate and nature of attack. Corrosion is generally uniform however high velocities and turbulence will cause localized thickness losses. For carbon steel, common velocity limits are generally limited to 3 to 6 fps for rich amine and about 20 fps for lean amine.

5.1.1.1.4 Affected Units or Equipment

a) Amine units are used in refineries to remove H₂S, CO₂ and mercaptans from process streams originating in many units including the crude, coker, FCC, hydrogen reforming, hydrotreating, and tail gas units.

b) The regenerator reboiler and the regenerator are areas where the temperature and turbulence of the amine stream are the highest and can cause significant corrosion problems.
c) The rich amine side of the lean/rich exchangers, hot lean amine piping, hot rich amine piping, the amine solution pumps, and the reclaimers are also areas where corrosion problems occur.

5.1.1.1.5  \textit{Appearance or Morphology of Damage}

a) Carbon steel and low alloy steels suffer general uniform thinning, localized corrosion or localized underdeposit attack (Figure 5-1 to 5-6).

b) Thinning will be uniform in nature when the process stream velocity is low while it will be localized for high velocities associated with turbulence.

5.1.1.1.6  \textit{Prevention / Mitigation}

a) Proper operation of the amine system is the most effective way to control corrosion, with particular attention to acid gas loading levels. In addition, to avoid corrosive amine degradation products, the process temperature should not exceed recommended limits. Proper control of the reboiler rate and temperature is necessary in order to maintain a regenerator top temperature.

b) Proper attention should be given to avoid the buildup of HSAS to unacceptable levels.

c) The system design should incorporate measures to control local pressure drop to minimize flashing. In areas where it is unavoidable, upgrading to 300 Series SS or other corrosion resistant alloys may be required. SS410 trays and internals are also used in absorber and stripping towers.

d) Oxygen inleakage causes high corrosion rates and contributes to heat stable salt formation. Storage tanks and surge vessels should be blanketed with inert gas.

e) Solids and hydrocarbons should be removed from the amine solution by filtration and through process control. Filtration of rich amine solutions has the potential to be more effective than lean amine filtration for solids removal.

f) Corrosion inhibitors may be required to control amine corrosion within acceptable levels.

5.1.1.1.7  \textit{Inspection and Monitoring}

a) Visual examination and UT thickness measurement are the methods used for internal equipment inspection. UT scans or profile radiography are used for external inspection.

b) Corrosion monitoring can also be achieved with corrosion coupons and/or corrosion probes.

c) Monitoring should target the hot areas of the unit such as the reboiler feed and return line, the hot lean/rich amine piping, and the stripper overhead condenser piping.

d) Fouling of exchangers and filters can be a sign of corrosion problems on the unit.

5.1.1.1.8  \textit{Related Mechanisms}

Amine stress corrosion cracking may also be found in 5.1.2.2.

5.1.1.1.9  \textit{References}


4. API Recommended Practice 945, Avoiding Environmental Cracking in Amine Units, American Petroleum Institute, Washington, D.C.


Figure 5-1 – Localized amine corrosion at the weld found in piping from reboiler to regenerator tower in an MEA unit. Many other similar cases found, some going as deep as half thickness. They were originally found and mistaken as cracks with shear wave UT inspection.

Figure 5-2 – Hot Lean Amine Corrosion of Carbon Steel:
Figure 5-3 – Preferential weld corrosion in lean amine (Ref. 5)

Figure 5-4 – Preferential corrosion in amine regenerator reboiler return elbow (Ref. 6).
Figure 5-5 – Corroded reboiler exchanger shell near liquid level from an amine regeneration unit, (Numbers drawn on figure are UT thicknesses in inches. Nominal wall 0.550 inch (Ref 7).

Figure 5-6 – Corroded amine regenerator column shell near a downcomer (Numbers drawn on figure are UT thicknesses in inches). Nominal Wall 0.500 inch (Ref. 7).
5.1.1.2 Ammonium Bisulfide Corrosion (Alkaline Sour Water)

5.1.1.2.1 Description of Damage
a) Aggressive corrosion occurring in hydروprocessing reactor effluent streams and in units handling alkaline sour water.
b) Several major failures have occurred in hydروprocessing reactor effluent systems due to localized corrosion.

5.1.1.2.2 Affected Materials
a) Carbon steel is less resistant.
b) 300 Series SS, duplex SS, aluminum alloys and nickel base alloys are more resistant, depending on ammonium bisulfide (NH₄HS) concentration and velocity.

5.1.1.2.3 Critical Factors
a) NH₄HS concentration, H₂S partial pressure, velocity and/or localized turbulence, pH, temperature, alloy composition and flow distribution are all critical factors to consider.
b) Corrosion increases with increasing NH₄HS concentration and increasing velocity. Below 2 wt %, solutions are not generally corrosive. Above 2 wt % NH₄HS, solutions are increasingly corrosive.
c) In hydروprocessing reactors, FCC reactors and coker furnaces, nitrogen in the feed is converted to ammonia and reacts with H₂S to form NH₄HS. NH₄HS precipitates out of the gas phase in the reactor effluent stream at temperatures below about 150°F (66°C), depending on the concentration of NH₃ and H₂S, and may cause fouling and plugging unless flushed away with wash water.
d) NH₄HS salt deposits lead to underdeposit corrosion and fouling. The salts are not corrosive unless they become hydrated at which point they are very corrosive.
e) Oxygen and iron in the wash water injected into hydروprocessing reactor effluent can lead to increased corrosion and fouling.
f) Presence of cyanides increases severity of corrosion in FCC gas plants, coker gas plants and sour water stripper overheads by destroying the normally protective sulfide film.

5.1.1.2.4 Affected Units or Equipment
a) Hydروprocessing Units
   i) NH₄HS salts precipitate in the reactor effluent streams when temperatures drop to within the range of 120°F to 150°F (49°C to 66°C).
   ii) Fouling and/or velocity accelerated corrosion may be found at:
   iii) Air cooler header boxes.
   iv) Inlet and outlet piping of air coolers, as well as exchanger tubes.
   v) Effluent separators, and piping into and out of the reactor effluent separators.
   vi) Sour water draw piping from reactor effluent separators; flashing may cause severe erosion-corrosion downstream of control valves (Figure 5-7).
   vii) Vapor line from the high pressure separators.
   viii) Hydrocarbon lines from reactor effluent separators due to entrained sour water.
   ix) Stripper Column overhead sour water.
b) FCC Units
   NH₄HS concentrations are usually less than 2 wt % but high velocities and/or the presence of cyanides can remove protective iron sulfide scales.
c) Sour Water Strippers (SWS)
   High concentrations of NH₄HS in stripper overhead piping, condensers, accumulator and reflux piping,
and possible presence of cyanides.

d) Amine Units

High concentrations of NH₄HS may be found in regenerator overheads and reflux piping depending on unit operation.

e) Delayed Coker

High concentrations of NH₄HS may be found in the gas concentration plant downstream of the fractionator tower.

5.1.1.2.5 Appearance or Morphology of Damage

a) General loss in thickness of carbon steel, with the potential for extremely high localized rates of wall loss can occur at changes in direction or turbulent flow areas above 2 wt % concentration.

b) Low velocities may result in extremely localized under-deposit corrosion if insufficient water is available to dissolve the NH₄HS salts that precipitated.

c) Heat exchangers may show plugging and loss of duty due to fouling.

d) NH₄HS rapidly corrodes admiralty brass tubes and other copper alloys.

5.1.1.2.6 Prevention / Mitigation

a) Good design practice should consist of symmetrical and hydraulically balanced flow in and out of air cooled exchangers.

b) Carefully review design and localized velocities as process conditions change, particularly as NH₄HS concentrations exceed 2 wt % and begin to approach 8 wt % or higher.

c) Maintain velocities within industry guidelines of 10 to 20 fps for carbon steel. Carbon steel may be susceptible to high corrosion rates above about 8 wt % NH₄HS concentration.

d) Use resistant materials of construction (e.g. Alloy 825, duplex SS) at velocities above 20 fps, depending on NH₄HS concentration.

e) Properly design and maintain water wash injection with low oxygen content; provide sufficient excess water to ensure that an adequate amount of water remains as liquid to dilute the NH₄HS salts. Use proper injection spray nozzles and metallurgy.

f) Titanium and Alloy C276 have been used in overhead condensers in SWS units.

g) Aluminum exchanger tubes are extremely susceptible to erosion-corrosion damage.

5.1.1.2.7 Inspection and Monitoring

a) A carefully designed plan should include input from process engineers and materials/corrosion engineers to determine specific areas of vulnerability. Determine ammonium bisulfide content through sampling and calculation.

b) Frequent UT scanning and/or RT profile thickness of high and low velocity areas.

c) UT downstream of control valves at high NH₄HS concentrations.

d) IRIS, RFEC and flux leakage inspection of steel air cooler tubes.

e) EC inspect non-magnetic air cooler tubes.

f) Monitor water injection facilities and flow meters to ensure proper operation.

5.1.1.2.8 Related Mechanisms

Erosion/erosion corrosion (see 4.2.14).

5.1.1.2.9 References


2. E. F. Ehmke, “Corrosion Correlation with Ammonia and Hydrogen Sulfide in Air Coolers,” Materials


9. Richard J. Horvath, Michael S. Cayard, Russell D. Kane, “Prediction and assessment of ammonium bisulfide corrosion under refinery sour water service conditions”, paper # 06576, NACE International, Houston, TX.


Figure 5-7 – 2-inch CS elbow and straight section in a sour water line off the cold HPS on an HDT unit.
5.1.1.3 Ammonium Chloride Corrosion

5.1.1.3.1 Description of Damage
General or localized corrosion, often pitting, normally occurring under ammonium chloride or amine salt deposits, often in the absence of a free water phase.

5.1.1.3.2 Affected Materials
All commonly used materials are susceptible, in order of increasing resistance: carbon steel, low alloy steels, 300 Series SS, Alloys 400, duplex SS, 800, and 825, Alloys 625 and C276 and titanium.

5.1.1.3.3 Critical Factors
a) Concentration (NH₃, HCl, H₂O or amine salts), temperature and water availability are the critical factors.
b) Ammonium chloride salts may precipitate from high temperature streams as they are cooled, depending upon the concentration of NH₃ and HCl, and may corrode piping and equipment at temperatures well above the water dewpoint (> 300°F (149°C)).
c) Ammonium chloride salts are hygroscopic and readily absorb water. A small amount of water can lead to very aggressive corrosion (>100 mpy (>2.5 mm/y)).
d) Ammonium chloride and amine hydrochloride salts are highly water soluble, highly corrosive and form an acidic solution when mixed with water. Some neutralizing amines react with chlorides to form amine hydrochlorides that can act in a similar fashion.
e) Corrosion rates increase with increasing temperature.
f) When they deposit above the water dewpoint, a water wash injection may be required to dissolve the salts.

5.1.1.3.4 Affected Units or Equipment
a) Crude Tower Overheads
   i) Tower top, top trays, overhead piping and exchangers may be subject to fouling and corrosion. Deposits may occur in low flow zones due to ammonia and/or amine chloride salts condensing from the vapor phase.
   ii) Top pumparound streams may be affected if ammonia or amine chloride salts are present.
b) Hydrosprocessing
   Reactor effluent streams are subject to ammonium chloride salt fouling and corrosion. Water washing may be required if exchanger fouling or loss in duty occurs.
c) Catalytic Reforming
   Reactor effluent streams and the H₂ recycle system are subject to ammonium chloride salting and corrosion.
d) FCCU and coker fractionator overheads and top pumparounds are subject to ammonium chloride corrosion and salting.

5.1.1.3.5 Appearance or Morphology of Damage
a) The salts have a whitish, greenish or brownish appearance. Water washing and/or steamout will remove deposits so that evidence of fouling may not be evident during an internal visual inspection.
b) Corrosion underneath the salts is typically very localized and results in pitting.
c) Corrosion rates can be extremely high.

5.1.1.3.6 Prevention / Mitigation
Alloys that are more pitting resistant will have improved resistance to ammonium chloride salts but even the most corrosion resistant nickel base alloys and titanium alloys may suffer pitting corrosion.
a) Crude Unit
   i) Limit salts by limiting chlorides in the tower feed through desalting and/or the addition of caustic to the desalted crude.
   ii) A water wash may be required in the crude tower overhead line to flush the salt deposits.
   iii) Filming amine inhibitors are often added to control corrosion.

b) Hydroprocessing
   i) Limit chlorides in the hydrocarbon feed to the reactor.
   ii) Limit chlorides in the make-up hydrogen supply.
   iii) A continuous or intermittent water wash may be required in the reactor effluent to flush out the salt deposits.

c) Catalytic Reforming
   i) Reactor effluent can be treated to remove the chlorides.
   ii) Water washing has been used in some cases but the system must be carefully designed.
   iii) Some tower overheads may require neutralizing or filming amines.

5.1.1.3.7 Inspection and Monitoring
a) Accumulation of ammonium chloride salts can be very localized and the resulting corrosion may be difficult to detect.

b) RT or UT thickness monitoring can be used to determine remaining wall thickness.

c) Monitoring of the feed streams and effluent waters will give an indication of the amount of ammonia and chlorides present, however process simulation may be required to determine the concentration and dewpoint temperatures. If the ammonium chloride salt deposition temperature has been calculated, temperature monitoring and control may be effective for maintaining metal temperatures above the salt deposition temperature.

d) The presence of deposits is often detected when the pressure drop increases or the thermal performance of exchangers has deteriorated.

e) Corrosion probes or coupons can be useful, but the salt must deposit on the corrosion probe element to detect the corrosion.

5.1.1.3.8 Related Mechanisms
HCl corrosion (see 5.1.1.4), chloride SCC (4.5.1) and organic acid corrosion of distillation tower overhead systems (5.1.1.12).

5.1.1.3.9 References
5.1.1.4 Hydrochloric Acid (HCl) Corrosion

5.1.1.4.1 Description of Damage

a) Hydrochloric acid (aqueous HCl) causes both general and localized corrosion and is very aggressive to most common materials of construction across a wide range of concentrations.

b) Damage in refineries is most often associated with dew point corrosion in which vapors containing water and hydrogen chloride condense from the overhead stream of a distillation, fractionation or stripping tower. The first water droplets that condense can be highly acidic (low pH) and promote high corrosion rates.

5.1.1.4.2 Affected Materials

All common materials of construction used in refineries.

5.1.1.4.3 Critical Factors

a) HCl acid concentration, temperature and alloy composition.

b) The severity of corrosion increases with increasing HCl concentration and increasing temperature.

c) Aqueous HCl can form beneath deposits of ammonium chloride or amine hydrochloride salts in exchangers and piping. The deposits readily absorb water from the process stream or from injected wash water. Hydrogen chloride is normally not corrosive in dry process streams, but becomes very corrosive where water is available to form hydrochloric acid.

d) Carbon steel and low alloy steels are subject to excessive corrosion when exposed to any concentration of HCl acid that produces at pH below about 4.5

e) 300 series SS and 400 series SS are not usefully resistant to HCl at any concentration or temperature.

f) Alloy 400, titanium and some other nickel base alloys have good resistance to dilute HCl acid in many refinery applications.

g) The presence of oxidizing agents (oxygen, ferric and cupric ions) will increase the corrosion rate, particularly for alloy 400 and Alloy B-2. Titanium performs well in oxidizing conditions but fails rapidly in dry HCl service.

5.1.1.4.4 Affected Units or Equipment

HCl corrosion is found in several units, especially crude and vacuum units, hydroprocessing units and catalytic reformer units.

a) Crude Unit

i) In the atmospheric tower overhead system, corrosion from HCl acid occurs as the first droplets of water condense from the vapor stream off the top of the tower. This water can have a very low pH and can result in high rates of corrosion in piping, as well as exchanger shells, tubes and header boxes, and cold dead legs.

ii) HCl corrosion can also be a problem in the vacuum ejector and condensing equipment off the top of the vacuum tower.

b) Hydroprocessing Units

i) Chlorides may enter the unit as organic chloride in the hydrocarbon feed or with the recycle hydrogen and react to form HCl.

ii) Ammonium chloride salts can form in various parts of the unit including the effluent side of the hot feed/effluent exchangers because both NH₃ and HCl are present or they may condense with water in the effluent train.

HCl containing streams can migrate through the fractionation section resulting in severe acid dewpoint corrosion at the mixing point where it contacts water.
c) Catalytic Reforming Units
   i) Chlorides may be stripped from the catalyst and react to form HCl that carries through the effluent train, regeneration system, stabilizer tower, debutanizer tower and feed/preheat exchangers.
   ii) HCl containing vapors can migrate through the gas plant fractionation section resulting in mix point or acid dew point corrosion.

5.1.1.4.5 Appearance or Morphology of Damage
a) Carbon steel and low alloy steels suffer general uniform thinning, localized corrosion or underdeposit attack.
b) 300 Series SS and 400 Series SS will often suffer pitting attack and 300 Series SS may experience chloride stress corrosion cracking.

5.1.1.4.6 Prevention/Mitigation
a) Crude Units
   i) Optimize the crude oil tank water separation and withdrawal and crude desalting operation to reduce chloride in the feed to the crude tower. A common target is 20 ppm or fewer chlorides in the overhead accumulator water.
   ii) Upgrading carbon steel to nickel base alloys or titanium can reduce HCl acid corrosion problems. Titanium tubes will solve most overhead condenser tube corrosion problems.
   iii) Water washing can be added to quench the overhead stream and to help dilute the condensing hydrochloric acid concentration.
   iv) Caustic injection downstream of the desalter is another common method used to reduce the amount of HCl going overhead. Proper design and operating guidelines must be used to avoid caustic SCC and fouling in the feed preheat train.
   v) Various combinations of ammonia, neutralizing amines and filming amines can be injected in the atmospheric tower overhead line before the water dewpoint.
b) Hydrodroprocessing
   i) Minimize carryover of water and chloride salts from upstream units including neutralizing amine hydrochloride salts.
   ii) Minimize HCl in H₂ streams (e.g., install scrubbers or guard beds to remove Cl⁻ ions from hydrogen produced in catalytic reforming units).
   iii) Selective use of corrosion resistant nickel base alloys.
c) Catalytic Reforming
   i) Same as hydroprocessing, but in addition, water washing the hydrocarbon stream has also been used to remove the highly water soluble chlorides. Special care in the design and operation of this equipment is recommended. Minimizing water and/or oxygenates in the feed will reduce stripping of chlorides from the catalyst.
   ii) Special adsorbents in chloride beds and chloride treaters can be used to remove chlorides from the recycle hydrogen streams and from liquid hydrocarbon streams.

5.1.1.4.7 Inspection and Monitoring
a) For carbon steel, damage is usually in the form of general thinning but may be highly localized where a water phase is condensing.
b) Serious corrosion can also be found at mix points where dry chloride containing streams mix with streams containing free water or where water saturated streams are cooled below the dewpoint.
c) Evidence of locally thinned areas can be found using automatic ultrasonic scanning methods or profile radiography.
d) Process and corrosion monitoring are important aspects of a well-developed program to minimize the effects of HCl corrosion.

e) The pH of the water in the boot of the atmospheric tower overhead accumulator is normally checked every shift. Other variables including chloride and iron content are checked on a less frequent basis but do need to be monitored regularly.

f) Water phases in other units are also monitored by periodic sampling of water draws from the overhead drums of fractionating or stripping towers.

g) Strategically placed corrosion probes and/or corrosion coupons can provide additional information on the rate and extent of damage.

5.1.1.4.8 Related Mechanisms

Ammonium chloride corrosion (see 5.1.1.3), chloride SCC (4.5.1) and organic acid corrosion of distillation tower overhead systems (5.1.1.12).

5.1.1.4.9 References

5.1.1.5 High Temp H₂/H₂S Corrosion

5.1.1.5.1 Description of Damage
The presence of hydrogen in H₂S-containing hydrocarbon streams increases the severity of high temperature sulfide corrosion at temperatures above about 500°F (260°C). This form of sulfidation usually results in a uniform loss in thickness associated with hot circuits in hydroprocessing units.

5.1.1.5.2 Affected Materials
In order of increasing resistance: carbon steel, low alloy steels, 400 Series SS, and 300 Series SS.

5.1.1.5.3 Critical Factors
a) The major factors affecting high temperature sulfidation are the temperature, the presence of hydrogen, the concentration of H₂S and the alloy composition.
b) Depending on the quantity of hydrogen that is present, corrosion rates may be significantly different than those associated with high temperature sulfidation in the absence of hydrogen (see 4.4.2).
c) Sulfidation rates increase with increasing H₂S content and especially increasing temperature as illustrated in Figure 5-8.
d) Higher corrosion rates are found more in gas oil desulfurizers and hydrocrackers than naphtha desulfurizers by a factor of almost ‘2’.
e) Susceptibility to sulfidation is determined by the chemical composition of the alloy.
f) Increasing chromium content of the alloy improves resistance (Figure 5-9). However, there is little improvement with increasing chromium content until about 7-9Cr as shown by the relative rate reduction factors in Table 5-1.
g) Chromium-containing nickel base alloys are similar to stainless steel. Similar levels of chromium provide similar corrosion resistance.

5.1.1.5.4 Affected Units or Equipment
a) This form of corrosion occurs in piping and equipment in units where high temperature H₂/H₂S streams are found including all hydroprocessing units such desulfurizers, hydrotreaters and hydrocracking units.
b) Noticeable increases in corrosion may be found downstream of hydrogen injection points.

5.1.1.5.5 Appearance or Morphology of Damage
a) Corrosion will appear as a uniform loss in thickness from the process side and is accompanied by the formation of an iron sulfide scale.
b) Scale is about 5 times the volume of lost metal and may be in multiple layers.
c) The tightly adherent shiny gray scale attached to the surface may be mistaken for unaffected metal.

5.1.1.5.6 Prevention / Mitigation
a) The corrosion damage is minimized by using alloys with high chromium content.
b) The 300 Series SS such as Types 304L, 316L, 321 and 347 are highly resistant at service temperatures.

5.1.1.5.7 Inspection and Monitoring
a) UT, VT and RT thickness readings are used to monitor loss in thickness.
b) Actual operating temperatures should be verified in the field to compare against design.
c) Process simulations should be checked periodically to confirm that H₂S levels have not significantly increased.
5.1.1.5.8 Related Mechanisms

High temperature sulfidation in the absence of hydrogen is discussed in 4.4.2

5.1.1.5.9 References

### Table 5-1– Rate Factors vs. Chromium Content. (Ref. 2)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Rate Factor</th>
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</thead>
<tbody>
<tr>
<td>CS, C-0.5Mo</td>
<td>1</td>
</tr>
<tr>
<td>1 Cr-0.5Mo</td>
<td>0.96</td>
</tr>
<tr>
<td>2.25Cr-1Mo</td>
<td>0.91</td>
</tr>
<tr>
<td>5Cr-0.5Mo</td>
<td>0.80</td>
</tr>
<tr>
<td>7Cr-1Mo</td>
<td>0.74</td>
</tr>
<tr>
<td>9Cr-1Mo</td>
<td>0.68</td>
</tr>
</tbody>
</table>
Figure 5-8 – Corrosion rate of carbon steel in H₂/H₂S service in a naphtha desulfurizer from the modified Couper-Gorman curves. (Ref. 1)

Figure 5-9 – Corrosion rate curves for various alloys in H₂/H₂S service. (Ref. 1)
5.1.1.6 Hydrofluoric (HF) Acid Corrosion

5.1.1.6.1 Description of Damage

Corrosion by HF acid can result in high rates of general or localized corrosion and may be accompanied by hydrogen cracking, blistering and/or HIC/SOHIC (see 5.1.2.3 and 5.1.2.4).

5.1.1.6.2 Affected Materials

a) Carbon steel, copper-nickel alloys, Alloy 400.
b) Other nickel base alloys such as Alloy C276 have also been used in some applications.
c) Low alloy steels, 300 Series SS and the 400 Series SS are susceptible to corrosion and/or cracking and are generally not suitable for HF service.

5.1.1.6.3 Critical Factors

a) HF acid concentration (water content), temperature, alloy composition and the presence of contaminants including oxygen and sulfur compounds are the controlling factors.
b) Carbon steel forms a protective fluoride scale in dry concentrated acid. Loss of the protective scale through high velocities or turbulence, will result in greatly accelerated corrosion rates.
c) The presence of water can destabilize the fluoride scale and convert it into a voluminous nonprotective scale.
d) The primary concern is the “HF-in-water” concentration of the acid phase. Although the process stream may be comprised primarily of hydrocarbon, the acid is considered as a separate phase. Concentration is determined by the amount of water present in the acid phase.
e) Typical HF alkylation units operate with 1% to 3% water in the acid, equivalent to an HF-in-water concentration of 97% to 99% and the temperatures are generally below 150°F (66°C). Under these conditions carbon steel is widely used for all equipment except where close tolerances are required for operation (i.e., pumps, valves, instruments).
f) Corrosion rates increase with increasing temperature and decreasing HF concentration (increasing water content) as shown in Figures 5-10 to 5-11.
g) In carbon steel, the “Residual Element” (RE) content of base metal and weld metal may have an affect on corrosion rates in certain parts of the unit. This RE content refers to the effect of trace elements, primarily %C, %Cu, %Ni, %Cr that are present in carbon steel during the steel manufacturing process (Ref. 1-4).
h) Industry guidelines regarding RE content have been developed and implemented into some industry consensus standards as indicated below. A more detailed discussion of these guidelines is outlined in References 1 and 2.

i) For Base Metal: %C > 0.18 wt.% and %Cu + %Ni < 0.15 wt.%
ii) For Weld Metal: %Cu + %Ni + %Cr < 0.15 wt.%
i) Oxygen contamination increases the corrosion rate of carbon steel and promotes accelerated corrosion and SCC of Alloy 400.

5.1.1.6.4 Affected Units or Equipment

a) Piping and equipment in the HF alkylation unit, flare piping and downstream units exposed to acid carryover are also affected.
b) Most equipment is made from carbon steel with the exception of the HF acid rerun/regenerator tower and the acid relief neutralizer vessel which are usually made partially or completely from Alloy 400.
c) High corrosion rates have been observed:

i) In piping and equipment operating above 150°F (66°C);
ii) In deadlegs including inlets to relief valves, as well as small bore vents and drains;
iii) Condensing overhead vapors in piping and exchangers off top of the Isostripper, Depropanizer and HF Stripper/Propane Stripper;

iv) On flange faces;

v) Heat exchanger bundles that heat acid-containing streams such as the acid vaporizer.

d) Severe fouling due to iron fluoride corrosion product has been observed in the piping, heat exchangers and in the tops of the Isostripper and Depropanizer towers.

5.1.1.6.5 Appearance or Morphology of Damage

a) Corrosion is in the form of localized general or severe thinning of carbon steel. Preferential corrosion may not always conform to behavior predicted by the RE guidelines in API RP 751 (Figure 5-12 to 5-15).

b) Corrosion may be accompanied by cracking due to hydrogen stress cracking, blistering and/or HIC/SOHIC damage.

c) Significant fouling due to iron fluoride scales may also accompany corrosion.

d) Alloy 400 shows uniform loss in thickness but is not accompanied by significant scaling.

e) Alloy 400 is susceptible to stress corrosion cracking when in contact with moist HF vapors in the presence of oxygen.

5.1.1.6.6 Prevention / Mitigation

a) Carbon steel operating above 150°F (66°C) should be closely monitored for loss in thickness and may need to be upgraded to Alloy 400.

b) Corrosion can be prevented by careful operation of the unit to minimize water, oxygen, sulfur and other contaminants in the feed.

c) Maintain strict controls on the water content of the circulating acid.

d) Alloy 400 (solid or clad) can be used to eliminate the problems associated with blistering and HIC/SOHIC. A stress relieving heat treatment is required to help minimize, but not eliminate, the possibility of SCC (Figure 5-16 to 5-17).

e) Alloy C276 has been used where there have been cracking problems with Alloy 400.

5.1.1.6.7 Inspection and Monitoring

a) UT and RT are used to monitor for loss in thickness.

b) Special emphasis programs to monitor small bore piping, flange face corrosion, blistering and HIC/SOHIC are recommended as outlined in API RP 751.

c) Track and monitor RE content of carbon steel components in accordance with API 751 guidelines. Inspect for the potential for localized corrosion of piping components and or welds in accordance with API 751 and industry best practices.

5.1.1.6.8 Related Mechanisms

Environmental cracking of carbon steel and Alloy 400 can occur in HF. Refer to 5.1.2.4 hydrogen stress cracking in HF and to 5.1.2.3 for a discussion of blistering and HIC/SOHIC damage.

5.1.1.6.9 References

1. API Recommended Practice 751, Safe Operation of Hydrofluoric Acid Alkylation Units, American Petroleum Institute, Washington, D.C.

2. NACE Publication 5A171, Materials for Receiving, Handling, and Storing Hydrofluoric Acid, NACE International, Houston, TX.


Figure 5-10 – Corrosion rate as a function of temperature for carbon steel in anhydrous HF acid under stagnant conditions in 100-hr laboratory test (Ref. 2).  

Figure 5-11 – The corrosion rate of carbon steel at 70° to 100°F (21° to 38°C) based on laboratory testing and field experience at low flow and no-flow conditions (Ref. 2).
Figure 5-12 – Cross-section of a carbon steel pipe showing preferential corrosion of the pipe with high residual element content on the right, as compared to the low residual pipe section to the left of the weld (Ref. 3).

Figure 5-13 - Ruptured NPS 3 Sch. 80 0.216 in (5.49 mm) Depropanizer Feed Line operating <120°F
Residual element content is as follows:
Both Base metals: %C > 0.18 & %Cu + %Ni < 0.15
Weld Metal: %Cu + %Ni + %Cr < 0.15
Figure 5-14 – A cross-section of a line in fresh acid service showing accelerated corrosion of the weld and base metal of the component on the left (Ref. 8).

Figure 5-15 - Accelerated corrosion in the heat affected zone of a carbon steel weldment. 
Residual element content is as follows (Ref. 8):
Both Base metals: \%C > 0.18 wt. & \%Cu + \%Ni < 0.15
Weld Metal: \%Cu + \%Ni + \%Cr < 0.15
Figure 5-16 - HF stress corrosion cracking of Alloy 400 vent line in an acid dump system (Ref. 8).

Figure 5-17 - HF stress corrosion cracking of Alloy 400 instrument tubing (Ref. 8).
Figure 5-18 - HF Corrosion at manway in HF acid storage service.
5.1.1.7 Naphthenic Acid Corrosion (NAC)

5.1.1.7.1 Description of Damage
A form of high temperature corrosion that occurs primarily in crude and vacuum units, and downstream units that process certain fractions or cuts that contain naphthenic acids.

5.1.1.7.2 Affected Materials
Carbon steel, low alloy steels, 300 Series SS, 400 Series SS and nickel base alloys.

5.1.1.7.3 Critical Factors
a) NAC is a function of the naphthenic acid content (neutralization number), temperature, sulfur content, velocity and alloy composition.
b) Severity of corrosion increases with increasing acidity of the hydrocarbon phase.
c) Neutralization number or Total Acid Number (TAN) is a measure of the acidity (organic acid content) as determined by various test methods such as ASTM D-664. However, NAC corrosion is associated with hot dry hydrocarbon streams that do not contain a free water phase.
d) The Total Acid Number (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. Therefore, NAC is determined by the acidity of the actual stream not the crude charge.
e) The various acids which comprise the naphthenic acid family can have distinctly different corrosivity.
f) No widely accepted prediction methods have been developed to correlate corrosion rate with the various factors influencing it.
g) Sulfur promotes iron sulfide formation and has an inhibiting effect on NAC, up to a point.
h) Naphthenic acids remove protective iron sulfide scales on the surface of metals.
i) NAC can be a particular problem with very low sulfur crudes with TAN’s as low as 0.10.
j) NAC normally occurs in hot streams above 425°F (218°C) but has been reported as low as 350°F (177°C). Severity increases with temperature up to about 750°F (400°C), however, NAC has been observed in hot coker gas oil streams up to 800°F (427°C)
k) Naphthenic acids are destroyed by catalytic reactions in downstream hydrossprocessing and FCCU units.
l) Alloys containing increasing amounts of molybdenum show improved resistance. A minimum of 2% to 2.5% is required depending on the TAN of the whole crude and its side cuts.
m) 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.

5.1.1.7.4 Affected Units or Equipment
a) Crude and vacuum heater tubes; crude and vacuum transfer lines; vacuum bottoms piping, AGO circuits; HVGO and sometimes LVGO circuits. NAC has also been reported in the LCGO and HCGO streams on delayed coking units processing high TAN feed.
b) Piping systems are particularly susceptible in areas of high velocity, turbulence or change of flow direction, such as pump internals, valves, elbows, tees and reducers as well as areas of flow disturbance such as weld beads and thermowells.
c) Crude and vacuum tower internals may also be corroded in the flash zones, packing and internals where high acid streams condense or high velocity droplets impinge.
d) NAC may be found in hot hydrocarbon streams downstream of the crude and vacuum units, upstream of any hydrogen mix points.

5.1.1.7.5 Appearance or Morphology of Damage
a) NAC is characterized by localized corrosion, pitting corrosion, or flow induced grooving in high velocity
areas (Figure 5-19 and Figure 5-20).

b) In low velocity condensing conditions, many alloys including carbon steel, low alloy steels and 400 Series SS may show uniform loss in thickness and/or pitting.

5.1.1.7.6 Prevention / Mitigation

a) For units and/or components of systems which have not been designed for resistance to NAC, the options are to change or blend crudes, upgrade metallurgy, utilize chemical inhibitors or some combination thereof.

b) NAC can be reduced by blending crude to reduce the TAN and/or increase the sulfur content.

c) Use alloys with higher molybdenum content for improved resistance (Table 5-2).

d) High temperature NAC inhibitors have been used with moderate success, however potential detrimental effects on downstream catalyst activity must be considered. Inhibitors effectiveness needs to be monitored carefully.

e) For severe conditions, Type 317L stainless steel or other alloys with higher molybdenum content may be required.

5.1.1.7.7 Inspection and Monitoring

a) UT and RT are used for thickness monitoring but localized erosion may be difficult to locate so RT should be the primary detection method followed by UT thickness measurement.

b) Monitor TAN and sulfur content of the crude charge and side streams to determine the distribution of acids in the various cuts.

c) Electrical resistance corrosion probes and corrosion coupon racks can be used.

d) Streams can be monitored for Fe and Ni content to assess corrosion in the system.

e) Hydrogen probes have also been reported to detect NAC.

5.1.1.7.8 Related Mechanisms

Sulfidation is a competing and complimentary mechanism which must be considered in most situations with NAC. In cases where thinning is occurring, it is difficult to distinguish between NAC and sulfidation.

5.1.1.7.9 References


6. API Publication 581, Risk-Based Inspection Technology, American Petroleum Institute, Washington, D.C.
<table>
<thead>
<tr>
<th>Table 5-2 – Alloys listed in approximate order of increasing resistance to NAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS, 1.25C-0.5Mo, 2.25Cr-1Mo, 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>
Figure 5-19 – Erosion-corrosion damage due to NAC in a 10-inch 5Cr elbow in the outlet of a vacuum heater in a VDU.

Figure 5-20 – Severe NAC of 410 SS trays and bubble caps in the HVGO section of the vacuum tower fed by the vacuum heater in Figure 5-19.
5.1.1.8 Phenol (Carbolic Acid) Corrosion

5.1.1.8.1 Description of Damage
Corrosion of carbon steel can occur in plants using phenol as a solvent to remove aromatic compounds from lubricating oil feedstocks.

5.1.1.8.2 Affected Materials
In order of increasing resistance: carbon steel, 304L, 316L and Alloy C276.

5.1.1.8.3 Critical Factors
a) Temperature, water content, alloy chemistry and velocity are the critical factors.
b) Corrosion is usually minimal in the treating section when the temperature is below 250°F (121°C).
c) Corrosion can occur in the recovery section where spent phenol is separated by vaporization.
d) Sulfur and organic acids may lead to naphthenic acid attack and sulfidation in the hot extract circuit.
e) Carbon steel and 304/304L stainless steel corrode rapidly in phenol service above 450°F (232°C).
f) Dilute aqueous solutions (5-15% phenol) are very corrosive to the extract dryer condensers.
g) High velocities may promote localized corrosion.

5.1.1.8.4 Affected Units or Equipment
Phenol extraction facilities in lubes plant.

5.1.1.8.5 Appearance or Morphology of Damage
a) Corrosion will be in the form of general or localized corrosion of carbon steel.
b) Localized loss in thickness due to erosion-corrosion may occur.
c) Erosion-corrosion and/or condensation corrosion may be observed in tower overhead circuits.

5.1.1.8.6 Prevention / Mitigation
a) Corrosion is best prevented through proper materials selection and control of phenol solvent chemistry.
b) Overhead piping circuits should be designed for a maximum velocity of 30 fps in the recovery section.
c) Recovery tower overhead temperatures should be maintained to at least 30°F (17°C) above the dew point.
d) Type 316L stainless steel may be used in the top of the dry tower, phenol flash tower and various condenser shells and separator drums that handle phenol-containing water.
e) Tubes and headers in extract furnaces should be 316L.
f) Alloy C276 has been used in areas of high velocity or other locations where 316L is inadequate.

5.1.1.8.7 Inspection and Monitoring
a) UT and RT to monitor for loss in thickness.
b) ER corrosion probes and corrosion coupons have been used for corrosion monitoring.

5.1.1.8.8 Related Mechanisms
Not applicable.

5.1.1.8.9 References
5.1.1.9  Phosphoric Acid Corrosion

5.1.1.9.1  Description of Damage

Phosphoric acid is most often used as a catalyst in polymerization units. It can cause both pitting corrosion and localized corrosion of carbon steels depending on water content.

5.1.1.9.2  Affected Materials

In order of increasing resistance: carbon steel, 304L SS, 316L SS and Alloy 20.

5.1.1.9.3  Critical Factors

a) Acid concentration, temperature and contaminants.
b) Solid phosphoric acid catalysts are not corrosive to carbon steel unless free water is present. When water is present, severe corrosion of carbon steel may occur.
c) Corrosion rates increase with increasing temperature.
d) Corrosion can penetrate a 1/4-inch thick steel tube in eight hours.
e) Most corrosion probably occurs during water washing operations at shutdowns.
f) Contaminants, such as chlorides, can increase phosphoric acid corrosion.

5.1.1.9.4  Affected Units or Equipment

a) Piping and equipment in the polymerization unit where water mixes with catalyst.
b) Corrosion is usually found in low velocity areas where there is little or no circulation such as piping manifolds, the bottom of kettle-type reboilers, partial penetration welds, and exchangers where there is sufficient residence time to permit the settling of acid droplets.

5.1.1.9.5  Appearance or Morphology of Damage

General or localized thinning of carbon steel.

5.1.1.9.6  Prevention / Mitigation

a) Selective upgrading to corrosion resistant materials is the only option where water cannot be eliminated.
b) Type 304L SS is satisfactory for phosphoric acid concentration of 100% up to about 120°F (49°C). Type 316L SS is required from 120°F to 225°F (49°C to 107°C)).
c) Type 316L SS and Alloy 20 are effective at concentrations up to 85% at boiling temperatures.

5.1.1.9.7  Inspection and Monitoring

a) UT and RT for loss of thickness.
b) Sample iron in water from first column overhead receiver.
c) Online corrosion monitoring using ER probes and/or corrosion coupons in the water draw from the first column overhead condenser and the reboiler.

5.1.1.9.8  Related Mechanisms

Not applicable.

5.1.1.9.9  References

5.1.1.10  Sour Water Corrosion (Acidic)

5.1.1.10.1  Description of Damage

a) Corrosion of steel due to acidic sour water containing H₂S at a pH between 4.5 and 7.0. Carbon dioxide (CO₂) may also be present.

b) Sour waters containing significant amounts of ammonia, chlorides or cyanides may significantly affect pH but are outside the scope of this section.

5.1.1.10.2  Affected Materials

a) Primarily affects carbon steel.

b) Stainless steels, copper alloys and nickel base alloys are usually resistant.

5.1.1.10.3  Critical Factors

a) H₂S content, pH, temperature, velocity and oxygen concentration are all critical factors.

b) The H₂S concentration in the sour water is dependent on the H₂S partial pressure in the gas phase as well as temperature and pH.

c) At a given pressure, the H₂S concentration in the sour water decreases as temperature increases.

d) Increasing concentrations of H₂S tend to decrease solution pH down to about 4.5. Streams with a pH below 4.5 indicate the presence of a strong acid which would be the main corrosion concern (see 5.1.1).

e) Above a pH of about 4.5, a protective, thin iron sulfide layer limits the corrosion rate.

f) In some instances at a pH above 4.5, a thicker, porous sulfide film layer can form. This can promote pitting under sulfide deposits. Typically, this does not affect the general corrosion rate.

g) Other contaminants have a significant affect on water pH. For example, HCl and CO₂ lower pH (more acidic). Ammonia significantly increases pH and is more often associated with alkaline sour water where the main concern is ammonia bisulfide corrosion (see 5.1.1.2).

h) The presence of air or oxidants may increase the corrosion and usually produces pitting or underdeposit attacks.

5.1.1.10.4  Affected Units or Equipment

Acid sour water corrosion is a concern in overhead systems of FCC and coker gas fractionation plants with high H₂S levels and low NH₃ levels.

5.1.1.10.5  Appearance or Morphology of Damage

a) Corrosion damage from acidic sour water is typically general thinning. However, localized corrosion or localized underdeposit attack can occur, especially if oxygen is present. Corrosion in CO₂ containing environments may be accompanied by carbonate stress corrosion cracking (see 5.1.2.5).

b) 300 Series SS are susceptible to pitting attack and may experience crevice corrosion and/or chloride stress corrosion cracking (see 4.5.1).

5.1.1.10.6  Prevention / Mitigation

a) 300 Series SS can be used at temperatures below about 140°F (60°C) where Chloride Stress Corrosion Cracking (CSCC) is not likely.

b) Copper alloys and nickel alloys are generally not susceptible to acid sour water corrosion. However, copper alloys are vulnerable to corrosion in environments with ammonia.

5.1.1.10.7  Inspection and Monitoring

a) Evidence of locally thinned areas can be found using scanning ultrasonic thickness methods or profile radiography.

b) For carbon steel, damage is usually in the form general thinning but may be highly localized to specific
areas of high velocity or turbulence, typically where a water phase is condensing.

c) Process and corrosion monitoring are important aspects of a well-developed program to minimize the effects of acidic sour water corrosion.

d) The water draws of overhead accumulators should be monitored periodically to measure pH.

e) Properly placed corrosion probes and corrosion coupons provide additional information on the rate and extent of potential damage.

5.1.1.10.8 Related Mechanisms

Other factors to consider in these environments include wet H₂S damage (see 5.1.2.3) and carbonate SCC. (see 5.1.2.5).

5.1.1.10.9 References

5.1.1.11 Sulfuric Acid Corrosion

5.1.1.11.1 Description of Damage
Sulfuric acid promotes general and localized corrosion of carbon steel and other alloys. Carbon steel heat affected zones may experience severe corrosion.

5.1.1.11.2 Affected Materials
In order of increasing resistance: carbon steel, 316L SS, Alloy 20, high silicon cast iron, high nickel cast iron, Alloy B-2 and Alloy C276.

5.1.1.11.3 Critical Factors
a) Acid concentration, temperature, alloy content, velocity, contamination and presence of oxidizers.
b) Figure 5-21 shows a plot of carbon steel corrosion rates as a function of sulfuric acid concentration and temperature.
c) Carbon steel corrosion rates increase significantly if the flow velocity exceeds about 2 to 3 fps (0.6 to 0.9 m/s) or at acid concentrations below 65%.
d) Mix points with water cause heat to be released and high corrosion rates can occur where the acid becomes diluted.
e) The presence of oxidizers can greatly increase the corrosion rate.

5.1.1.11.4 Affected Units or Equipment
a) Sulfuric acid alkylation units and waste water treatment plants are affected.
b) Areas of vulnerability in sulfuric acid alkylation units include reactor effluent lines, reboilers, deisobutanizer overhead systems and the caustic treating section (Figure 5-22 and Figure 5-23).
c) Acid usually ends up in the bottom of fractionation towers and reboilers where it becomes concentrated.

5.1.1.11.5 Appearance or Morphology of Damage
a) Mostly general in nature, but attacks carbon steel weld heat affected zones rapidly.
b) Hydrogen grooving may occur in low flow or stagnant areas such as in storage tanks or rail cars.
c) Sulfuric acid attacks slag left from welding.
d) If the corrosion rate and velocity are high, there will be no scale.
e) Corrosion of steel by dilute acid is usually in the form of overall metal loss or pitting and becomes more severe with increasing temperature and velocity.

5.1.1.11.6 Prevention / Mitigation
a) Corrosion is minimized through materials selection and proper operation within design velocities.
b) Alloys such as Alloy 20, Alloy 904L and Alloy C-276 resist dilute acid corrosion and form a protective iron sulfate film on the surface.
c) Acidified product streams can be washed with caustic to neutralize the acid.

5.1.1.11.7 Inspection and Monitoring
a) UT or RT inspection of turbulent zones and hottest areas.
b) Corrosion monitoring with coupons and ER probes.

5.1.1.11.8 Related Mechanisms
Not applicable.
5.1.1.11.9 References
1. NACE Publication 5A151, Materials of Construction for Handling Sulfuric Acid, NACE International, Houston, TX, 1985.
6. NACE Standard RP0294, Design, Fabrication, and Inspection of Tanks for the Storage of Concentrated Sulfuric Acid and Oleum at Ambient Temperatures, NACE International, Houston, TX.
Figure 5-21 – Sulfuric acid corrosion data for carbon steel.

Figure 5-22 – Accelerated corrosion under a baffle.
Figure 5-23 – Grooving corrosion in the carbon steel vapor line from an alkaline water wash drum in a sulfuric acid alkylation unit.
5.1.1.12 Aqueous Organic Acid Corrosion

5.1.1.12.1 Description of Damage.
Organic compounds present in some crude oils decompose in the crude furnace to form low molecular weight organic acids which condense in distillation tower overhead systems. They may also result from additives used in upstream operations or desalting. These naturally occurring acids may contribute significantly to aqueous corrosion depending on the type and quantity of acids, and the presence of other contaminants.

5.1.1.12.2 Affected Materials
a) All grades of carbon steel are affected.
b) Most other corrosion resistant alloys used in crude tower overhead systems are generally not affected.

5.1.1.12.3 Critical Factors
a) Corrosion is a function of the type and quantity of organic acids, metal temperature, fluid velocity, system pH, and presence of other acids.
b) The low molecular weight organic acids that are formed include formic acid, acetic acid, propionic acid, and butyric acid.
c) The lower molecular weight acids such as formic acid and acetic acid are the most corrosive. They are soluble in naphtha and are extracted into the water phase, once the water condenses, and contribute to a reduction of pH.
d) The presence of organic acids will contribute to the overall demand for neutralizing chemicals but their affects may be completely masked by the presence of other acids such as HCl, H2S, carbonic acid and others.
e) Corrosion is most likely to be a problem where relatively ‘non-corrosive’ conditions exist in an overhead system and there is a sudden increase in low molecular weight organic acids that reduces the pH of the water in the overhead system requiring a potentially unexpected increase in neutralizer demand.
f) The type and quantity of organic acids formed in the overhead system are crude specific. One source of acid is believed to be the result of thermal decomposition of naphthenic acids in the crude may be precursors to light organic acid formation and that processing of higher TAN crudes may increase organic acid in the overheads but very little published data is available on this subject.
g) Some of the higher molecular weight organic acids condense above the water dew point in overhead systems but are generally not present in sufficient quantities to cause corrosion.
h) Light organic acids such as acetic acid are sometimes added to upstream dehydrators or desalters to improve performance and inhibit calcium naphthenate salt deposition (Ref. 2). Such acids will vaporize in the crude preheat and furnace, and go up the column into the crude tower overhead system.
i) Other high molecular weight acids used as additives can thermally decompose at crude unit temperatures forming volatile acidic species, such as acetic and formic acids.
j) In general, these light organic acids do not generate the severity of corrosion associated with inorganic acids such as HCl. Table 5-3 shows the HCl equivalent factor for corrosion in overhead systems. To calculate the HCl equivalent of an organic acid, multiply the content of the organic acid (in ppm-weight) by the factor for that acid, and result will be the equivalent content of HCl (in ppm). This number can then be used to estimate the neutralizer demand in the overhead system, and the additional neutralizer needed to compensate for organic acids in overhead systems. Excess neutralizer can lead to amine hydrochloride salts in overhead systems.

5.1.1.12.4 Affected Units or Equipment
a) All carbon steel piping and process equipment in crude tower, vacuum tower and coker fractionator overhead systems including heat exchangers, towers and drums are susceptible to damage where acidic conditions occur.
b) Corrosion tends to occur where water accumulates or where hydrocarbon flow directs water droplets
against metal surfaces. For example, the bottoms of overhead exchangers, separator drums, boots of separator drums, elbows, tees, pumps, and downstream of control valves.

c) Corrosion is also sensitive to flow rate and will tend to be more severe in turbulent areas in piping systems including overhead transfer lines, overhead condensers, separator drums, control valves, pipe elbows and tees, exchanger tubes, etc.

5.1.1.12.5 Appearance or Morphology of Damage

a) Light organic acid corrosion typically leaves the corroded surface smooth and damage may be difficult to distinguish from corrosion by other acids in the overhead system. It is sometimes mistaken for HCl corrosion or carbonic acid corrosion.

b) In pipe or other equipment where there is significant flow, the surfaces are sometimes smoothly grooved.

5.1.1.12.6 Prevention / Mitigation

a) Corrosion caused by light organic acids in crude unit overhead systems can be minimized through the injection of a chemical neutralizing additive. However, problems may arise when frequent changes in crude blends lead to changes in neutralizer demand.

b) The TAN of the crudes being processed can be used as an initial guide to setting the neutralizer by anticipating an increase in the acid concentration in the overhead system. After a new crude is processed, a review of analyses of water samples from the boot of the overhead separator drum can be used to determine how much light organic acid reaches the overhead system optimize future additions.

c) Filming amines can be used to prevent corrosion if the filming amine selected does not react with the organic acid. However, using filming amines is not as effective as neutralization.

d) Upgrading to corrosion-resistant alloys will prevent organic acid corrosion but the selection of suitable materials should account for other potential damage mechanisms in the overhead system.

5.1.1.12.7 Inspection and Monitoring

a) UT and RT inspection for loss in thickness are the most common methods of inspection.

b) Long range UT techniques can also be used for long runs of pipe.

c) For carbon steel, damage is usually in the form of general thinning but may be highly localized where a water phase is condensing.

d) Evidence of locally thinned areas can be found using automatic ultrasonic scanning methods or profile radiography.

e) Process monitoring should include pH measurement and analysis of water in the crude tower overhead drum to analyze for the presence of organic acids.

f) Strategically placed corrosion probes and/or corrosion coupons can provide additional information on the rate and extent of damage.

5.1.1.12.8 Related Mechanisms

This form of damage may be difficult to differentiate from HCl corrosion in crude tower overhead systems. See also HCl corrosion (see 5.1.1.4). Ammonium chloride corrosion (see 5.1.1.3), and chloride SCC (4.5.1).

5.1.1.12.9 References


5. NACE Publication 34109, “Crude Distillation Unit - Distillation Tower Overhead System Corrosion”,
Table 5-3: Light Organic Acid Corrosion Equivalency Factors

<table>
<thead>
<tr>
<th>Acid</th>
<th>HCl Equivalent Factor</th>
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<tr>
<td>Formic</td>
<td>0.76</td>
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<tr>
<td>Acetic</td>
<td>0.61</td>
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<tr>
<td>Propionic</td>
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<tr>
<td>Hexanoic</td>
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<tr>
<td>Heptanoic</td>
<td>0.28</td>
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</tbody>
</table>
5.1.2  Environment-Assisted Cracking

5.1.2.1  Polythionic Acid Stress Corrosion Cracking (PASCC)

5.1.2.1.1  Description of Damage

a) A form of stress corrosion cracking normally occurring during shutdowns, startups or during operation when air and moisture are present. Cracking is due to sulfur acids forming from sulfide scale, air and moisture acting on sensitized austenitic stainless steels.

b) Usually adjacent to welds or high stress areas.

c) Cracking may propagate rapidly through the wall thickness of piping and components in a matter of minutes or hours.

5.1.2.1.2  Affected Materials

300 Series SS, Alloy 600/600H and Alloy 800/800H.

5.1.2.1.3  Critical Factors

a) A combination of environment, material, and stress are required.

i) Environment - Metallic components form a surface sulfide scale when exposed to sulfur compounds. The scale may react with air (oxygen) and moisture to form sulfur acids (polythionic acid).

ii) Material - The material must be in a susceptible or "sensitized" condition.

iii) Stress - Residual or applied.

b) Affected alloys become sensitized during exposure to elevated temperatures during manufacture, welding or high temperature service. "Sensitization" refers to the composition/time/temperature dependent formation of chromium carbide in the grain boundaries of the metal. Sensitization occurs in the 750°F to 1500°F (400°C to 815°C) temperature range.

c) The carbon content and the thermal history of the alloy have a significant effect on sensitization susceptibility. Regular and controlled carbon grades of stainless steels such as types 304/304H and 316/316H are particularly susceptible to sensitizing in the weld HAZ. Low carbon "L" grades (< 0.03% C) are less susceptible and usually can be welded without sensitizing. The L grades will not sensitize provided long term operating temperatures do not exceed about 750°F (399°C).

d) Residual stresses in most components are usually sufficient to promote cracking.

5.1.2.1.4  Affected Units or Equipment

a) All units where sensitized alloys are used in sulfur-containing environments. Commonly damaged equipment includes heat exchanger tubes, furnace tubes and piping.

b) Fired heaters burning oil, gas, coke and most other sources of fuel may be affected depending on sulfur levels in the fuel.

c) Severe cases have been found in FCC units (air rings, plenums, slide valves, cyclone components, expansion joint bellows and piping).

d) In hydroprocessing units (heater tubes, hot feed/effluent exchanger tubes, bellows).

e) Crude and coker units (piping).

f) Boilers and high temperature equipment exposed to sulfur-containing combustion products.

5.1.2.1.5  Appearance or Morphology of Damage

a) Typically occurs next to welds, but can also occur in the base metal (Figure 5-24). It is usually quite localized and may not be evident until a leak appears during start-up or, in some cases, operation.

b) Cracking propagates intergranularly (Figure 5-25).
5.1.2.1.6  **Prevention / Mitigation**

c) Corrosion or loss in thickness is usually negligible.

5.1.2.1.6  **Prevention / Mitigation**

a) If equipment will be opened or exposed to air, preventive measures should be taken to minimize or eliminate PASCC include flushing the equipment with alkaline or soda ash solution to neutralize sulfur acids immediately after or during shutdown or purging with dry nitrogen or nitrogen/ammonia during the shutdown to prevent air exposure. Refer to guidelines in NACE RP0170.

b) For furnaces, keep the firebox heated above the dewpoint to prevent acids from forming on heater tubes.

c) Low carbon grades such as 304L/316L/317L provide some measure of improvement over controlled carbon grades. The L grades will sensitize if exposed more than several hours above about 1000°F (538°C) or long term above 750°F (400°C).

d) Improved resistance to PASCC cracking can be achieved with modified versions of these alloys containing small amounts of Ti and Nb. Typically used are the chemically stabilized grades (austenitic stainless steel types 321 and 347 and nickel base Alloys 825 and 625).

e) ASTM specifications allow mill products to be shipped in a stabilized condition rather than solution annealed. This heat treatment will minimize potential sensitization problems especially with type 321.

f) A thermal stabilization heat treatment at 1650°F (899°C) may be applied to chemically stabilized austenitic stainless steel welds after all welding is complete in an attempt to reduce sensitization and PTA susceptibility. This heat treatment is difficult to apply in the field.

g) Susceptibility to PASCC can be determined by laboratory corrosion testing according to ASTM A262 Practice C. A sensitizing heat treatment is often applied to L and/or chemically stabilized grades prior to testing.

5.1.2.1.7  **Inspection and Monitoring**

a) PT examination can be used to detect PASCC cracking (Figure 5-24 through Figure 5-28). However, because the cracks are filled with a tight deposit, flapper disc sanding may be needed to improve the PT sensitivity.

b) PASCC cracking can be an inspection challenge because the cracking may not occur until well into a turnaround.

c) Monitoring for PASCC cracking during operation is not usually practical. Conditions causing the cracking are not usually present while operating.

5.1.2.1.8  **Related Mechanisms**

Also known as Polythionic Acid Stress Corrosion Cracking (PTA SCC), Intergranular Corrosion (IGC) and Intergranular Attack (IGA).

5.1.2.1.9  **References**


2. NACE Recommended Practice RP0170, Protection of Austenitic Stainless Steels and Other Austenitic Alloys from Polythionic Acid Stress Corrosion Cracking during Shutdown of Refinery Equipment, NACE International, Houston, TX.


Figure 5-24 – Dye penetrant inspection showing extensive O.D. cracking around welds.

Figure 5-25 – High magnification photomicrograph of metallographic sample showing intergranular cracking and grain dropping.
Figure 5-26 – PT inspection of a type 304 stainless steel catalyst withdrawal line piping and weld neck flange.

Figure 5-27 – Cross-section of the catalyst withdrawal line attached to the flange in Figure 5-26 showing cracking in the weld HAZ. Mag. 3X.
Figure 5-28 – Higher magnification view showing intergranular cracking. Mag. 200X.
5.1.2.2 Amine Stress Corrosion Cracking

5.1.2.2.1 Description of Damage
a) Amine cracking is a common term applied to the cracking of steels under the combined action of tensile stress and corrosion in aqueous alkanolamine systems used to remove/absorb H₂S and/or CO₂ and their mixtures from various gas and liquid hydrocarbon streams.
b) Amine cracking is a form of alkaline stress corrosion cracking.
c) It is most often found at or adjacent to non-PWHT’d carbon steel weldments or in highly cold worked parts.
d) Amine cracking should not be confused with several other types of SCC that can occur in amine environments which are further described in 5.1.2.3 and 5.1.2.5.

5.1.2.2.2 Affected Materials
Carbon steel and low alloy steels.

5.1.2.2.3 Critical Factors
a) The critical factors are the level of tensile stress, amine concentration and temperature.
b) Cracking is associated with residual stresses from welding, cold working or fabrication that have not been removed through an effective stress-relieving heat treatment.
c) Cracking is more likely to occur in lean MEA and DEA services but is also found in most amines including MDEA and DiPA (ADIP).
d) Cracking has been reported down to ambient temperatures with some amines. Increasing temperature and stress levels increases the likelihood and severity of cracking. Refer to API RP 945 for guidelines on PWHT requirements for various amine services.
e) Amine cracking is most often associated with lean amine services. The pure alkanolamine does not cause cracking. Cracking in rich amine services are most often associated with wet H₂S problems (see 5.1.2.3).
f) Cracking can occur in non-PWHT’d piping and equipment as a result exposure to steamout and to short-term amine carryover.
g) Amine concentration does not appear to have a significant effect on the propensity for cracking.
h) Some refiners believe cracking will not occur below an amine concentration of about 2% to 5%. However, local enrichment and steamout can reduce this limit and some plants have used lower limits down to 0.2%.

5.1.2.2.4 Affected Units or Equipment
All non-PWHT carbon steel piping and equipment in lean amine service including contactors, absorbers, strippers, regenerators and heat exchangers as well as any equipment subject to amine carryover.

5.1.2.2.5 Appearance or Morphology of Damage
a) Amine cracking results in surface breaking flaws that initiate on the ID of piping and equipment primarily in the weld HAZ but has also been found in weld metal and high stress areas adjacent to the HAZ.
b) Cracking typically develops parallel to the weld and there may be parallel cracks. In weld metal, the cracks are either transverse or longitudinal with the weld.
c) At set-on nozzles, the cracks are radial in the base metal, i.e., they fan out from the bore. At set-in nozzles, the cracks are usually parallel to the weld.
d) The appearance of the cracks on the surface may be similar to those caused by wet H₂S cracking.
e) Since the driving force for cracking is residual stress, cracks are often found on the process side, opposite external attachment welds.
f) Positive identification of amine cracking can be confirmed by metallographic analysis. The cracking is typically intergranular, oxide filled with some branching (Figure 5-29 through Figure 5-32).

5.1.2.2.6 **Prevention / Mitigation**

a) PWHT all carbon steel welds in piping and equipment in accordance with API RP 945. The same requirement applies to repair welds and to internal and external attachment welds (Figure 5-33).

b) Use solid or clad stainless steel, Alloy 400 or other corrosion resistant alloys in lieu of carbon steel.

c) Water wash non-PWHT carbon steel piping and equipment prior to welding, heat treatment or steamout.

5.1.2.2.7 **Inspection and Monitoring**

a) Although cracks may be seen visually, crack detection is best performed with WFMT or ACFM techniques. Surface preparation by grit blasting, high pressure water blasting or other methods is required for WFMT but may not be necessary for ACFM.

b) PT is usually not effective in finding tight and/or scale filled cracks and should not be used.

c) If the cracks have minimum branching, crack depths can be measured with a suitable UT technique including external SWUT.

d) AET can also be used for monitoring crack growth and locating growing cracks.

5.1.2.2.8 **Related Mechanisms**

Amine cracking is more properly termed amine stress corrosion cracking and is a form of Alkaline Stress Corrosion Cracking (ASCC). Caustic stress corrosion cracking (see 4.3.10) and carbonate stress corrosion cracking (see 5.1.2.5) are two other forms of ASCC that are similar in appearance.

5.1.2.2.9 **References**

1. API Recommended Practice 945, Avoiding Environmental Cracking in Amine Units, American Petroleum Institute, Washington, D.C.


Figure 5-29 – A photomicrograph of a cross-section of a weld in non-PWHT piping showing a SCC in the vicinity of a piping weld. Mag. 6X (From API 945)

Figure 5-30 – A higher magnification view of the crack tip in Figure 5-29. Mag. 200X. (From API RP 945.)
Figure 5-31 – A photomicrograph of a cross-section of a piping weld showing stress corrosion cracking in section of the line from the MEA absorber column normally operated at 100°F (38°C). Mag. 6X. (From API RP 945.)

Figure 5-32 – A higher magnification view of the cracks in Figure 5-31 which illustrates the
intergranular nature of cracking. Mag. 200X. (From API RP 945.)

Figure 5-33 – Amine SCC developed on the ID, beneath an arc strike on the OD of a 3 inch line in 20% MEA. The original line was PWHT’d during original fabrication but not the arc strike. Leaks occurred after 30 years service.
5.1.2.3 Wet H₂S Damage (Blistering/HIC/SOHIC/SSC)

5.1.2.3.1 Description of Damage

This section describes four types of damage that result in blistering and/or cracking of carbon steel and low alloy steels in wet H₂S environments.

a) Hydrogen Blistering

Hydrogen blisters may form as surface bulges on the ID, the OD or within the wall thickness of a pipe or pressure vessel. The blister results from hydrogen atoms that form during the sulfide corrosion process on the surface of the steel, that diffuse into the steel, and collect at a discontinuity in the steel such as an inclusion or lamination. The hydrogen atoms combine to form hydrogen molecules that are too large to diffuse out and the pressure builds to the point where local deformation occurs, forming a blister. Blistering results from hydrogen generated by corrosion, not hydrogen gas from the process stream. (Figure 5-34 and Figure 5-35.)

b) Hydrogen Induced Cracking (HIC)

Hydrogen blisters can form at many different depths from the surface of the steel, in the middle of the plate or near a weld. In some cases, neighboring or adjacent blisters that are at slightly different depths (planes) may develop cracks that link them together. Interconnecting cracks between the blisters often have a stair step appearance, and so HIC is sometimes referred to as "stepwise cracking" (Figure 5-36, Figure 5-37 and Figure 5-38).

c) Stress Oriented Hydrogen Induced Cracking (SOHIC)

SOHIC is similar to HIC but is a potentially more damaging form of cracking which appears as arrays of cracks stacked on top of each other. The result is a through-thickness crack that is perpendicular to the surface and is driven by high levels of stress (residual or applied). They usually appear in the base metal adjacent to the weld heat affected zones where they initiate from HIC damage or other cracks or defects including sulfide stress cracks (Figure 5-39 and Figure 5-40).

d) Sulfide Stress Cracking (SSC)

Sulfide Stress Cracking (SSC) is defined as cracking of metal under the combined action of tensile stress and corrosion in the presence of water and H₂S. SSC is a form of hydrogen stress cracking resulting from absorption of atomic hydrogen that is produced by the sulfide corrosion process on the metal surface.

SSC can initiate on the surface of steels in highly localized zones of high hardness in the weld metal and heat affected zones. Zones of high hardness can sometimes be found in weld cover passes and attachment welds which are not tempered (softened) by subsequent passes. PWHT is beneficial in reducing the hardness and residual stresses that render steel susceptible to SSC. High strength steels are also susceptible to SSC but these are only used in limited applications in the refining industry. (Figure 5-41 and Figure 5-42). Some carbon steels contain residual elements that form hard areas in the heat affected zones that will not temper at normal stress relieving temperatures. Using preheat helps minimize these hardness problems.

5.1.2.3.2 Affected Materials

Carbon steel and low alloy steels.

5.1.2.3.3 Critical Factors

a) The most important variables that affect and differentiate the various forms of wet H₂S damage are environmental conditions (pH, H₂S level, contaminants, temperature), material properties (hardness, microstructure, strength) and tensile stress level (applied or residual). These factors are outlined below.
b) All of these damage mechanisms are related to the absorption and permeation of hydrogen in steels.

i) pH

- Hydrogen permeation or diffusion rates have been found to be minimal at pH 7 and increase at both higher and lower pH. The presence of hydrogen cyanide (HCN) in the water phase significantly increases permeation in alkaline (high pH) sour water.

- Conditions which are known to promote blistering, HIC, SOHIC and SSC are those containing free water (in liquid phase) and:
  - >50 wppm dissolved H₂S in the free water, or
  - free water with pH <4 and some dissolved H₂S present, or
  - free water with pH >7.6 and 20 wppm dissolved hydrogen cyanide (HCN) in the water and some dissolved H₂S present, or
  - >0.0003 MPa (0.05 psia) partial pressure of H₂S in the gas phase.

- Increasing levels of ammonia may push the pH higher into the range where cracking can occur.

ii) H₂S

- Hydrogen permeation increases with increasing H₂S partial pressure due to a concurrent increase in the H₂S concentration in the water phase.

- An arbitrary value of 50 wppm H₂S in the water phase is often used as the defining concentration where wet H₂S damage becomes a problem. However, there are cases where cracking has occurred at lower concentrations or during upset conditions where wet H₂S was not ordinarily anticipated. The presence of as little as 1 wppm of H₂S in the water has been found to be sufficient to cause hydrogen charging of the steel.

- Susceptibility to SSC increases with increasing H₂S partial pressures above about 0.05 psi (0.0003 Mpa) H₂S in steels with a tensile strength above about 90 ksi or in steels with localized zones of weld or weld HAZ hardness above 237 HB.

iii) Temperature

- Blistering, HIC, and SOHIC damage have been found to occur between ambient and 300°F (150°C) or higher.

- SSC generally occurs below about 180°F (82°C). However, equipment operating above this temperature are susceptible to SSC if there is an aqueous phase with H₂S as outlined above. Some susceptible equipment can fail even during short sour water excursions such as those encountered during equipment shutdowns.

- Hydrogen charging potential increases with increasing temperature if the aqueous phase is not eliminated by elevated temperature. Elevated temperature promotes dissociation of H₂S (thereby producing more monatomic hydrogen), together with an increase in the diffusion rates of hydrogen in metals, resulting in increased level of hydrogen charging. However, the SSC cracking potential is maximized at near-ambient temperature. This distinction is important because metals can become charged during high-temperature exposure and subsequently crack during excursions to lower temperatures (Ref. 8).

iv) Hardness

- Hardness is primarily an issue with SSC. Typical low-strength carbon steels used in refinery applications should be controlled to produce weld hardness <200 HB in accordance with NACE RP0472. These steels are not generally susceptible to SSC unless localized zones of hardness above 237 HB are present.

- The time to failure by SSC decreases as material strength, applied tensile stress, and environmental charging potential increase.

- Blistering, HIC and SOHIC damage are not related to steel hardness.

v) Steelmaking
- Blistering and HIC damage are strongly affected by the presence of inclusions and laminations which provide sites for diffusing hydrogen to accumulate.

- Steel chemistry and manufacturing methods also affect susceptibility and can be tailored to produce the HIC resistant steels outlined in NACE Publication 8X194.

- Improving steel cleanliness and processing to minimize blistering and HIC damage may still leave the steel susceptible to SOHIC.

- The disadvantage is that an absence of visual blistering may leave a false sense of security that H₂S damage is not active yet subsurface SOHIC damage may be present.

- HIC is often found in so-called “dirty” steels with high levels of inclusions or other internal discontinuities from the steel-making process.

vi) PWHT

- Blistering and HIC damage develop without applied or residual stress so that PWHT will not prevent them from occurring.

- High local stresses or notch-like discontinuities such as shallow sulfide stress cracks can serve as initiation sites for SOHIC. PWHT is highly effective in preventing or eliminating SSC by reduction of both hardness and residual stress.

- SOHIC is driven by localized stresses so that PWHT is also somewhat effective in reducing SOHIC damage.

5.1.2.3.4 Affected Units or Equipment

a) Blistering, HIC, SOHIC and SSC damage can occur throughout the refinery wherever there is a wet H₂S environment present.

b) In hydroprocessing units, increasing concentration of ammonium bisulfide above 2% increases the potential for blistering, HIC and SOHIC.

c) Cyanides significantly increase the probability and severity of blistering, HIC and SOHIC damage. This is especially true for the vapor recovery sections of the fluid catalytic cracking and delayed coking units. Typical locations include fractionator overhead drums, fractionation towers, absorber and stripper towers, compressor interstage separators and knockout drums and various heat exchangers, condensers, and coolers. Sour water stripper and amine regenerator overhead systems are especially prone to wet H₂S damage because of generally high ammonia bisulfide concentrations and cyanides.

d) SSC is most likely found in hard weld and heat affected zones and in high strength components including bolts, relief valve springs, 400 Series SS valve trim, compressor shafts, sleeves and springs.

5.1.2.3.5 Appearance or Morphology of Damage

a) All four forms of wet H₂S damage are best illustrated though the pictures and diagrams shown in Figure 5-33 through Figure 5-42.

b) Hydrogen blisters appear as bulges on the ID or OD surface of the steel and can be found anywhere in the shell plate or head of a pressure vessel. Blistering has been found on rare occasions in pipe and very rarely in the middle of a weld. HIC damage can occur wherever blistering or subsurface laminations are present.

c) In pressure-containing equipment, SOHIC and SSC damage is most often associated with the weldments. SSC can also be found at any location where zones of high hardness are found in vessels or in high strength steel components.

5.1.2.3.6 Prevention / Mitigation

a) Effective barriers that protect the surface of the steel from the wet H₂S environment can prevent damage including alloy cladding and coatings.

b) Process changes that affect the pH of the water phase and/or ammonia or cyanide concentration can help to reduce damage. A common practice is to utilize wash water injection to dilute the HCN concentration, for example, in FCC gas plants. Cyanides can be converted to harmless thiocyanates by
injecting dilute streams of ammonium polysulfides. Injection facilities require careful design.

c) HIC-resistant steels can be used to minimize the susceptibility to blistering and HIC damage. Detailed materials and fabrication guidance can be found in NACE Publication 8X194.

d) SSC can generally be prevented by limiting the hardness of welds and heat affected zones to 200 HB maximum through preheat, PWHT, weld procedures and control of carbon equivalents. Depending on the service environment, small zones of hardness up to 22 HRC should be resistant to SSC. Refer to NACE RP0472 for additional details.

e) PWHT can also help to minimize susceptibility to SOHIC. PWHT has limited value in preventing blistering and HIC damage from initiating but is beneficial in reducing residual stresses and strength levels that might otherwise contribute to crack propagation.

f) Specialized corrosion inhibitors can be used.

5.1.2.3.7 Inspection and Monitoring

a) Process conditions should be evaluated by process engineers and corrosion/materials specialists to identify piping and equipment where conditions are most likely to promote wet H₂S damage. Field sampling of the free water phase should be performed on a periodic or as-needed basis to monitor conditions or changes in conditions, particularly if water washing or polysulfide injection is used.

b) Inspection for wet H₂S damage generally focuses on weld seams and nozzles. Since the consequences can be severe, refineries generally have a procedure to prioritize and execute inspection for this type of damage. General notes on inspection for wet H₂S damage are included below. However, for the development of more detailed inspection plans including methods, coverage and surface preparation, the reader is directed to extensive recommendations on detection and repair outlined in NACE RP0296.

c) Although cracks may be seen visually, crack detection is best performed with WFMT, EC, RT or ACFM techniques. Surface preparation by grit blasting, high pressure water blasting or other methods is usually required for WFMT but not for ACFM. PT cannot find tight cracks and should not be depended on.

d) UT techniques including external SWUT can be used. SWUT is especially useful for volumetric inspection and crack sizing. Electrical resistance instruments are not effective for measuring crack depth.

e) Grinding out the crack or removal by thermal arc gouging is a viable method of crack depth determination.

f) AET can be used for monitoring crack growth.

5.1.2.3.8 Related Mechanisms

a) SSC is a form of hydrogen stress cracking (hydrogen embrittlement). Refer to 4.5.7.

b) Amine cracking (see 5.1.2.2) and carbonate cracking (see 5.1.2.5) can also occur in wet H₂S environments, may be similar in appearance, and are sometimes confused with the various forms of wet H₂S damage.

5.1.2.3.9 References

1. NACE Standard RP0296, Guidelines for Detection, Repair and Mitigation of Cracking of Existing Petroleum Refinery Pressure Vessels in Wet H₂S Environments, NACE International, Houston, TX.


5. NACE Standard RP0472, Methods and Controls to Prevent in-Service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments, NACE International, Houston,

7. R.D. Kane, R.J. Horvath, and M.S. Cayard, editors, "Wet H₂S Cracking of Carbon Steels and Weldments," NACE International, Houston, TX, 1996.

8. NACE Standard MR0103, Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments, NACE International, Houston, TX.
Figure 5-34 – Schematic of hydrogen blistering and HIC damage.

Figure 5-35 – Extensive hydrogen blistering on the surface of steel pressure vessel.
Figure 5-36 – Cross-section of plate showing HIC damage in the shell of a trim cooler which had been cooling vapors off a HHPS vessel in a hydroprocessing unit.

Figure 5-37 – High magnification photomicrograph of HIC damage.
Figure 5-38 – High magnification photomicrograph showing stepwise cracking nature of HIC damage.

Figure 5-39 – Schematic showing hydrogen blistering that is accompanied by SOHIC damage at the weld.
Figure 5-40– Schematic of SOHIC damage at a fillet weld that is usually a combination of SSC and SOHIC.

Figure 5-41 – Photograph showing WFMT of SOHIC damage.
Figure 5-42 – Schematic of SSC damage of a hard weld.

Figure 5-43 – Schematic showing morphology of sulfide stress cracking in a hard heat affected zone.
5.1.2.4 Hydrogen Stress Cracking - HF

5.1.2.4.1 Description of Damage

Hydrogen Stress Cracking is a form of environmental cracking that can initiate on the surface of high strength low alloy steels and carbon steels with highly localized zones of high hardness in the weld metal and HAZ as a result of exposure to aqueous HF acid environments.

5.1.2.4.2 Affected Materials

Carbon steel and low alloy steels.

5.1.2.4.3 Critical Factors

a) Steel hardness, strength and stress are the critical factors.
b) Susceptibility increases with increasing hardness. Hardness levels above Rockwell C 22 (237 BHN) are highly susceptible. Time-to-failure decreases as the hardness increases (higher strength materials).
c) Under high levels of applied or residual tensile stress (from cold-forming or welding) embrittlement results in cracking of susceptible steels.
d) Cracking may occur very rapidly, within hours after exposure to the HF environment, or considerable time may pass before cracking initiates.
e) Hard microstructures may arise in welds, particularly in low heat input welds in the heat affected zones, in low alloy steels, or may result from inadequate heat treatment.

5.1.2.4.4 Affected Units or Equipment

a) All piping and equipment exposed to HF acid at any concentration with hardness levels above the recommended limit are subject to hydrogen stress cracking.
b) High strength low alloy steels such as ASTM A193-B7 bolts and compressor components are susceptible.
c) ASTM A193B7M bolts are also susceptible if overtorqued.

5.1.2.4.5 Appearance or Morphology of Damage

a) This mode of cracking can only be confirmed by metallographic examination. The cracking will be intergranular.
b) Produces surface breaking cracks, usually associated with weldments.

5.1.2.4.6 Prevention / Mitigation

a) PWHT is beneficial in reducing the hardness and residual stresses that render a steel susceptible to SSC.
b) Typical low-strength carbon steels used in refinery applications should be controlled to produce weld hardness <200 HB in accordance with NACE SP0472. These steels are not generally susceptible to SCC unless localized zones of hardness above 237 HB are present.
c) Use carbon steels with Carbon Equivalents (CE) less than 0.43. Where CE is defined as:

\[
CE = \%C + \%Mn/6 + \%(Cr + Mo + V)/5 + \%(Cu + Ni)/15
\]

d) ASTM A193 grade B7M bolts are softer and lower strength than B7 bolts and are more resistant to cracking.
e) Alloy cladding or nonmetallic coatings that provide an effective barrier and protect the surface of the steel from hydrogen permeation will prevent cracking.
f) Alloy 400 is not susceptible to this form of cracking but may be susceptible to intergranular stress corrosion cracking, particularly in the non-stress relieved condition (see 5.1.1.6).
5.1.2.4.7 Inspection and Monitoring

a) Surface breaking cracks can be found by WFMT.

b) Hardness testing is the best method to determine the susceptibility of suspect material.

c) Zones of high hardness can sometimes be found on the process side in weld cover passes and attachment welds that are not tempered (softened) by subsequent passes.

5.1.2.4.8 Related Mechanisms

This is the same mechanism that is responsible for sulfide stress corrosion cracking in wet H₂S environments except that HF acid is generating the hydrogen. Blistering, HIC and SOHIC damage is similar to that found in wet H₂S (see 5.1.2.3).

5.1.2.4.9 References


3. NACE SP0472, Methods and Controls to Prevent in-Service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments, NACE International, Houston, TX.
5.1.2.5 Carbonate Stress Corrosion Cracking (ACSCC)

5.1.2.5.1 Description of Damage
Carbonate stress corrosion cracking (often referred to as carbonate cracking) is the term applied to surface breaking cracks that occur adjacent to carbon steel welds under the combined action of tensile stress in systems containing a free water phase with carbonate, where some amount of H$_2$S is also present. It is a form of Alkaline Stress Corrosion Cracking (ACSCC).

This type of damage has also been observed in other environments which are outside the scope of this discussion. Those environments include the outside surface of buried pipelines; and piping and equipment containing aqueous carbonate solutions (e.g., potassium carbonate) used in the carbon dioxide (CO$_2$) removal facilities associated with hydrogen reformers.

5.1.2.5.2 Affected Materials
Carbon steel and low alloy steels.

5.1.2.5.3 Critical Factors

a) The residual stress level of carbon steel and the water chemistry are the critical factors that determine the likelihood of carbonate cracking.

b) Carbonate stress corrosion cracking can occur at relatively low levels of residual stress but usually occurs at welds or cold worked areas that have not been stress relieved.

c) Additional details of water chemistry affecting susceptibility in FCC units are outlined below. More detailed information can be found in a NACE industry review published in 2008 (Ref. 4).

i) Water - In all areas in which ACSCC has been reported, there has been a separate liquid water phase present.

ii) pH - The pH of the sour water is a critical factor; most failures have occurred in the range of pH 8 to 10.

iii) H$_2$S – Cracking occurs where alkaline water is present. Although H$_2$S is often present, no threshold level has been established.

iv) Ammonia - NH$_3$ in the sour water is usually higher in cases where ACSCC has been observed than in cases with no ACSCC (e.g., 4,800 ppmw vs. 2,500 ppmw). Increasing NH$_3$ and decreasing H$_2$S together increase the likelihood of ACSCC.

v) Carbonate ion concentration – Cracking occurs above a certain threshold concentration. It has been suggested that levels above 100 ppmw can cause ACSCC, depending on the pH of the system. However, specific guidelines are difficult to define, largely as a result of the difficulty of sampling for carbonate ions and the lack of available data.

vi) Cyanides – Cracking can occur with or without the presence of cyanides.

vii) Polysulfides - There is no evidence to suggest that ammonium polysulfide injection increases or decreases the potential for ACSCC.

d) FCCU feed quality and unit operation appear to have an effect on cracking susceptibility:

i) Feed Nitrogen - The total nitrogen in FCCU feed is usually higher in cases where ACSCC has been observed than in cases with no ACSCC (e.g., 2,645 ppmw vs. 940 ppmw).

ii) Feed Sulfur – In general, cracking is associated with low sulfur FCCU feeds as opposed to high sulfur feeds. Susceptibility to cracking appears to be much more likely with hydrotreated feed.

iii) N to S ratio – Most cases of ACSCC have been associated with N/S ratio in the FCCU feed of 0 to 70

iv) Full burn vs. partial burn – The likelihood of cracking occurring in the FCC Regenerator partial-burn mode is approximately the same as full burn mode.
e) In CO₂ removal units, cracking may occur when the CO₂ content is above 2% and temperatures exceed 200°F (93°C).

5.1.2.5.4 **Affected Units or Equipment**

a) Carbonate cracking has been most prevalent in the fluid catalytic cracking unit main fractionator overhead condensing and reflux system, the downstream wet gas compression system, and the sour water systems emanating from these areas. Both piping and vessels are affected. See Figure 5-44 and 5-45 for typical locations where cracking has occurred.

b) Carbonate cracking has also been observed in SWS units of the side-pumparound type in the pumparound return line to the SWS tower; on the OD (process side) of highly cold worked SA179 condenser tube u-bends; and in the floor of tank storing sour water from an FCC unit.

c) Carbonate cracking has also occurred in piping and equipment in potassium carbonate in Catacarb and CO₂ removal facilities of hydrogen manufacturing units.

5.1.2.5.5 **Appearance or Morphology of Damage**

a) Carbonate cracking typically propagates parallel to the weld in the heat-affected zone, or adjacent base metal within 2 inches (50 mm) of the weld. At least two cases have been reported to occur more than 3 inches away (80 mm) in highly cold worked fittings including an elbow and reducer.

b) Cracking can also occur in the weld deposit.

c) The pattern of cracking observed on the steel surface is sometimes described as a spider web of small cracks, which often initiate at or interconnect with weld-related flaws that serve as local stress raisers.

d) These cracks may be easily mistaken for SSC or SOHIC, however, the carbonate cracks are usually further from the toe of the weld and have multiple parallel cracks (Figure 5-46 to Figure 5-47).

e) Carbonate cracks are surface breaking flaws that are predominantly intergranular in nature and typically occur in as-welded carbon steel fabrications as a network of very fine, oxide-filled cracks similar in appearance to caustic stress corrosion cracking and amine stress corrosion cracking. See Figures 5-48 to Figure 5-55.

5.1.2.5.6 **Prevention / Mitigation**

a) Application of a post-fabrication stress-relieving heat treatment of 1200°F to 1225°F (649°C to 663°C) in accordance with WRC 452 (Ref. 8) is a proven method of preventing carbonate cracking. Heat treatment requirements apply to repair welds as well as internal and external attachment welds.

b) Cracking can be eliminated through the use of effective barrier coatings, solid or clad 300 Series SS, Alloy 400 or other corrosion resistant alloys in lieu of carbon steel.

c) Water wash non-PWHT piping and equipment prior to steamout or heat treatment in hot carbonate systems.

d) A metavanadate inhibitor can be used in hot carbonate systems in CO₂ removal units in hydrogen manufacturing units to prevent cracking. Proper dosing and oxidation of the inhibitor must be maintained.

5.1.2.5.7 **Inspection and Monitoring**

a) Monitoring the pH of FCC sour waters is the fastest and most practical and cost effective method to locate areas where there is a potential for ASCC to occur.

b) The cracking can involve sporadic and rapid growth, depending on subtle changes in the process. Periodic monitoring of CO₃²⁻ concentration in FCC sour waters should be done to determine cracking susceptibility.

c) Although cracks may be seen visually, crack detection is best performed with WFMT or ACFM techniques. Surface preparation by grit blasting, high pressure water blasting or other methods is usually required for WFMT. PT usually cannot find tight or scale filled cracks and should not be used.

d) There is usually much branching so crack depths may be measured with a suitable UT technique including external SWUT. Electrical resistance type instruments that measure crack depth are not
effective because the cracks typically contain magnetic iron oxide.

e) This cracking is not susceptible to extension by grinding. Grinding out the cracks is a viable method of crack depth determination.

f) AET can be used for monitoring crack growth and locating growing cracks.

5.1.2.5.8 Related Mechanisms

Carbonate cracking is more properly termed carbonate stress corrosion cracking and is a form of Alkaline Stress Corrosion Cracking (ASCC). Amine cracking (see 5.1.2.2) and caustic stress corrosion cracking (see 4.5.3) are two other similar forms of ASCC.

5.1.2.5.9 References


8. WRC Bulletin 452, “Recommended Practices for Local Heating of Welds in Pressure Vessels” Welding Research Council (WRC), Shaker Heights, OH.
Figure 5-44 Simplified PFD of an FCCU gas plant showing where ACSCC has been reported Ref. 5).
Figure 5-45 – In a span of 7 months, a refinery experienced 23 leaks in piping in the Fractionator Overhead and the Wet Gas Comp sections. Follow-up with SWUT located 73 more indications (Ref. 6)
Figure 5-46 – Overhead interstage knockout drum vapor outlet nozzle.

Figure 5-47 – Carbonate cracking adjacent to a weld (Ref. 6).
Figure 5-48 – Metallographic sample showing intergranular carbonate cracking developed after 6 months service (Ref. 6).

Figure 5-49 – Most cracks originate in base metal but this weldment contained a crack that originated at the root and propagated through the weld metal. Other cracks appear to have initiated in the HAZ (Ref. 7).
Figure 5-50 – Photomicrograph of a cross-section of carbonate cracking in the base metal. Cracks initiate from the I.D. surface (left side). Unetched.

Figure 5-51 – Photomicrograph of a cross-section of carbonate cracking in the base metal, initiating at a corrosion pit on the ID surface. Unetched.
Figure 5-52 – Photomicrograph of a cross-section of carbonate cracking in the base metal, showing the branched nature of the cracking. Etched.

Figure 5-53 - Photomicrograph of a cross-section of a weld from a 4 inch (100 mm) ASTM A53 reflux line on the Main Fractionator that leaked after 52 years service.
Figure 5-54 – An 18 inch (460 mm) diameter API 5L Grade B pipe section with two 1 in (25 mm) water wash injection nozzles at the inlet to the 2nd stage compressor. Note the cracks on the ID of the two injection nozzles after blast cleaning. The line leaked after 21 years service.
Figure 5-55 – A 3 in x 4 in (76 mm x 100 mm) diameter tee in a hydrocarbon line off a water knockout pot in the FCC light ends recovery section. Cracking developed after 6 months service.
5.1.3 Other Mechanisms

5.1.3.1 High Temperature Hydrogen Attack (HTHA)

5.1.3.1.1 Description of Damage
a) High temperature hydrogen attack results from exposure to hydrogen at elevated temperatures and pressures. The hydrogen reacts with carbides in steel to form methane (CH₄) which cannot diffuse through the steel. The loss of carbide causes an overall loss in strength.
b) Methane pressure builds up, forming bubbles or cavities, microfissures and fissures that may combine to form cracks.
c) Failure can occur when the cracks reduce the load carrying ability of the pressure containing part.

5.1.3.1.2 Affected Materials
In order of increasing resistance: carbon steel, C-0.5Mo, Mn-0.5Mo, 1Cr-0.5Mo, 1.25Cr-0.5Mo, 2.25Cr-1Mo, 2.25Cr-1Mo-V, 3Cr-1Mo, 5Cr-0.5Mo and similar steels with variations in chemistry.

5.1.3.1.3 Critical Factors
a) For a specific material, HTHA is dependent on temperature, hydrogen partial pressure, time and stress. Service exposure time is cumulative.
b) HTHA is preceded by a period of time when no noticeable change in properties is detectable by normal inspection techniques.
c) The incubation period is the time period during which enough damage has occurred to be measured with available inspection techniques and may vary from hours at very severe conditions to many years.
d) Figure 5-56 contains curves that show a temperature/hydrogen partial pressure safe operating envelope for carbon and low alloy steels. Additional information on HTHA can be found in API RP 941.
e) The curves are reasonably conservative for carbon steel up to about 10,000 psi hydrogen partial pressure.
f) 300 Series SS, as well as 5Cr, 9Cr and 12 Cr alloys, are not susceptible to HTHA at conditions normally seen in refinery units.

5.1.3.1.4 Affected Units
a) Hydroprocessing units, such as hydrotreaters (desulfurizers) and hydrocrackers, catalytic reformers, hydrogen producing units and hydrogen cleanup units, such as pressure swing absorption units, are all susceptible to HTHA.
b) Boiler tubes in very high pressure steam service.

5.1.3.1.5 Appearance or Morphology of Damage
a) HTHA can be confirmed through the use of specialized techniques including metallographic analysis of damaged areas as described below.
b) The hydrogen/carbon reaction can cause surface decarburization of steel. If the diffusion of carbon to the surface is limiting, the reaction can result in internal decarburization, methane formation and cracking (Figures 5-57 to 5-59).
c) In the early stages of HTHA, bubbles/cavities can be detected in samples by a scanning microscope, although it may be difficult to tell the difference between HTHA cavities and creep cavities. Some refinery services expose low alloy steels to both HTHA and creep conditions. Early stages of HTHA can only be confirmed through advanced metallographic analysis of damaged areas.
d) In later stages of damage, decarburization and/or fissures can be seen by examining samples under a microscope and may sometimes be seen by in-situ metallography (Figure 5-60 and 5-61).
e) Cracking and fissuring are intergranular and occur adjacent to pearlite (iron carbide) areas in carbon steels.
f) Some blistering may be visible to the naked eye, due to either molecular hydrogen or methane accumulating in laminations in the steel.

5.1.3.1.6 Prevention/Mitigation

a) Use alloy steels with chromium and molybdenum to increase carbide stability thereby minimizing methane formation. Other carbide stabilizing elements include tungsten and vanadium.

b) Normal design practice is to use a 25°F to 50°F (14°C to 28°C) safety factor approach when using the API RP 941 curves.

c) While the curves have served the industry well, there have been several failures of C-0.5Mo steels in refinery service under conditions that were previously considered safe. C-0.5Mo carbide stability under HTHA conditions may be due at least in part to the different carbides formed during the various heat treatments applied to the fabricated equipment.

d) As a result of the problems with the 0.5Mo alloy steels, its curve has been removed from the main set of curves and the material is not recommended for new construction in hot hydrogen services. For existing equipment, this concern has prompted an economic review of inspection cost versus replacement with a more suitable alloy. Inspection is very difficult because problems have occurred in weld heat affected zones as well as base metal away from welds.

e) 300 Series SS overlay and/or roll bond clad material is used in hydrogen service where the base metal does not have adequate sulfidation resistance. Although it is recognized that properly metallurgically bonded austenitic overlay/clad will decrease the hydrogen partial pressure seen by the underlying metal, most refiners make sure the base metal has adequate resistance to HTHA under service conditions. In some cases, refiners take the decrease in partial pressure into account when evaluating the need for hydrogen outgassing while shutting down heavy wall equipment.

5.1.3.1.7 Inspection and Monitoring

a) Damage may occur randomly in welds or weld heat affected zones as well as the base metal, making monitoring and detection of HTHA in susceptible materials extremely difficult.

b) Ultrasonic techniques using a combination of velocity ratio and AUBT have been the most successful in finding fissuring and/or serious cracking. HTHA damage can only be found using these techniques if damage has progressed to the point where microvoids would be visible at a magnification of 1500X or lower, if a sample of the metal was removed for examination.

c) HTHA can occur in the base metal at locations remote from welds. In clad vessels, in particular, HTHA damage can occur in base metal at locations where cladding has become disbonded. Bulging of the cladding away from the underlying base metal may be a tell tale sign that HTHA has occurred. Localized damage under cladding might be overlooked if inspection methods focus only on the weld seams and nozzles (Ref.4).

d) In-situ metallography can only detect microfissuring, fissuring and decarburization near the surface. However, most equipment has decarburized surfaces due to the various heat treatments used during fabrication.

e) Visual inspection for blisters on the inside surface may indicate methane formation and potential HTHA. However, HTHA may frequently occur without the formation of surface blisters.

f) Other conventional forms of inspection, including WFM and RT, are severely limited in their ability to detect anything except the advanced stages of damage where cracking has already developed.

g) AET is not a proven method for the detection of damage.

5.1.3.1.8 Related Mechanisms

A form of HTHA can occur in boiler tubes and is referred to by the fossil utility industry as hydrogen damage.

5.1.3.1.9 References


2. J. Vitovec, F.H., “The Growth Rate of Fissures During Hydrogen Attack of Steels,” API Division of
Refining, Vol. 44 {III} 1964, pp. 179-188.
Figure 5-56 – Recommended pressure and $H_2$ partial pressure limits per API 941. (Ref. 1)
Figure 5-57 – A pair of 10 inch Carbon-0.5Mo flanged pipe sections (SA335-P1 & SA234-WP1) from a hot bypass line in a catalytic reformer that was designed to remain closed but operated partially or fully open for unknown lengths of time. They were in service for ~34 years at temperatures up to 960°F (516°C) and a hydrogen partial pressure of 198 psig (1.37 MPa).

Figure 5-58 – A photomicrograph of the outside surface of a pipe section, shown in the previous figure, exhibits a normal ferritic-pearlitic structure. Mag. 200X
Figure 5-59 – A photomicrograph at the pipe ID surface exhibiting of the pipe shown in the previous pictures, exhibiting complete decarburization of the original structure. Mag. 200X

Figure 5-60 – A photomicrograph illustrating decarburization and fissuring of C-0.5Mo steel.
Figure 5-61 – High magnification photomicrograph showing linkup of microfissures to form continuous cracks. Note that damage is accompanied by a significant amount of decarburization.
5.1.3.2 Titanium Hydriding

5.1.3.2.1 Description of Damage
Hydriding of titanium is a metallurgical phenomenon in which hydrogen diffuses into the titanium and reacts to form an embrittling hydride phase. This can result in a complete loss of ductility with no noticeable sign of corrosion or loss in thickness.

5.1.3.2.2 Affected Materials
Titanium alloys.

5.1.3.2.3 Critical Factors
a) The critical factors are metal temperature, solution chemistry and alloy composition.
b) This is a phenomenon that occurs in specific environments at temperatures above 165°F (74°C) and at a pH below 3, pH above 8 or neutral pH with high H₂S content.
c) Galvanic contact between titanium and more active materials such as carbon steel and 300 Series SS promotes damage. However, hydriding can occur in the absence of a galvanic coupling.
d) Embrittlement occurs over a period of time as hydrogen is absorbed by the component and reacts to form embrittling hydride phases. The depth and extent of hydriding will continue to increase until a complete loss of ductility results.
e) Hydriding has also occurred in some chemical environments as a result of the corrosion of iron which has been accidentally embedded into the surface of titanium during fabrication. Corrosion of iron and iron sulfide scale in the process streams brought in from upstream units can result in hydrogen pickup.
f) The solubility of hydrogen in pure titanium and alpha-beta alloys is limited (50 - 300 ppm) and once this is exceeded, hydride is formed. Beta alloys, on the other hand, are more tolerant of hydrogen and 2000 ppm can be tolerated.

5.1.3.2.4 Affected Units or Equipment
a) Damage has occurred primarily in sour water strippers and amine units in the overhead condensers, heat exchanger tubes, piping and other titanium equipment operating above about 165°F (74°C).
b) Hydriding can also occur in hydrogen atmospheres at temperatures >350°F (177°C), especially in the absence of moisture or oxygen.
c) Cathodically protected equipment with protection potentials <-0.9 v SCE.

5.1.3.2.5 Appearance or Morphology of Damage
a) Titanium hydriding is a metallurgical change that is not readily apparent, and can only be confirmed through metallurgical techniques (Figure 5-62, Figure 5-63 and Figure 5-64) or mechanical testing.
b) A quick test for embrittlement is a bend test or a crush test in a vice. Unaffected titanium will be crushed in a ductile fashion while embrittled components will crack and/or shatter with little or no sign of ductility.
c) Heat exchanger tubes that have become embrittled may remain intact until disturbed by removal of the bundle for inspection. The tubes crack as the bundle flexes when it is removed.
d) Cracking can occur if there is an attempt to re-roll tube ends that have become embrittled.
e) Another possible damage mode that has occurred is ignition and fire of titanium tubes. Metallographic examination of titanium tubes from a bundle that burned showed significant amounts of hydride, especially in the vicinity of the metal that had been melted.

5.1.3.2.6 Prevention / Mitigation
a) Titanium should not be used in known hydriding services such as amine or sour water, where the possibility of a leak is not acceptable.
b) Where galvanic contact has promoted hydriding, the problem can be avoided by using all titanium
construction or by electrically isolating the titanium from non-titanium components. Eliminating the galvanic couple may not prevent hydriding in alkaline sour water environments.

5.1.3.2.7 **Inspection and Monitoring**

a) Specialized eddy current techniques are reported to have been able to detect hydriding damage.

b) There are no other techniques to monitor or inspect for titanium hydriding other than the metallurgical and/or mechanical methods mentioned above.

5.1.3.2.8 **Related Mechanisms**

Hydriding is a damage mechanism that is unique to a few materials including alloys of titanium and zirconium.

5.1.3.2.9 **References**

Figure 5-62 – Titanium heat exchanger tube that failed from hydriding in a sour water cooler. The cooling medium is sea water.

Figure 5-63 – High magnification photomicrograph of a cross-section of the tube shown in Figure 5-63 through the crack tip. Mag. 200X.
Figure 5-64 – Another high magnification photomicrograph of a cross-section of the tube showing more of the cross section through the tip of the crack. Titanium hydrides are more clearly discernable. Mag. 400X.