SECTION 4.0

GENERAL DAMAGE MECHANISMS – ALL INDUSTRIES

4.1 General ........................................................................................................................................... 3
4.2 Mechanical and Metallurgical Failure Mechanisms ................................................................. 3
4.2.1 Graphitization .............................................................................................................................. 3
4.2.2 Softening (Spheroidization) ......................................................................................................... 7
4.2.3 Temper Embrittlement ............................................................................................................... 10
4.2.4 Strain Aging ............................................................................................................................... 14
4.2.5 885°F (475°C) Embrittlement .................................................................................................... 16
4.2.6 Sigma Phase Embrittlement ....................................................................................................... 19
4.2.7 Brittle Fracture ............................................................................................................................ 27
4.2.8 Creep and Stress Rupture ........................................................................................................... 32
4.2.9 Thermal Fatigue ........................................................................................................................ 38
4.2.10 Short Term Overheating – Stress Rupture ................................................................................. 44
4.2.11 Steam Blanketing .................................................................................................................... 48
4.2.12 Dissimilar Metal Weld (DMW) Cracking ................................................................................ 51
4.2.13 Thermal Shock .......................................................................................................................... 60
4.2.14 Erosion/Erosion – Corrosion .................................................................................................... 62
4.2.15 Cavitation ..................................................................................................................................... 68
4.2.16 Mechanical Fatigue ................................................................................................................... 72
4.2.17 Vibration-Induced Fatigue ....................................................................................................... 79
4.2.18 Refractory Degradation ........................................................................................................... 82
4.2.19 Reheat Cracking ....................................................................................................................... 85
4.2.20 Gaseous Oxygen-Enhanced Ignition and Combustion ............................................................ 91
4.3 Uniform or Localized Loss of Thickness ....................................................................................... 99
4.3.1 Galvanic Corrosion ....................................................................................................................... 99
4.3.2 Atmospheric Corrosion .............................................................................................................. 103
4.3.3 Corrosion Under Insulation (CUI) ............................................................................................. 106
4.3.4 Cooling Water Corrosion .......................................................................................................... 115
4.3.5 Boiler Water Condensate Corrosion ......................................................................................... 118
4.3.6 CO₂ Corrosion ............................................................................................................................ 122
4.3.7 Flue-Gas Dew-Point Corrosion ................................................................................................. 126
4.3.8 Microbiologically Induced Corrosion (MIC) ........................................................................... 128
4.3.9 Soil Corrosion ............................................................................................................................. 134
4.3.10 Caustic Corrosion ..................................................................................................................... 138
4.3.11 Dealloying ................................................................................................................................... 141
4.3.12 Graphitic Corrosion ................................................................................................................ 145
4.4 High Temperature Corrosion [>400°F (204°C)] .................................................................................. 151
4.4.1 Oxidation ...................................................................................................................................... 151
4.4.2 Sulfidation .................................................................................................................................... 157
4.4.3 Carburization ............................................................................................................................. 163
4.4.4 Decarburization .......................................................................................................................... 166
4.4.5 Metal Dusting ............................................................................................................................. 169
4.4.6 Fuel Ash Corrosion ..................................................................................................................... 172
4.4.7 Nitriding ..................................................................................................................................... 177
4.5 Environment – Assisted Cracking ................................................................................................. 181
4.5.1 Chloride Stress Corrosion Cracking (Cl’SCC) ............................................................................. 181
4.5.2 Corrosion Fatigue ....................................................................................................................... 190
4.5.3 Caustic Stress Corrosion Cracking (Caustic Embrittlement) ..................................................... 196
4.5.4 Ammonia Stress Corrosion Cracking ....................................................................................... 203
4.5.5 Liquid Metal Embrittlement (LME) .......................................................................................... 207
4.5.6 Hydrogen Embrittlement (HE) ................................................................................................. 212
4.5.7 Ethanol Embrittlement .............................................................................................................. 217
4.5.8 Sulfate Stress Corrosion Cracking ............................................................................................ 224
4.1 General
Damage mechanisms that are common to a variety of industries including refining and petrochemical, pulp and paper, and fossil utility are covered in this Section. The mechanisms are divided into the following sections:

a) Mechanical and Metallurgical Failure
b) Uniform or Localized Loss of Thickness
c) High Temperature Corrosion
d) Environment Assisted Cracking

4.2 Mechanical and Metallurgical Failure Mechanisms

4.2.1 Graphitization

4.2.1.1 Description of Damage

a) Graphitization is a change in the microstructure of certain carbon steels and 0.5Mo steels after long-term operation in the 800°F to 1100°F (427°C to 593°C) range that may cause a loss in strength, ductility, and/or creep resistance.

b) At elevated temperatures, the carbide phases in these steels are unstable and may decompose into graphite nodules. This decomposition is known as graphitization.

4.2.1.2 Affected Materials

Some grades of carbon steel and 0.5Mo steels.

4.2.1.3 Critical Factors

a) The most important factors that affect graphitization are the chemistry, stress, temperature, and time of exposure.

b) In general, graphitization is not commonly observed. Some steels are much more susceptible to graphitization than others, but exactly what causes some steels to graphitize while others are resistant is not well understood. It was originally thought that silicon and aluminum content played a major role but it has been shown that they have negligible influence on graphitization.

c) Graphitization has been found in low alloy C-Mo steels with up to 1% Mo. The addition of about 0.7% chromium has been found to eliminate graphitization.

d) Temperature has an important effect on the rate of graphitization. Below 800°F (427°C), the rate is extremely slow. The rate increases with increasing temperature.

e) There are two general types of graphitization. First is random graphitization in which the graphite nodules are distributed randomly throughout the steel. While this type of graphitization may lower the room-temperature tensile strength, it does not usually lower the creep resistance.

f) The second and more damaging type of graphitization results in chains or local planes of concentrated graphite nodules. This form of graphitization can result in a significant reduction in load bearing capability while increasing the potential for brittle fracture along this plane. The two forms of this type of graphitization are weld heat-affected zone graphitization and non-weld graphitization.

i) Weld heat-affected zone graphitization is most frequently found in the heat-affected zone adjacent to welds in a narrow band, corresponding to the low temperature edge of the heat-affected zone. In multipass welded butt joints, these zones overlap each other, covering the entire cross-section. Graphite nodules can form at the low temperature edge of these heat-affected zones, resulting in a band of weak graphite extending across the section. Because of its appearance, this graphite formation within heat-affected zones is called eyebrow graphitization.
Non-weld graphitization is a form of localized graphitization that sometimes occurs along planes of localized yielding in steel. It also occurs in a chain-like manner in regions that have experienced significant plastic deformation as a result of cold working operations or bending.

g) The extent and degree of graphitization is usually reported in a qualitative fashion (none, slight, moderate, severe). Although it is difficult to predict the rate at which it forms, severe heat-affected zone graphitization can develop in as little as five years at service temperatures above 1000°F (538°C). Very slight graphitization would be expected to be found after 30 to 40 years at 850°F (454°C). Time-Temperature-Transformation curves for heat-affected zone graphitization can be found in Reference 2.

4.2.1.4  Affected Units or Equipment
a) Primarily hot-wall piping and equipment in the FCC, catalytic reforming and coker units.
b) Bainitic grades are less susceptible than coarse pearlitic grades.
c) Few failures directly attributable to graphitization have been reported in the refining industry. However, graphitization has been found where failure resulted primarily from other causes.
d) Several serious cases of graphitization have occurred in the reactors and piping of fluid catalytic cracking units, as well as with carbon steel furnace tubes in a thermal cracking unit and the failure of seal welds at the bottom tube sheet of a vertical waste heat boiler in a fluid catalytic cracker. A graphitization failure was reported in the long seam weld of a C-0.5Mo catalytic reformer reactor/interheater line.
e) Where concentrated eyebrow graphitization occurs along heat-affected zones, the creep rupture strength may be drastically lowered. Slight to moderate amounts of graphite along the heat-affected zones do not appear to significantly lower room or high-temperature properties.
f) Graphitization seldom occurs on boiling surface tubing but did occur in low alloy C-0.5Mo tubes and headers during the 1940's. Economizer tubing, steam piping and other equipment that operates in the range of temperatures of 850°F to 1025°F (441°C to 552°C) is more likely to suffer graphitization.

4.2.1.5  Appearance or Morphology of Damage
a) Damage due to graphitization is not visible or readily apparent and can only be observed by metallographic examination (Figure 4-1 and Figure 4-2).
b) Advanced stages of damage related to loss in creep strength may include microfissuring/microvoid formation, subsurface cracking or surface connected cracking.

4.2.1.6  Prevention / Mitigation
Graphitization can be prevented by using chromium containing low alloy steels for long-term operation above 800°F (427°C).

4.2.1.7  Inspection and Monitoring
a) Evidence of graphitization is most effectively evaluated through removal of full thickness samples for examination using metallographic techniques. Damage may occur midwall so that field replicas may be inadequate.
b) Advanced stages of damage related to loss in strength include surface breaking cracks or creep deformation that may be difficult to detect.

4.2.1.8  Related Mechanisms
Spheroidization (see 4.2.2) and graphitization are competing mechanisms that occur at overlapping temperature ranges. Spheroidization tends to occur preferentially above 1025°F (551°C), while graphitization predominates below this temperature.

4.2.1.9  References


Figure 4-1 – High magnification photomicrograph of metallographic sample showing graphite nodules. Compare to normal microstructure shown in Figure 4-2.

Figure 4-2 – High magnification photomicrograph of metallographic sample showing typical ferrite-pearlite structure of carbon steel.
4.2.2 Softening (Spheroidization)

4.2.2.1 Description of Damage

Spheroidization is a change in the microstructure of steels after exposure in the 850°F to 1400°F (440°C to 760°C) range, where the carbide phases in carbon steels are unstable and may agglomerate from their normal plate-like form to a spheroidal form, or from small, finely dispersed carbides in low alloy steels like 1Cr-0.5Mo to large agglomerated carbides. Spheroidization may cause a loss in strength and/or creep resistance.

4.2.2.2 Affected Materials

All commonly used grades of carbon steel and low alloy steels including C-0.5Mo, 1Cr-0.5Mo, 1.25Cr-0.5Mo, 2.25Cr-1Mo, 3Cr-1Mo, 5Cr-0.5Mo, and 9Cr-1Mo steels.

4.2.2.3 Critical Factors

a) Metal chemistry, microstructure, exposure time, and temperature are critical factors.

b) The rate of spheroidization depends on the temperature and initial microstructure. Spheroidization can occur in a few hours at 1300°F (552°C), but may take several years at 850°F (454°C).

c) Annealed steels are more resistant to spheroidization than normalized steels. Coarse-grained steels are more resistant than fine-grained. Fine grained silicon-killed steels are more resistant than aluminum-killed.

4.2.2.4 Affected Units or Equipment

a) Spheroidization can occur in piping and equipment after exposure to temperatures above 850°F (454°C). The loss in strength may be as high as about 30% but failure is not likely to occur except under very high applied stresses, in areas of stress concentration, or in combination with other damage mechanisms.

b) The loss in strength is usually accompanied by an increase in ductility which allows for deformation at stress concentrations.

c) Spheroidization affects hot wall piping and equipment in the FCC, catalytic reforming and coker units. Fired heater tubes in boilers or process units may be affected by a loss in creep strength, but equipment, in general, is seldom renewed or repaired because of spheroidization.

4.2.2.5 Appearance or Morphology of Damage

a) Spheroidization is not visible or readily apparent and can only be observed through metallography. The pearlitic phase undergoes a time dependant transformation from partial to complete spheroidization (Figure 4–3 and Figure 4–4).

b) In the case of the 5% to 9% CrMo alloys, spheroidization is the process of transforming the carbides from their original finely dispersed morphology to large agglomerated carbides.

4.2.2.6 Prevention / Mitigation

Spheroidization is difficult to prevent except by minimizing long-term exposure to elevated temperatures.

4.2.2.7 Inspection and Monitoring

Spheroidization can only be found through field metallography or removal of samples for metallographic observation. A reduction in tensile strength and/or hardness may indicate a spheroidized microstructure.
4.2.2.8  Related Mechanisms

a) Closely related to graphitization (see 4.2.1).

b) Spheroidization and graphitization are competing mechanisms which occur at overlapping temperature ranges. At temperatures above about 1025°F (552°C), graphitization may occur after spheroidization. Below 1025°F (552°C), graphitization occurs before the steel is fully spheroidized.

4.2.2.9  References

Figure 4-3 – High magnification photomicrograph of metallographic sample showing typical ferrite-pearlite structure of carbon steel.

Figure 4-4 – High magnification photomicrograph of metallographic sample showing spheroidized carbides.
4.2.3 Temper Embrittlement

4.2.3.1 Description of Damage
Temper embrittlement is the reduction in toughness due to a metallurgical change that can occur in some low alloy steels as a result of long-term exposure in the temperature range of about 650°F to 1070°F (343°C to 577°C). This change causes an upward shift in the ductile-to-brittle transition temperature as measured by Charpy impact testing. Although the loss of toughness is not evident at operating temperature, equipment that is temper embrittled may be susceptible to brittle fracture during start-up and shutdown.

4.2.3.2 Affected Materials
a) Primarily 2.25Cr-1Mo low alloy steel, 3Cr-1Mo (to a lesser extent), and the high-strength low alloy Cr-Mo-V rotor steels.
b) Older generation 2.25Cr-1Mo materials manufactured prior to 1972 may be particularly susceptible. Some high strength low alloy steels are also susceptible.
c) The C-0.5Mo, 1Cr-0.5Mo and 1.25Cr-0.5Mo alloy steels are not significantly affected by temper embrittlement. However, other high-temperature damage mechanisms promote metallurgical changes that can alter the toughness or high-temperature ductility of these materials. Refer to API 934-C and API 934-D for additional information.
d) Weld materials are generally more affected than today’s low-impurity base materials.

4.2.3.3 Critical Factors
a) Alloy steel composition, thermal history, metal temperature and exposure time are critical factors.
b) Susceptibility to temper embrittlement is largely determined by the presence of the alloying elements manganese and silicon, and the tramp elements phosphorus, tin, antimony, and arsenic. The strength level and heat treatment/fabrication history should also be considered.
c) Temper embrittlement of 2.25Cr-1Mo steels develops more quickly at 900°F (482°C) than in the 800°F to 850°F (427°C to 440°C) range, but the damage is more severe after long-term exposure at 850°F (440°C).
d) Some embrittlement can occur during fabrication heat treatments, but most of the damage occurs over many years of service in the embrittling temperature range.
e) This form of damage will significantly reduce the structural integrity of a component containing a crack-like flaw. An evaluation of the materials toughness may be required depending on the flaw type, the severity of the environment, and the operating conditions, particularly in hydrogen service.

4.2.3.4 Affected Units or Equipment
a) Temper embrittlement occurs in a variety of process units after long-term exposure to temperatures above 650°F (343°C). It should be noted that there have been very few industry failures related directly to temper embrittlement.
b) Equipment susceptible to temper embrittlement is most often found in hydrotreating units, particularly reactors, hot feed/effluent exchanger components, and hot HP separators. Other units with the potential for temper embrittlement include catalytic reforming units (reactors and exchangers), FCC reactors, coker and visbreaking units.
c) Welds in these alloys are often more susceptible than the base metal and should be evaluated.
4.2.3.5 **Appearance or Morphology of Damage**

a) Temper embrittlement is a metallurgical change that is not readily apparent and can be confirmed through impact testing. Damage due to temper embrittlement may result in catastrophic brittle fracture.

b) Temper embrittlement can be identified by an upward shift in the ductile-to-brittle transition temperature measured in a Charpy V-notch impact test, as compared to the non-embrittled or de-embrittled material (Figure 4-5). Another important characteristic of temper embrittlement is that there is no effect on the upper shelf energy.

c) SEM fractographs of severely temper embrittled material show primarily intergranular cracking due to impurity segregation at grain boundaries.

4.2.3.6 **Prevention / Mitigation**

a) Existing Materials

i) Temper embrittlement cannot be prevented if the material contains critical levels of the embrittling impurity elements and is exposed in the embrittling temperature range.

ii) To minimize the possibility of brittle fracture during startup and shutdown, many refiners use a pressurization sequence to limit system pressure to about 25 percent of the maximum design pressure for temperatures below a Minimum Pressurization Temperature (MPT). Note that MPT is not a single point but rather a pressure-temperature envelope which defines safe operating conditions to minimize the likelihood of brittle fracture.

iii) MPT's generally range from 350°F (171°C) for the earliest, most highly temper embrittled steels, down to 125°F (52°C) or lower for newer, temper embrittlement resistant steels (as required to also minimize effects of hydrogen embrittlement).

iv) If weld repairs are required, the effects of temper embrittlement can be temporarily reversed (de-embrittled) by heating at 1150°F (620°C) for two hours per inch of thickness, and rapidly cooling to room temperature. It is important to note that re-embrittlement will occur over time if the material is re-exposed to the embrittling temperature range.

b) New Materials

i) The best way to minimize the likelihood and extent of temper embrittlement is to limit the acceptance levels of manganese, silicon, phosphorus, tin, antimony, and arsenic in the base metal and welding consumables. In addition, strength levels and PWHT procedures should be specified and carefully controlled.

ii) A common way to minimize temper embrittlement is to limit the "J" Factor for base metal and the "X" Factor for weld metal, based on material composition as follows:

\[
J^* = (\text{Si} + \text{Mn}) \times (\text{P} + \text{Sn}) \times 10^4 \quad \text{elements in wt%}
\]

\[
X = (10\text{P} + 5\text{Sb} + 4\text{Sn} + \text{As})/100 \quad \text{elements in ppm}
\]

iii) Typical J* and X factors used for 2.25 Cr steel are a maximum of 100 and 15, respectively. Studies have also shown that limiting the (P + Sn) to less than 0.01% is sufficient to minimize temper embrittlement because (Si + Mn) control the rate of embrittlement.

iv) A newer and less widely used factor called the Equivalent Phosphorus content has been developed for base metal and weld metal and is defined as follows is given by:

\[
P = \text{C} + \text{Mn} + (\text{Mo Cr})/3 + \text{Si} / 4 + 3.5 \times [(10 \times \text{P} + (5 \times \text{Sb}) + (4 \times \text{Sn}) + \text{As}) \quad \text{elements in wt%}
\]

v) Expert metallurgical advice should be solicited to determine acceptable composition, toughness and strength levels, as well as appropriate welding, fabricating and heat treating procedures for new low alloy steel heavy wall equipment and low alloy equipment operating in the temper embrittlement and/or creep range.
4.2.3.7 **Inspection and Monitoring**

a) A common method of monitoring is to install blocks of original heats of the alloy steel material inside the reactor. Samples are periodically removed from these blocks for impact testing to monitor/establish the ductile-brittle transition temperature. The test blocks should be strategically located near the top and bottom of the reactor to make sure that the test material is exposed to both inlet and outlet conditions.

b) Process conditions should be monitored to ensure that a proper pressurization sequence is followed to help prevent brittle fracture due to temper embrittlement.

4.2.3.8 **Related Mechanisms**

Not applicable.

4.2.3.9 **References**

5. API Recommended Practice 934-B, Fabrication Considerations for ¼V Steel Heavy Wall Pressure Vessels for High Temperature, High Pressure Hydrogen Service, American Petroleum Institute, Washington, D.C.
6. API Recommended Practice 934-C, Materials and Fabrication Requirements for 1 1/4Cr-1/2Mo Steel Heavy Wall Pressure Vessels for High Temperature, High Pressure Hydrogen Service, American Petroleum Institute, Washington, D.C.
7. API Recommended Practice 934-D, Technical Report on the Materials and Fabrication Issues of 1¼ Cr - ½ Mo and 1 Cr - ½ Mo Steel Pressure Vessels, American Petroleum Institute, Washington, D.C.,
8. API RP 934-E, Recommended Practice for Materials and Fabrication of 1¼Cr-½Mo Steel Pressure Vessels for Service above 825°F (441°C), American Petroleum Institute, Washington, D.C.,
Figure 4-5 – Plot of CVN toughness as a function of temperature showing a shift in the 40-ft-lb transition temperature.
4.2.4 Strain Aging

4.2.4.1 Description of Damage
Strain aging is a form of damage found mostly in older vintage carbon steels and C-0.5 Mo low alloy steels under the combined effects of deformation and aging at an intermediate temperature. This results in an increase in hardness and strength with a reduction in ductility and toughness.

4.2.4.2 Affected Materials
Mostly older (pre-1980’s) carbon steels with a large grain size and C-0.5 Mo low alloy steel.

4.2.4.3 Critical Factors
a) Steel composition and manufacturing process determine steel susceptibility.
b) Steels manufactured by the Bessemer or open hearth process contain higher levels of critical impurity elements than newer steels manufactured by the Basic Oxygen Furnace (BOF) process.
c) In general, steels made by BOF and fully killed with aluminum will not be susceptible. The effect is found in rimmed and capped steels with higher levels of nitrogen and carbon, but not in the modern fully killed carbon steels manufactured to a fine grain practice.
d) Strain aging effects are observed in materials that have been cold worked and placed into service at intermediate temperatures without stress relieving.
e) Strain aging is a major concern for equipment that contains cracks. If susceptible materials are plastically deformed and exposed to intermediate temperatures, the zone of deformed material may become hardened and less ductile. This phenomenon has been associated with several vessels that have failed by brittle fracture.
f) The pressurization sequence versus temperature is a critical issue to prevent brittle fracture of susceptible materials.
g) Strain aging can also occur when welding in the vicinity of cracks and notches in a susceptible material.

4.2.4.4 Affected Units or Equipment
Strain aging is most likely to occur in thick wall vessels manufactured from susceptible materials that have not been stress relieved.

4.2.4.5 Appearance or Morphology of Damage
Strain aging can result in the formation of brittle cracks that are revealed through detailed metallurgical analyses, but damage most likely will not be identified as strain aging until fracture has already occurred.

4.2.4.6 Prevention / Mitigation
a) Strain aging is not an issue for newer steels that contain low levels of interstitial impurity elements and sufficient aluminum (>0.015 wt%) to fully deoxidize the steel.
b) For older equipment, extra care should be taken to avoid the potentially damaging effects of strain aging by avoiding stressing or pressurizing equipment until the metal temperature reaches an acceptable level where the risk of brittle fracture is low. Refer to curve “A” in UCS 66 of the ASME Code Section VIII, Division I for pressurization temperatures of vessels susceptible to strain aging effects.
c) Applying PWHT to weld repairs of susceptible materials will eliminate the effects of strain aging. Where PWHT is not possible, buttering should be considered to minimize welding on old material under restraint.
4.2.4.7  **Inspection and Monitoring**  
Inspection and monitoring are not used to control strain aging.

4.2.4.8  **Related Mechanisms**  
When deformation occurs at the intermediate temperature, the mechanism is referred to as dynamic strain aging. Blue brittleness is another form of strain aging.

4.2.4.9  **References**  
1. ASME Boiler and Pressure Vessel Code, Section VIII, Division I, American Society of Mechanical Engineers, NY.
4.2.5 885°F (475°C) Embrittlement

4.2.5.1 Description of Damage

885°F (475°C) embrittlement is a loss in toughness due to a metallurgical change that can occur in alloys containing a ferrite phase, as a result of exposure in the temperature range 600°F to 1000°F (316°C to 540°C).

4.2.5.2 Affected Materials

a) 400 Series SS (e.g., 405, 409, 410, 410S, 430 and 446).
b) Duplex stainless steels such as Alloys 2205, 2304 and 2507.

4.2.5.3 Critical Factors

a) The alloy composition, particularly chromium content, amount of ferrite phase, and operating temperature are critical factors.
b) Increasing amounts of ferrite phase increase susceptibility to damage when operating in the high temperature range of concern. A dramatic increase in the ductile-to-brittle transition temperature will occur.
c) A primary consideration is operating time at temperature within the critical temperature range. Damage is cumulative and results from the precipitation of an embrittling intermetallic phase that occurs most readily at approximately 885°F (475°C). Additional time is required to reach maximum embrittlement at temperatures above or below 885°F (475°C). For example, many thousands of hours may be required to cause embrittlement at 600°F (316°C).
d) Since 885°F embrittlement can occur in a relatively short period of time, it is often assumed that susceptible materials that have been exposed to temperatures in the 700°F to 1000°F (371°C to 538°C) range are affected.
e) The effect on toughness is not pronounced at the operating temperature, but is significant at lower temperatures experienced during plant shutdowns, startups or upsets.
f) Embrittlement can result from tempering at higher temperatures or by holding within or cooling through the transformation range.

4.2.5.4 Affected Units or Equipment

a) 885°F embrittlement can be found in any unit where susceptible alloys are exposed to the embrittling temperature range.
b) Most refining companies limit the use of ferritic stainless steels to non-pressure boundary applications because of this damage mechanism.
c) Common examples include fractionator trays and internals in high temperature vessels used in FCC, crude, vacuum and coker units. Typical failures include cracking when attempting to weld or to straighten bent, upset tower trays of Type 409 and 410 material (occurs often with vacuum tower trays of this material).
d) Other examples include duplex stainless steel heat exchanger tubes and other components exposed to temperatures above 600°F (316°C) for extended time periods.
4.2.5.5  Appearance or Morphology of Damage
a) 885°F embrittlement is a metallurgical change that is not readily apparent with metallography but can be confirmed through bend or impact testing (Fig 4-6).

b) The existence of 885°F embrittlement can be identified by an increase in hardness in affected areas. Failure during bend testing or impact testing of samples removed from service is the most positive indicator of 885°F embrittlement.

4.2.5.6  Prevention / Mitigation
a) The best way to prevent 885°F embrittlement is to use low ferrite or non-ferritic alloys, or to avoid exposing the susceptible material to the embrittling range.

b) It is possible to minimize the effects of embrittlement through modifications in the chemical composition of the alloy, however, resistant material may not always be readily available in most commercial forms.

c) 885°F embrittlement is reversible by heat treatment to dissolve precipitates, followed by rapid cooling. The de-embrittling heat treatment temperature is typically 1100°F (593°C) or higher and may not be practical for many equipment items. If the de-embrittled component is exposed to the same service conditions it will re-embrittle faster than it did initially.

4.2.5.7  Inspection and Monitoring
a) Impact or bend testing of samples removed from service is the most positive indicator of a problem.

b) Most cases of embrittlement are found in the form of cracking during turnarounds, or during startup or shutdown when the material is below about 200°F (93°C) and the effects of embrittlement are most detrimental.

c) An increase in hardness is another method of evaluating 885°F embrittlement.

4.2.5.8  Related Mechanisms
Not applicable.

4.2.5.9  References
Figure 4-6 – Sample of cracked material with craze cracks running through the grains suggesting severe embrittlement.
4.2.6 Sigma Phase Embrittlement

4.2.6.1 Description of Damage
Formation of a metallurgical phase known as sigma phase can result in a loss of fracture toughness in some stainless steels as a result of high temperature exposure.

4.2.6.2 Affected Materials
a) 300 Series SS wrought metals, weld metal, and castings. Cast 300 Series SS including the HK and HP alloys are especially susceptible to sigma formation because of their high (10% to 40%) ferrite content.
b) The 400 Series SS and other ferritic and martensitic SS with 17% Cr or more are also susceptible (e.g., Types 430 and 440).
c) Duplex stainless steels.

4.2.6.3 Critical Factors
a) Alloy composition, time and temperature are the critical factors.
b) In susceptible alloys, the primary factor that affects sigma phase formation is the time of exposure at elevated temperature.
c) Sigma phase occurs in ferritic (Fe-Cr), martensitic (Fe-Cr), austenitic (Fe-Cr-Ni) and duplex stainless steels when exposed to temperatures in the range of 1000°F to 1700°F (538°C to 927°C). Embrittlement can result by holding within or cooling through the transformation range.
d) Sigma forms most rapidly from the ferrite phase that exists in 300 Series SS and duplex SS weld deposits. It can also form in the 300 Series SS base metal (austenite phase) but usually more slowly.
e) The 300 Series SS can exhibit about 10% to 15% sigma phase. Cast austenitic stainless steels can develop considerably more sigma.
f) Formation of sigma phase in austenitic stainless steels can also occur in a few hours, as evidenced by the known tendency for sigma to form if an austenitic stainless steel is subjected to a post weld heat treatment at 1275°F (690°C).
g) The tensile and yield strength of sigmatized stainless steels increases slightly compared with solution annealed material. This increase in strength is accompanied by a reduction in ductility (measured by percent elongation and reduction in area) and a slight increase in hardness.
h) Stainless steels with sigma can normally withstand normal operating stresses, but upon cooling to temperatures below about 500°F (260°C) may show a complete lack of fracture toughness as measured in a Charpy impact test. Laboratory tests of embrittled weld metal have shown a complete lack of fracture toughness below 1000°F (538°C).
i) The metallurgical change is actually the precipitation of a hard, brittle intermetallic compound that can also render the material more susceptible to intergranular corrosion. The precipitation rate increases with increasing chromium and molybdenum content.

4.2.6.4 Affected Units or Equipment
a) Common examples include stainless steel cyclones, piping ductwork and valves in high temperature FCC Regenerator service.
b) 300 Series SS weld overlays and tube-to-tubesheet attachment welds can be embrittled during PWHT treatment of the underlying CrMo base metal.
c) Stainless steel heater tubes are susceptible and can be embrittled.
4.2.6.5  Appearance or Morphology of Damage

a) Sigma phase embrittlement is a metallurgical change that is not readily apparent, and can only be confirmed through metallographic examination and impact testing. (Tables 4-1 and 4-2)

b) Damage due to sigma phase embrittlement appears in the form of cracking, particularly at welds or in areas of high restraint.

c) Tests performed on sigmatized 300 Series SS (304H) samples from FCC regenerator internals have shown that even with 10% sigma formation, the Charpy impact toughness was 39 ft-lbs (53 J) at 1200°F (649°C).

d) For the 10% sigmatized specimen, the values ranged from 0% ductility at room temperature to 100% at 1200°F (649°C). Thus, although the impact toughness is reduced at high temperature, the specimens broke in a 100% ductile fashion, indicating that the wrought material is still suitable at operating temperatures. See Figures 4-7 to 4-11.

e) Cast austenitic stainless steels typically have high ferrite/sigma content (up to 40%) and may have very poor high temperature ductility.

4.2.6.6  Prevention / Mitigation

a) The best way to prevent sigma phase embrittlement is to use alloys that are resistant to sigma formation or to avoid exposing the material to the embrittling range.

b) The lack of fracture ductility at room temperature indicates that care should be taken to avoid application of high stresses to sigmatized materials during shutdown, as a brittle fracture could result.

c) The 300 Series SS can be de-sigmatized by solution annealing at 1950°F (1066°C) for four hours followed by a water quench. However, this is not practical for most equipment.

d) Sigma phase in welds can be minimized by controlling ferrite in the range of 5% to 9% for Type 347 and somewhat less ferrite for Type 304. The weld metal ferrite content should be limited to the stated maximum to minimize sigma formation during service or fabrication, and must meet the stated minimum in order to minimize hot short cracking during welding.

e) For stainless steel weld overlay clad Cr-Mo components, the exposure time to PWHT temperatures should be limited wherever possible.

4.2.6.7  Inspection and Monitoring

a) Physical testing of samples removed from service is the most positive indicator of a problem.

b) Most cases of embrittlement are found in the form of cracking in both wrought and cast (welded) metals during turnarounds, or during startup or shutdown when the material is below about 500°F (260°C) and the effects of embrittlement are most pronounced.

4.2.6.8  Related Mechanisms

Not applicable.

4.2.6.9  References

Table 4-1 – Data for Property Trends of Toughness vs. Temperature

<table>
<thead>
<tr>
<th>Test Temperature</th>
<th>304 SS 2 % Sigma</th>
<th>321 SS 10% Sigma</th>
<th>304 SS 1% Sigma</th>
<th>304 SS 2% Sigma</th>
<th>347 SS 1% Sigma</th>
</tr>
</thead>
<tbody>
<tr>
<td>70°F (21°C)</td>
<td>21 % Impact</td>
<td>0 % Shear</td>
<td>7 % Impact</td>
<td>0 % Shear</td>
<td>21 % Impact</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10 % Impact</td>
</tr>
<tr>
<td>500°F (260°C)</td>
<td>38 % Impact</td>
<td>25 % Shear</td>
<td>10 % Impact</td>
<td>20 % Shear</td>
<td>10 % Impact</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100 % Impact</td>
</tr>
<tr>
<td>900°F (480°C)</td>
<td>44 % Impact</td>
<td>50 % Shear</td>
<td>15 % Impact</td>
<td>40 % Shear</td>
<td>20 % Impact</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10 % Impact</td>
</tr>
<tr>
<td>1200°F (650°C)</td>
<td>63 % Impact</td>
<td>100 % Shear</td>
<td>21 % Impact</td>
<td>60 % Shear</td>
<td>71 % Impact</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>77 % Shear</td>
</tr>
</tbody>
</table>

Notes:
1. Percent of impact is a comparison to original impact strength of non-embrittled materials.
2. The results for 304 SS in columns one and four are for different heats of material under different exposure conditions and are intended to exemplify variability of embrittlement.
Table 4-2 – Charpy V-notch Impact Test Results, absorbed energy in Joules (ft-lbs) from Ref. 6

<table>
<thead>
<tr>
<th>Refinery</th>
<th>Location</th>
<th>Years of Service</th>
<th>Sigma Phase Content (%)</th>
<th>Temperature 85 (63)</th>
<th>Temperature 145 (107)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Base Metal</td>
<td>17</td>
<td>4.0</td>
<td>85 (63)</td>
<td>145 (107)</td>
</tr>
<tr>
<td>A</td>
<td>Weld Metal</td>
<td>17</td>
<td>8.7</td>
<td>37 (27)</td>
<td>100 (74)</td>
</tr>
<tr>
<td>B</td>
<td>Base Metal</td>
<td>19</td>
<td>12.0</td>
<td>12 (9)</td>
<td>43 (32)</td>
</tr>
<tr>
<td>C</td>
<td>Base Metal</td>
<td>13</td>
<td>1.5</td>
<td>35 (26)</td>
<td>75 (55)</td>
</tr>
</tbody>
</table>

Figure 4-7 - Tensile tests from 304H stainless steel FCC flue gas line with 12% sigma phase. The top bar (a) failed in a brittle manner at room temperature. The bottom sample (b) was tested at the operating temperature and shows significantly ductility and elongation 1,320°F (716°C), Ref. 6.
Figure 4-8 - Microstructure of FCC regenerator plenum chamber wall, electrolytic etch in 33% KOH, 100X. Dark-etching particles are sigma phase, estimated amount 6.0% (Ref. 6).

Figure 4-9 - Dark-etching particles are sigma phase that are concentrated near the outside surface of FCC regenerator plenum chamber, electrolytic etch in 33% KOH, 100X. (Ref. 6).
Figure 4-10 - Stainless steel 304H with 14 years operation at a nominal temperature of 1,320°F (716°C) after (a) etching in Vilella's reagent, 100X; and (b) electrolytic etching in KOH, 200X. The estimated amount of sigma phase was 5.0%. (Ref. 6)
Figure 4-11 - Charpy V-Notch Impact Test Results as absorbed energy in ft-lbf, at room temperature and service temperature (Ref. 6).
4.2 Brittle Fracture

4.2.7 Description of Damage
Brittle fracture is the sudden rapid fracture under stress (residual or applied) where the material exhibits little or no evidence of ductility or plastic deformation.

4.2.7.2 Affected Materials
Carbon steels and low alloy steels are of prime concern, particularly older steels. 400 Series SS are also susceptible.

4.2.7.3 Critical Factors
a) For a material containing a flaw, brittle fracture can occur. Following are three important factors:
   i) The materials’ fracture toughness (resistance to crack like flaws) as measured in a Charpy impact test;
   ii) The size, shape and stress concentration effect of a flaw;
   iii) The amount of residual and applied stresses on the flaw.

b) Susceptibility to brittle fracture may be increased by the presence of embrittling phases.

c) Steel cleanliness and grain size have a significant influence on toughness and resistance to brittle fracture.

d) Thicker material sections also have a lower resistance to brittle fracture due to higher constraint which increases triaxial stresses at the crack tip.

e) In most cases, brittle fracture occurs only at temperatures below the Charpy impact transition temperature (or ductile-to-brittle transition temperature), the point at which the toughness of the material drops off sharply.

4.2.7.4 Affected Units or Equipment
a) Equipment manufactured to the ASME Boiler and Pressure Vessel Code, Section VIII, Division 1, prior to the December 1987 Addenda, were made with limited restrictions on notch toughness for vessels operating at cold temperatures. However, this does not mean that all vessels fabricated prior to this date will be subject to brittle fracture. Many designers specified supplemental impact tests on equipment that was intended to be in cold service.

b) Equipment made to the same code after this date were subject to the requirements of UCS 66 (impact exemption curves).

c) Most processes run at elevated temperature so the main concern is for brittle fracture during startup, shutdown, or hydrotest/tightness testing. Thick wall equipment on any unit should be considered.

d) Brittle fracture can also occur during an autorefrigeration event in units processing light hydrocarbons such as methane, ethane/ethylene, propane/propylene, or butane. This includes alkylation units, olefin units and polymer plants (polyethylene and polypropylene). Storage bullets/spheres for light hydrocarbons may also be susceptible.

e) Brittle fracture can occur during ambient temperature hydrotesting due to high stresses and low toughness at the testing temperature.
4.2.7.5  Appearance or Morphology of Damage
a) Cracks will typically be straight, non-branching, and largely devoid of any associated plastic deformation (although fine shear lips may be found along the free edge of the fracture, or localized necking around the crack (Figure 4-12 to Figure 4-16).

b) Microscopically, the fracture surface will be composed largely of cleavage, with limited intergranular cracking and very little microvoid coalescence.

4.2.7.6  Prevention / Mitigation
a) For new equipment, brittle fracture is best prevented by using materials specifically designed for low temperature operation including upset and autorefrigeration events. Materials with controlled chemical composition, special heat treatment and impact test verification may be required. Refer to UCS 66 in Section VIII of the ASME BPV Code.

b) Brittle fracture is an "event" driven damage mechanism. For existing materials, where the right combination of stress, material toughness and flaw size govern the probability of the event, an engineering study can be performed in accordance with API RP 579, Section 3, Level 1 or 2.

c) Preventative measures to minimize the potential for brittle fracture in existing equipment are limited to controlling the operating conditions (pressure, temperature), minimizing pressure at ambient temperatures during startup and shutdown, and periodic inspection at high stress locations.

d) Some reduction in the likelihood of a brittle fracture may be achieved by:
   i) Performing a post weld heat treatment (PWHT) on the vessel if it was not originally done during manufacturing; or if the vessel has been weld repaired/modified while in service without the subsequent PWHT.
   ii) Perform a "warm" pre-stress hydrotest followed by a lower temperature hydrotest to extend the Minimum Safe Operating Temperature (MSOT) envelope.

4.2.7.7  Inspection and Monitoring
a) Inspection is not normally used to mitigate brittle fracture.

b) Susceptible vessels should be inspected for pre-existing flaws/defects.

4.2.7.8  Related Mechanisms
Temper embrittlement (see 4.2.3), strain age embrittlement (see 4.2.4), 885°F (475°C) embrittlement (see 4.2.5), titanium hydriding (see 5.1.3.2) and sigma embrittlement (see 4.2.6).

4.2.7.9  References
1. API RP 579, Fitness-For-Service, American Petroleum Institute, Washington, D.C.
2. Jeffery A. Smith and Stanley T. Rolfe, "The Effect of Crack Depth (a) and Crack-Depth to Width Ratio (a/W) on the Fracture Toughness of A533-B Steel," WRC Bulletin 418, Welding Research Council, Shaker Heights, OH.
4. ASME Boiler and Pressure Vessel Code, Section III, Division I, Rules for Construction of Nuclear Power Plant Components ASME, New York, N.Y.
Figure 4-12 – 20-inch carbon steel pipeline that failed during hydrotest at gouges on the O.D.

Figure 4-13 – Close-up photograph showing the gouges and the fracture origin (arrow) in one of the gouges.
Figure 4-14 – Brittle Fracture of 2.2 inch wall C-0.5Mo exchanger channel PWHT during hydrotest.

Figure 4-15 – Brittle Fracture of vessel shell during hydrotest.
Figure 4-16 – Classic example of brittle fracture that occurred during hydrotest.
4.2.8 Creep and Stress Rupture

4.2.8.1 Description of Damage

a) At high temperatures, metal components can slowly and continuously deform under load below the yield stress. This time dependent deformation of stressed components is known as creep.

b) Deformation leads to damage that may eventually lead to a rupture.

4.2.8.2 Affected Materials

All metals and alloys.

4.2.8.3 Critical Factors

a) The rate of creep deformation is a function of the material, load, and temperature. The rate of damage (strain rate) is sensitive to both load and temperature. Generally, an increase of about 25°F (12°C) or an increase of 15% on stress can cut the remaining life in half or more, depending on the alloy.

b) Table 4-3 lists threshold temperatures above which creep damage is a concern. If the metal temperature exceeds these values, then creep damage and creep cracking can occur.

c) The level of creep damage is a function of the material and the coincident temperature/stress level at which the creep deformation occurs.

d) The life of metal components becomes nearly infinite at temperatures below the threshold limit (Table 4-3) even at the high stresses near a crack tip.

e) The appearance of creep damage with little or no apparent deformation is often mistakenly referred to as creep embrittlement, but usually indicates that the material has low creep ductility.

f) Low creep ductility is:

i) More severe for higher tensile strength materials and welds.

ii) More prevalent at the lower temperatures in the creep range, or low stresses in the upper creep range.

iii) More likely in a coarse-grained material than a fine-grained material.

iv) Not evidenced by a deterioration of ambient temperature properties.

v) Promoted by certain carbide types in some CrMo steels.

g) Increased stress due to loss in thickness from corrosion will reduce time to failure.

4.2.8.4 Affected Units or Equipment

a) Creep damage is found in high temperature equipment operating above the creep range. Heater tubes in fired heaters are especially susceptible as well as tube supports, hangers and other furnace internals.

b) Piping and equipment, such as hot-wall catalytic reforming reactors and furnace tubes, hydrogen reforming furnace tubes, hot wall FCC reactors, FCC main fractionator and regenerator internals all operate in or near the creep range.

c) Low creep ductility failures have occurred in weld heat-affected zones (HAZ) at nozzles and other high stress areas on catalytic reformer reactors. Cracking has also been found at long seam welds in some high temperature piping and in reactors on catalytic reformers.

d) Welds joining dissimilar materials (ferritic to austenitic welds) may suffer creep related damage at high temperatures due to differential thermal expansion stresses.
4.2.8.5 Appearance or Morphology of Damage

a) The initial stages of creep damage can only be identified by scanning electron microscope metallography. Creep voids typically show up at the grain boundaries and in later stages form fissures and then cracks.

b) At temperatures well above the threshold limits, noticeable deformation may be observed. For example, heater tubes may suffer long term creep damage and exhibit significant bulging before final fracture occurs. The amount of deformation is highly dependent on the material, and the combination of temperature and stress level (Figure 4-17 to 4-19).

c) In vessels and piping, creep cracking can occur where high metal temperatures and stress concentrations occur together, such as near major structural discontinuities including pipe tee joints, nozzles, or welds at flaws. Creep cracking, once initiated, can progress rapidly.

4.2.8.6 Prevention / Mitigation

a) There is little that inspectors or operators can do to prevent this damage once a susceptible material has been placed into creep service, other than to minimize the metal temperature, particularly with fired heater tubes. Avoiding stress concentrators is important during design and fabrication.

b) Low creep ductility can be minimized by the careful selection of chemistry for low alloy materials. Higher post weld heat treatment temperatures may help minimize creep cracking of materials with low creep ductility such as 1.25Cr-0.5Mo.

c) Creep damage is not reversible. Once damage or cracking is detected much of the life of the component has been used up and typically the options are to repair or replace the damaged component. Higher PWHT in some cases can produce a more creep ductile material with longer life.

i) Equipment – Repair of creep damaged catalytic reformer reactor nozzles has been successfully accomplished by grinding out the affected area (making sure all the damaged metal is removed), re-welding and careful blend grinding to help minimize stress concentration. PWHT temperatures must be carefully selected and may require a higher PWHT than originally specified.

ii) Fired Heater Tubes

- Alloys with improved creep resistance may be required for longer life.
- Heaters should be designed and operated to minimize hot spots and localized overheating (Figure 4-9).
- Visual inspection followed by thickness measurements and or strap readings may be required to assess remaining life of heater tubes in accordance with API RP 579.
- Minimizing process side fouling/deposits and fire side deposits/scaling can maximize tube life.

4.2.8.7 Inspection and Monitoring

a) Creep damage with the associated microvoid formation, fissuring and dimensional changes is not effectively found by any one inspection technique. A combination of techniques (UT, RT, EC, dimensional measurements and replication) should be employed. Destructive sampling and metallographic examination are used to confirm damage.

b) For pressure vessels, inspection should focus on welds of CrMo alloys operating in the creep range. The 1 Cr-0.5Mo and 1.25Cr-0.5Mo materials are particularly prone to low creep ductility. Most inspections are performed visually and followed by PT or WFMT on several-year intervals. Angle beam (shear wave) UT can also be employed, although the early stages of creep damage are very difficult to detect. Initial fabrication flaws should be mapped and documented for future reference.

c) Fired heater tubes should be inspected for evidence of overheating, corrosion, and erosion as follows:

i) Tubes should be VT examined for bulging, blistering, cracking, sagging and bowing.

ii) Wall thickness measurements of selected heater tubes should be made where wall losses are most likely to occur.
iii) Tubes should be examined for evidence of diametric growth (creep) with a strap or go/no go gauge, and in limited cases by metallography on in place replicas or tube samples. However, metallography on the OD of a component may not provide a clear indication of subsurface damage.

iv) Retirement criteria based on diametric growth and loss of wall thickness is highly dependent on the tube material and the specific operating conditions.

4.2.8.8 Related Mechanisms

a) Creep damage that occurs as a result of exposure to very high temperatures is described in 4.2.10.

b) Reheat cracking (see 4.2.19) is a related mechanism found in heavy wall equipment.

4.2.8.9 References


2. API Standard 530, Calculation of Heater Tube Thickness in Petroleum Refineries, American Petroleum Institute, Washington, D.C.

Table 4-3 – Threshold Temperatures for Creep (Ref. 1)

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Steel ( UTS \leq 414 \text{MPa} \ (60 \text{ksi}) )</td>
<td>343°C (650°F)</td>
</tr>
<tr>
<td>Carbon Steel ( UTS &gt; 414 \text{MPa} \ (60 \text{ksi}) )</td>
<td>371°C (700°F)</td>
</tr>
<tr>
<td>Carbon Steel – Graphitized</td>
<td>371°C (700°F)</td>
</tr>
<tr>
<td>C-1/2Mo</td>
<td>399°C (750°F)</td>
</tr>
<tr>
<td>1-1/4Cr-1/2Mo – Normalized &amp; Tempered</td>
<td>427°C (800°F)</td>
</tr>
<tr>
<td>1-1/4Cr-1/2Mo – Annealed</td>
<td>427°C (800°F)</td>
</tr>
<tr>
<td>2-1/4Cr-1Mo – Normalized &amp; Tempered</td>
<td>427°C (800°F)</td>
</tr>
<tr>
<td>2-1/4Cr-1Mo – Annealed</td>
<td>427°C (800°F)</td>
</tr>
<tr>
<td>2-1/4Cr-1Mo – Quenched &amp; Tempered</td>
<td>427°C (800°F)</td>
</tr>
<tr>
<td>2-1/4Cr-1Mo – V</td>
<td>441°C (825°F)</td>
</tr>
<tr>
<td>3Cr-1Mo-V</td>
<td>441°C (825°F)</td>
</tr>
<tr>
<td>5Cr-1/2Mo</td>
<td>427°C (800°F)</td>
</tr>
<tr>
<td>7Cr-1/2Mo</td>
<td>427°C (800°F)</td>
</tr>
<tr>
<td>9Cr-1Mo</td>
<td>427°C (800°F)</td>
</tr>
<tr>
<td>9Cr-1Mo – V</td>
<td>454°C (850°F)</td>
</tr>
<tr>
<td>12 Cr</td>
<td>482°C (900°F)</td>
</tr>
<tr>
<td>AISI Type 304 &amp; 304H</td>
<td>510°C (950°F)</td>
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<tr>
<td>AISI Type 316 &amp; 316H</td>
<td>538°C (1000°F)</td>
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<tr>
<td>AISI Type 321</td>
<td>538°C (1000°F)</td>
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<tr>
<td>AISI Type 321H</td>
<td>538°C (1000°F)</td>
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<tr>
<td>AISI Type 347</td>
<td>538°C (1000°F)</td>
</tr>
<tr>
<td>AISI Type 347H</td>
<td>538°C (1000°F)</td>
</tr>
<tr>
<td>Alloy 800</td>
<td>565°C (1050°F)</td>
</tr>
<tr>
<td>Alloy 800H</td>
<td>565°C (1050°F)</td>
</tr>
<tr>
<td>Alloy 800HT</td>
<td>565°C (1050°F)</td>
</tr>
<tr>
<td>HK-40</td>
<td>649°C (1200°F)</td>
</tr>
</tbody>
</table>
Figure 4-17 – Pinched Alloy 800H pigtail opened up creep fissures on the surface.

Figure 4-18 – Creep rupture of an HK40 heater tube.
Figure 4-19 – Creep Failure of 310 SS Heater Tube Guide Bolt after approximately 7 years service at 1400°F (760°C). a.) Cross-section at 10X, as-polished. b) Voids and intergranular separation characteristic of long term creep, 100X, etched.
4.2.9 Thermal Fatigue

4.2.9.1 Description of Damage
Thermal fatigue is the result of cyclic stresses caused by variations in temperature. Damage is in the form of cracking that may occur anywhere in a metallic component where relative movement or differential expansion is constrained, particularly under repeated thermal cycling.

4.2.9.2 Affected Materials
All materials of construction.

4.2.9.3 Critical Factors
a) Key factors affecting thermal fatigue are the magnitude of the temperature swing and the frequency (number of cycles).

b) Time to failure is a function of the magnitude of the stress and the number of cycles and decreases with increasing stress and increasing cycles.

c) Startup and shutdown of equipment increase the susceptibility to thermal fatigue. There is no set limit on temperature swings; however, as a practical rule, cracking may be suspected if the temperature swings exceed about 200°F (93°C).

d) Damage is also promoted by rapid changes in surface temperature that result in a thermal gradient through the thickness or along the length of a component. For example: cold water on a hot tube (thermal shock); rigid attachments and a smaller temperature differential; inflexibility to accommodate differential expansion.

e) Notches (such as the toe of a weld) and sharp corners (such as the intersection of a nozzle with a vessel shell) and other stress concentrations may serve as initiation sites.

4.2.9.4 Affected Units or Equipment
a) Examples include the mix points of hot and cold streams such as hydrogen mix points in hydroprocessing units, and locations where condensate comes in contact with steam systems, such as de-superheating and attemporating equipment (Figures 4-20 and 4-23).

b) Thermal fatigue cracking has been a major problem in coke drum shells. Thermal fatigue can also occur on coke drum skirts where stresses are promoted by a variation in temperature between the drum and skirt (Figure 4–21 and Figure 4–22).

c) In steam generating equipment, the most common locations are at rigid attachments between neighboring tubes in the superheater and reheater. Slip spacers designed to accommodate relative movement may become frozen and act as a rigid attachment when plugged with fly ash.

d) Tubes in the high temperature superheater or reheater that penetrate through the cooler waterwall tubes may crack at the header connection if the tube is not sufficiently flexible. These cracks are most common at the end where the expansion of the header relative to the waterwall will be greatest.

e) Steam actuated soot blowers may cause thermal fatigue damage if the first steam exiting the soot blower nozzle contains condensate. Rapid cooling of the tube by the liquid water will promote this form of damage. Similarly, water lancing or water cannon use on waterwall tubes may have the same effect.
4.2.9.5 **Appearance or Morphology of Damage**

a) Thermal fatigue cracks usually initiate on the surface of the component. They are generally wide and often filled with oxides due to elevated temperature exposure. Cracks may occur as single or multiple cracks.

b) Thermal fatigue cracks propagate transverse to the stress and they are usually dagger-shaped, transgranular, and oxide filled (Figure 4-24 and 4-25). However, cracking may be axial or circumferential, or both, at the same location.

c) In steam generating equipment, cracks usually follow the toe of the fillet weld, as the change in section thickness creates a stress raiser. Cracks often start at the end of an attachment lug and if there is a bending moment as a result of the constraint, they will develop into circumferential cracks into the tube.

d) Water in soot blowers may lead to a crazing pattern. The predominant cracks will be circumferential and the minor cracks will be axial. (Figure 4-26 to 4-27).

4.2.9.6 **Prevention / Mitigation**

a) Thermal fatigue is best prevented through design and operation to minimize thermal stresses and thermal cycling. Several methods of prevention apply depending on the application.

i) Designs that incorporate reduction of stress concentrators, blend grinding of weld profiles, and smooth transitions should be used.

ii) Controlled rates of heating and cooling during startup and shutdown of equipment can lower stresses.

iii) Differential thermal expansion between adjoining components of dissimilar materials should be considered.

b) Designs should incorporate sufficient flexibility to accommodate differential expansion.

i) In steam generating equipment, slip spacers should slip and rigid attachments should be avoided.

ii) Drain lines should be provided on soot-blowers to prevent condensate in the first portion of the soot blowing cycle.

c) In some cases, a liner or sleeve may be installed to prevent a colder liquid from contacting the hotter pressure boundary wall.

4.2.9.7 **Inspection and Monitoring**

a) Since cracking is usually surface connected, visual examination, MT and PT are effective methods of inspection.

b) External SWUT inspection can be used for non-intrusive inspection for internal cracking and where reinforcing pads prevent nozzle examination.

c) Heavy wall reactor internal attachment welds can be inspected using specialized ultrasonic techniques.

4.2.9.8 **Related Mechanisms**

Corrosion fatigue (see 4.5.2) and dissimilar metal weld cracking (see 4.2.12).

4.2.9.9 **References**


Figure 4-20 – Thermal fatigue cracks on the inside of a heavy wall SS pipe downstream of a cooler H₂ injection into a hot hydrocarbon line.

Figure 4-21 – Bulging in a skirt of a coke drum.
Figure 4-22 – Thermal fatigue cracking associated with bulged skirt shown in Figure 4-21.

Figure 4-23 – Thermal fatigue of 304L stainless at mix point in the BFW preheater bypass line around the high temperature shift effluent exchanger in a hydrogen reformer. The delta T is 325°F (181°C) at an 8 inch bypass line tying into a 14 inch line, 3 yrs after startup.
Figure 4-24 – In a carbon steel sample, metallographic section through a thermal fatigue crack indicates origin at the toe of an attachment weld. Mag. 50X, etched.

Figure 4-25 – Older cracks fill with oxide, may stop and restart (note jog part way along the crack), and do not necessarily require a change in section thickness to initiate the crack. Mag. 100X, etched.
Figure 4-26 – Metallographic cross-section of a superheated steam outlet that failed from thermal fatigue. Unetched.

Figure 4-27 – Photomicrograph of the failed superheated steam outlet shown in Figure 4-26. Etched.
4.2.10 Short Term Overheating – Stress Rupture

4.2.10.1 Description of Damage
Permanent deformation occurring at relatively low stress levels as a result of localized overheating. This usually results in bulging and eventually failure by stress rupture.

4.2.10.2 Affected Materials
All fired heater tube materials and common materials of construction.

4.2.10.3 Critical Factors
a) Temperature, time and stress are critical factors.
b) Usually due to flame impingement or local overheating.
c) Time to failure will increase as internal pressures or loading decrease. However, bulging and distortion can be significant at low stresses, as temperatures increase.
d) Local overheating above the design temperature.
e) Loss in thickness due to corrosion will reduce time to failure by increasing the stress.

4.2.10.4 Affected Units or Equipment
a) All boiler and fired heater tubes are susceptible.
b) Furnaces with coking tendencies such as crude, vacuum, heavy oil hydroprocessing and coker units are often fired harder to maintain heater outlet temperatures and are more susceptible to localized overheating.
c) Hydroprocessing reactors may be susceptible to localized overheating of reactor beds due to inadequate hydrogen quench or flow maldistribution.
d) Refractory lined equipment in the FCC, sulfur plant and other units may suffer localized overheating due to refractory damage and/or excessive firing.

4.2.10.5 Appearance or Morphology of Damage
a) Damage is typically characterized by localized deformation or bulging on the order of 3% to 10% or more, depending on the alloy, temperature and stress level.
b) Ruptures are characterized by open “fishmouth” failures and are usually accompanied by thinning at the fracture surface (Figure 4-28 to 4-31).

4.2.10.6 Prevention / Mitigation
a) Minimize localized temperature excursions.
b) Fired heaters require proper burner management and fouling/deposit control to minimize hot spots and localized overheating.
c) Utilize burners which produce a more diffuse flame pattern.
d) In hydroprocessing equipment, install and maintain bed thermocouples in reactors and minimize the likelihood of hot spots through proper design and operation.
e) Maintain refractory in serviceable condition in refractory lined equipment.
4.2.10.7 **Inspection and Monitoring**

a) In fired heaters, visual observation, IR monitoring of tubes and tubeskin thermocouples are used to monitor temperatures.

b) Refractory lined equipment can be monitored with heat indicating paint and periodic IR scans. Inspect for refractory damage during shutdowns.

c) Maintain and monitor reactor bed thermocouples as well as reactor skin thermocouples.

4.2.10.8 **Related Mechanisms**

Creep/stress rupture (see 4.2.8).

4.2.10.9 **References**

1. API RP 579, Fitness-For-Service, American Petroleum Institute, Washington, D.C.
2. API Standard 530, Calculation of Heater Tube Thickness in Petroleum Refineries, American Petroleum Institute, Washington, D.C.
Figure 4-28 – Short term overheating failure of a vertical 4.5-in. OD, Schedule 160 2.25Cr-1Mo (SA335-P2) hydrocracker radiant that was 21 years old. Failure occurred due process side starvation with burners running.

Figure 4-29 – Short term overheating tube failed by bulging and rupture due to short term overheating at a temperature well over 1380°F (750°C).
Figure 4-30 – 1Cr-0.5Mo boiler superheater tube in 700 psig steam service that failed due to overheating.

Figure 4-31 – The fracture-edge microstructure displays severely elongated ferrite grains, proof of the ductility of the rupture. The thickness at the edge here is about 0.01 inch for a reduction in the wall thickness of more than 95%. 50X, etched.
4.2.11 Steam Blanketing

4.2.11.1 Description of Damage

The operation of steam generating equipment is a balance between the heat flow from the combustion of the fuel and the generation of steam within the waterwall or generating tube. The flow of heat energy through the wall of the tube results in the formation of discrete steam bubbles (nucleate boiling) on the ID surface. The moving fluid sweeps the bubbles away. When the heat flow balance is disturbed, individual bubbles join to form a steam blanket, a condition known as Departure From Nucleate Boiling (DNB). Once a steam blanket forms, tube rupture can occur rapidly, as a result of short term overheating, usually within a few minutes.

4.2.11.2 Affected Materials

Carbon steel and low alloy steels.

4.2.11.3 Critical Factors

a) Heat flux and fluid flow are critical factors.

b) Flame impingement from misdirected or damaged burners can provide a heat flux greater than the steam generating tube can accommodate.

c) On the water side, anything that restricts fluid flow (for example, pinhole leaks lower in the steam circuit or dented tubes from slag falls) will reduce fluid flow and can lead to DNB conditions.

d) Failure occurs as a result of the hoop stress in the tube from the internal steam pressure at the elevated temperature.

4.2.11.4 Affected Units or Equipment

All steam-generating units including fired boilers, waste heat exchangers in sulfur plants, hydrogen reformers and FCC units. Failures can occur in superheaters and reheaters during start-up when condensate blocks steam flow.

4.2.11.5 Appearance or Morphology of Damage

a) These short-term, high-temperature failures always show an open burst with the fracture edges drawn to a near knife-edge (Figure 4-32).

b) The microstructure will always show severe elongation of the grain structure due to the plastic deformation that occurs at the time of failure.

4.2.11.6 Prevention / Mitigation

a) When a DNB condition has developed, tube rupture will quickly follow. Proper burner management should be practiced to minimize flame impingement.

b) Proper BFW treatment can help prevent some conditions that can lead to restricted fluid flow.

c) Tubes should be visually inspected for bulging.

4.2.11.7 Inspection and Monitoring

Burners should be properly maintained to prevent flame impingement.

4.2.11.8 Related Mechanisms

a) Steam blanketing can cause caustic corrosion (caustic gouging) as outlined in 4.3.10.

b) Very similar characteristics are observed in short term overheating (see 4.2.10).
4.2.11.9 References

Figure 4-32 – Short-term high-temperature failures from DNB are wide-open bursts with the failure lips drawn to a near knife edge. They are ductile ruptures. Mag. 25X.
4.2.12 Dissimilar Metal Weld (DMW) Cracking

4.2.12.1 Description of Damage

Cracking of dissimilar metal welds occurs in the ferritic (carbon steel or low alloy steel) side of a weld between an austenitic (300 Series SS or Nickel base alloy) and a ferritic material operating at high temperature (Figure 4-33 and 4-44). Cracking can result from creep damage, from fatigue cracking, from sulfide stress cracking or hydrogen disbonding.

4.2.12.2 Affected Materials

The most common are ferritic materials such as carbon steel and low alloy steels that are welded to the austenitic stainless steels as well as any material combinations that have widely differing thermal expansion coefficients.

4.2.12.3 Critical Factors

a) Important factors include the type of filler metal used to join the materials, heating and cooling rate, metal temperature, time at temperature, weld geometry and thermal cycling.

b) Cracking can occur because of the different coefficients of thermal expansion between ferritic and austenitic (e.g. 300 Series stainless steel or nickel-base alloys) which differ by about 25 to 30% or more. At high operating temperatures, the differences in thermal expansion leads to high stress at the heat-affected zone on the ferritic side (Table 4-4).

c) As the operating temperature increases, differential thermal expansion between the metals results in increasing stress at the weldment, particularly if a 300 Series SS weld metal is used. Ferritic/austenitic joints can generate significant thermal expansion/thermal fatigue stresses at temperatures greater than 510°F (260°C).

d) Thermal cycling aggravates the problem. Stresses during start up and shut down can be significant.

e) Stresses acting on the weldment are significantly higher when an austenitic stainless steel filler metal is used. A nickel base filler metal has a coefficient of thermal expansion that is closer to carbon steel, resulting in significantly lower stress at elevated temperatures.

f) For dissimilar welds that operate at elevated temperatures, the problem is aggravated by the diffusion of carbon out of the heat-affected zone of the ferritic material and into the weld metal. The loss of carbon reduces the creep strength of the ferritic material heat-affected zone, thereby increasing the cracking probability (Figure 4-35). The temperature at which carbon diffusion becomes a concern is above 800°F to 950°F (427°C to 510°C) for carbon steels and low alloy steels, respectively.

g) Dissimilar metal welds on a ferritic steel that are made with a 300 Series SS weld metal or a nickel-based filler metal result in a narrow region (mixed zone) of high hardness at the toe of the weld, near the fusion line on the ferritic steel side. These high hardness zones render the material susceptible to various forms of environmental cracking such as sulfide stress cracking or hydrogen stress cracking (Figures 4-36 and 4-37). PWHT of the weldment will not prevent environmental cracking if the weld is exposed to wet H₂S conditions.

h) DMW’s for high temperature service in hydrogen environments must be carefully designed and inspected to prevent hydrogen disbonding (Figures 4-38 to 4-41).

i) In environments that promote liquid ash corrosion, weld cracking problems may be accelerated by stress-assisted corrosion. The ferritic heat-affected zone will preferentially corrode due to the large thermal strain. The results are long, narrow, oxide wedges that parallel the fusion line of the weld (Figure 4-42).

j) Poor geometry of the weld, excessive undercut, and other stress intensification factors will promote crack formation.
**4.2.12.4 Affected Units or Equipment**

a) Dissimilar metal welds are utilized in special applications in refineries and other process plants.

b) Examples of DMW’s include:
   - Welds used to join clad pipe in locations such as transitions in hydroprocessing reactor outlet piping from overlaid low alloy CrMo nozzles or piping to solid 300 Series stainless steel pipe.
   - Hydroprocessing exchanger inlet and outlet piping.
   - Alloy transitions inside fired heaters (e.g. 9Cr to 317L in a crude furnace)
   - Hydrogen reformer furnace 1.25 Cr inlet pig tails to Alloy 800 socketlets or weldolets on Hydrogen reformer tubes.
   - Hydrogen reformer furnace Alloy 800 outlet cones to CS or 1.25 Cr refractory lined transfer lines.
   - Alloy transitions inside fired heaters (e.g. 9Cr to 317L in a crude or vacuum furnace)
   - Welds joining clad pipe sections to themselves or to unclad carbon or low alloy steel pipe (e.g. Alloy C276 clad CS piping in crude unit overhead system)
   - Nickel base alloy welds joining socket weld valves in 5 and 9 Cr piping systems.
   - 300 series SS weld overlay in numerous refinery reactors and pressure vessels.
   - Similar DMWs have been used in FCCU reactors and regenerator vessels and in Coker Units.

c) All superheaters and reheaters that have welds between ferritic materials (1.25Cr-0.5Mo and 2.25Cr-1Mo) and the austenitic materials (300 Series SS, 304H, 321H and 347H).

**4.2.12.5 Appearance or Morphology of Damage**

a) In most cases, the cracks form at the toe of the weld in the heat-affected zone of the ferritic material (Figure 4-36 to Figure 4-43).

b) Welds joining tubes are the most common problem area, but support lugs or attachments of cast or wrought 300 Series SS to 400 Series SS are also affected.

**4.2.12.6 Prevention / Mitigation**

a) For high temperature applications, nickel base filler metals which have a coefficient of thermal expansion closer to carbon steel and low alloy steels may dramatically increase the life of the joint, because of the significant reduction in thermal stress acting on the steel (ferritic) side of the joint. Refer to API 577 and API 582 for additional information on filler metal selection, welding procedures and weld inspection.

b) If 300 Series SS welding electrodes are used, the dissimilar metal weld should be located in a low temperature region.

c) Consider buttering the ferritic side of the joint with the SS or nickel base filler metal and perform PWHT prior to completing the DMW to minimize the hardness of the mixed weld zone in order to minimize susceptibility to environmental cracking. See Figure 4-34 and 35.

d) On buttered joints, the thickness of the weld metal should be a minimum of 0.25 inch (6.35 mm) after the bevel is machined. Figure 4-35.

e) In steam generating equipment, the weld at the high temperature end should be made in the penthouse or header enclosure, out of the heat transfer zone.

f) For high temperature installations, consider installing a pup piece that has an intermediate thermal expansion coefficient between the two materials to be joined.
4.2.12.7 **Inspection and Monitoring**

a) The following elements should be considered for non-destructive examination of critical dissimilar butt welds before they are put into service:
   - 100% PT after buttering and completion
   - 100% UT on butter layer after PWHT (check bonding)
   - 100% RT
   - 100% UT – recordable
   - PMI

b) For dissimilar welds in fired heater tubes, RT and UT shear wave inspection should be performed.

c) Environmental cracking will also result in surface breaking cracks initiating on the ID surface exposed to the corrosive environment, which can be detected using WFMT or external SWUT methods.

4.2.12.8 **Related Mechanisms**

Thermal fatigue (see 4.2.9), corrosion fatigue (see 4.5.2), creep (see 4.2.8), and sulfide stress cracking (see 5.1.2.3.)

4.2.12.9 **References**

11. API RP 577, “Welding Inspection and Metallurgy”, American Petroleum Institute,
12. Washington, D.C.
13. API Subcommittee on Corrosion and Materials, Roundtable on Dissimilar Welds April 17, 2007, Seattle, WA.
Table 4-4: Coefficients of thermal expansion for common materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Coefficient (in/in/F \times 10^{-6}) to 800°F (427°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS</td>
<td>7.97</td>
</tr>
<tr>
<td>1 Cr-1/2 Mo</td>
<td>7.53</td>
</tr>
<tr>
<td>2 1/4 Cr-1 Mo</td>
<td>7.53</td>
</tr>
<tr>
<td>300 Series SS</td>
<td>10.05</td>
</tr>
<tr>
<td>Alloy 600</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 4-33 – Two primary DMW configurations.
a) Ferritic steel pipe (left) welded to clad or weld overlaid pipe (right)
b) Solid Stainless steel pipe (left) welded to clad or weld overlaid pipe (right)
Figure 4-34 – Schematic of typical weld detail used to join a solid stainless steel pipe to a clad or weld overlaid pipe. The sequence is: 1) Butter the weld bevel on the ferritic steel side, 2) Perform PWHT of the ferritic side prior to making dissimilar weld, 3) Complete the dissimilar weld using alloy filler metal, 4) Do not PWHT the completed dissimilar weld.

Figure 4-35 – High magnification photomicrograph of a DMW joining a ferritic alloy (SA213 T-22) used in high temperature service. Creep cracks (black specks) can be observed in the ferritic alloy heat-affected zones. Mag. 50X, etched.
Figure 4-36 – Weld detail used to join a carbon steel elbow (bottom) to a weld overlaid pipe section (top) in high pressure wet H₂S service. Sulfide stress cracking (SSC) occurred along the toe of the weld (arrow), in a narrow zone of high hardness.

Figure 4-37 – High magnification photomicrograph of SSC in pipe section shown in Figure 4-36.
Figure 4-38 – Failure of DMW joining 1.25Cr-0.5Mo to Alloy 800H in a Hydro-dealkylation (HAD) Reactor Effluent Exchanger. Crack propagation due to stresses driven at high temperature of 875°F (468°C) and a hydrogen partial pressure of 280 psig (1.93 MPa).

Figure 4-39 - High magnification photomicrograph of the crack in Figure 4-38 showing blistering and disbondment along the weld fusion line interface.
Figure 4-40 - High magnification photomicrograph of the crack shown above in Figure 4-39. Plastic deformation of the grain structure can be found at the vicinity of the blister.

Figure 4-41 - Failure of nickel alloy DMW joining HP40 (Nb modified) tube to 1.25Cr-0.5Mo flange in a Steam Methane Reformer due to cold hydrogen disbonding of the buttering layer. Process temperature 914°-941°F (490° to 505°C), Pressure (2.14 Mpa), H₂ content 10-20% (off-gas).
Figure 4-42 – When both liquid phase coal ash corrosion and a DMW exists, stress assisted corrosion of the 2.25Cr-1Mo heat-affected zone may occur. Note that there is a lack of creep damage at the crack tip. Mag. 25X, etched.
4.2.13 Thermal Shock

4.2.13.1 Description of Damage
A form of thermal fatigue cracking – thermal shock – can occur when high and non-uniform thermal stresses develop over a relatively short time in a piece of equipment due to differential expansion or contraction. If the thermal expansion/contraction is restrained, stresses above the yield strength of the material can result. Thermal shock usually occurs when a colder liquid contacts a warmer metal surface.

4.2.13.2 Affected Materials
All metals and alloys.

4.2.13.3 Critical Factors
a) The magnitude of the temperature differential and the coefficient of thermal expansion of the material determine the magnitude of the stress.
b) Cyclic stresses generated by temperature cycling of the material may initiate fatigue cracks.
c) Stainless steels have higher coefficients of thermal expansion than carbon and alloy steels or nickel base alloys and are more likely to see higher stresses.
d) High temperature exposure during a fire.
e) Temperature changes that can result from water quenching as a result of rain deluges.
f) Fracture is related to constraint on a component that prevents the component from expanding or contracting with a change in temperature.
g) Cracking in cast components such as valves may initiate at casting flaws on the ID and progress through the thickness.
h) Thick sections can develop high thermal gradients.

4.2.13.4 Affected Units or Equipment
a) FCC, cokers, catalytic reforming and high severity hydroprocessing units are high temperature units where thermal shock is possible.
b) High temperature piping and equipment in any unit can be affected.
c) Materials that have lost ductility, such as CrMo equipment (temper embrittlement) are particularly susceptible to thermal shock.
d) Equipment subjected to accelerated cooling procedures to minimize shutdown time.

4.2.13.5 Appearance or Morphology of Damage
Surface initiating cracks may also appear as “craze” cracks.

4.2.13.6 Prevention / Mitigation
a) Prevent interruptions in the flow of high temperature lines.
b) Design to minimize severe restraint.
c) Install thermal sleeves to prevent liquid impingement on the pressure boundary components.
d) Minimize rain or fire water deluge situations.
e) Review hot/cold injection points for potential thermal shock.
4.2.13.7 **Inspection and Monitoring**

a) This type of damage is highly localized and difficult to locate.

b) PT and MT can be used to confirm cracking.

4.2.13.8 **Related Mechanisms**

Thermal fatigue (see 4.2.9).

4.2.13.9 **References**

2. API RP 579, Fitness-For-Service, American Petroleum Institute, Washington, D.C.
4.2.14 Erosion/Erosion – Corrosion

4.2.14.1 Description of Damage

a) Erosion is the accelerated mechanical removal of surface material as a result of relative movement between, or impact from solids, liquids, vapor or any combination thereof.

b) Erosion-corrosion is a description for the damage that occurs when corrosion contributes to erosion by removing protective films or scales, or by exposing the metal surface to further corrosion under the combined action of erosion and corrosion.

4.2.14.2 Affected Materials

All metals, alloys and refractories.

4.2.14.3 Critical Factors

a) In most cases, corrosion plays some role so that pure erosion (sometimes referred to as abrasive wear) is rare. It is critical to consider the role that corrosion contributes.

b) Metal loss rates depend on the velocity and concentration of impacting medium (i.e., particles, liquids, droplets, slurries, two-phase flow), the size and hardness of impacting particles, the hardness and corrosion resistance of material subject to erosion, and the angle of impact.

c) Softer alloys such as copper and aluminum alloys that are easily worn from mechanical damage may be subject to severe metal loss under high velocity conditions.

d) Although increasing hardness of the metal substrate is a common approach to minimize damage, it is not always a good indicator of improved resistance to erosion, particularly where corrosion plays a significant role.

e) For each environment-material combination, there is often a threshold velocity above which impacting objects may produce metal loss. Increasing velocities above this threshold result in an increase in metal loss rates as shown in Table 4-5. This table illustrates the relative susceptibility of a variety of metals and alloys to erosion/corrosion by seawater at different velocities.

f) The size, shape, density and hardness of the impacting medium affect the metal loss rate.

g) Increasing the corrosivity of the environment may reduce the stability of protective surface films and increase the susceptibility to metal loss. Metal may be removed from the surface as dissolved ions, or as solid corrosion products which are mechanically swept from the metal surface.

h) Factors which contribute to an increase in corrosivity of the environment, such as temperature, pH, etc., can increase susceptibility to metal loss.
4.2.14.4 **Affected Units or Equipment**

a) All types of equipment exposed to moving fluids and/or catalyst are subject to erosion and erosion-corrosion. This includes piping systems, particularly the bends, elbows, tees and reducers; piping systems downstream of letdown valves and block valves; pumps; blowers; propellers; impellers; agitators; agitated vessels; heat exchanger tubing; measuring device orifices; turbine blades; nozzles; ducts and vapor lines; scrapers; cutters; and wear plates.

b) Erosion can be caused by gas borne catalyst particles or by particles carried by a liquid such as a slurry. In refineries, this form of damage occurs as a result of catalyst movement in FCC reactor/regenerator systems in catalyst handling equipment (valves, cyclones, piping, reactors) and slurry piping (Figure 4-43); coke handling equipment in both delayed and fluidized bed cokers (Figure 4-44); and as wear on pumps (Figure 4-45), compressors and other rotating equipment.

c) Hydroprocessing reactor effluent piping may be subject to erosion-corrosion by ammonium bisulfide. The metal loss is dependent on several factors including the ammonium bisulfide concentration, velocity and alloy corrosion resistance.

d) Crude and vacuum unit piping and vessels exposed to naphthenic acids in some crude oils may suffer severe erosion-corrosion metal loss depending on the temperature, velocity, sulfur content and TAN level.

4.2.14.5 **Appearance or Morphology of Damage**

a) Erosion and erosion-corrosion are characterized by a localized loss in thickness in the form of pits, grooves, gullies, waves, rounded holes and valleys. These losses often exhibit a directional pattern.

b) Failures can occur in a relatively short time.

4.2.14.6 **Prevention / Mitigation**

a) Improvements in design involve changes in shape, geometry and materials selection. Some examples are: increasing the pipe diameter to decrease velocity; streamlining bends to reduce impingement; increasing the wall thickness; and using replaceable impingement baffles.

b) Improved resistance to erosion is usually achieved through increasing substrate hardness using harder alloys, hardfacing or surface-hardening treatments. Erosion resistant refractories in cyclones and slide valves have been very successful.

c) Erosion-corrosion is best mitigated by using more corrosion-resistant alloys and/or altering the process environment to reduce corrosivity, for example, deaeration, condensate injection or the addition of inhibitors. Resistance is generally not improved through increasing substrate hardness alone.

d) Heat exchangers utilize impingement plates and occasionally tube ferrules to minimize erosion problems.

e) Higher molybdenum containing alloys are used for improved resistance to naphthenic acid corrosion.

4.2.14.7 **Inspection and Monitoring**

a) Visual examination of suspected or troublesome areas, as well as UT checks or RT can be used to detect the extent of metal loss.

b) Specialized corrosion coupons and on-line corrosion monitoring electrical resistance probes have been used in some applications.

c) IR scans are used to detect refractory loss on stream.

4.2.14.8 **Related Mechanisms**

Specialized terminology has been developed for various forms of erosion and erosion-corrosion in specific environments and/or services. This terminology includes cavitation, liquid impingement erosion, fretting and other similar terms.
4.2.14.9 References

<table>
<thead>
<tr>
<th>Material</th>
<th>1 fps (tidal current)</th>
<th>4 fps (Immersed in seawater flume)</th>
<th>27 fps (rotating disk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel</td>
<td>6</td>
<td>13</td>
<td>47</td>
</tr>
<tr>
<td>Cast iron</td>
<td>9</td>
<td>--</td>
<td>54</td>
</tr>
<tr>
<td>Silicon bronze</td>
<td>0.2</td>
<td>0.3</td>
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<tr>
<td>Admiralty brass</td>
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<tr>
<td>Hydraulic bronze</td>
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<td>55</td>
</tr>
<tr>
<td>G bronze</td>
<td>1</td>
<td>0.3</td>
<td>46</td>
</tr>
<tr>
<td>Al bronze</td>
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<td>--</td>
<td>44</td>
</tr>
<tr>
<td>Aluminum brass</td>
<td>0.4</td>
<td>--</td>
<td>19</td>
</tr>
<tr>
<td>90-10 CuNi</td>
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<td>16</td>
</tr>
<tr>
<td>70-30 CuNi (0.05%Fe)</td>
<td>0.3</td>
<td>--</td>
<td>32</td>
</tr>
<tr>
<td>70-30 CuNi (0.5% Fe)</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
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<tr>
<td>Monel</td>
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<tr>
<td>316 SS</td>
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<td>0</td>
<td>&lt;0.2</td>
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<tr>
<td>Hastelloy C</td>
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<td>--</td>
<td>0.05</td>
</tr>
<tr>
<td>Titanium</td>
<td>0</td>
<td>--</td>
<td>0</td>
</tr>
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</table>
Figure 4-43 – Erosion Corrosion of a 1.25Cr 300 # valve flange on an FCC Catalyst withdrawal line.

Figure 4-44 – Erosion of a 9Cr-1Mo coker heater return bend.
Figure 4-45 – Erosion-Corrosion of is ASTM A48 Class 30 Cast Iron Impeller in recycle water pump.
4.2.15 Cavitation

4.2.15.1 Description of Damage

a) Cavitation is a form of erosion caused by the formation and instantaneous collapse of innumerable tiny vapor bubbles.
b) The collapsing bubbles exert severe localized impact forces that can result in metal loss referred to as cavitation damage.
c) The bubbles may contain the vapor phase of the liquid, air or other gas entrained in the liquid medium.

4.2.15.2 Affected Materials

Most common materials of construction including copper and brass, cast iron, carbon steel, low alloy steels, 300 Series SS, 400 Series SS and nickel base alloys.

4.2.15.3 Critical Factors

a) In a pump, the difference between the actual pressure or head of the liquid available (measured on the suction side) and the vapor pressure of that liquid is called the Net Positive Suction Head (NPSH) available. The minimum head required to prevent cavitation with a given liquid at a given flow rate is called the net positive suction head required. Inadequate NPSH can result in cavitation.
b) Temperatures approaching the boiling point of the liquid are more likely to result in bubble formation than lower temperature operation.
c) The presence of solid or abrasive particles is not required for cavitation damage but will accelerate the damage.

4.2.15.4 Affected Units or Equipment

a) Cavitation is most often observed in pump casings, pump impellers (low pressure side) and in piping downstream of orifices or control valves.
b) Damage can also be found in restricted-flow passages or other areas where turbulent flow is subjected to rapid pressure changes within a localized region. Examples of affected equipment include heat exchanger tubes, venturis, seals and impellers.

4.2.15.5 Appearance or Morphology of Damage

Cavitation damage generally looks like sharp-edged pitting but may also have a gouged appearance in rotational components. However, damage occurs only in localized low-pressure zones (see Figure 4-46, Figure 4-47 to Figure 4-49).

4.2.15.6 Prevention / Mitigation

a) Resistance to cavitation damage in a specific environment may not be significantly improved by a material change. A mechanical modification, design or operating change is usually required.
b) Cavitation is best prevented by avoiding conditions that allow the absolute pressure to fall below the vapor pressure of the liquid or by changing the material properties. Examples include:
   i) Streamline the flow path to reduce turbulence.
   ii) Decrease fluid velocities.
   iii) Remove entrained air.
   iv) Increase the suction pressure of pumps.
   v) Alter the fluid properties, perhaps by adding additives.
   vi) Use hard surfacing or hardfacing.
   vii) Use of harder and/or more corrosion resistant alloys.
c) Attack is accelerated by the mechanical disruption of protective films at the liquid-solid interface (such as a protective corrosion scale or passive films). Therefore, changing to a more corrosion resistant and/or higher hardness material may not improve cavitation resistance. Excessively hard materials may not be suitable if they lack the toughness required to withstand the high local pressures and impact (shear loads) of the collapsing bubbles.

4.2.15.7 Inspection and Monitoring

a) Cavitating pumps may sound like pebbles are being thrashed around inside.

b) Techniques include limited monitoring of fluid properties as well as acoustic monitoring of turbulent areas to detect characteristic sound frequencies.

c) Visual examination of suspected areas, as well as external UT and RT can be used to monitor for loss in thickness.

4.2.15.8 Related Mechanisms

Liquid impingement or erosion (see 4.2.14).

4.2.15.9 References

Figure 4-46 – Cutaway of a CS butterfly valve with cavitation damage after two years of service due to a high pressure drop across the valve in a hydrocarbon drain line off a cold low pressure separator in an atmospheric resid desulfurizing unit.

Figure 4-47 – Closer view of damaged surface of butterfly valve.
Figure 4-48 – Cavitation pitting on the low-pressure side of a stainless steel pump impeller.

Figure 4-49 – Cavitation pitting on the water side of a cast iron cylinder liner in a large engine.
4.2.16 Mechanical Fatigue

4.2.16.1 Description of Damage
a) Fatigue cracking is a mechanical form of degradation that occurs when a component is exposed to cyclical stresses for an extended period, often resulting in sudden, unexpected failure.

b) These stresses can arise from either mechanical loading or thermal cycling and are typically well below the yield strength of the material.

4.2.16.2 Affected Materials
All engineering alloys are subject to fatigue cracking although the stress levels and number of cycles necessary to cause failure vary by material.

4.2.16.3 Critical Factors
Geometry, stress level, number of cycles, and material properties (strength, hardness, microstructure) are the predominant factors in determining the fatigue resistance of a component.

a) Design: Fatigue cracks usually initiate on the surface at notches or stress raisers under cyclic loading. For this reason, design of a component is the most important factor in determining a component's resistance to fatigue cracking. Several common surface features can lead to the initiation of fatigue cracks as they can act as stress concentrations. Some of these common features are:
   i) Mechanical notches (sharp corners or groves);
   ii) Key holes on drive shafts of rotating equipment;
   iii) Weld joint, flaws and/or mismatches;
   iv) Quench nozzle areas;
   v) Tool markings;
   vi) Grinding marks;
   vii) Lips on drilled holes;
   viii) Thread root notches;
   ix) Corrosion.

b) Metallurgical Issues and Microstructure
   i) For some materials such as titanium, carbon steel and low alloy steel, the number of cycles to fatigue fracture decreases with stress amplitude until an endurance limit reached. Below this stress endurance limit, fatigue cracking will not occur, regardless of the number of cycles.
   ii) For alloys with endurance limits, there is a correlation between Ultimate Tensile Strength (UTS) and the minimum stress amplitude necessary to initiate fatigue cracking. The ratio of endurance limit over UTS is typically between 0.4 and 0.5. Materials like austenitic stainless steels and aluminum that do not have an endurance limit will have a fatigue limit defined by the number of cycles at a given stress amplitude.
   iii) Inclusions found in metal can have an accelerating effect on fatigue cracking. This is of importance when dealing with older, “dirty” steels or weldments, as these often have inclusions and discontinuities that can degrade fatigue resistance.
   iv) Heat treatment can have a significant effect on the toughness and hence fatigue resistance of a metal. In general, finer grained microstructures tend to perform better than coarse grained. Heat treatments such as quenching and tempering, can improve fatigue resistance of carbon and low alloy steels.

c) Carbon Steel and Titanium: These materials exhibit an endurance limit below which fatigue cracking will not occur, regardless of the number of cycles.
d) 300 Series SS, 400 Series SS, aluminum and most other non-ferrous alloys:
   i) These alloys have a fatigue characteristic that does not exhibit an endurance limit. This means that fatigue fracture can be achieved under cyclical loading eventually, regardless of stress amplitude.
   ii) Maximum cyclical stress amplitude is determined by relating the stress necessary to cause fracture to the desired number of cycles necessary in a component’s lifetime. This is typically 106 to 107 cycles.

4.2.16.4 Affected Units or Equipment

a) Thermal Cycling
   i) Equipment that cycles daily in operation such as coke drums.
   ii) Equipment that may be auxiliary or on continuous standby but sees intermittent service such as auxiliary boiler.
   iii) Quench nozzle connections that see significant temperature deltas during operations such as water washing systems.

b) Mechanical Loading
   i) Pressure Swing Absorbers on hydrogen purification units.
   ii) Rotating shafts on centrifugal pumps and compressors that have stress concentrations due to changes in radii and key ways.
   iii) Components such as small diameter piping that may see vibration from adjacent equipment and/or wind. For small components, resonance can also produce a cyclical load and should be taken into consideration during design and reviewed for potential problems after installation.
   iv) High pressure drop control valves or steam reducing stations can cause serious vibration problems in connected piping.

4.2.16.5 Appearance or Morphology of Damage

a) The signature mark of a fatigue failure is a “clam shell” type fingerprint that has concentric rings called “beach marks” emanating from the crack initiation site (Figure 4-50 and Figure 4-51). This signature pattern results from the “waves” of crack propagation that occur during cycles above the threshold loading. These concentric cracks continue to propagate until the cross-sectional area is reduced to the point where failure due to overload occurs.

b) Cracks nucleating from a surface stress concentration or defect will typically result in a single “clam shell” fingerprint (Figure 4-52 to Figure 4-56).

c) Cracks resulting from cyclical overstress of a component without significant stress concentration will typically result in a fatigue failure with multiple points of nucleation and hence multiple “clam shell” fingerprints. These multiple nucleation sites are the result of microscopic yielding that occurs when the component is momentarily cycled above its yield strength.
4.2.16.6 **Prevention / Mitigation**

a) The best defense against fatigue cracking is good design that helps minimize stress concentration of components that are in cyclic service.

b) Select a metal with a design fatigue life sufficient for its intended cyclic service.

c) Allow for a generous radius along edges and corners.

d) Minimize grinding marks, nicks and gouges on the surface of components.

e) Insure good fit up and smooth transitions for welds. Minimize weld defects as these can accelerate fatigue cracking.

f) Remove any burrs or lips caused by machining.

g) Use low stress stamps and marking tools.

4.2.16.7 **Inspection and Monitoring**

a) NDE techniques such as PT, MT and SWUT can be used to detect fatigue cracks at known areas of stress concentration.

b) VT of small diameter piping to detect oscillation or other cyclical movement that could lead to cracking.

c) Vibration monitoring of rotating equipment to help detect shafts that may be out of balance.

d) In high cycle fatigue, crack initiation can be a majority of the fatigue life making detection difficult.

4.2.16.8 **Related Mechanisms**

Vibration induced fatigue (see 4.2.17).

4.2.16.9 **References**


Figure 4-50 – Schematic of a fatigue fracture surface showing “beach marks”.

Figure 4-51 – Compressor rod fracture surface showing “beach marks”
Figure 4-52 – Higher magnification view of figure above showing “beach marks”.

Figure 4-53 – Fatigue fracture surface of a carbon steel pipe.
Figure 4-54 – Fatigue crack in a 16-inch pipe-to-elbow weld in the fill line of crude oil storage tank after 50 years in service.

Figure 4-55 – A cross-section through the weld showing the crack location.
Figure 4-56 – The surface of the fracture faces of the crack shown in Figure 4-54 and Figure 4-55.
4.2.17 Vibration-Induced Fatigue

4.2.17.1 Description of Damage
A form of mechanical fatigue in which cracks are produced as the result of dynamic loading due to vibration, water hammer, or unstable fluid flow.

4.2.17.2 Affected Materials
All engineering materials.

4.2.17.3 Critical Factors
a) The amplitude and frequency of vibration as well as the fatigue resistance of the components are critical factors.
b) There is a high likelihood of cracking when the input load is synchronous or nearly synchronizes with the natural frequency of the component.
c) A lack of or excessive support or stiffening allows vibration and possible cracking problems that usually initiate at stress raisers or notches.

4.2.17.4 Affected Units or Equipment
a) Socket welds and small bore piping at or near pumps and compressors that are not sufficiently gusseted.
b) Small bore bypass lines and flow loops around rotating and reciprocating equipment.
c) Small branch connections with unsupported valves or controllers.
d) Safety relief valves are subject to chatter, premature pop-off, fretting and failure to operate properly.
e) High pressure drop control valves and steam reducing stations.
f) Heat exchanger tubes may be susceptible to vortex shedding.

4.2.17.5 Appearance or Morphology of Damage
a) Damage is usually in the form of a crack initiating at a point of high stress or discontinuity such as a thread or weld joint (Figure 4-57 and Figure 4-58).
b) A potential warning sign of vibration damage to refractories is the visible damage resulting from the failure of the refractory and/or the anchoring system. High skin temperatures may result from refractory damage.

4.2.17.6 Prevention / Mitigation
a) Vibration-induced fatigue can be eliminated or reduced through design and the use of supports and vibration dampening equipment. Material upgrades are not usually a solution.
b) Install gussets or stiffeners on small bore connections. Eliminate unnecessary connections and inspect field installations.
c) Vortex shedding can be minimized at the outlet of control valves and safety valves through proper side branch sizing and flow stabilization techniques.
d) Vibration effects may be shifted when a vibrating section is anchored. Special studies may be necessary before anchors or dampeners are provided, unless the vibration is eliminated by removing the source.
4.2.17.7 Inspection and Monitoring

a) Look for visible signs of vibration, pipe movement or water hammer.
b) Check for the audible sounds of vibration emanating from piping components such as control valves and fittings.
c) Conduct visual inspection during transient conditions (such as startups, shutdowns, upsets, etc.) for intermittent vibrating conditions.
d) Measure pipe vibrations using special monitoring equipment.
e) The use of surface inspection methods (such as PT, MT) can be effective in a focused plan.
f) Check pipe supports and spring hangers on a regular schedule.
g) Damage to insulation jacketing may indicate excessive vibration. This can result in wetting the insulation which will cause corrosion.

4.2.17.8 Related Mechanisms

Mechanical fatigue (see 4.2.16) and refractory degradation (see 4.2.18).

4.2.17.9 References

2. API Publication 581, Risk-Based Inspection Technology, American Petroleum Institute, Washington, D.C.
Figure 4-57 – Vibration induced fatigue of a 1-inch socket weld flange in a thermal relief system shortly after startup.

Figure 4-58 – Cross-sectional view of the crack in the socket weld in Figure 4-57.
4.2.18 Refractory Degradation

4.2.18.1 Description of Damage
Both thermal insulating and erosion resistant refractories are susceptible to various forms of mechanical damage (cracking, spalling and erosion) as well as corrosion due to oxidation, sulfidation and other high temperature mechanisms.

4.2.18.2 Affected Materials
Refractory materials include insulating ceramic fibers, castables, refractory brick and plastic refractories.

4.2.18.3 Critical Factors
a) Refractory selection, design and installation are the keys to minimizing damage.
b) Refractory lined equipment should be designed for erosion, thermal shock and thermal expansion.
c) Dry out schedules, cure times and application procedures should be in accordance with the manufacturer’s specifications and the appropriate ASTM requirements.
d) Anchor materials must be compatible with thermal coefficients of expansion of the base metal.
e) Anchors must be resistant to oxidation in high temperature services.
f) Anchors must be resistant to condensing sulfurous acids in heaters and flue gas environments.
g) Refractory type and density must be selected to resist abrasion and erosion based on service requirements.
h) Needles and other fillers must be compatible with the process environment composition and temperature.

4.2.18.4 Affected Units or Equipment
a) Refractories are extensively used in FCC reactor regenerator vessels, piping, cyclones, slide valves and internals; in fluid cokers; in cold shell catalytic reforming reactors; and in waste heat boilers and thermal reactors in sulfur plants.
b) Boiler fire boxes and stacks which also use refractory are affected.

4.2.18.5 Appearance or Morphology of Damage
a) Refractory may show signs of excessive cracking, spalling or lift-off from the substrate, softening or general degradation from exposure to moisture.
b) Coke deposits may develop behind refractory and promote cracking and deterioration.
c) In erosive services, refractory may be washed away or thinned, exposing the anchoring system. (Figure 4-59)

4.2.18.6 Prevention / Mitigation
Proper selection of refractory, anchors and fillers and their proper design and installation are the keys to minimizing refractory damage.

4.2.18.7 Inspection and Monitoring
a) Conduct visual inspection during shutdowns.
b) Survey cold-wall equipment onstream using IR to monitor for hot spots to help identify refractory damage.
4.2.18.8  Related Mechanisms
Oxidation (see 4.4.1), sulfidation (see 4.4.2) and flue gas dew point corrosion (see 4.3.7).

4.2.18.9  References
Figure 4-59 – Damaged refractory and ferrules.
4.2.19 Reheat Cracking

4.2.19.1 **Description of Damage**
Cracking of a metal due to stress relaxation during Post Weld Heat Treatment (PWHT) or in service at elevated temperatures above 750°F (399°C). It is most often observed in heavy wall sections.

4.2.19.2 **Affected Materials**
Low alloy steels, especially the Cr-Mo steels with vanadium added, as well as 300 Series SS and nickel base alloys such as Alloy 800H.

4.2.19.3 **Critical Factors**
Important parameters include the type of material (chemical composition, impurity elements), grain size, residual stresses from fabrication (cold working, welding), section thickness (which controls restraint and stress state), notches and stress concentrators, weld metal and base metal strength, welding and heat treating conditions.

From the various theories of reheat cracking for both 300 Series SS and low alloy steels, cracking features are as follows:

a) Reheat cracking requires the presence of high stresses and is therefore more likely to occur in thicker sections and higher strength materials.

b) Reheat cracking occurs at elevated temperatures when creep ductility is insufficient to accommodate the strains required for the relief of applied or residual stresses.

c) In the first half of 2008, numerous cases of reheat cracking occurred during 2 ¼ Cr-1 Mo-V reactor fabrication. The cracks were in weld metal only, transverse to the welding direction, and in only SAW welds. It was traced to a contaminant in the welding flux.

d) Reheat cracking can either occur during PWHT or in service at high temperature. In both cases, cracks are intergranular and show little or no evidence of deformation.

e) Fine intragranular precipitate particles make the grains stronger than the grain boundaries and force the creep deformation to occur at the grain boundaries.

f) Stress relief and stabilization heat treatment of 300 Series SS for maximizing chloride SCC and PTASCC resistance can cause reheat cracking problems, particularly in thicker sections.

4.2.19.4 **Affected Units or Equipment**

a) Reheat cracking is most likely to occur in heavy wall vessels in areas of high restraint including nozzle welds and heavy wall piping.

b) HSLA steels are very susceptible to reheat cracking.

4.2.19.5 **Appearance or Morphology of Damage**

a) Reheat cracking is intergranular and can be surface breaking or embedded depending on the state of stress and geometry. It is most frequently observed in coarse-grained sections of a weld heat-affected zone.

b) In many cases, cracks are confined to the heat-affected zone, initiate at some type of stress concentration, and may act as an initiation site for fatigue. Figure 4-60 to figure 4-63.
4.2.19.6 Prevention / Mitigation

a) Joint configurations in heavy wall sections should be designed to minimize restraint during welding and PWHT. Adequate preheat must also be applied.

b) The grain size has an important influence on the high temperature ductility and on the reheat cracking susceptibility. A large grain size results in less ductile heat-affected zones, making the material more susceptible to reheat cracking.

c) Metallurgical notches arising from the welding operation are frequently the cause of heat-affected zone cracking (at the boundary between the weld and the heat-affected zone).

d) In design and fabrication, it is advisable to avoid sharp changes in cross section, such as short radius fillets or undercuts that can give rise to stress concentrations. Long-seam welds are particularly susceptible to mismatch caused by fitup problems.

e) For 2 ¼ Cr-1 Mo-V SAW weld materials, prequalification screening tests for reheat cracking such as high temperature (650°C) Gleeble tensile tests should be considered.

f) For Alloy 800H, the risk of in-service cracking can be reduced by using base metal and matching weld metal with Al+Ti <0.7%.

g) For Alloy 800H which will operate >540°C, the material may need to be purchased with a thermal stabilization heat treatment, and with PWHT of welds and cold worked sections. Welds should be made with matching Alloy 800H filler material and should be stress relieved. Refer to ASME Section VIII, Div. 1 Code in UNF-56(e) for additional information.

h) For thick-wall SS piping, PWHT should be avoided whenever possible.

4.2.19.7 Inspection and Monitoring

a) Surface cracks can be detected with UT and MT examination of carbon and low alloy steels

b) UT and PT examination can be used to detect cracks in 300 Series SS and nickel base alloys.

c) Embedded cracks can only be found through UT examination.

d) Inspection for reheat cracking in 2 ¼ Cr-1 Mo-V reactors during fabrication is typically done with TOFD or manual shearwave UT with the demonstration block having defects as small as 3 mm side drilled holes

4.2.19.8 Related Mechanisms

Reheat cracking has also been referred to in the literature as “stress relief cracking” and “stress relaxation cracking”.

4.2.19.9 References

8. H. Van Wortel, “Control of relaxation cracking in austenitic high temperature components”, Paper
Figure 4-60 – Samples removed from a cracked 12-inch NPS 321SS elbow in hot recycle H\textsubscript{2} line that operated at 985°F in hydrocracker.

Figure 4-61 – Crack at weld from SS321 elbow shown in the Figure 4-60.
Figure 4-62 – Cross-section through the weldment showing the crack in Figure 4-61.
Figure 4-63 – Photomicrographs of the weldment area.
4.2.20 Gaseous Oxygen-Enhanced Ignition and Combustion

4.2.20.1 Description of Damage

Many metals are flammable in oxygen and enriched air (>25% oxygen) services even at low pressures, whereas they are non-flammable in air. The spontaneous ignition or combustion of metallic and non-metallic components can result in fires and explosions in certain oxygen-enriched gaseous environments if not properly designed, operated and maintained. Once ignited, metals and non-metals burn more vigorously with higher oxygen purity, pressure and temperature.

4.2.20.2 Affected Materials

a) Carbon steels and low alloy steels are flammable in low pressure oxygen, greater than about 15 psig (0.103 MPa). With special precautions, these materials are safely used in high pressure oxygen.

b) Austenitic stainless steels (300 series) have better resistance to low pressure oxygen and are generally difficult to ignite at pressures below about 200 psig (1.38 MPa).

c) Copper alloys (with >55% copper) and nickel alloys (with >50% nickel) are very fire resistant and are generally considered non-flammable. Because of their excellent oxygen “compatibility” they are often selected for impingement and turbulent services such as valves and instrumentation (Figure 4-69). Alloy 400 is highly resistant.

d) Although widely used for oxygen cylinders and in oxygen manufacturing plants, aluminum is usually avoided for flowing oxygen. If ignited it burns quickly and with a large energy release.

e) The easiest materials to ignite are plastics, rubbers, and hydrocarbon lubricants and these are minimized in oxygen systems.

f) Titanium alloys are generally avoided in oxygen and oxygen-enriched service because they have low ignition energies and release a large amount of energy during combustion. Tests indicate that titanium can sustain combustion at oxygen pressure as low as 7 kPa (1 psi) absolute. Most industry documents caution against the use of titanium in oxygen systems (Ref 6 and 7).

Note: These are general guidelines and should not be considered for design.

4.2.20.3 Critical Factors

a) Many factors affect the likelihood of combustion and ignition in oxygen services including the system pressure, oxygen content of the stream, line velocity, component thickness, design and piping configuration, cleanliness and temperature.

b) The primary concern under high velocity oxygen flow conditions is the entrainment of particulate and their subsequent impingement on a surface, such as at a pipe bend. Oxygen velocities in carbon steel and stainless steel piping should comply with industry limits as shown in Reference 1. Allowable velocity is a function of pressure and flow condition (direct impingement or non-impingement).

c) The temperature of a material affects its flammability. As temperature increases, a lower amount of additional energy is required for ignition and sustained combustion. The minimum temperature at which a substance will support combustion, under a specific set of conditions is referred to as the ignition temperature. Published ignition temperatures for most alloys are near the alloy’s melting temperature. However, these are measured in non-flowing conditions. Actual systems can suffer ignition and combustion at room temperature (and lower) due to particle impact and other mechanisms.

d) System cleanliness is important for the safe operation of oxygen systems. Contamination of with metallic fines or hydrocarbons such as oils and greases during construction or maintenance activities can lead to fires during subsequent start up of the unit. These materials are easy to ignite and can lead to a large fire and breach of the system.

e) Impingement areas such as sharp elbows, tees and valves have a higher risk of ignition than straight pipe. Particles in the flowing oxygen can strike these areas and cause ignition. Operation of valves and regulators (opening / closing) cause high turbulence and impingement and only components selected and cleaned specifically for oxygen service should be used.
4.2.20.4 **Affected Units or Equipment**

a) These guidelines apply to any unit that uses oxygen or enriched air for combustion or other process reasons.

b) Oxygen is sometimes used in sulfur recovery units (SRU) and fluid catalytic cracking units (FCCU), Gasification, and Partial Oxidation (POX) units. Figure 4-64 to 4-66.

c) Oxygen piping systems especially valves, regulators, and other impingement areas are potentially vulnerable. Non-metals such as those used for seats and seals, are easier to ignite than metals (Figure 4-69).

4.2.20.5 **Appearance or Morphology of Damage**

a) In some cases a small component will burn, such as a valve seat, without kindling other materials and without any outward sign of fire damage. It is noticed when the component is removed because it is not functioning properly. Figure 4-67 to 4-68.

b) Also, external heat damage (glowing pipe or heat tint) is a strong indication of an internal fire. This can be caused by accumulation of flammable debris at a low point or other location and combustion or smoldering of the debris.

c) The worst situation is when the pressure envelope is breached because of fire. Oxygen fires can cause significant burning of metal components and extensive structural damage (Figures 4-68).

4.2.20.6 **Prevention / Mitigation**

Refer to industry recommended guidelines included in the references listed below. Some general considerations are as follows:

a) Oxygen fires are a sudden occurrence and not a progressive degradation or weakening of the material. Prevention is best accomplished be keeping systems clean, or cleaning them after maintenance or inspections.

b) Maintain velocity within recommended limits. If practical, avoid velocities that are nominally above 100 feet/second (30 m/sec) in gaseous oxygen.

c) Ensure that replacement components are suitable for oxygen service.

d) Oxygen systems should be thoroughly cleaned after maintenance.

e) Minimize lubricants and use only “oxygen compatible” lubricants.

f) Do not unnecessarily open oxygen systems for visual or other inspections as this could introduce contamination.

g) A thorough review is needed before modifying oxygen systems to operate at higher pressures, temperatures, or velocities.

h) Minimize sudden changes in pressure in the system. If high pressure oxygen suddenly enters a system initially at low pressure by quick operation of a valve, the “dead end” of that system experiences heating from adiabatic compression of the oxygen. Adiabatic compression heating can ignite plastics and rubbers, but will not ignite metals. Valve seats, seals, non-metallic hoses, etc can be ignited by this mechanism.

i) Do not use plastic pipe in oxygen piping systems.

j) Personnel activities near oxygen piping and systems should be minimized during start ups.

4.2.20.7 **Inspection and Monitoring**

a) Most commercial oxygen is dry and non-corrosive at normal ambient temperatures. Because of the sudden catastrophic ignition of metals under certain conditions this type of damage is difficult to inspect for in advance.

b) Tell-tale signs of a minor fire such as external heat damage, or signs of malfunctioning valves or other components containing non-metallic components may be indicative of a problem.
c) Blacklights can be used to check for hydrocarbon contamination.

4.2.20.8 Related Mechanisms

Not applicable.

4.2.20.9 References

Figure 4-64 - Thermal combustor on the front end of a reaction furnace on a sulfur recovery unit.
Figure 4-65 - Same as figure above after damage due to oxygen combustion resulting from oxygen injection into the thermal combustor on the front end of the reaction furnace.
Figure 4-66 - Same as figure above when viewed from a different angle.
Figure 4-67 Photograph of a burned 304 SS elbow. The fire started in an upstream stainless steel wire filter (due to particle impact) and the burning filter material impacted the elbow and ignited it. Thin stainless steel components (e.g., filter) are much more flammable than thicker SS. Thin SS (<1/8") is usually avoided in oxygen systems.

Figure 4-68 - Photograph illustrating burn through of a brass pressure gage. Brass is generally suitable for oxygen service. However, the gauge was not intended for oxygen service and was not "oil free". Hydrocarbon contamination, probably from manufacture, caused the fire.
Figure 4-69 - Burnthrough of a PTFE-lined stainless steel hose in high pressure gaseous oxygen (GOX) service. Grease contamination ignited and penetrated the hose.
4.3 Uniform or Localized Loss of Thickness

4.3.1 Galvanic Corrosion

4.3.1.1 Description of Damage
A form of corrosion that can occur at the junction of dissimilar metals when they are joined together in a suitable electrolyte, such as a moist or aqueous environment, or soils containing moisture.

4.3.1.2 Affected Material
All metals with the exception of most noble metals.

4.3.1.3 Critical Factors
a) For galvanic corrosion, three conditions must be met:
   i) Presence of an electrolyte, a fluid that can conduct a current. Moisture or a separate water phase is usually required for the solution to have enough conductivity.
   ii) Two different materials or alloys known as the anode and the cathode, in contact with an electrolyte.
   iii) An electrical connection must exist between the anode and the cathode.
b) The more noble material (cathode) is protected by sacrificial corrosion of the more active material (anode). The anode corrodes at a higher rate than it would if it were not connected to the cathode.
c) A typical listing of the relative position of alloys in seawater is shown in Table 4-6.
d) The farther the alloys are apart in the table, the higher the driving force for corrosion.
e) The relative exposed surface areas between anodic material and the cathodic material has a significant affect.
   i) Corrosion rates of the anode can be high, if there is a small anode to cathode ratio.
   ii) Corrosion rates of the anode will be less affected if there is a large anode to cathode ratio.
   iii) If there is a galvanic couple, the more noble material may need to be coated. If the active material were coated, a large cathode to anode area can accelerate corrosion of the anode at any breaks in the coating.
   iv) The same alloy may act as both an anode and a cathode due to surface films, scale, and/or local environment (for example, old steel pipe connected to new steel pipe).

4.3.1.4 Affected Units or Equipment
a) Galvanic corrosion can occur in any unit where there is a conductive fluid and alloys are coupled. Heat exchangers are susceptible if the tube material is different from the tubesheet and/or baffles, particularly if salt water cooling is utilized.
b) Buried pipelines, electrical transmission support towers and ship hulls are typical locations for galvanic corrosion.

4.3.1.5 Appearance or Morphology of Damage
a) Damage occurs where two materials are joined at welded or bolted connections.
b) The more active material can suffer generalized loss in thickness or may have the appearance of a crevice, groove or pitting corrosion, depending on the driving force, conductivity and relative anodic/cathodic areas ratio.
c) Corrosion of the anode may be significantly higher immediately adjacent to the connection to the cathode, depending on solution conductivity (Figure 4-70 and Figure 4-71).
4.3.1.6  **Prevention / Mitigation**

a) The best method for prevention/mitigation is through good design.

b) Differing alloys should not be in intimate contact in conductive environments unless the anode/cathode surface area ratio is favorable.

c) Coatings can be helpful, but the more noble material should be coated.

d) For piping, specially designed electric insulating bolt sleeves and gaskets can eliminate the electrical connection.

e) Galvanic corrosion is the principle used in galvanized steel, where the Zn corrodes preferentially to protect the underlying carbon steel. (If there is a break in the galvanized coating, a large anode to small cathode area prevents accelerated corrosion of the steel). This anode-to-cathode relationship reverses at water temperatures over about 150°F (66°C).

4.3.1.7  **Inspection and Monitoring**

Visual inspection and UT thickness gauging are very effective methods for detecting galvanic corrosion. The damage may sometimes be hidden underneath a bolt or rivet head.

4.3.1.8  **Related Mechanisms**

Soil corrosion (see 4.3.9).

4.3.1.9  **References**

Table 4-6 – Galvanic Series in Seawater. (Ref. 1)

<table>
<thead>
<tr>
<th>Corroded End Anodic—More Active</th>
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<tbody>
<tr>
<td>Magnesium</td>
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<tr>
<td>Magnesium alloys</td>
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<tr>
<td>Zinc</td>
<td></td>
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<tr>
<td>Aluminum</td>
<td></td>
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<tr>
<td>Aluminum alloys</td>
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<tr>
<td>Steel</td>
<td></td>
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<tr>
<td>Cast iron</td>
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<tr>
<td>Type 410 SS (active state)</td>
<td></td>
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<tr>
<td>Ni-Resist</td>
<td></td>
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<tr>
<td>Type 304 SS (active state)</td>
<td></td>
</tr>
<tr>
<td>Type 316 SS (active state)</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td></td>
</tr>
<tr>
<td>Tin</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>Passivity: Nickel is more noble in seawater.</td>
</tr>
<tr>
<td>Brass</td>
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<tr>
<td>Copper</td>
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<td>Bronze</td>
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<td>Copper-Nickel</td>
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<td>Monel</td>
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<tr>
<td>Nickel (passive state)</td>
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<tr>
<td>Type 410 SS (passive state)</td>
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<tr>
<td>Type 304 SS (passive state)</td>
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<tr>
<td>Type 316 SS (passive state)</td>
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<tr>
<td>Titanium</td>
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<td>Gold</td>
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<tr>
<td>Platinum</td>
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<tr>
<td>Protected End—Cathode - More Noble</td>
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</tbody>
</table>
Figure 4-70 – Preferential galvanic corrosion of the more active component of the two materials.

Figure 4-71 – Galvanic corrosion of a carbon steel nipple in a SS vessel in warm water service.
4.3.2 Atmospheric Corrosion

4.3.2.1 Description of Damage
A form of corrosion that occurs from moisture associated with atmospheric conditions. Marine environments and moist polluted industrial environments with airborne contaminants are most severe. Dry rural environments cause very little corrosion.

4.3.2.2 Affected Materials
Carbon steel, low alloy steels and copper alloyed aluminum.

4.3.2.3 Critical Factors
a) Critical factors include the physical location (industrial, marine, rural); moisture (humidity), particularly designs that trap moisture or when present in a cooling tower mist; temperature; presence of salts, sulfur compounds and dirt.
b) Marine environments can be very corrosive (20 mpy) as are industrial environments that contain acids or sulfur compounds that can form acids (5-10 mpy).
c) Inland locations exposed to a moderate amount of precipitation or humidity are considered moderately corrosive environments (~1-3 mpy).
d) Dry rural environments usually have very low corrosion rates (<1 mpy).
e) Designs that trap water or moisture in crevices are more prone to attack.
f) Corrosion rates increase with temperature up to about 250°F (121°C). Above 250°F (121°C), surfaces are usually too dry for corrosion to occur except under insulation (see 4.3.3).
g) Chlorides, H₂S, fly ash and other airborne contaminates from cooling tower drift, furnace stacks and other equipment accelerate corrosion.
h) Bird turds can also cause accelerated corrosion and unsightly stains.

4.3.2.4 Affected Units or Equipment
a) Piping and equipment with operating temperatures sufficiently low to allow moisture to be present.
b) A paint or coating system in poor condition.
c) Equipment may be susceptible if cycled between ambient and higher or lower operating temperatures.
d) Equipment shut down or idled for prolonged periods unless properly mothballed.
e) Tanks and piping are particularly susceptible. Piping that rests on pipe supports is very prone to attack due to water entrapment between the pipe and the support.
f) Orientation to the prevailing wind and rain can also be a factor.
g) Piers and docks are very prone to attack.
h) Bimetallic connections such as copper to aluminum electrical connections

4.3.2.5 Appearance or Morphology of Damage
a) The attack will be general or localized, depending upon whether or not the moisture is trapped.
b) If there is no coating or if there is a coating failure, corrosion or loss in thickness can be general.
c) Localized coating failures will tend to promote corrosion.
d) Metal loss may not be visually evident, although normally a distinctive iron oxide (red rust) scale forms as shown in Figure 4-72.
4.3.2.6  **Prevention / Mitigation**
Surface preparation and proper coating application are critical for long-term protection in corrosive environments.

4.3.2.7  **Inspection and Monitoring**
VT and UT are techniques that can be used.

4.3.2.8  **Related Mechanisms**
Corrosion under insulation (see 4.3.3).

4.3.2.9  **References**
Figure 4-72 – Atmospheric Corrosion of an LPG line in close proximity to a cooling tower.
4.3.3 Corrosion Under Insulation (CUI)

4.3.3.1 Description of Damage
Corrosion of piping, pressure vessels and structural components resulting from water trapped under insulation or fireproofing.

4.3.3.2 Affected Materials
Carbon steel, low alloy steels, 300 Series SS, and duplex stainless steels.

4.3.3.3 Critical Factors
a) It affects externally-insulated vessels and those that are in intermittent service or operate between:
   i) 10°F (−12°C) and 350°F (175°C) for carbon and low alloy steels,
   ii) 140°F (60°C) and 400°F (205°C) for austenitic stainless steels and duplex stainless steels
b) Corrosion rates increase with increasing metal temperature up to the point where the water evaporates quickly. For insulated components, corrosion becomes more severe at metal temperatures between the boiling point 212°F (100°C) and 350°F (121°C), where water is less likely to vaporize and insulation stays wet longer.
c) Design of insulation system, insulation type, temperature and environment are critical factors.
d) Poor design and/or installations that allow water to become trapped will increase CUI.
e) Insulating materials that hold moisture (wick) can be more of a problem.
f) Cyclic thermal operation or intermittent service can increase corrosion.
g) Equipment that operates below the water dewpoint tends to condense water on the metal surface thus providing a wet environment and increasing the risk of corrosion.
h) Damage is aggravated by contaminants that may be leached out of the insulation, such as chlorides.
i) Plants located in areas with high annual rainfall or warmer, marine locations are more prone to CUI than plants located in cooler, drier, mid-continent locations.
j) Environments that provide airborne contaminants such as chlorides (marine environments, cooling tower drift) or SO₂ (stack emissions) can accelerate corrosion.

4.3.3.4 Affected Units or Equipment
a) All insulated piping and equipment are susceptible to CUI under conditions noted above even on piping and equipment where the insulation system appears to be in good condition and no visual signs of corrosion are present.
b) Examples of locations where CUI can occur are listed below:
   i) CUI can be found on equipment with damaged insulation, vapor barriers, weatherproofing or mastic, or protrusions through the insulation or at insulation termination points such as flanges.
   ii) Equipment designed with insulation support rings welded directly to the vessel wall (no standoff); particularly around ladder and platform clips, and lifting lugs, nozzles and stiffener rings.
   iii) Piping or equipment with damaged/leaking steam tracing.
   iv) Localized damage at paint and/or coating systems.
   v) Locations where moisture/water will naturally collect (gravity drainage) before evaporating (insulation support rings on vertical equipment) and improperly terminated fireproofing.
   vi) Vibrating piping systems that have a tendency to inflict damage to insulation jacketing providing a path for water ingress.
vii) Deadlegs (vents, drains, and other similar items).
viii) Pipe hangers and other supports.
ix) Valves and fittings (irregular insulation surfaces).
x) Bolted-on pipe shoes.
x) Steam tracer tubing penetrations.
xii) Termination of insulation at flanges and other piping components.
xiii) Insulation jacketing seams located on the top of horizontal piping or improperly lapped or sealed insulation jacketing.
xiv) Termination of insulation in a vertical pipe.
xv) Caulking that has hardened, has separated, or is missing.
xvi) Bulges or staining of the insulation or jacketing system or missing bands. (Bulges may indicate corrosion product buildup.)
xvii) Low points in piping systems that have a known breach in the insulation system, including low points in long unsupported piping runs.
xviii) Carbon or low-alloy steel flanges, bolting, and other components under insulation in high-alloy piping systems.
xix) Locations where insulation plugs have been removed to permit piping thickness measurements on insulated piping and equipment should receive particular attention. These plugs should be promptly replaced and sealed. Several types of removable plugs are commercially available that permit inspection and identification of inspection points for future reference.
xx) The first few feet of a horizontal pipe run adjacent to the bottom of a vertical run.

4.3.3.5 Appearance or Morphology of Damage
a) Carbon and low alloy steels are subject to localized pitting corrosion and or localized loss in thickness.
b) 300 Series SS are also subject to Stress Corrosion Cracking (SCC) if chlorides are present, while the duplex SS are less susceptible.
c) 300 Series SS and duplex SS are subject to pitting and localized corrosion. For 300 Series SS, specifically in older calcium silicate insulation (known to contain chlorides), localized pitting and chloride stress corrosion cracking can occur.
d) After insulation is removed from carbon and low alloy steels, CUI damage often appears as loose, flaky scale covering the corroded component. Damage may be highly localized (Figure 4-73 to 4-79).
e) In some localized cases, the corrosion can appear to be carbuncle type pitting (usually found under a failed paint/coating system).
f) Tell tale signs of insulation and paint/coating damage often accompany CUI.

4.3.3.6 Prevention / Mitigation
a) Since the majority of construction materials used in plants are susceptible to CUI degradation, mitigation is best achieved by using appropriate paints/coatings and maintaining the insulation/sealing/vapor barriers to prevent moisture ingress.
b) Flame-sprayed aluminum coatings have been used on carbon steels. The coating corrodes preferentially by galvanic action, thereby protecting the base metal.
c) High quality non-metallic coatings, properly applied to the surfaces to be insulated can provide long term protection.
d) Thin aluminum foil wrapped on stainless steel piping and equipment has been used on stainless steels as an effective barrier under insulation.
e) Careful selection of insulating materials is important. Closed-cell foam glass materials will hold less
water against the vessel/pipe wall than mineral wool and potentially be less corrosive.

f) Low chloride insulation should be used on 300 Series SS to minimize the potential for pitting and chloride SCC.

g) It is not usually possible to modify operating conditions. However, consideration should be given to removing the insulation on equipment where heat conservation is not as important.

4.3.3.7 Inspection and Monitoring

a) An inspection plan for corrosion under insulation should be a structured and systematic approach starting with prediction/analysis, then looking at the more invasive procedures. The inspection plan should consider operating temperature; type and age/condition of coating; and type and age/condition of insulation material. Additional prioritization can be added from a physical inspection of the equipment, looking for evidence of insulation, mastic and/or sealant damage, signs of water penetration and rust in gravity drain areas around the equipment.

b) Although external insulation may appear to be in good condition, CUI damage may still be occurring. CUI inspection may require removal of some or all insulation. If external coverings are in good condition and there is no reason to suspect damage behind them, it may not be necessary to remove them for inspection of the vessel.

c) Considerations for insulation removal are not limited to but include:
   i) History of CUI for the vessel or comparable equipment.
   ii) Visual condition of the external covering and insulation.
   iii) Evidence of fluid leakage, e.g. stains.
   iv) Equipment in intermittent service.
   v) Condition/age of the external coating, if applicable.

d) Common areas of concern in process units are high moisture areas such as those down-wind from cooling towers, near steam vents, deluge systems, acid vapors, or near supplemental cooling with water spray.

e) When developing the inspection plan for CUI inspection, the inspector should consider
   i) Areas that are most susceptible to CUI. If CUI damage is found, the inspector should inspect other susceptible areas on the vessel.
   ii) Utilize multiple inspection techniques to produce the most cost effective approach, including:
       • Partial and/or full stripping of insulation for visual examination.
       • UT for thickness verification.
       • Real-time profile x-ray (for small bore piping).
       • Neutron backscatter techniques for identifying wet insulation.
       • Deep penetrating eddy-current inspection (can be automated with a robotic crawler).
       • IR thermography looking for wet insulation and/or damaged and missing insulation under the jacket.
       • Guided wave UT.

4.3.3.8 Related Mechanisms

Atmospheric corrosion (see 4.3.2), oxidation (see 4.4.1) and chloride SCC (see 4.5.1).

4.3.3.9 References

1. API Publication 581, Risk-Based Inspection Technology, American Petroleum Institute, Washington, D.C.
2. NACE Standard RP0198, The Control of Corrosion Under Thermal Insulation, and Fireproofing – A
Systems Approach, NACE International, Houston, TX.


6. API 570, Piping Inspection Code, American Petroleum Institute, Washington, D.C.
Figure 4-73 – Tee in a 1000 psig ethylene line before insulation removal.

Figure 4-74 Close-up of Tee CUI of a Tee in Figure 4-73 after insulation removal.
Figure 4-75 - CUI of a 30 inch CS Butadiene line showing highly localized corrosion which could only be found by stripping the entire line. Note the 0.25 in (6.5 mm) diameter hole at arrow.
Figure 4-76 - CUI of nozzle on a bottom head.

Figure 4-77 - CUI of nozzle on a top head.
Figure 4-78 - CUI of vessel wall. Note leak at arrow.

Figure 4-79 - CUI at attachment supports and vessel head.
Figure 4-80 – CUI of CS level bridle.
4.3.4 Cooling Water Corrosion

4.3.4.1 Description of Damage
General or localized corrosion of carbon steels and other metals caused by dissolved salts, gases, organic compounds or microbiological activity.

4.3.4.2 Affected Materials
Carbon steel, all grades of stainless steel, copper, aluminum, titanium and nickel base alloys.

4.3.4.3 Critical Factors
a) Cooling water corrosion and fouling are closely related and should be considered together. Fluid temperature, type of water (fresh, brackish, salt water) and the type of cooling system (once-through, open circulating, closed circulating), oxygen content, and fluid velocities are critical factors.

b) Increasing cooling water outlet temperatures and or process side inlet temperatures tend to increase corrosion rates as well as fouling tendency.

c) Increasing oxygen content tends to increase carbon steel corrosion rates.

d) If the process side temperature is above 140°F (60°C), a scaling potential exists with fresh water and becomes more likely as process temperatures increase and as cooling water inlet temperatures rise. Brackish and salt water outlet temperatures above about 115°F (46°C) may cause serious scaling.

e) Fouling may occur from mineral deposits (hardness), silt, suspended organic materials, corrosion products, mill scale, marine and microbiological growth.

f) Velocities should be high enough to minimize fouling and drop out of deposits but not so high as to cause erosion. Velocity limits depend on the tube material and water quality.

g) Low velocities can promote increased corrosion. Velocities below about 3 fps (1 m/s) are likely to result in fouling, sedimentation and increased corrosion in fresh and brackish water systems. Accelerated corrosion can also result from dead spots or stagnant areas if cooling water is used on the shell side of condensers/coolers rather than the preferred tube side.

h) 300 Series SS can suffer pitting corrosion, crevice corrosion and SCC in fresh, brackish and salt water systems.

i) Copper/zinc alloys can suffer dezincification in fresh, brackish and salt water systems. The copper/zinc alloys can suffer SCC if any ammonia or ammonium compounds are present in the water or on the process side.

j) ERW carbon steel may suffer severe weld and/or heated affected zone corrosion in fresh and/or brackish water.

k) When connected to a more anodic material, titanium may suffer severe hydriding embrittlement. Generally, the problem occurs at temperatures above 180°F (82°C) but can occur at lower temperatures.

4.3.4.4 Affected Units or Equipment
Cooling water corrosion is a concern with water-cooled heat exchangers and cooling towers in all applications across all industries.

4.3.4.5 Appearance or Morphology of Damage
a) Cooling water corrosion can result in many different forms of damage including general corrosion, pitting corrosion (Figure 4-81), MIC, stress corrosion cracking and fouling.

b) General or uniform corrosion of carbon steel occurs when dissolved oxygen is present.

c) Localized corrosion may result from underdeposit corrosion, crevice corrosion or microbiological corrosion.
d) Deposits or crevices can lead to underdeposit or crevice corrosion of any of the affected materials.

e) Wavy or smooth corrosion at nozzle inlets/outlets and tube inlets may be due to flow induced corrosion, erosion or abrasion.

f) Corrosion at ERW weld areas will appear as grooving along the weld fusion lines.

g) Metallurgical analysis of tube samples may be required to confirm the mode of failure.

4.3.4.6  Prevention / Mitigation

a) Cooling water corrosion (and fouling) can be prevented by proper design, operation and chemical treatment of cooling water systems.

b) Design for process side inlet temperatures below 140°F (60°C).

c) Minimum and maximum water velocities must maintained, particularly in salt water systems.

d) The metallurgy of heat exchanger components may need to be upgraded for improved resistance, especially in waters with high chloride content, low velocity, high process temperatures, and/or poorly maintained water chemistry.

e) Periodic mechanical cleaning of tube ID’s and OD’s should be performed in order to maintain clean heat transfer surfaces.

f) With very few exceptions, cooling water should be on the tube side to minimize stagnant areas.

4.3.4.7  Inspection and Monitoring

a) Cooling water should be monitored for variables that affect corrosion and fouling including, pH, oxygen content, cycles of concentration, biocide residual, biological activity, cooling water outlet temperatures, hydrocarbon contamination and process leaks.

b) Periodic calculation of U-factors (heat exchanger performance measurement) will provide information on scaling and fouling.

c) Ultrasonic flow meters can be used to check the velocity of water in the tubes.

d) EC or IRIS inspection of tubes.

e) Splitting representative tubes.

4.3.4.8  Related Mechanisms

Microbiologically induced corrosion (see 4.3.8), chloride stress corrosion cracking (see 4.5.1) and galvanic corrosion (see 4.3.1).

4.3.4.9  References


Figure 4-81 – Cooling water corrosion on the I.D. of a CS heat exchanger tube operating at 86°F (30°C).
4.3.5 Boiler Water Condensate Corrosion

4.3.5.1 Description of Damage
General corrosion and pitting in the boiler system and condensate return piping.

4.3.5.2 Affected Materials
Primarily carbon steel, some low alloy steel, some 300 Series SS and copper based alloys.

4.3.5.3 Critical Factors
a) Corrosion in boiler feedwater and condensate return systems is usually the result of dissolved gases, oxygen and carbon dioxide, which lead to oxygen pitting corrosion and carbonic acid corrosion, respectively.
b) Critical factors are the concentration of dissolved gas (oxygen and or carbon dioxide), pH, temperature, quality of the feedwater, and the specific feedwater treating system.
c) Corrosion protection in the boiler is accomplished by laying down and continuously maintaining a layer of protective Fe₃O₄ (magnetite).
d) The chemical treatment for scale and deposit control must be adjusted to coordinate with the oxygen scavenger for the specific water service and boiler feedwater treating system.
e) Ammonia SCC of Cu-Zn alloys can occur due to hydrazine, neutralizing amines or ammonia-containing compounds.

4.3.5.4 Affected Units or Equipment
Corrosion can occur in the external treatment system, deaerating equipment, feedwater lines, pumps, stage heaters and economizers as well as the steam generation system on both the water and fire sides and the condensate return system.

4.3.5.5 Appearance or Morphology of Damage
a) Corrosion from oxygen tends to be a pitting type damage and can show up anywhere in the system even if only very small quantities break through the scavenging treatment. Oxygen is particularly aggressive in equipment such as closed heaters and economizers where there is a rapid water temperature rise (Fig. 4-82).
b) Corrosion in the condensate return system tends to be due to carbon dioxide although some oxygen pitting problems can occur if the oxygen scavenging treatment is not working correctly. Carbon dioxide corrosion tends to be a smooth grooving of the pipe wall (Fig. 4-83 and 4-84).

4.3.5.6 Prevention/Mitigation
a) Oxygen scavenging treatments typically include catalyzed sodium sulfite or hydrazine depending on the system pressure level along with proper mechanical deaerator operation. A residual of the oxygen scavenger is carried into the steam generation system to handle any oxygen ingress past the deaerator.
b) If the scale/deposit control/magnetite maintenance treatment scheme does not minimize carbon dioxide in the condensate return system, an amine inhibitor treatment might be required.

4.3.5.7 Inspection and Monitoring
a) Water analysis is the common monitoring tool used to assure that the various treatment systems are performing in a satisfactory manner. Parameters which can be monitored for signs of upset include the pH, conductivity, chlorine or residual biocide, and total dissolved solids to check for leaks in the form of organic compounds.
b) There are no proactive inspection methods other than developing an appropriate program when problems such as a ruptured boiler tube or condensate leaks are recognized in the various parts of complex boiler water and condensate systems.
c) Deaerator cracking problems can be evaluated off-line at shutdowns by utilizing properly applied wet fluorescence magnetic particle inspection.

4.3.5.8 Related Mechanisms

CO₂ corrosion (see 4.3.6), corrosion fatigue (see 4.5.2), and erosion/erosion-corrosion (see 4.2.14).

4.3.5.9 References

Figure 4-82 – Pits caused by oxygen corrosion.

Figure 4-83 – General metal loss (left end of tube) on steel resulting from oxygen corrosion. The color of hydrous ferric oxide is orange to red brown.
Figure 4-84 – Jagged fir-tree pattern of corrosion inside a tilted steel pipe caused by condensing steam containing high concentrations of carbon dioxide.
4.3.6 CO₂ Corrosion

4.3.6.1 Description of Damage
Carbon dioxide (CO₂) corrosion results when CO₂ dissolves in water to form carbonic acid (H₂CO₃). The acid may lower the pH and sufficient quantities may promote general corrosion and/or pitting corrosion of carbon steel.

4.3.6.2 Affected Materials
Carbon steel and low alloy steels.

4.3.6.3 Critical Factors
a) The partial pressure of CO₂, pH and temperature are critical factors.
b) Increasing partial pressures of CO₂ result in lower pH condensate and higher rates of corrosion.
c) Corrosion occurs in the liquid phase, often at locations where CO₂ condenses from the vapor phase.
d) Increasing temperatures increase corrosion rate up to the point where CO₂ is vaporized.
e) Increasing the level of chromium in steels offers no major improvement in resistance until a minimum of 12% is reached.

4.3.6.4 Affected Units or Equipment
a) Boiler feedwater and condensate systems in all units are affected.
b) Effluent gas streams of the shift converters in hydrogen plants can be affected. Corrosion usually occurs when the effluent stream drops below the dew point, approximately 300°F (149°C). Corrosion rates as high as 1000 mpy have been observed.
c) Overhead systems of regenerators in CO₂ removal plants are affected.

4.3.6.5 Appearance or Morphology of Damage
a) Localized thinning and/or pitting corrosion of carbon steel (Figure 4-85, Figure 4-86 and Figure 4-87).
b) Carbon steel may suffer deep pitting and grooving in areas of turbulence (Figure 4-88).
c) Corrosion generally occurs in areas of turbulence and impingement and sometimes at the root of piping welds.

4.3.6.6 Prevention / Mitigation
a) Corrosion inhibitors can reduce corrosion in steam condensate systems. Vapor phase inhibitors may be required to protect against condensing vapors.
b) Increasing condensate pH above 6 can reduce corrosion in steam condensate systems.
c) The 300 Series SS are highly resistant to corrosion in most applications. Selective upgrading to stainless steels is usually required in operating units designed to produce and/or remove CO₂ (such as hydrogen plants and CO₂ removal units).
d) Steam condensate systems that experience CO₂ corrosion are usually the result of operating problems.
e) 400 Series SS and duplex SS are also resistant.

4.3.6.7 Inspection and Monitoring
a) VT, UT and RT inspection techniques should focus on general and local loss in thickness where water wetting is anticipated.
b) Preferential corrosion of weld seams may require angle probe UT or RT.
c) Corrosion may occur along the bottom surface of the pipe if there is a separate water phase, at the top
surface of the pipe if condensation in wet gas systems is anticipated, and in the turbulent flow areas at elbow and tees.

d) Monitor water analyses (pH, Fe, etc.) to determine changes in operating conditions.

4.3.6.8 Related Mechanisms

Boiler water condensate corrosion (see 4.3.5) and carbonate cracking (see 5.1.2.5).

4.3.6.9 References

Figure 4-85 – \( \text{CO}_2 \) corrosion of a carbon steel oil and gas production flow line.

Figure 4-86 – Higher magnification view of the corrosion pits in Figure 4-41.
Figure 4-87 – CO₂ corrosion of CS pipe nipple in CO₂ contaminated water.

Figure 4-88 – A view inside the nipple in Figure 4-87 showing “Mesa” type corrosion typical of CO₂ corrosion.
4.3.7 Flue-Gas Dew-Point Corrosion

4.3.7.1 Description of Damage

a) Sulfur and chlorine species in fuel will form sulfur dioxide, sulfur trioxide and hydrogen chloride within the combustion products.

b) At low enough temperatures, these gases and the water vapor in the flue gas will condense to form sulfurous acid, sulfuric acid and hydrochloric acid which can lead to severe corrosion.

4.3.7.2 Affected Materials

Carbon steel, low alloy steels and 300 Series SS.

4.3.7.3 Critical Factors

a) The concentration of contaminants (sulfur and chlorides) in the fuel and the operating temperature of flue gas metal surfaces determine the likelihood and severity of corrosion.

b) Since all fuels contain some amount of sulfur, sulfuric and sulfurous acid dewpoint corrosion can occur if the metal temperatures are below the dewpoint.

c) The dewpoint of sulfuric acid depends on the concentration of sulfur trioxide in the flue gas, but is typically about 280°F (138°C).

d) Similarly, the dewpoint of hydrochloric acid depends on the concentration of hydrogen chloride. It is typically about 130°F (54°C).

4.3.7.4 Affected Units or Equipment

a) All fired process heaters and boilers that burn fuels containing sulfur have the potential for sulfuric acid dewpoint corrosion in the economizer sections and in the stacks.

b) Heat-Recovery Steam Generators (HRSG’s) that have 300 Series SS feedwater heaters may suffer chloride-induced stress corrosion cracking from the gas side (OD) when the temperature of the inlet water is below the dewpoint of hydrochloric acid.

c) 300 Series SS feedwater heaters in HRSG’s are potentially at risk if the atmosphere of the combustion turbine includes chlorine. Cooling tower drift from cooling towers that use chlorine-based biocides may blow into the combustion turbine and lead to potential damage in the feedwater heaters.

4.3.7.5 Appearance or Morphology of Damage

a) Sulfuric acid corrosion on economizers or other carbon steel or low alloy steel components will have general wastage often with broad, shallow pits, depending on the way the sulfuric acid condenses.

b) For the 300 Series SS feedwater heaters in HRSG’s, stress corrosion cracking will have surface breaking cracks and the general appearance will be somewhat crazed.

4.3.7.6 Prevention / Mitigation

a) Maintain the metallic surfaces at the back end of the boilers and fired heaters above the temperature of sulfuric acid dewpoint corrosion.

b) For HRSG’s, avoid the use of 300 Series SS in the feedwater heaters if the environment is likely to contain chlorides.

c) Similar damage occurs in oil-fired boilers when the units are water-washed to remove ash if the final rinse does not neutralize the acid salts. Sodium carbonate should be added to the final rinse as a basic solution to neutralize the acidic ash constituents.

4.3.7.7 Inspection and Monitoring

a) Wall-thickness measurements by UT methods will monitor the wastage in economizer tubes.

b) Stress corrosion cracking of 300 Series SS can be found using VT and PT inspection.
4.3.7.8 Related Mechanisms

At lower temperatures, hydrochloric acid may condense and promote HCL corrosion of carbon steels (see 5.1.1.4) and chloride stress corrosion cracking of 300 Series SS (see 4.5.1).

4.3.7.9 References

4.3.8  Microbiologically Induced Corrosion (MIC)

4.3.8.1  Description of Damage
A form of corrosion caused by living organisms such as bacteria, algae or fungi. It is often associated with the presence of tubercles or slimy organic substances.

4.3.8.2  Affected Materials
Most common materials of construction including carbon and low alloy steels, 300 Series SS and 400 Series SS, aluminum, copper and some nickel base alloys.

4.3.8.3  Critical Factors
a) MIC is usually found in aqueous environments or services where water is always or sometimes present, especially where stagnant or low-flow conditions allow and/or promote the growth of microorganisms.

b) Because there are several types, organisms can survive and grow under severe conditions including lack of oxygen, light or dark, high salinity, pH range of 0 to 12, and temperatures from 0°F to 235°F (–17°C to 113°C).

c) Systems may become “inoculated” by the introduction of organisms that multiply and spread unless controlled.

d) Different organisms thrive on different nutrients including inorganic substances (e.g., sulfur, ammonia, H₂S) and inorganic substances (e.g., hydrocarbons, organic acids). In addition, all organisms require a source of carbon, nitrogen and phosphorous for growth.

e) In-leakage of process contaminants such as hydrocarbons or H₂S may lead to a massive increase in biofouling and corrosion.

4.3.8.4  Affected Units or Equipment
a) MIC is most often found in heat exchangers, bottom water of storage tanks, piping with stagnant or low flow, and piping in contact with some soils.

b) MIC is also found in equipment where the hydrotest water has not been removed or equipment has been left outside and unprotected.

c) Product storage tanks and water cooled heat exchangers in any unit where cooling water is not properly treated can be affected.

d) Fire water systems can be affected.

4.3.8.5  Appearance or Morphology of Damage
a) MIC corrosion is usually observed as localized pitting under deposits or tubercles that shield the organisms.

b) Damage is often characterized by cup-shaped pits within pits in carbon steel or subsurface cavities in stainless steel (Figure 4-89 through Figure 4-95).

4.3.8.6  Prevention / Mitigation
a) Microbes require water to thrive. Systems that contain water (cooling water, storage tanks, etc.) should be treated with biocides such as chlorine, bromine, ozone, ultraviolet light or proprietary compounds.

b) Proper application of biocides will control but not eliminate microbes so that continued treatment is necessary.

c) Maintain flow velocities above minimum levels. Minimize low flow or stagnant zones.

d) Systems that are not designed or intended for water containment should be kept clean and dry.

e) Empty hydrotest water as soon as possible. Blow dry and prevent moisture intrusion.
f) Wrapping and cathodically protecting underground structures have been effective in preventing MIC.

g) Effective mitigation of established organisms requires complete removal of deposits and organisms using a combination of pigging, blasting, chemical cleaning and biocide treatment.

h) Add biocides to water phase in storage tanks.

i) Maintain coatings on the interior of storage tanks.

4.3.8.7  Inspection and Monitoring

a) In cooling water systems, effectiveness of treatment is monitored by measuring biocide residual, microbe counts and visual appearance.

b) Special probes have been designed to monitor for evidence of fouling which may precede or coincide with MIC damage.

c) An increase in the loss of duty of a heat exchanger may be indicative of fouling and potential MIC damage.

d) Foul smelling water may be a sign of trouble.

4.3.8.8  Related Mechanisms

Cooling water corrosion (see 4.3.4).

4.3.8.9  References


Figure 4-89 – MIC of diesel tank bottom.

Figure 4-90 – Pitting corrosion on the I.D. of a 6-inch CS sour crude line after 2.5 years of service. Pits are approximately 1-inch to 2-inch wide. Note the halo effect in Figure 4-91.
Figure 4-91 – Same pipe as Figure 4-90. Note the halo effect.

Figure 4-92 – Oil line with MIC damage beneath tubercles.
Figure 4-93 – Same oil line as Figure 4-92. Hemispherical pitting typical of MIC can be seen after grit blasting to remove the scale.

Figure 4-94 – Type 304 stainless steel exchanger tubes failed from pitting corrosion on the shell side in cooling water service after 2.5 years without biocide treatment.
Figure 4-95 – A cross section of the tube (Figure 4-94) revealing severe subsurface tunneling, typical of MIC.
4.3.9  Soil Corrosion

4.3.9.1  Description of Damage
The deterioration of metals exposed to soils is referred to as soil corrosion.

4.3.9.2  Affected Materials
Carbon steel, cast iron and ductile iron.

4.3.9.3  Critical Factors
a) The severity of soil corrosion is determined by many factors including operating temperature, moisture and oxygen availability, soil resistivity (soil condition and characteristics), soil type (water drainage), and homogeneity (variation in soil type), cathodic protection, stray current drainage, coating type, age, and condition.
b) There is no single parameter that can be used to determine soil corrosivity. Instead, a number of characteristics must be combined to estimate the corrosion in particular soil as outlined in ASTM STP 741 as well as API RP 580 and Publ 581.
c) Soil resistivity is frequently used to estimate soil corrosivity, mainly because it is easy to measure. Soil resistivity is related to soil moisture content and dissolved electrolytes in the soil water.
d) Soils having high moisture content, high dissolved salt concentrations, and high acidity are usually the most corrosive.
e) Soil-to-air interface areas are often much more susceptible to corrosion than the rest of the structure because of moisture and oxygen availability (Figure 4-96).
f) Corrosion rates increase with increasing metal temperature.
g) Other factors that affect soil corrosion include galvanic corrosion, dissimilar soils, stray currents, differential aeration corrosion cells, and microbiologically induced corrosion.

4.3.9.4  Affected Units or Equipment
a) Underground piping and equipment as well as buried tanks and the bottoms of above ground storage tanks (Figure 4-97).
b) Ground supported metal structures (Figure 4-98).

4.3.9.5  Appearance or Morphology of Damage
a) Soil corrosion appears as external thinning with localized losses due to pitting. The severity of corrosion depends on the local soil conditions and changes in the immediate environment along the equipment metal surface.
b) Poor condition of a protective coating is a tell tale sign of potential corrosion damage.

4.3.9.6  Prevention / Mitigation
Soil corrosion of carbon steel can be minimized through the use of special backfill, coatings and cathodic protection. The most effective protection is a combination of a corrosion resistant coating and a cathodic protection system.

4.3.9.7  Inspection and Monitoring
a) The most common method used for monitoring underground structures is measuring the structure to soil potential using dedicated reference electrodes near the structure (corrected for IR drop error). Cathodic protection should be performed and monitored in accordance with NACE RP 0169.
b) There are many techniques for inspecting buried or on-grade metallic components. Piping may be inspected by inline inspection devices, guided ultrasonic thickness tools, indirectly by pressure testing, or visually by evaluation. The same or similar techniques may be used on other structures.
4.3.9.8 Related Mechanisms

Galvanic corrosion (see 4.3.1).

4.3.9.9 References

11. NACE RP 0169, Standard Recommended Practice: Control of External Corrosion on Underground or Submerged Metallic Piping Systems, NACE International, Houston, TX.
Figure 4-96 – Corrosion of carbon steel pipe at the soil-air interface where the pipe emerges from underground.

Figure 4-97 – Coupons removed from the bottom of an unprotected steel condensate storage tank after 3 years of service. The external surface is shown.
Figure 4-98 – Cross section through location (A) showing severe corrosion. The arrows point to a location that was at the original thickness.
4.3.10 Caustic Corrosion

4.3.10.1 Description of Damage
Localized corrosion due to the concentration of caustic or alkaline salts that usually occurs under evaporative or high heat transfer conditions. However, general corrosion can also occur depending on alkali or caustic solution strength.

4.3.10.2 Affected Materials
Primarily carbon steel, low alloy steels and 300 Series SS.

4.3.10.3 Critical Factors
Major contributing factors are the presence of caustic (NaOH or KOH). The following are sources of caustic:

a) Caustic is sometimes added to process streams for neutralization or as a reactant.
b) It is sometimes intentionally added to boiler feedwater at low concentrations or may enter inadvertently during regeneration of demineralizers.
c) Alkaline salts may also enter process streams through leaks in condensers or process equipment.
d) Some process units utilize caustic solutions for neutralizing, for removal of sulfur compounds, or for removal of chloride compounds.
e) A concentrating mechanism must exist to build up the caustic strength.
f) Caustic may become concentrated by departure from DNB, evaporation and deposition.

4.3.10.4 Affected Units or Equipment

a) Caustic corrosion is most often associated with boilers and steam generating equipment including heat exchangers.
b) Similar concentrating effects of caustic may occur where caustic is added to crude unit charge.
c) Accelerated localized corrosion can occur in preheat exchangers, furnace tubes and transfer lines, unless the caustic is effectively mixed in the oil stream.
d) Units that use caustic for removing sulfur compounds from product streams.

4.3.10.5 Appearance or Morphology of Damage

a) Typically characterized by localized metal loss which may appear as grooves in a boiler tube or locally thinned areas under insulating deposits (Figure 4-99 and Figure 4-100).
b) Deposits may fill corroded depressions and mask damage below. Probing suspect areas with a sharp instrument may be required.
c) Localized gouging may result along a waterline where corrosives concentrate. In vertical tubes, this may appear as a circumferential groove.
d) In horizontal or sloped tubes, grooving may appear at the top of the tube or as longitudinal grooves on opposite sides of the tube.
e) Exposure to high solution strength caustic can result in general corrosion of carbon steel above 175°F (79°C) and very high corrosion rates above 200°F (93°C).

4.3.10.6 Prevention / Mitigation

a) In steam generating equipment, caustic corrosion is best prevented through proper design. Damage can be minimized by reducing the amount of free caustic, by ensuring adequate water flooding and water flow, by ensuring proper burner management to minimize hot spots on heater tubes, and by minimizing the ingress of alkaline producing salts into condensers.
b) In process equipment, caustic injection facilities should be designed to allow proper mixing and dilution
of caustic in order to avoid the concentration of caustic on hot metal surfaces.

c) Carbon steel and 300 Series SS have serious corrosion problems in high strength caustic solutions above about 150°F (66°C). Alloy 400 and some other nickel base alloys exhibit much lower corrosion rates.

4.3.10.7 **Inspection and Monitoring**

a) For process equipment, UT thickness gauging is useful to detect and monitor general corrosion due to caustic. However, localized losses due to caustic corrosion may be difficult to locate.

b) Injection points should be inspected in accordance with API 570.

c) UT scans and radiography can be used.

d) Steam generation equipment may require visual inspection with the use a boroscope.

4.3.10.8 **Related Mechanisms**

Caustic corrosion is also referred to as caustic gouging or ductile gouging. A related mechanism is known as Departure from Nucleate Boiling (DNB) as discussed in steam blanketing (See 4.2.11).

4.3.10.9 **References**


Figure 4-99 – I.D. deposits on CS boiler tube with damage due to caustic corrosion.

Figure 4-100 – Cross-section of tube in Figure 4-99 showing localized attack due to caustic corrosion.
4.3.11 Dealloying

4.3.11.1 Description of Damage

a) Dealloying is a selective corrosion mechanism in which one or more constituents of an alloy are preferentially attacked leaving a lower density (dealloyed) often porous structure.
b) Component failure may occur suddenly and unexpectedly because mechanical properties of the dealloyed material are significantly degraded.

4.3.11.2 Affected Materials

Primarily copper alloys (brass, bronze, tin) as well as Alloy 400 and cast iron.

4.3.11.3 Critical Factors

a) Factors which influence dealloying include the composition of the alloy and exposure conditions including temperature, degree of aeration, pH and exposure time.
b) Dealloying occurs with several different alloys but is usually limited to very specific alloy-environment combinations.
c) Exact conditions under which dealloying occurs are often hard to define and damage may occur progressively over many years in service.
d) Common examples of where dealloying has been found to occur are listed in Table 4-7.

4.3.11.4 Affected Units or Equipment

a) Underground cast iron piping when exposed to certain soils.
b) In cooling water applications, heat exchanger tubing (brass, Al brass) is susceptible to dealloying in some brackish and seawater applications but often the tubesheets suffer significant damage. Problems may also occur in some fresh or domestic water systems.
c) Boiler feedwater piping systems and afterboiler components may suffer dealloying including bronze pumps, Monel strainers and brass pressure gage fittings.

4.3.11.5 Appearance or Morphology of Damage

a) There is often a significant color change or a deep etched (corroded) appearance as one element is removed from the alloy. However, depending on the alloy, the outward appearance of the affected material may not be noticeable upon visual inspection, even where the full wall thickness is degraded.
b) Attack may be uniform through the cross-section (layer-type) or it can be localized (plug-type) (Figure 4-101 and Figure 4-102).
c) In some cases, the original material is completely dealloyed yet the component exhibits virtually no dimensional or other visible changes.

4.3.11.6 Prevention / Mitigation

a) It is often difficult to predict whether conditions will be conducive to dealloying in a particular environment or service, so that one must be cognizant of the susceptibility of certain alloys, and the possible resulting consequences.
b) Resistance to dealloying can sometimes be improved by the addition of certain alloying elements so that a similar alloy with a different composition may be resistant. For example, tin tends to inhibit dealloying of copper alloys; admiralty brass is inhibited by the addition of a very small amount of phosphorous, antimony or arsenic; and dealuminification of aluminum-bronze can be prevented by heat treatment to produce an $\alpha$ and $\beta$ microstructure.
c) Continued degradation of a dealloyed component can only be prevented by altering the exposure conditions or replacing it with a resistant material.
d) Depending on the alloy-environment combination, cathodic protection or barrier coatings may be effective.

4.3.11.7 Inspection and Monitoring

a) Many alloys change color in the affected area, however, scale removal may be required to determine the depth of attack.
b) Dealloying in brasses is visually evident by a reddish, copper color instead of the yellow brass color.
c) Graphitic corrosion turns cast iron charcoal gray and the material can be cut or gouged with a knife.
d) Metallographic examination may be required to confirm the extent of damage.
e) A significant reduction in hardness may accompany dealloying, although affected areas may be localized.
f) Acoustic techniques (loss of “metallic ring”) and ultrasonic attenuation are applicable, but UT thickness measurements are not.
g) Fitness-For-Service (FFS) analysis of dealloyed components should consider that the dealloyed portion may be brittle and contribute little or no mechanical strength or load bearing capability.

4.3.11.8 Related Mechanisms

a) Dealloying is often referred to by the element removed, as in dezincification, destannification, denickelification, dealuminification and graphitic corrosion. Dealloying has also been referred to as selective leaching.
b) Graphitic corrosion affects cast irons and is further described in 4.3.12.

4.3.11.9 References

Table 4-7 – Combinations of Alloys and Environment Subject to Dealloying. (Ref. 1)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Environment</th>
<th>Element Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brasses (&gt;15% Zn) *</td>
<td>Many waters, especially stagnant conds.</td>
<td>Zinc (dezincification)</td>
</tr>
<tr>
<td>Gray Cast Iron</td>
<td>Soils, many waters</td>
<td>Iron (graphitic corrosion)</td>
</tr>
<tr>
<td>Aluminum bronze</td>
<td>HF acid, acids w/chloride ions, seawater</td>
<td>Aluminum (dealuminification)</td>
</tr>
<tr>
<td>(primarily w/&gt; 8% Al)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicon bronzes</td>
<td>High-temp steam and acidic species</td>
<td>Silicon (desiliconification)</td>
</tr>
<tr>
<td>Tin bronzes</td>
<td>Hot brine or steam</td>
<td>Tin (destannification)</td>
</tr>
<tr>
<td>Copper nickels (70-30)</td>
<td>High heat flux and low water velocity</td>
<td>Nickel (denickelification)</td>
</tr>
<tr>
<td>Monel</td>
<td>Hydrofluoric and other acids</td>
<td>Nickel (denickelification)</td>
</tr>
</tbody>
</table>

* The extent of dezincification increases with increasing zinc content.
Figure 4-101 – Cross section of a silicon-brass alloy C87500 pump impeller from stagnant fire-water service. Layer-type dezincification depleted the zinc and left this porous red color of the copper. Mag. 50X

Figure 4-102 – A zone of denickelification in a Monel valve plug (at the port), due to oxygen contamination in hot hydrofluoric acid.
4.3.12  Graphitic Corrosion

4.3.12.1  Description of Damage

a) Cast irons are comprised of graphite particles embedded in an iron matrix. Graphitic corrosion is a form of dealloying in which the iron matrix is corroded, leaving corrosion products and porous graphite.

b) Attack results in a porous structure with a loss of strength, ductility and density. It usually occurs under low pH and stagnant conditions, especially in contact with soils or waters high in sulfates.

4.3.12.2  Affected Materials

Primarily gray cast iron, but also nodular and malleable cast irons experience graphitic corrosion. However, nodular and malleable cast irons tend to crumble when attacked. White iron is not subject to this damage because there is no free graphite.

4.3.12.3  Critical Factors

a) Graphitic corrosion occurs with several different cast iron alloys but is usually limited to very specific microstructure-environment combinations. Factors that influence graphitic corrosion include the composition of the alloy and exposure conditions including temperature, degree of aeration, pH and exposure time.

b) Damage occurs in the presence of moisture or an aqueous phase, usually below 200°F (93°C).

c) Damage may take many months or years to progress but can increase in severity if the pH drops. Much of the damage occurs during stagnant conditions when high concentrations of sulfates are present.

d) Graphite is cathodic to the iron matrix. The iron matrix preferentially corrodes and cathodically protects the graphite in certain conductive waters or soils.

e) Graphitic corrosion may affect adjacent components by causing galvanic corrosion.

4.3.12.4  Affected Units or Equipment

Graphitic corrosion can occur in soft water, salt water, mine waters, dilute acids and in underground piping as well as in boiler feedwater equipment. Typical examples include feedwater piping, pumps (including pump impellers), valves, and underground cast iron pipe. Fire water systems are particularly vulnerable.

4.3.12.5  Appearance or Morphology of Damage

a) Damage may be widespread or it may also occur in localized areas in which the majority of the component is unaffected.

b) The damage may not be noticeable upon visual inspection even where the full wall thickness is degraded.

c) Damaged areas will be soft and easily gouged with a knife or hand tool.

d) Metallographic examination may be required to confirm the extent of damage (Figure 4-103 through Figure 4-110).

4.3.12.6  Inspection and Monitoring

a) UT is not a good method for detecting damage.

b) Acoustic techniques (loss of “metallic ring”) and ultrasonic attenuation are applicable.

c) A significant reduction in hardness may accompany dealloying, although affected areas may be localized.

4.3.12.7  Prevention / Mitigation

a) It is often difficult to predict if exposure conditions will cause this form of dealloying in a particular environment or service. One must be aware of the potential susceptibility of cast irons.
b) Internal graphitic corrosion can be prevented by coatings and/or cement linings.

c) External graphitic corrosion can be prevented by external coatings or cathodic protection in severely corrosive soils.

4.3.12.8 Related Mechanisms

Also known as selective leaching, graphitic corrosion is a form of dealloying (see 4.3.11) of cast irons. It should not be confused with graphitization, the decomposition of carbides at high temperatures (see 4.2.1).

4.3.12.9 References


Figure 4-103 – Graphitic Corrosion of cast iron impeller due to glycol acidification.

Figure 4-104 - Cut away of cast iron impeller shown above. The dark phase around the outside perimeter (at arrows) is graphite which surround the unaffected metal in the middle.
Figure 4-105 – View of the outside of an underground concrete-lined salt water service line that failed from graphitic corrosion.

Figure 4-106 – View of concrete lining inside the failed line shown in Figure 105.
Figure 4-107 – Cross section of a gray cast iron drainpipe showing charcoal colored thru-wall graphitic corrosion encroaching from both sides. Note the through wall crack at the bottom.

Figure 4-108 – Cross section of a gray cast iron pipe with graphitic corrosion coming from O.D. (Point B).
Figure 4-109 – Higher magnification view of unaffected area “A” shown in Figure 4-108.

Figure 4-110 – Higher magnification view of the damage from shown in 4-108 (area “B”).
4.4 High Temperature Corrosion [>400°F (204°C)]

4.4.1 Oxidation

4.4.1.1 Description of Damage
a) Oxygen reacts with carbon steel and other alloys at high temperature converting the metal to oxide scale.
b) It is most often present as oxygen is in the surrounding air (approximately 20%) used for combustion in fired heaters and boilers.

4.4.1.2 Affected Materials
a) All iron based materials including carbon steel and low alloy steels, both cast and wrought.
b) All 300 Series SS, 400 Series SS and nickel base alloys also oxidize to varying degrees, depending on composition and temperature.

4.4.1.3 Critical Factors
a) The primary factors affecting high temperature oxidation are metal temperature and alloy composition.
b) Oxidation of carbon steel begins to become significant above about 1000°F (538°C). Rates of metal loss increase with increasing temperature.
c) In general, the resistance of carbon steel and other alloys is determined by the chromium content of the material. Increasing chromium levels produce a more protective oxide scale. The 300 Series SS are resistant to scaling up to about 1500°F (816°C). See Table 4-8.
d) The presence of water vapor can significantly accelerate oxidation rates of some steels including 9Cr-1Mo (Ref 4.)

4.4.1.4 Affected Units or Equipment
Oxidation occurs in fired heaters and boilers as well as other combustion equipment, piping and equipment that operates in high temperature environments when metal temperatures exceed about 1000°F (538°C).

4.4.1.5 Appearance or Morphology of Damage
a) Most alloys, including carbon steels and low alloy steels, suffer general thinning due to oxidation. Usually, the component will be covered on the outside surface with an oxide scale, depending on the temperature and exposure time (Figure 4-111 to 4-113).
b) 300 Series SS and nickel alloys generally have a very thin dark scale unless exposed to extremely high temperatures where metal loss rates are excessive.

4.4.1.6 Prevention / Mitigation
a) Resistance to oxidation is best achieved by upgrading to a more resistant alloy.
b) Chromium is the primary alloying element that affects resistance to oxidation. Other alloying elements, including silicon and aluminum, are effective but their concentrations are limited due to adverse affects on mechanical properties. They are often used in special alloys for applications such as heater supports, burner tips and components for combustion equipment.

4.4.1.7 Inspection and Monitoring
a) Process conditions should be monitored for establishing trends of high temperature equipment where oxidation can occur.
b) Temperatures can be monitored through the use of tubeskin thermocouples and/or infrared thermography.
c) Loss in thickness due to oxidation is usually measured using external ultrasonic thickness measurements.
4.4.1.8 Related Mechanisms

Oxidation damage referred to in this section is due to surface scaling. Some damage mechanisms result in internal oxidation which is outside the scope of this document.

4.4.1.9 References

### Table 4-8 Estimated Corrosion Rates (mpy) for Oxidation (Ref. 1)

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<tr>
<th>Material</th>
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<td></td>
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</tr>
<tr>
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<td>2</td>
</tr>
<tr>
<td>1 1/4 Cr</td>
<td>2</td>
</tr>
<tr>
<td>2 1/4 Cr</td>
<td>1</td>
</tr>
<tr>
<td>5 Cr</td>
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<td>1</td>
</tr>
<tr>
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<td>310 SS / HK</td>
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<tr>
<td>800 H / HP</td>
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<tr>
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<td>800 H / HP</td>
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<td>3</td>
</tr>
</tbody>
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Figure 4-111 – Oxidation of a carbon steel nut on a stainless steel stud at 1300°F (704°C).

Figure 4-112 – Oxidation of a carbon steel grid from a sulfur reactor.
Figure 4-113 – Oxidation of the O.D. of a carbon steel furnace transfer line.
4.4.2 Sulfidation

4.4.2.1 Description of Damage
Corrosion of carbon steel and other alloys resulting from their reaction with sulfur compounds in high temperature environments. The presence of hydrogen accelerates corrosion. This mechanism is also known as sulfidic corrosion.

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

4.4.2.3 Critical Factors
a) Major factors affecting sulfidation are alloy composition, temperature and concentration of corrosive sulfur compounds.
b) Susceptibility of an alloy to sulfidation is determined by its ability to form protective sulfide scales.
c) Sulfidation of iron-based alloys usually begins at metal temperatures above 500°F (260°C). The typical effects of increasing temperature, chromium content and sulfur content on metal loss are shown in Figure 4-114 and Figure 115.
d) Note: These graphs are provided for reference only for general estimating of corrosion behavior and trends, and should not be used to make an exact determination of corrosion rates. The references at the end of this section should be consulted for additional background on the development of these curves.
e) In general, the resistance of iron and nickel base alloys is determined by the chromium content of the material. Increasing the chromium content significantly increases resistance to sulfidation. 300 Series SS, such as Types 304, 316, 321 and 347, are highly resistant in most refining process environments. Nickel base alloys are similar to stainless steels in that similar levels of chromium provide similar resistance to sulfidation.
f) Crude oils, coal and other hydrocarbon streams contain sulfur at various concentrations. Total sulfur content is made up of many different sulfur-containing compounds.
g) Sulfidation is primarily caused by H₂S and other reactive sulfur species as a result of the thermal decomposition of sulfur compounds at high temperatures. Some sulfur compounds react more readily to form H₂S. Therefore, it can be misleading to predict corrosion rates based on weight percent sulfur alone.
h) A sulfide scale on the surface of the component offers varying degrees of protection depending on the alloy and the severity of the process stream.

4.4.2.4 Affected Units or Equipment
a) Sulfidation occurs in piping and equipment in high temperature environments where sulfur-containing streams are processed.
b) Common areas of concern are the crude, FCC, coker, vacuum, visbreaker and hydroprocessing units.
c) Heaters fired with oil, gas, coke and most other sources of fuel may be affected depending on sulfur levels in the fuel.
d) Boilers and high temperature equipment exposed to sulfur-containing gases can be affected.

4.4.2.5 Appearance or Morphology of Damage
a) Depending on service conditions, corrosion is most often in the form of uniform thinning but can also
occur as localized corrosion or high velocity erosion-corrosion damage (Figure 4-116 to 4-120).

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

4.4.2.6  Prevention / Mitigation

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

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

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

4.4.2.7  Inspection and Monitoring

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

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

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

d) Proactive and retroactive PMI programs are used for alloy verification and to check for alloy mix-ups in services where sulfidation is anticipated (Ref. 7).

4.4.2.8  Related Mechanisms

Sulfidation is also known as sulfidic corrosion. High temperature sulfidation in the presence of hydrogen is covered in 5.1.1.5.

4.4.2.9  References


6. API RP 939-C Guidelines for Avoiding Sulfidation Corrosion Failures in Oil Refineries, American Petroleum Institute, Washington, D.C.,

Figure 4-114 – Modified McConomy curves showing typical effect of temperature on high temperature sulfidation of steels and stainless steels. (Ref. 3)
Figure 4-115 – Multiplier for corrosion rates in Figure 4-112 based on differing sulfur content of process fluid. (Ref. 3)

Figure 4-116 – Sulfidation failure of NPS 8 carbon steel pipe. Note the relatively uniform thinning that resulted in a sizeable rupture.
Figure 4-117 – Sulfidation failure illustrating the effect of accelerated corrosion due to low silicon content. This 8 inch NPS pipe section in FCC bottoms piping was in service at 150 psig (1Mpa) at 650° to 700°F (340° to 370°C). The piping sketch in Figure 118 illustrates the difference in corrosion rate as compared to adjacent high-silicon components.

Figure 4-118 - Thickness survey of 8 inch pipe shown in Figure 4-117 above.
Figure 4-119 – Sulfidation failure of carbon steel sight glass nipple on the right after 2 years in crude unit. Original thickness is shown on left for comparison. Material was supposed to be 9Cr-1Mo.

Figure 4-120 – Sulfidation failure of piping elbow.
4.4.3 Carburization

4.4.3.1 Description of Damage
Carbon is absorbed into a material at elevated temperature while in contact with a carbonaceous material or carburizing environment.

4.4.3.2 Affected Materials
Carbon steel and low alloy steels, 300 Series SS and 400 Series SS, cast stainless steels, nickel base alloys with significant iron content (e.g., Alloys 600 and 800) and HK/HP alloys.

4.4.3.3 Critical Factors
a) Three conditions must be satisfied:
   i) Exposure to a carburizing environment or carbonaceous material.
   ii) Temperature high enough to allow diffusion of carbon into the metal [typically above 1100°F (593°C)].
   iii) Susceptible material.

b) Conditions favoring carburization include a high gas phase carbon activity (hydrocarbons, coke, gases rich in CO, CO₂, methane, ethane) and low oxygen potential (minimal O₂ or steam).

c) Initially, carbon diffuses into the component at a high rate and then tapers off as the depth of carburization increases.

d) In carbon steels and low alloy steels, carbon reacts to form a hard, brittle structure at the surface that may crack or spall upon cooling.

e) 300 Series SS are more resistant than carbon steel and the low alloy steels due to higher chromium and nickel content.

f) Carburization can result in the loss of high temperature creep ductility, loss of ambient temperature mechanical properties (specifically toughness/ductility), loss of weldability, and corrosion resistance.

4.4.3.4 Affected Units or Equipment
a) Fired heater tubes are the most common type of equipment susceptible to carburization in the environments mentioned earlier.

b) Coke deposits are a source of carbon that may promote carburization, particularly during decoke cycles where temperatures exceed the normal operating temperatures, accelerating the carburization.

c) Carburization is sometimes found in heater tubes in catalytic reformers and coker units or other heaters where steam/air decoking is performed.

d) Carburization is also encountered in ethylene pyrolysis and steam reformer furnaces. Significant carburization occurs during decoking cycles.

4.4.3.5 Appearance or Morphology of Damage
a) The depth of carburization can be confirmed by metallography. Figure 4-121 to 4-122.

b) Carburization can be confirmed by substantial increases in hardness and loss in ductility.

c) In a more advanced stage, there may be a volumetric increase in the affected component.

d) A change (increase) in the level of ferromagnetism can occur in some alloys.

e) Carburization results in the formation of metal carbides depleting the surrounding matrix of the carbide-forming element.
4.4.3.6 **Prevention / Mitigation**

a) Select alloys with adequate resistance to carburization including alloys with a strong surface oxide or sulfide film formers (silicon and aluminum).

b) Reduce the carbon activity of the environment through lower temperatures and higher oxygen/sulfur partial pressures. Sulfur inhibits carburization and is often added in the process stream in small amounts in steam/gas cracking in olefin and thermal hydrodealkylation units.

4.4.3.7 **Inspection and Monitoring**

a) Inspection for carburization in the initial stages of attack is difficult. If the process side surfaces are accessible, hardness testing and field metallography can be used. Destructive sampling and magnetic based techniques (Eddy Current) have also been used.

b) Inspection techniques based on determining increased levels of ferromagnetism (magnetic permeability) are also useful for alloys that are paramagnetic when initially installed (austenitic alloys). However, surface oxides may interfere with the results.

c) In the advanced stages of carburization where cracking has initiated, RT, UT and some magnetic techniques may be used.

4.4.3.8 **Related Mechanisms**

A severe form of carburization known as metal dusting is discussed in 4.4.5.

4.4.3.9 **References**

Figure 4-121 – Carburization (dark areas) of an HP-modified tube from an ethylene furnace after 3 years at 1900°F (1038°C).

Figure 4-122 – A photomicrograph of a cross-section of a 304H cyclone from a fluid coker showing surface carburization after 24 years. Mag. 35X.
4.4.4 Decarburization

4.4.4.1 Description of Damage
A condition where steel loses strength due to the removal of carbon and carbides leaving only an iron matrix. Decarburization occurs during exposure to high temperatures, during heat treatment, from exposure to fires, or from high temperature service in a gaseous environment.

4.4.4.2 Affected Materials
Carbon steels and low alloy steels.

4.4.4.3 Critical Factors
a) Time, temperature and carbon activity of the process stream are the critical factors.
b) The material must be exposed to a gas phase that has a low carbon activity so that carbon in the steel will diffuse to the surface to react with gas phase constituents.
c) The extent and depth of decarburization is a function of the temperature and exposure time.
d) Typically, shallow decarburization can slightly decrease the strength of the material, but has no detrimental effect on the overall performance of the component. However, it is indicative that the steel may have been overheated and suggests other effects may be present (e.g. decarburization associated with HTHA in hydrogen services).
e) Potential loss in room temperature tensile strength and creep strength may occur.

4.4.4.4 Affected Units or Equipment
a) Decarburization can occur in almost any equipment that is exposed to elevated temperatures, heat treated or exposed to a fire.
b) Piping and equipment in hot hydrogen service in hydroprocessing units or catalytic reforming units as well as fired heater tubes can be affected. Pressure vessel components that are hot formed during fabrication can be affected.

4.4.4.5 Appearance or Morphology of Damage
a) Damage can be verified by metallography.
b) Damage occurs on the surface exposed to the gas environment but in extreme cases may be through wall.
c) The decarburized layer will be free of carbide phases. Carbon steel will be pure iron (Figure 4-123 to 4-124).

4.4.4.6 Prevention / Mitigation
a) Decarburization can be controlled by controlling the chemistry of the gas phase and alloy selection (API RP 941).
b) Alloy steels with chromium and molybdenum form more stable carbides and are more resistant to decarburization.
c) Steels operating in high temperature hydrogen environments should be selected in accordance with API RP 941.

4.4.4.7 Inspection and Monitoring
a) Field Metallography and Replication (FMR) can confirm decarburization.
b) Decarburization results in a softening that can be confirmed by hardness testing.
4.4.4.8  Related Mechanisms
High Temperature Hydrogen Attack (HTHA) (see 5.1.3.1).

4.4.4.9  References
2. API Recommended Practice 941, Steels for Hydrogen Service at Elevated Temperatures in Petroleum Refineries and Petrochemical Plants, American Petroleum Institute, Washington, D.C.
Figure 4-123 – Typical low carbon steel microstructure showing ferrite phase (light grains) and pearlite carbide (dark layered phases).

Figure 4-124 – Microstructure illustrating a decarburized low carbon steel where the strength-providing pearlitic phases have been decomposed as a result of the removal of carbon atoms by diffusion to the surface.
4.4.5 Metal Dusting

4.4.5.1 Description of Damage
Metal dusting is form of carburization resulting in accelerated localized pitting which occurs in carburizing gases and/or process streams containing carbon and hydrogen. Pits usually form on the surface and may contain soot or graphite dust.

4.4.5.2 Affected Materials
Low alloy steels, 300 Series SS, nickel base alloys and heat resisting alloys. There is currently no known metal alloy that is immune to metal dusting under all conditions.

4.4.5.3 Critical Factors
a) Process stream composition, operating temperature and alloy composition are critical factors.

b) Metal dusting is preceded by carburization and is characterized by rapid metal wastage.

c) Metal dusting involves a complex series of reactions involving a reducing gas such as hydrogen, methane, propane or CO.

d) It usually occurs in the operating temperature range of 900°F to 1500°F (482°C to 816°C). Damage increases with increasing temperature.

e) The mechanism of metal dusting is considered to be:
   i) Saturation of the metal matrix by carburization;
   ii) Precipitation of metal carbides at the metal surface and grain boundaries;
   iii) Deposition of graphite from the atmosphere onto the metal carbides at the surface;
   iv) Decomposition of the metal carbides under the graphite and metal particles; and
   v) Further deposition of graphite catalyzed by the metal particles on the surface.

f) In high nickel alloys, it is thought that metal dusting occurs without the formation of metal carbides.

g) Metal dusting can also occur under alternating reducing and oxidizing conditions.

4.4.5.4 Affected Units or Equipment
a) Primarily fired heater tubes, thermowells and furnace components operating in carburizing environments are affected.

b) Metal dusting has been reported in catalytic reforming unit heater tubes, coker heaters, gas turbines, methanol reforming unit outlet piping and thermal hydrodealkylation furnaces and reactors.

4.4.5.5 Appearance or Morphology of Damage
a) In low alloy steels, the wastage can be uniform but usually is in the form of small pits filled with a crumbly residue of metal oxides and carbides.

b) The corrosion product is a voluminous carbon dust containing metal particles and sometimes metal oxides and carbides. Frequently, this dust will be swept away by the flowing process stream, leaving behind only the thinned or pitted metal.

c) In stainless and high alloy steels, the attack is frequently local, appearing as deep, round pits (Figure 4-125).

d) Metallography will show that the metal is heavily carburized under the attacked surface (Figure 4-126).

4.4.5.6 Prevention / Mitigation
a) Sulfur in the carburizing atmosphere (usually as H₂S), forms a protective sulfide that minimizes carburization and metal dusting. It is thought that sulfur retards the carbon transfer from the atmosphere
to the metal and suppresses graphite nucleation and growth. For protection, sufficient H₂S must always be in the process environment. If the H₂S level drops too low, even for a short period of time, damage may occur. Sulfur is a catalyst poison in some processing units so that the introduction of H₂S into a process stream may not always be practical.

b) There is currently no known metal alloy that is immune to metal dusting under all conditions. Materials selection must be made based on the specific application and environment.

c) An aluminum diffusion treatment to the base metal substrate can be beneficial in some applications.

4.4.5.7 Inspection and Monitoring

a) For heater tubes with suspected damage, compression wave ultrasonic testing is probably the most efficient method of inspection since large areas can be inspected relatively quickly.

b) RT techniques can be employed to look for pitting and wall thinning.

c) If internal surfaces are accessible, visual inspection is effective.

d) Filtering the cooled furnace or reactor effluent may yield metal particles that are a tell tale indication of a metal dusting problem upstream.

4.4.5.8 Related Mechanisms

Metal dusting is also known as catastrophic carburization. Carburization is discussed in 4.4.3.

4.4.5.9 References

Figure 4-125 – Metal dusting of a 304H stainless steel pipe.

Figure 4-126 - Carbon steel separator plate in a natural gas preheater showing classical pattern of carburization and pitting
4.4.6 Fuel Ash Corrosion

4.4.6.1 Description of Damage

a) Fuel ash corrosion is accelerated high temperature wastage of materials that occurs when contaminants in the fuel form deposits and melt on the metal surfaces of fired heaters, boilers and gas turbines.

b) Corrosion typically occurs with fuel oil or coal that is contaminated with a combination of sulfur, sodium, potassium and/or vanadium.

c) The resulting molten salts (slags) dissolve the surface oxide and enhance the transport of oxygen to the surface to re-form the iron oxide at the expense of the tube wall or component.

4.4.6.2 Affected Materials

a) All conventional alloys used for process heater and boiler construction are susceptible.

b) Alloys of the 50Cr-50Ni family show improved resistance.

4.4.6.3 Critical Factors

a) The concentration of molten salt forming contaminants, metal temperature and alloy composition are the critical factors.

b) The severity of damage depends on the type of fuel (i.e., the concentrations of contaminants in the fuel), sulfur content and metal temperature.

c) Corrosion occurs by this mechanism only if the metal temperature is above the temperature of the liquid species formed, and it is most severe where the temperatures are the highest.

d) The corrosion rates differ depending on the alloy and location within the heater.

4.4.6.4 Affected Units or Equipment

a) Fuel ash corrosion can occur in any fired heater or gas turbine utilizing fuels with the aforementioned contaminants.

b) Fuel ash corrosion is most often associated with fired heaters burning vanadium and sodium contaminated fuel oils or residue.

c) Heater tubes are sometimes not affected because their skin temperatures are cooler than the threshold melting point of the slags in most heaters. Tube hangers and supports, however, operate hotter and can suffer severe fuel ash corrosion.

d) Some gas turbines suffer blade corrosion when switched over to burning fuel oil.
e) In some cases, coking of the heater tubes may cause operators to increase heat flux that may push some components above the threshold temperature where fuel ash corrosion is possible.

f) Since the melting points of these liquid species are around 1000°F (538°C) and higher in the superheaters and reheaters, any unit that has metal temperatures above the melting point of the sulfates may have the problem.

g) For oil-fired boilers, fuel oils that do not contain vanadium are less prone to liquid ash corrosion.

h) For waterwalls, if the temperature can be maintained below the melting point of the pyrosulfates [that is below 700°F (371°C)], damage will be minimized. Thus, steam generating pressures below about 1800 psi are nearly immune.

4.4.6.5 Appearance or Morphology of Damage

a) Oil ash corrosion is manifested as severe metal loss associated with slagging. In some cases, corrosion rates of 100 to 1000 mpy may be experienced.

b) Metallographic examination and deposit-analysis techniques can be used to verify the presence of fuel ash corrosion.

c) For oil ash corrosion of superheaters and reheaters, the appearance of the ash deposit will be in at least two distinct layers. The important deposit is adjacent to the component, which will have a dark gray or black appearance at room temperature. As the liquid sulfates sinter the corrosion debris to the surface, a hard, glassy, tenacious scale is formed. When removed, the surface of the steel will have an "alligator-hide" appearance (Figure 4-127 and Figure 4-128) as shallow grooves will have penetrated the steel in a cross-hatched pattern.

d) For waterwalls, the cracks are predominantly circumferential and, to a lesser extent, axial. The overall appearance on the waterwalls is one of circumferential grooving.

i) After the liquid ash layer develops, the "slush" can only hold a certain weight of ash. When the weight is excessive, the slag is shed, exposing a bare, uninsulated tube to the heat flux of the firebox. The temperatures will spike on waterwalls, by perhaps 100°F (38°C) and the cracking is then similar to thermal fatigue.

ii) The mechanism for the steam-cooled tubes is similar, except that the temperature spike is probably less and, therefore, the thermal fatigue damage is less severe.

iii) The alligator-hide morphology of superheaters and reheaters and the circumferential cracking on waterwalls in coal-fired boilers is caused by a similar mechanism.

e) For coal ash, the appearance will be a smooth interface between a glassy slag layer and the metal.

4.4.6.6 Prevention / Mitigation

a) Fuel ash corrosion can be prevented by blending or changing fuel sources (minimizing the contaminants) and by operating equipment so that hot components are below the temperature where molten deposits are formed.

b) Proper burner design and burner management can help to reduce flame impingement and localized hot spots.

c) In some cases, the characteristics and melting points of the slags can be changed by firing with low excess oxygen or by injecting special additives into the fuel. These changes can increase the melting point of the slags and reduce the tendency of the deposits to stick to metal surfaces or dissolve the protective oxide scale. Even with changes to reduce slag formation, corrosion may continue if metal surfaces are not cleaned to remove slag and corrosion products.

d) Corrosion of some components, such as tube hangers and supports, can be minimized by changing to a 50%Cr-50%Ni alloy, such as Alloy 657. Designs of tube hangers may need to be modified to account for the lower stress-rupture strength of the 50Cr-50Ni alloys.

4.4.6.7 Inspection and Monitoring

a) Visual inspection is usually sufficient to detect hot ash corrosion.
b) Metal loss is likely to be severe and the presence of a slag will be apparent.

c) Tubes need to be grit blasted in order to remove the tenacious glass-like ash deposit. UT examination may be useful to measure loss of thickness.

4.4.6.8 Related Mechanisms

a) Hot corrosion, hot ash corrosion, molten salt corrosion, oil ash corrosion and coal ash corrosion are all terms used to describe this mechanism.

b) Circumferential cracking in waterwall tubes is similar to thermal fatigue aggravated by a corrosive environment (Figure 4-129).

4.4.6.9 References

Figure 4-127 – The “alligator hide” morphology of liquid coal-ash corrosion is evident when the dense, glassy deposit is removed. Mag. 2.4X

Figure 4-128 – In cross-section, the surface grooving is, in actuality, broad, V-shaped corrosion-fatigue cracks. Mag. 100X, etched.
Figure 4-129 – On waterwall tubes, even with a corrosion-resistant weld-overly, circumferential cracking will develop. Mag. 37½X, etched.
4.4.7 Nitriding

4.4.7.1 Description of Damage
A hard, brittle surface layer will develop on some alloys due to exposure to high temperature process streams containing high levels of nitrogen compounds such as ammonia or cyanides, particularly under reducing conditions.

4.4.7.2 Affected Materials
a) Carbon steels, low alloy steels, 300 Series SS and 400 Series SS.
b) Nickel base alloys are more resistant.

4.4.7.3 Critical Factors
a) Nitriding is a diffusion controlled process dependent on temperature, time, partial pressure of nitrogen and metal composition.
b) Temperatures must be high enough to allow for the thermal breakdown/disassociation of nitrogen from ammonia or other compounds and for diffusion of nitrogen into the metal.
c) Nitriding begins above 600°F (316°C) and becomes severe above 900°F (482°C).
d) High gas phase nitrogen activity (high partial pressures of nitrogen) promotes nitriding.
e) Corrosion resistance may be adversely affected by nitriding.
f) Alloys containing 30% to 80% nickel are more resistant.
g) A loss of high temperature creep strength, ambient temperature mechanical properties (specifically toughness/ductility), weldability and corrosion resistance may result.

4.4.7.4 Affected Units or Equipment
Nitriding can occur at any location where appropriate environment and temperature conditions are met, but it is considered to be fairly rare. Nitriding has been observed in steam methane-reformers, steam gas cracking (olefin plants) and ammonia synthesis plants.

4.4.7.5 Appearance or Morphology of Damage
a) Nitriding is usually confined to the surface of most components and will have a dull, dark gray appearance. However, during initial stages of nitriding, damage can only be seen with metallography as shown in Figure 4-130, Figure 4-131 and Figure 4-132.
b) In a more advanced stage, the material will exhibit very high surface hardness. In most cases, a slightly harder surface layer of a vessel or component will not affect the mechanical integrity of the equipment. However, the concern is for the potential development of cracks in the nitrided layer that could propagate into the base metal.
c) Nitriding of low alloy steels containing up to 12% chromium is accompanied by an increase in volume. The nitrided layer tends to crack and flake.
d) Above 770°F (410°C), preferential grain boundary nitriding may lead to microcracking and embrittlement.
e) Stainless steels tend to form thin, brittle layers that may crack and spall from thermal cycling or applied stress.
f) Nitrogen diffuses into the surface and forms needle-like particles of iron nitrides (Fe₃N or Fe₄N) that can only be confirmed by metallography.

4.4.7.6 Prevention / Mitigation
Changing to more resistant alloys with 30% to 80% nickel is usually required. It is usually not practical to modify the process conditions to reduce the nitrogen partial pressure or to lower temperatures.
4.4.7.7 Inspection and Monitoring

a) A change in surface color to a dull gray may indicate nitriding.

b) Materials exposed to nitriding conditions should be inspected thoroughly because good appearance may mask damage.

c) Hardness testing of the affected surfaces (400 to 500 BHN or higher) can help indicate nitriding.

d) Nitrided layers are magnetic. Therefore, 300 Series SS should be checked for magnetism as an initial screening.

e) Metallography is generally required to confirm nitriding.

f) EC testing may be used in some cases to detect nitriding.

g) In the advanced stages of nitriding, where cracking may have initiated, appropriate inspection techniques include PT, RT and UT.

4.4.7.8 Related Mechanisms

Similar gas-metal surface reactions occur in other environments including carburization (see 4.4.3) and metal dusting (see 4.4.5).

4.4.7.9 References


Figure 4-130 – A nitrided 5Cr-0.5Mo thermowell from an ammonia synthesis plant with surface cracking.

Figure 4-131 – A photomicrograph of a cross-section through the tube showing the interface between the shallow nitrided layer on the surface (gray) and the unaffected base metal (white). Cracks initiate from the O.D. surface at the top. Mag. 50X.
Figure 4-132 – A higher magnification photomicrograph showing the diamond-shaped hardness indentations in the hard nitrided layer (540 BHN) versus the softer base metal (210 BHN). Mag. 150X.
4.5 Environment – Assisted Cracking

4.5.1 Chloride Stress Corrosion Cracking (Cl-SCC)

4.5.1.1 Description of Damage

Surface initiated cracks caused by environmental cracking of 300 Series SS and some nickel base alloys under the combined action of tensile stress, temperature and an aqueous chloride environment. The presence of dissolved oxygen increases propensity for cracking.

4.5.1.2 Affected Materials

a) All 300 Series SS are highly susceptible.
b) Duplex stainless steels are more resistant.
c) Nickel base alloys are highly resistant, but not immune.

4.5.1.3 Critical Factors

a) Chloride content, pH, temperature, stress, presence of oxygen and alloy composition are critical factors.
b) Increasing temperatures increase the susceptibility to cracking.
c) Increasing levels of chloride increase the likelihood of cracking.
d) No practical lower limit for chlorides exists because there is always a potential for chlorides to concentrate.
e) Heat transfer conditions significantly increase cracking susceptibility because they allow chlorides to concentrate. Alternate exposures to wet-dry conditions or steam and water are also conducive to cracking.
f) SCC usually occurs at pH values above 2. At lower pH values, uniform corrosion generally predominates. SCC tendency decreases toward the alkaline pH region.
g) Cracking usually occurs at metal temperatures above about 140°F (60°C), although exceptions can be found at lower temperatures.
h) Stress may be applied or residual. Highly stressed or cold worked components, such as expansion bellows, are highly susceptible to cracking.
i) Oxygen dissolved in the water normally accelerates SCC but it is not clear whether there is an oxygen concentration threshold below which chloride SCC is impossible.
j) Nickel content of the alloy has a major affect on resistance. The greatest susceptibility is at a nickel content of 8% to 12%. Alloys with nickel contents above 35% are highly resistant and alloys above 45% are nearly immune.
k) Low-nickel stainless steels, such as the duplex (ferrite-austenite) stainless steels, have improved resistance over the 300 Series SS but are not immune.
l) Carbon steels, low alloy steels and 400 Series SS are not susceptible to Cl-SCC.

4.5.1.4 Affected Units or Equipment

a) All 300 Series SS piping and pressure vessel components in any process units are susceptible to Cl-SCC.
b) Cracking has occurred in water-cooled condensers and in the process side of crude tower overhead condensers.
c) Drains in hydroprocessing units are susceptible to cracking during startup/shutdown if not properly purged.
d) Bellows and instrument tubing, particularly those associated with hydrogen recycle streams
contaminated with chlorides, can be affected.
e) External Cl–SCC has also been a problem on insulated surfaces when insulation gets wet.
f) Cracking has occurred in boiler drain lines.

4.5.1.5 Appearance or Morphology of Damage

a) Surface breaking cracks can occur from the process side or externally under insulation (Figures 4-133 to 4-134).
b) The material usually shows no visible signs of corrosion.
c) Characteristic stress corrosion cracks have many branches and may be visually detectable by a craze-cracked appearance of the surface (Figure 4-135 to Figure 4-136).
d) Metallography of cracked samples typically shows branched transgranular cracks (Figure 4-137 to 4-139).
e) Sometimes intergranular cracking of sensitized 300 Series SS may also be seen.
f) Welds in 300 Series SS usually contain some ferrite, producing a duplex structure that is usually more resistant to Cl–SCC.
g) Corrosion-resistant nickel-based alloys are also susceptible to cracking under severe conditions (Figure 4-140).
h) Fracture surfaces often have a brittle appearance.

4.5.1.6 Prevention / Mitigation

a) Use resistant materials of construction.
b) When hydrotesting, use low chloride content water and dry out thoroughly and quickly.
c) Properly applied coatings under insulation.
d) Avoid designs that allow stagnant regions where chlorides can concentrate or deposit.
e) A high temperature stress relief of 300 Series SS after fabrication may reduce residual stresses. However, consideration should be given to the possible effects of sensitization that may occur, increasing susceptibility to polythionic SCC, possible distortion problems and potential reheat cracking.

4.5.1.7 Inspection and Monitoring

a) Cracking is surface connected and may be detected visually in some cases.
b) PT or phase analysis EC techniques are the preferred methods.
c) Eddy current inspection methods have also been used on condenser tubes as well as piping and pressure vessels.
d) Extremely fine cracks may be difficult to find with PT. Special surface preparation methods, including polishing or high-pressure water blast, may be required in some cases, especially in high pressure services.
e) UT.
f) Often, RT is not sufficiently sensitive to detect cracks except in advanced stages where a significant network of cracks has developed.

4.5.1.8 Related Mechanisms

Caustic SCC (see 4.5.3) and polythionic acid SCC (see 5.1.2.1).

4.5.1.9 References

Figure 4-133 – External cracking of Type 304SS instrument tubing under insulation.

Figure 4-134 – External cracking of Type 304SS instrument tubing under insulation.
Figure 4-135 – Cracking on the shell side of Type 316L SS tubes in steam service at 450°F (232°C), showing tubes after PT inspection. The cracks can be seen in the center tube (arrow).
Figure 4-136 – Close-up of the tube in Figure 4-135 showing tight cracks with a spider web appearance.
Figure 4-137 - Photomicrograph of a cross-section of sample in Figure 4-136 showing fine branching cracks. (Unetched, Mag. 50X)

Figure 4-138 – Another photomicrograph of a cross-section of a cracked tube illustrating the
transgranular mode of cracking initiating on the surface. (Etched)

Figure 4-139 - Chloride SCC on the thread surface of a failed 303SS bolt.
Figure 4-140 – Severe cracking of a finned Alloy C-276 tube in a Deethanizer reboiler after 8 years service due to ammonium chloride carryover. (a.) Hundreds of cracks initiated on the OD (process side) of the tube associated with the cold worked portion of the tube at the fins (b.). Branching transgranular cracks (c.)
4.5.2 Corrosion Fatigue

4.5.2.1 Description of Damage
A form of fatigue cracking in which cracks develop under the combined effects of cyclic loading and corrosion. Cracking often initiates at a stress concentration such as a pit in the surface. Cracking can initiate at multiple sites.

4.5.2.2 Affected Materials
All metals and alloys.

4.5.2.3 Critical Factors
a) The critical factors are the material, corrosive environment, cyclic stresses and stress raisers.
b) Cracking is more likely to occur in environments that promote pitting or localized corrosion under cyclic stress due to thermal stress, vibration or differential expansion.
c) Contrary to a pure mechanical fatigue, there is no fatigue limit load in corrosion-assisted fatigue. Corrosion promotes failure at a lower stress and number of cycles than the materials’ normal endurance limit in the absence of corrosion and often results in propagation of multiple parallel cracks.
d) Crack initiation sites include concentrators such as pits, notches, surface defects, changes in section or fillet welds.

4.5.2.4 Affected Units or Equipment
Rotating equipment, deaerators and cycling boilers, as well as any equipment subjected to cyclic stresses in a corrosive environment. Some examples include:

a) Rotating Equipment
Galvanic couples between the impeller and the pump shaft or other corrosion mechanisms may result in a pitting problem on the shaft. The pitting can act as a stress concentrator or stress riser to promote cracking. Most cracking is transgranular with little branching.

b) Deaerators
In the late 1980’s, deaerators in the pulp and paper, refining and petrochemical and fossil fueled utility industries had major deaerator cracking problems. Complete vessel failures in the pulp and paper industry resulted in a diligent inspection program that found major cracking problems across the various industries. It was concluded that residual welding and fabrication stresses, stress risers (attachments and weld reinforcement) and the normal deaerator environment could produce multiple corrosion fatigue cracking problems.

c) Cycling Boilers
A cycling boiler may see several hundred cold starts over its useful life which, because of differential expansion, continually cracks the protective magnetite scale, allowing corrosion to continue.
4.5.2.5 **Appearance or Morphology of Damage**

a) The fatigue fracture is brittle and the cracks are most often transgranular, as in stress-corrosion cracking, but not branched, and often results in propagation of multiple parallel cracks.

b) Fatigue cracking will be evidenced by very little plastic deformation except that final fracture may occur by mechanical overload accompanied by plastic deformation.

c) In cycling boilers, the damage usually appears first on the water side of buckstay (structural) attachments (Figure 4-141). The cracking pattern may be circular cracks surrounding the weld between the buckstay attachment and the waterwall tube. In cross-section, the cracks tend to be bulbous with numerous lobes (Figure 4-142). The crack tips themselves may be somewhat blunted but are oxide filled and transgranular (Figure 4-143 to 4-135).

d) In sulfidizing environments, cracks will have a similar appearance but will be filled with a sulfide scale.

e) In rotating equipment, most cracking is transgranular with minimal branching.

4.5.2.6 **Prevention / Mitigation**

a) Rotating Equipment
   i) Modify the corrosive environment by using coatings and/or inhibitors.
   ii) Minimize galvanic couple effects.
   iii) Use more corrosion resistant materials.

b) Deaerators
   i) Proper feedwater and condensate chemical control.
   ii) Minimize residual welding and fabrication stresses through PWHT.
   iii) Minimize weld reinforcement by grinding weld contours smooth.

c) Cycling Boilers
   i) Start up slowly to minimize the differential expansion strains.
   ii) Always start up with the chemistry of the boiler water under proper control.

4.5.2.7 **Inspection and Monitoring**

a) Rotating Equipment
   i) UT and MT techniques can be used for crack detection.

b) Deaerators
   i) Cracking is generally detected with WFMT inspection.
   ii) Many of the cracks are very tight and difficult to detect.

c) Cycling Boilers
   i) The first sign of damage is usually a pinhole leak on the cold side of a waterwall tube at a buckstay attachment.
   ii) Inspect highly stressed regions in the boiler by UT or EMATS techniques.
   iii) Cracking may occur at the membranes in the highly stressed regions, particularly corners at buckstays.

4.5.2.8 **Related Mechanisms**

Mechanical fatigue (see 4.2.16) and vibration induced fatigue (see 4.2.17).
4.5.2.9 References

Figure 4-141 - Corrosion fatigue failure of a boiler tube.

Figure 4-142 - Metallographic mount of sample taken from failed boiler tube in Figure 4-141.
Figure 4-143 – Higher magnification view of sample shown in Figure 142.

Figure 4-144 – Photograph of a carbon steel boiler tube cut in half lengthwise. Corrosion fatigue cracks initiate at the I.D. of a tube, opposite a buckstay attachment on the O.D. (Mag. 1X)
Figure 4-145 – Photomicrograph showing the crack morphology that is rounded with multiple lobes, and may branch to form “rabbit ears.” (Mag. 25X, etched.)
4.5.3 Caustic Stress Corrosion Cracking (Caustic Embrittlement)

4.5.3.1 Description of Damage
Caustic embrittlement is a form of stress corrosion cracking characterized by surface-initiated cracks that occur in piping and equipment exposed to caustic, primarily adjacent to non-PWHT’d welds.

4.5.3.2 Affected Materials
Carbon steel, low alloy steels and 300 Series SS are susceptible. Nickel base alloys are more resistant.

4.5.3.3 Critical Factors
a) Susceptibility to caustic embrittlement in caustic soda (NaOH) and caustic potash (KOH) solutions is a function of caustic strength, metal temperature and stress levels.
b) Increasing caustic concentration and increasing temperatures increase the likelihood and severity of cracking. Conditions likely to result in cracking have been established through plant experience and are presented in Figure 4-146.
c) Cracking can occur at low caustic levels if a concentrating mechanism is present. In such cases, caustic concentrations of 50 to 100 ppm are sufficient to cause cracking.
d) Stresses that promote cracking can be residual that result from welding or from cold working (such as bending and forming) as well as applied stresses (Figure 4-147 and Figure 4-148).
e) It is generally accepted that stresses approaching yield are required for SCC so that thermal stress relief (PWHT) is effective in preventing caustic SCC (Figure 4-142). Although failures have occurred at stresses that are low relative to yield, they are considered more rare (Figure 4-149 to Figure 4-150).
f) Crack propagation rates increase dramatically with temperature and can sometimes grow through wall in a matter of hours or days during temperature excursions, especially if conditions promote caustic concentration. Concentration can occur as a result of alternating wet and dry conditions, localized hot spots or high temperature steamout.
g) Special care must be taken with steam tracing design and steamout of non-PWHT’d carbon steel piping and equipment (Figure 4-151 to Figure 4-152).

4.5.3.4 Affected Units or Equipment
a) Caustic embrittlement is often found in piping and equipment that handles caustic, including H₂S and mercaptan removal units, as well as equipment that uses caustic for neutralization in sulfuric acid alkylation units and HF alkylation units. Caustic is sometimes injected into the feed to the crude tower for chloride control.
b) Failures have occurred in improperly heat-traced piping or equipment as well as heating coils and other heat transfer equipment.
c) Caustic embrittlement may occur in equipment as a result of steam cleaning after being in caustic service.
d) Traces of caustic can become concentrated in BFW and can result in caustic embrittlement of boiler tubes that alternate between wet and dry conditions due to overfiring.

4.5.3.5 Appearance or Morphology of Damage
a) Caustic stress corrosion cracking typically propagates parallel to the weld in adjacent base metal but can also occur in the weld deposit or heat-affected zones.
b) 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.
c) Cracks can be confirmed through metallographic examination as surface breaking flaws that are predominantly intergranular. The cracking typically occurs in as-welded carbon steel fabrications as a network of very fine, oxide-filled cracks.
d) Cracking in 300 Series SS is typically transgranular and is very difficult to distinguish from chloride stress corrosion cracking (Figure 4-153).

4.5.3.6  **Prevention / Mitigation**

a) Cracking can be effectively prevented by means of a stress-relieving heat treatment (e.g. PWHT). A heat treatment at 1150°F (621°C) is considered an effective stress relieving heat treatment for carbon steel. The same requirement applies to repair welds and to internal and external attachment welds.

b) 300 Series SS offer little advantage in resistance to cracking over CS.

c) Nickel base alloys are more resistant to cracking and may be required at higher temperatures and/or caustic concentrations.

d) Steamout of non-PWHT’d carbon steel piping and equipment should be avoided. Equipment should be water washed before steamout. Where steamout is required, only low-pressure steam should be used for short periods of time to minimize exposure.

e) Proper design and operation of the injection system is required to ensure that caustic is properly dispersed before entering the high-temperature crude preheat system.

4.5.3.7  **Inspection and Monitoring**

a) 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.

b) PT may not be effective for finding tight, scale-filled cracks and should not be used as the only means of detection.

c) Fine cracks may be difficult to find with RT.

d) Crack depths can be measured with a suitable UT technique including external SWUT.

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

4.5.3.8  **Related Mechanisms**

Amine cracking (see 5.1.2.2) and carbonate cracking (see 5.1.2.5) are two other similar forms of alkaline SCC.

4.5.3.9  **References**

1. NACE 37519, NACE Corrosion Data Survey - Metals Section, Fifth Edition, NACE International, Houston, TX.
4. NACE SP0403, Avoiding Caustic Stress Corrosion Cracking of Carbon Steel Refinery Equipment and Piping, NACE International, Houston, TX.
Figure 4-146 – Recommended operating limits for carbon steel in caustic service. (Ref. 1)
Figure 4-147 – Cracking initiating on the inside surface of a non-stress relieved CS heat exchanger bend after 8 years in 15% to 20% caustic service at 140°F to 240°F (60°C to 115°C).

Figure 4-148 – Photomicrograph of a crack in the tube shown in Figure 4-147.
Figure 4-149 – Cracking at a boiler tubesheet due to caustic concentrating between the tube and the tubesheet.

Figure 4-150 – Photomicrograph of a crack in the tubesheet shown in Figure 4-149.
Figure 4-151 – Photomicrograph of caustic cracking initiating on the I.D. of a carbon steel socket weld in a non-PWHT’d piping in a suction drum downstream of a caustic scrubber. Unetched.

Figure 4-152 – Figure 4-151 in the etched condition.
Figure 4-153 – Stainless steel expansion bellows from a steam-driven turbine previously subjected to a caustic carryover upset condition.
4.5.4 Ammonia Stress Corrosion Cracking

4.5.4.1 Description of Damage

a) Aqueous streams containing ammonia may cause Stress Corrosion Cracking (SCC) in some copper alloys.

b) Carbon steel is susceptible to SCC in anhydrous ammonia.

4.5.4.2 Affected Materials

a) Some copper alloys in environments with aqueous ammonia and/or ammonium compounds.

b) Carbon steel in anhydrous ammonia.

4.5.4.3 Critical Factors

a) For copper alloys

i) Susceptible alloys may suffer cracking under the combination of residual stress and chemical compounds.

ii) Copper-zinc alloys (brasses), including admiralty brass and aluminum brasses, are susceptible.

iii) Zinc content of brasses affects susceptibility, especially as zinc increases above 15%.

iv) A water phase with ammonia or ammoniacal compounds must be present.

v) Oxygen is necessary, but trace amounts are sufficient.

vi) pH above 8.5.

vii) Occurs at any temperature.

viii) Residual stresses from fabrication or tube rolling are sufficient to promote cracking.

b) For steel

i) Anhydrous ammonia with <0.2% water may cause cracking in carbon steel.

ii) Cracking has been reported as low as -27°F (-33°C) in laboratory testing. Crack growth rates and cracking susceptibility with increasing temperature and can occur at ambient or refrigerated conditions.

iii) PWHT eliminates susceptibility of most common steels (<70 ksi tensile strength).

iv) Contamination with air or oxygen increases tendency toward cracking.

v) High residual stresses from fabrication and welding increase susceptibility.

4.5.4.4 Affected Units or Equipment

a) Copper-zinc alloy tubes in heat exchangers.

b) Ammonia is present as a process contaminant in some services or may be intentionally added as an acid neutralizer.

c) Carbon steel is used for ammonia storage tanks, piping and equipment in ammonia refrigeration units as well as some lube oil refining processes.

4.5.4.5 Appearance or Morphology of Damage

a) Copper alloys

i) Surface breaking cracks may show bluish corrosion products.

ii) Exchanger tubes show single or highly branched cracks on the surface.

iii) Cracking can be either transgranular (Figure 4-154 to 4-155 or intergranular (Figure 4-156), depending on the environment and stress level.
b) For carbon steel
   i) Cracking will occur at exposed non-PWHT welds and heat-affected zones.
   ii) Cracking is primarily intergranular in nature.

4.5.4.6 Prevention / Mitigation
a) Copper alloys
   i) Copper-zinc alloys show improved resistance as zinc content decreases below 15%.
   ii) The 90-10CuNi and 70-30CuNi alloys are nearly immune.
   iii) SCC in steam service can sometimes be controlled by preventing the ingress of air.
   iv) 300 Series SS and nickel base alloys are immune.
b) Carbon steel
   i) SCC of steel can be prevented through the addition of small quantities of water to the ammonia (0.2% minimum). Consideration must be given to vapor spaces could have less than 0.2% water present due to partitioning of ammonia in water phase.
   ii) An effective PWHT of the vessel reduces residual stress to the point where ammonia SCC can be prevented.
   iii) Low strength steels (<70 ksi tensile strength) should be used.
   iv) Weld hardness should not exceed 225 BHN.
   v) Prevent ingress of oxygen into storage facilities. Low levels of oxygen (< 10 ppm) have been reported to lead to cracking under some conditions.

4.5.4.7 Inspection and Monitoring
a) For copper alloys
   i) Monitor pH and ammonia of water draw samples to assess susceptibility of copper alloys.
   ii) Inspect heat exchanger tubes for cracking using EC or visual inspection. Rolled area is highly susceptible.
b) For steel storage tanks and or piping in anhydrous ammonia
   i) WFMT welds inside tanks.
   ii) External UT Shear wave inspection using TOFD.
   iii) AET.

4.5.4.8 Related Mechanisms
Not applicable.

4.5.4.9 References
Figure 4-154 – Ammonia SCC in an inhibited admiralty tube UNS C44300, 0.75 in. diameter, BWG 16 (0.063 in. thick) with extruded fins.

Figure 4-155 – High magnification view of a cross-section of the tube in Figure 4-154 showing transgranular cracking. (Mag. 500X)
Figure 4-156 – High magnification view of a cross-section of a brass exchanger tube showing intergranular cracking.
4.5.5 Liquid Metal Embrittlement (LME)

4.5.5.1 Description of Damage
Liquid Metal Embrittlement (LME) is a form of cracking that results when certain molten metals come in contact with specific alloys. Cracking can be very sudden and brittle in nature.

4.5.5.2 Affected Materials
Many commonly used materials including carbon steel, low alloy steels, high strength steels, 300 Series SS, nickel base alloys and the copper alloys, aluminum alloys and titanium alloys.

4.5.5.3 Critical Factors
a) LME occurs in very specific combinations of metals in contact with low melting point metals such as zinc, mercury, cadmium, lead, copper and tin. Typical combinations of industrial significance are shown in Table 4-9.

b) High tensile stress promotes cracking, however, cracking can initiate simply through contacting the molten metal with the susceptible alloy. Very small quantities of the low melting point metal are sufficient to cause LME.

c) Tensile stress contributes to crack propagation rates. Cracking under load can be extremely rapid such that cracks may pass through the wall within seconds of contact with the molten metal.

d) Cracking can occur after long periods of time when contaminated surfaces are exposed to liquid metals.

e) A susceptible metal in contact with a low melting metal at low temperatures may crack later when the temperature rises above the melting temperature of the low melting alloy.

4.5.5.4 Affected Units or Equipment
a) During a fire, molten metals may drip onto or contact a susceptible metal. Examples include melted zinc galvanizing, cadmium electrical housings, tin or lead from solders, and melted copper components.

b) LME can occur in any location where the LME couples are found. A common example is 300 Series SS piping or vessels in contact with (or previously rubbed against) galvanized steel (Figure 4-157 and Figure 4-158).

c) In refineries, mercury is found in some crude oils and can condense in the atmospheric tower overhead system thereby embrittling brass, Alloy 400, titanium or aluminum exchanger components.

d) Failure of process instruments that utilize mercury can introduce the liquid metal into refinery streams (Figure 4-159).

e) LME of aluminum components has occurred in LNG facilities and cryogenic gas plant components due to condensation of liquid mercury.

4.5.5.5 Appearance or Morphology of Damage
a) Damage resulting from LME will appear as brittle cracks in an otherwise ductile material. LME can only be confirmed through metallography by the presence of intergranular cracks, usually filled with the low melting metal.

b) Techniques such as spectrographic analysis may be required to confirm the presence of the molten metal species.

4.5.5.6 Prevention / Mitigation
a) LME can only be prevented by protecting metal substrates from coming into contact with the low melting metal. For example, galvanized steel components should not be welded to 300 Series SS. 300 Series SS should be protected to avoid contact with galvanized components and overspray from zinc and inorganic zinc coatings.

b) Once cracking from LME has initiated, grinding out the affected area is not an acceptable fix.
4.5.5.7 **Inspection and Monitoring**

a) Cracks can be detected with MT examination for ferritic steel and PT examination for 300 Series SS and nickel base alloys.

b) Because of the high density of mercury, radiography has been used to locate deposits inside heat exchanger tubes.

4.5.5.8 **Related Mechanisms**

a) LME is also referred to as Liquid Metal Cracking (LMC).

b) Nickel alloys are susceptible to a similar mechanism caused by the nickel-nickel sulfide eutectic that forms at 1157°F (625°C).

4.5.5.9 **References**

Table 4-9 – Some LME Couples Susceptible to Embrittlement. (Ref. 1)

<table>
<thead>
<tr>
<th>Susceptible Alloy</th>
<th>Molten Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 Series SS</td>
<td>Zinc</td>
</tr>
<tr>
<td>Copper Alloys</td>
<td>Mercury</td>
</tr>
<tr>
<td>Alloy 400</td>
<td>Mercury</td>
</tr>
<tr>
<td>Aluminum Alloys</td>
<td>Mercury</td>
</tr>
<tr>
<td>High Strength Steels</td>
<td>Cadmium, Lead</td>
</tr>
</tbody>
</table>
Figure 4-157 – Sketch of a stainless steel elbow that suffered liquid metal embrittlement as a result of dripping molten zinc during a fire.

Figure 4-158 – Photomicrograph of a section of the elbow in Figure 4-157, illustrating the intergranular nature of zinc-filled cracks in stainless steel.
Figure 4-159 – Liquid metal embrittlement of Monel caused by mercury in an FCC gas plant overhead drum.
4.5.6 Hydrogen Embrittlement (HE)

4.5.6.1 Description of Damage

A loss in ductility of high strength steels due to the penetration of atomic hydrogen can lead to brittle cracking. Hydrogen Embrittlement (HE) can occur during manufacturing, welding, or from services that can charge hydrogen into the steel in an aqueous, corrosive, or a gaseous environment.

4.5.6.2 Affected Materials

Carbon steel and low alloy steels, 400 Series SS, Precipitation Hardenable (PH) SS and some high strength nickel base alloys.

4.5.6.3 Critical Factors

a) Three conditions must be satisfied:

i) Hydrogen must be present at a critical concentration within the steel/alloy.

ii) The strength level and microstructure of the steel/alloy must be susceptible to embrittlement.

iii) A stress above the threshold for HE must be present from residual stresses and/or applied stresses.

b) The hydrogen can come from:

i) Welding – if wet electrodes or high moisture content flux weld electrodes are used, hydrogen can be charged into the steel (delayed cracking).

ii) Cleaning and pickling in acid solutions.

iii) Service in high temperature hydrogen gas atmospheres, molecular hydrogen dissociates to form atomic hydrogen that can diffuse into the steel.

iv) Wet H₂S services or HF acid services in which atomic hydrogen diffuses into the steel. (Cyanides, arsenic and FeS can act as hydrogen recombination poisons that diminish the hydrogen gas reaction and allows for greater charging rates.)

v) Manufacturing – melting practices or manufacturing processes particularly where components are plated (hydrogen flaking).

vi) Cathodic protection.

c) The effect is pronounced at temperatures from ambient to about 300°F (149°C). Effects decrease with increasing temperature.

d) HE affects static properties to a much greater extent than impact properties. If the hydrogen is present and a sufficient stress is applied, failure can occur quickly.

e) The amount of trapped hydrogen depends on the environment, surface reactions and the presence of hydrogen traps in the metal such as imperfections, inclusions and pre-existing flaws or cracks.

f) The amount of hydrogen needed to have a measurable effect on the mechanical properties varies with the strength level, microstructure and heat treatment for the alloy. In some cases, thresholds of critical hydrogen concentrations have been established.

g) Stresses include cooling during manufacture, residual stresses from welding or applied loads.

h) Thick wall components are more vulnerable due to increased thermal stress and high restraint and take longer for hydrogen to diffuse out.

i) In general, as strength increases, susceptibility to HE increases. Certain microstructures, such as untempered martensite and pearlite, are more susceptible at the same strength level than tempered martensite. Carbon steel that is severely hydrogen charged will have lower toughness than with no hydrogen.
4.5.6.4 **Affected Units or Equipment**

a) Services where HE is a concern include carbon steel piping and vessels in wet H₂S services in FCC, hydprocessing, amine, sour water services and HF alkylation units. However, mild steel used for vessels and piping in most refining, fossil utility and process applications have low hardness and are usually not susceptible to HE except at weldments, particularly the HAZ, if suitable PWHT is not performed.

b) Storage spheres are often made of slightly higher strength steels and are more susceptible than most other refinery equipment.

c) Bolts and springs made of high strength steel are very prone to HE. (Alloys that have a tensile strength above 150 ksi can absorb hydrogen during electroplating and crack.)

d) Cr-Mo reactors, drums and exchanger shells on hydprocessing units and catalytic reforming units are susceptible if the weld heat-affected zone hardness exceeds 235 BHN.

4.5.6.5 **Appearance or Morphology of Damage**

a) Cracking due to HE can initiate sub-surface, but in most cases is surface breaking (Figure 4-160 to 4-161).

b) HE occurs at locations of high residual or tri-axial stresses (notches, restraint) and where the microstructure is conducive, such as in weld HAZ's.

c) On a macro-scale, there is often little evidence, although some materials will appear to have brittle fracture surfaces. On a microscale, the material will contain less ductile fracture surface, but must often be compared to a fracture without the presence of hydrogen.

d) In higher strength steels, cracking is often intergranular.

4.5.6.6 **Prevention / Mitigation**

a) Dependent on the source of the hydrogen, alloy composition and fabrication/heat treatment history.

b) Use lower strength steels and PWHT to temper the microstructure, improve ductility and reduce residual stresses and hardness.

c) During welding, use low hydrogen, dry electrodes and preheating methods. If hydrogen is expected to have diffused into the metal, an elevated temperature bake out [400°F or higher (204°C or higher)] may be required to drive the hydrogen out prior to welding.

d) Heavy wall equipment in hot hydrogen service requires controlled shutdown and start-up procedures to control the pressurization sequence as a function of temperature.

e) In corrosive aqueous services, apply a protective lining, SS cladding or weld overlay to prevent the surface hydrogen reactions.

4.5.6.7 **Inspection and Monitoring**

a) For surface cracking inspection use PT, MT or WFMT.

b) UT may also be useful in finding HE cracks.

c) RT often is not sufficiently sensitive to detect HE cracks.

d) If the source of hydrogen is a low temperature aqueous environment, hydrogen flux can be monitored using specialized instruments.

4.5.6.8 **Related Mechanisms**

Also known as hydrogen flaking, underbead cracking, delayed cracking, hydrogen assisted cracking, hydrogen induced cracking. Sulfide stress cracking (see 5.1.2.3) and hydrogen stress corrosion cracking in HF (see 5.1.2.4) are closely related forms of hydrogen embrittlement.
4.5.6.9 References


Figure 4-160 – a.) Cracking due to hydrogen embrittlement of a carbon steel tube. b.) Intergranular crack emanating from surface in the tube.
Figure 4-161 – a.) Hydrogen Embrittlement of Martensitic SS Pump Parts. b.) High magnification photomicrograph of fracture surface showing intergranular nature of cracking.
4.5.7 Ethanol Stress Corrosion Cracking (SCC)

4.5.7.1 Description of Damage
Surface-initiated cracks caused by environmental cracking of carbon steel under the combined action of tensile stress and a fuel grade ethanol (FGE, ASTM D 4806) or FGE / gasoline blend environment. Dissolved oxygen and the presence of variable stresses such as cyclic stress or component flexing, increase the propensity for cracking.

4.5.7.2 Affected Materials
a) All grades of carbon steel are susceptible.
b) Ethanol SCC has not been reported in materials other than carbon steel, but general corrosion may be a concern with other materials including some alloys of aluminum, copper and copper alloys, lead and zinc.
c) FGE and blends with gasoline may adversely affect non-metallic materials (e.g. coatings and seals) causing swelling, hardness changes, etc.

4.5.7.3 Critical Factors
a) Several factors have been identified by field observations.
i) Stress may be applied or residual. Highly stressed, locally cold worked components, or components with stress concentrators are susceptible to cracking. Variable stresses, such as those produced by loading and unloading of tanks, have led to cracking in tank bottoms and floating roofs.
ii) Cracking has been found to occur in FGE meeting ASTM D 4806 specifications, including the water content requirement.
iii) Corrosion inhibitors may be added to ethanol to prevent general corrosion in vehicle fuel systems, but their affect on SCC is not fully understood.
b) Other factors have been identified in controlled laboratory conditions using conservative Slow Strain Rate Test (SSRT) methods which stress the steel sample to failure. Evidence of SCC is based on the stress / strain behavior and an examination of the fracture surfaces.
i) Aeration (i.e. the dissolved oxygen content) of the ethanol appears to be the most important factor for determining ethanol SCC susceptibility. Cracking has not been found under deaerated conditions.
ii) The maximum potential for ethanol SCC occurs within a narrow range of water content between 0.1 and 4.5 vol%.
iii) Ethanol SCC has been found to occur in blends of FGE and gasoline containing as little as 20 vol% FGE.
iv) Galvanic coupling of a new steel to corroded steel increases the likelihood of ethanol SCC.
v) Increasing the chloride content of the ethanol tends to increase the severity of cracking and changes the crack type from mainly intergranular found in the field to transgranular cracking.

4.5.7.4 Affected Units or Equipment
a) Carbon steel storage tanks, rack piping, and associated equipment are susceptible to ethanol SCC. All grades of carbon steel are susceptible.
b) Cracking has also been reported in a pipeline used to transport FGE to and from a terminal.
c) Ethanol SCC has not been reported in FGE manufacturers’ equipment and tankage, or in transportation equipment (barges, trucks, railcars).
d) Cracking has not been reported in equipment handling FGE after it has been blended with gasoline at end-use concentrations in unleaded gasoline (10 vol%). There has been one reported failure of an end-user E-85 tank.
4.5.7.5 **Appearance or Morphology of Damage**

a) Ethanol SCC is often found in the vicinity of welds and can appear as cracks that are parallel to the weld or transverse to the weld (Figures 4-162 to 4-169).

b) Cracks are typically tight and may be filled with corrosion product.

c) Ethanol SCC cracks are typically branched and intergranular, but transgranular or mixed-mode cracking has also been reported. Field failures tend to be intergranular, while laboratory testing has produced all crack morphologies. The cracking mode appears to depend on the chloride level, with an increased chloride content tending to shift the cracking from intergranular to transgranular or mixed mode.

d) Microrostructure of materials subjected to ethanol SCC are typically ferrite, or ferrite and pearlite.

4.5.7.6 **Prevention / Mitigation**

a) The likelihood of ethanol SCC can be reduced though PWHT (when possible) or by applying coatings. Given the high threshold stress intensities required to initiate ethanol SCC, standard carbon steel PWHT is expected to be effective. Research to confirm this is currently under way.

b) Avoid designs with highly localized tensile stresses.

c) Avoid the usage of lap seam welds that may concentrate strain in components.

d) Minimize cold working during fabrication.

4.5.7.7 **Inspection and Monitoring**

a) It is difficult to visually detect ethanol SCC because the cracks are typically tight and filled with corrosion product. Some small leaks may occur before an ethanol crack can be visually detected.

b) WFMT is the preferred method for detecting ethanol cracking. Methods for ethanol SCC inspection are similar to those used for detecting other types of SCC.

c) Shear wave UT may be used in instances where WFMT is not feasible.

d) ACFM can be used with less surface preparation than WFMT in areas such as weld HAZ's.

e) EC is unproven as a method for detection of ethanol SCC.

4.5.7.8 **Related Mechanisms**

Ethanol SCC is assumed to be similar to other reported in methanol and various alkaline aqueous solutions.

4.5.7.9 **References**


Figure 162 - Ethanol SCC in steel tank bottom. Note crack running parallel to fillet weld in striker plate.

Figure 163 - Ethanol SCC in a steel air eliminator vessel. Note cracks running perpendicular to the weld.
Figure 164 - A leak in piping resulting from an ethanol SCC adjacent to the weld.

Figure 165 - SCC in steel pipe from a loading rack supply line. The top figure shows a 7-inch long crack parallel to the weld root on the pipe ID surface. The bottom picture is a cross-section of above crack showing initiation outside the weld heat affected zone on the pipe’s inside surface (Nital etch).
Figure 166 - SCC of steel piping in a fuel ethanol system return line/tank transfer line. The top picture shows the crack parallels the pipe-to-tee circumferential weld. The bottom picture shows the inside and outside of the pipe after splitting and cleaning the weld area. Parallel SCC cracks are clearly visible adjacent to the weld.
Figure 167 - The top picture shows cracking initiating in the base metal on the ID of a section of piping adjacent to the weld. The bottom picture is a high magnification photomicrograph of the crack above illustrating the predominately intergranular nature of the cracking. (380X – Nital etch)
Figure 168 - Transverse cross-section of a piping section exposed to fuel ethanol showing multiple crack initiation sites characteristics of SCC.

Figure 169 - Photomicrograph of SCC in a steel tank bottom showing highly branched, intergranular cracks at 100 X.
4.5.8 Sulfate Stress Corrosion Cracking

4.5.8.1 Description of Damage
Surface initiated cracks caused by environmental cracking of copper alloys in sulfate solutions over many years. Most commonly found in heat exchanger tubes, primarily in cooling water services.

4.5.8.2 Affected Materials
a) Some copper alloys are highly susceptible, especially admiralty brass.
b) The 90/10 and 70/30 copper nickel alloys are more resistant.

4.5.8.3 Critical Factors
a) Susceptible alloys may suffer cracking under the combination of stress and the presence of sulfate chemical compounds. Residual stresses are sufficient to promote cracking.
b) The process environment must contain sulfates as part of the process or where sulfates can form due to reactions with other chemical species.
c) Ammonia is usually present, often at very low concentrations.
d) Cracking usually occurs over a period of many years, sometimes taking as long as 10 to 15 years to cause tube leaks.

4.5.8.4 Affected Units or Equipment
Sulfate SCC is most often associated with tubes in heat exchanger bundles in overhead distillation systems where sulfates can form or are present in low concentrations. Crude tower overhead exchangers are one example where this form of damage has been observed.

4.5.8.5 Appearance or Morphology of Damage
a) Exchanger tubes show single or highly branched cracks on the surface.
b) Upon metallurgical examination, the cracks will have a branched, transgranular appearance which may be visually difficult to differentiate form ammonia stress corrosion cracking.
c) Tube failures usually result in slow leaks as opposed to tube rupture.

4.5.8.6 Prevention / Mitigation
a) It has been suggested that the life of susceptible copper alloy exchanger tubes may be lengthened by periodic cleaning once every five years but limited published information is available to support this claim.
b) Alloys that are highly resistant to ammonia stress corrosion cracking such as the 90-10CuNi and 70-30CuNi alloys are also highly resistant to sulfate SCC.
c) Non-copper based alloys are immune from this form of damage.

4.5.8.7 Inspection and Monitoring
a) Inspect heat exchanger tubes for cracking using EC or visual inspection.
b) Physical bending of sample tubes can also be performed to detect shallow cracks indicative of sulfate SCC in the beginning stages.
4.5.8.8 References