Damage Mechanisms Affecting Fixed Equipment in the Refining Industry

RECOMMENDED PRACTICE 571

FIRST EDITION, DECEMBER 2003

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4.2.3 Temper Embitterment

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 1100°F (343°C to 593°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 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.

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_{o}F (343_{o}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 hydroprocessing 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.

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).

iii) MPT's generally range from 350_{o}F (171_{o}C) for the earliest, most highly temper embrittled steels, down to 150_{o}F (38_{o}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 (deembrittled) by heating at 1150°F (620°C) for 2 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:

$J^* = (Si + Mn) \times (P + Sn) \times 10_4$ {elements in wt%}

$X = (10P + 5Sb + 4Sn + As)/100$ {elements in ppm}

iii) Typical J* and X factors used for 2.25 Cr steel are 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) 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 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 progress of temper embrittlement or until a major repair issue arises.

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*

1. R.A. Swift , “Temper Embrittlement in Low Alloy Ferritic Steels,” *CORROSION/76,* Paper #125, NACE, 1976.
2. R.A. White and E.F. Ehmke, “Materials Selection for Refineries and Associated Facilities,” National Association of Corrosion Engineers, NACE, 1991, pp. 53-54.
3. R. Viswanathan, “Damage Mechanisms and Life Assessment of High Temperature Components,” ASM International, 1989.

4. API Recommended Practice 934, *Materials and Fabrication Requirements for 2-1/4 Cr-1Mo and 3Cr-1Mo Steel Heavy Wall Pressure Vessels for High Temperature, High Pressure Service*, American Petroleum Institute, Washington, D.C.

4.2.7 Brittle Fracture

4.2.7.1 *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) When the critical combination of three factors is reached, brittle fracture can occur:

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 (no shear lip or localized necking around the crack) (Figure 4-6 to Figure 4-7).

b) Microscopically, the fracture surface will be composed largely of cleveage, 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$_o$F (475$_o$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, New York.
3. British Standard 7910, *Guidance on Methods for Assessing the Acceptability of Flaws in Fusion Welded Structures*, British Standards Institution, London, UK.
4. *ASME Boiler and Pressure Vessel Code*, Section III, Division I, *Rules for Construction of Nuclear Power Plant Components* ASME, New York, N.Y.

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 swing exceeds about 200°F (93$_o$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 locations where condensate comes in contact with steam systems, such as de-superheating or attemporating equipment (Figure 4-11).

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 4–12 and Figure 4–13).

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 4-14). 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 (Figure 4-15). 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.

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***

1. “Steam - Its Generation and Use,” 40th Edition, Babcock & Wilcox, 1992.
2. “Combustion Fossil Power Systems,” Third Edition, *Combustion Engineering*, CT, 1981.
3. H. Thielsch, “Defects And Failures In Pressure Vessels and Piping,” Krieger Publishing Co., NY, 1977.
4. R.D. Port and H.M. Herro, “The NALCO Guide To Boiler Failure Analysis,” McGraw Hill, NY, 1991.
5. D.N. French, “Metallurgical Failures In Fossil Fired Boilers,” John Wiley & Sons, Publishers, Inc., NY, 1993.
6. B. Dooley and W. McNaughton, “Boiler Tube Failures: Theory and Practice – 3 Volumes,” EPRI, CA, 1995.

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) Increasing hardness of the metal substrate 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 4-3. 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 affects 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 erosioncorrosion.

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; coke handling equipment in both delayed and fluidized bed cokers (Figure 4-23); and as wear on pumps (Figure 4-24 and Figure 4-25), 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 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*

1. *ASM Metals Handbook*, Volume 13, “Corrosion,” ASM International, Materials Park, OH.

2. *ASM Metals Handbook*, Volume 11, “Failure Analysis and Prevention,”, ASM International, Materials Park, OH.

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 amptitude.

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 10_6 to 10_7 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) Rotating shafts on centrifugal pumps and compressors that have stress concentrations due to changes in radii and key ways.

ii) 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.

iii) 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 4-29 and Figure 4-30). This signature pattern results from the “waves” of crack propagation that occur during every cycle 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 4-31, Figure 4-32 and Figure 4-33.).

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***

1. “Fracture and Fatigue Control in Structures,”J.M. Barsom and S.T. Rolfe, American Society for Testing and Materials, West Conshohocken, PA.

2. ASTM STP1428, T*hermo-mechanical Fatigue Behavior of Materials*, American Society for Testing and

Materials, West Conshohocken, PA.

3. ASTM MNL41, *Corrosion in the Petrochemical Industry*, ASM International, Mateirals Park, OH, 1995.

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, H_2S, 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*

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.

4.3.2.6 ***Prevention / Mitigation***

Surface preparation and proper coating application are critical for long-term protection in corrosive

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***

1. ASM Metals Handbook, Volume 13, “Corrosion,” ASM International, Materials Park, OH.

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) Design of insulation system, insulation type, temperature, environment (humidity, rainfall and chlorides from marine environment, industrial environments containing high SO_2) are critical factors.

b) Poor design and/or installations that allow water to become trapped will increase CUI.

c) Corrosion rates increase with increasing metal temperature up to the point where the water evaporates quickly.

d) Corrosion becomes more severe at metal temperatures between the boiling point 212$_o$F (100$_o$C) and 250$_o$F (121$_o$C), where water is less likely to vaporize and insulation stays wet longer.

e) In marine environments or areas where significant amounts of moisture may be present, the upper temperature range where CUI may occur can be extended significantly above 250$_o$F (121$_o$C).

f) Insulating materials that hold moisture (wick) can be more of a problem.

g) Cyclic thermal operation or intermittent service can increase corrosion.

h) 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.

i) Damage is aggravated by contaminants that may be leached out of the insulation, such as chlorides.

j) 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.

k) Environments that provide airborne contaminants such as chlorides (marine environments, cooling tower drift) or SO_2 (stack emissions) can accelerate corrosion.

4.3.3.4 ***Affected Units or Equipment***

a) Carbon and low alloy steels are subject to pitting and loss in thickness.

b) 300 Series SS, 400 Series SS and duplex SS are subject to pitting and localized corrosion.

c) 300 Series SS are also subject to Stress Corrosion Cracking (SCC) if chlorides are present, while the duplex SS are less susceptible.

4.3.3.5 ***Affected Units or Equipment***

a) Location Issues

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

b) Design Issues

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) The first few feet of a horizontal pipe run adjacent to the bottom of a vertical run is a typical a CUI location.

4.3.3.6 ***Appearance or Morphology of Damage***

a) 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 4-38 and Figure 4-39).

b) In some localized cases, the corrosion can appear to be carbuncle type pitting (usually found under a failed paint/coating system).

c) For 300 Series SS, specifically in older calcium silicate insulation (known to contain chlorides), localized pitting and chloride stress corrosion cracking can occur.

d) Tell tale signs of insulation and paint/coating damage often accompany CUI.

4.3.3.7 ***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) High quality coatings, properly applied, can provide long term protection.

c) 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.

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

e) 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.

f) 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.

g) Utilize multiple inspection techniques to produce the most cost effective approach, including:

i) Partial and/or full stripping of insulation for visual examination.

ii) UT for thickness verification.

iii) Real-time profile x-ray (for small bore piping).

iv) Neutron backscatter techniques for identifying wet insulation.

v) Deep penetrating eddy-current inspection (can be automated with a robotic crawler).

vi) IR thermography looking for wet insulation and/or damaged and missing insulation under the jacket.

vii) 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 - Base Resource Document*, 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.

3. W.I. Pollock and C.N. Steely, “Corrosion Under Wet Thermal Insulation,” NACE International, Houston, TX, 1990

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$_{o}$F (60$_{o}$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 $_{o}$F (46$_{o}$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$_{o}$F (82$_{o}$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 4-40), 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 135$_{o}$F (57$_{o}$C).

c) Minimum and maximum water velocities must be 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*

1. T.J. Tvedt, Jr., “Cooling Water Systems,” NACE Course Book on Corrosion Control in the Refining Industry, NACE International, Houston, TX, 1999.

2. H.M. Herro and R.D. Port, “NALCO Guide to Cooling Water System Failure Analysis,” McGraw-Hill, Inc., NY, 1991, pp. 259-263.

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.

b) Critical factors are the concentration of dissolved gas (oxygen and 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 Fe_3O_4 (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 ammoniacal 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.

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.

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 deareator 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***

CO_2 corrosion (see 4.3.6), corrosion fatigue (see 4.5.2), and erosion/erosion-corrosion (see 4.2.14).

4.3.5.9 ***References***

1. “Betz Handbook of Industrial Water Conditioning,” Eighth Edition, Betz Laboratories, Inc., PA, 1980.

2. R.D. Port and H.M. Herro, “The Nalco Guide to Boiler Failure Analysis,” McGraw-Hill, Inc., NY, 1991.

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.

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$_o$F (260$_o$C). The typical effects of increasing temperature, chromium content and sulfur content on metal loss are shown in Figure 4-65 and Figure 4-66.

d) In general, the resistance of iron and nickel base alloys is determined by the chromium content of the material. Increasing the chromium content significantly increases resistance to sulfidation. 300 Series SS, such as Types 304, 316, 321 and 347, are highly resistant in most refining process environments. Nickel base alloys are similar to stainless steels in that similar levels of chromium provide similar resistance to sulfidation.

e) Crude oils, coal and other hydrocarbon streams contain sulfur at various concentrations. Total sulfur content is made up of many different sulfur-containing compounds.

f) Sulfidation is primarily caused by H_2S 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 H_2S. Therefore, it can be misleading to predict corrosion rates based on weight percent sulfur alone.

g) 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.

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 (Figure 4-67).

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.

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*

1. H.F. McConomy, “High Temperature Sulfidic Corrosion in Hydrogen-Free Environments,” API Proceedings, Vol. 43, (III), pp. 78-96, 1963.

2. J. Gutzeit, “High Temperature Sulfidic Corrosion of Steels”, Process Industries Corrosion – The Theory and Practice,” NACE International, Houston, TX, 1986, pp. 171-189.

3. *ASM Metals Handbook*, “Corrosion in Petroleum Refining and Petrochemical Operations,” Volume 13, ASM International, Materials Park, OH.

4. E. B Backenstow et al, “ High Temperature Hydrogen Sulfide Corrosion”, *CORROSION*, Vol. 12, No. 1, 1956, pp 6t-16t.

5. NACE Task Group 176 Draft Report, “Overview of Sulfidic Corrosion in Petroleum Refining”, NACE International, Houston, TX, 2003.

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.

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$_{o}$F (60$_{o}$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 (Figure 4-77).

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 crazecracked appearance of the surface (Figure 4-78, Figure 4-79 and Figure 4-80).

d) Metallography of cracked samples typically shows branched transgranular cracks (Figure 4-81 and Figure 4-82). Sometimes intergranular cracking of sensitized 300 Series SS may also be seen.

e) Welds in 300 Series SS usually contain some ferrite, producing a duplex structure that is usually more resistant to Cl^-SCC.

f) 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*

1. C.P. Dillon, “Corrosion Control in The Chemical Process Industries,” Materials Technology Institute, MO, 1994, pp. 88-90.

2. “Corrosion Basics – An Introduction,” NACE International, Houston, TX, 1984, pp. 111-123.

4.5.2 Corrosion Fatigue

4.5.2.1 *Description of Damage*

A form of fatigue cracking in which cracks develop under the combined affects 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 attachments (Figure 4-83). 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 4-84). The crack tips themselves may be somewhat blunted but are oxide filled and transgranular.

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*

1. “Steam – Its Generation and Use,” 40th Edition, Babcock and Wilcox, 1992.
2. “Combustion Fossil Power Systems,” Third Edition, Combustion Engineering, CT, 1981.
3. H. Thielsch, “Defects and Failures In Pressure Vessels and Piping,” Krieger Publishing Co., NY, 1977.
4. R.D. Port and H.M. Herro, “The NALCO Guide To Boiler Failure Analysis,” McGraw Hill, NY, 1991.
5. D.N. French, “Metallurgical Failures in Fossil Fired Boilers,” John Wiley and Sons, Publishers, Inc., NY, 1993.
6. B. Dooley and W. McNaughton, “Boiler Tube Failures: Theory and Practice – 3 Volumes,” EPRI, 1995.
7. *ASM Metals Handbook*, “Materials Characterization,” Volume 10, ASM International, Materials Park, OH.

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 4-85.
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 4-86 and Figure 4-87).
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. Although failures have occurred at stresses that are low relative to yield, they are considered more rare (Figure 4-88 through Figure 4-91).
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.

4.5.3.4 *Affected Units or Equipment*

a) Caustic embrittlement is often found in piping and equipment that handles caustic, including H_2S 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 4-92).

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 is not effective for finding tight, scale-filled cracks and should not be used for detection.

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

d) 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.

2. “Fitness-For Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service,” *MPC Report FS-26*, Draft #5, Consultants Report, Materials Properties Council, NY, 1995.

3. J.K. Nelson, “Materials of Construction for Alkalies and Hypochlorites,” *Process Industries Corrosion - The Theory and Practice,* NACE International, Houston, TX, 1986, pp. 297-310.

5.1.2.3 Wet H2S Damage (Blistering/HIC/SOHIC/SSC)

5.1.2.3.1 *Description of Damage*

This section describes four types of damage that result in blistering and/or cracking of carbon steel and low alloy steels in wet H_2S environments.

a) Hydrogen Blistering

Hydrogen blisters may form as surface bulges on the ID, the OD or within the wall thickness of a pipe or pressure vessel. The blister results from hydrogen atoms that form during the sulfide corrosion process on the surface of the steel, that diffuse into the steel, and collect at a discontinuity in the steel such as an inclusion or lamination. The hydrogen atoms combine to form hydrogen molecules that are too large to diffuse out and the pressure builds to the point where local deformation occurs, forming a blister. Blistering results from hydrogen generated by corrosion, not hydrogen gas from the process stream. (Figure 5-21 and Figure 5-22.)

b) Hydrogen Induced Cracking (HIC)

Hydrogen blisters can form at many different depths from the surface of the steel, in the middle of the plate or near a weld. In some cases, neighboring or adjacent blisters that are at slightly different depths (planes) may develop cracks that link them together. Interconnecting cracks between the blisters often have a stair step appearance, and so HIC is sometimes referred to as “stepwise cracking” (Figure 5-23, Figure 5-24 and Figure 5-25).

c) Stress Oriented Hydrogen Induced Cracking (SOHIC)

SOHIC is similar to HIC but is a potentially more damaging form of cracking which appears as arrays of cracks stacked on top of each other. The result is a through-thickness crack that is perpendicular to the surface and is driven by high levels of stress (residual or applied). They usually appear in the base metal adjacent to the weld heat affected zones where they initiate from HIC damage or other cracks or defects including sulfide stress cracks (Figure 5-26 and Figure 5-27).

d) Sulfide Stress Corrosion Cracking (SSC)

Sulfide Stress Cracking (SSC) is defined as cracking of metal under the combined action of tensile stress and corrosion in the presence of water and H_2S. SSC is a form of hydrogen stress cracking resulting from absorption of atomic hydrogen that is produced by the sulfide corrosion process on the metal surface.

SSC can initiate on the surface of steels in highly localized zones of high hardness in the weld metal and heat affected zones. Zones of high hardness can sometimes be found in weld cover passes and attachment welds which are not tempered (softened) by subsequent passes. PWHT is beneficial in reducing the hardness and residual stresses that render a steel susceptible to SSC. High strength steels are also susceptible to SSC but these are only used in limited applications in the refining industry. (Figure 5-28 and Figure 5-29). Some carbon steels contain residual elements that form hard areas in the heat affected zones that will not temper at normal stress relieving temperatures. Using preheat helps minimize these hardness problems.

5.1.2.3.2 *Affected Materials*

Carbon steel and low alloy steels.

5.1.2.3.3 *Critical Factors*

a) The most important variables that affect and differentiate the various forms of wet H_2S damage are environmental conditions (pH, H_2S level, contaminants, temperature), material properties (hardness, microstructure, strength) and tensile stress level (applied or residual). These factors are outlined below.

b) All of these damage mechanisms are related to the absorption and permeation of hydrogen in steels.

i) pH

- Hydrogen permeation or diffusion rates have been found to be minimal at pH 7 and increase at both higher and lower pH’s. The presence of hydrogen cyanide (HCN) in the water phase significantly increases permeation in alkaline (high pH) sour water.
- Conditions which are known to promote blistering, HIC, SOHIC and SSC are those containing free water (in liquid phase) and:
- >50 wppm dissolved H_2S in the free water, or
- free water with pH <4 and some dissolved H_2S present, or
- free water with pH >7.6 and 20 wppm dissolved hydrogen cyanide (HCN) in the water and some dissolved H_2S present, or
- >0.0003 MPa (0.05 psia) partial pressure of H_2S in the gas phase.
- Increasing levels of ammonia may push the pH higher into the range where cracking can occur.

ii) H_2S

- Hydrogen permeation increases with increasing H_2S partial pressure due to a concurrent increase in the H_2S concentration in the water phase.
- An arbitrary value of 50 wppm H_2S in the water phase is often used as the defining concentration where wet H_2S damage becomes a problem. However, there are cases where cracking has occurred at lower concentrations or during upset conditions where wet H_2S was not ordinarily anticipated. The presence of as little as 1 wppm of H2S in the water has been found to be sufficient to cause hydrogen charging of the steel.
- Susceptibility to SSC increases with increasing H_2S partial pressures above about 0.05 psi (0.0003 mpa) H_2S in steels with a tensile strength above about 90 ksi or in steels with localized

zones of weld or weld HAZ hardness above 237 HB.

iii) Temperature

- Blistering, HIC, and SOHIC damage have been found to occur between ambient and 300$_o$F (150$_o$C) or higher.
- SSC generally occurs below about 180$_o$F (82$_o$C).

iv) Hardness

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

v) Steelmaking

- Blistering and HIC damage are strongly affected by the presence of inclusions and laminations which provide sites for diffusing hydrogen to accumulate.
- Steel chemistry and manufacturing methods also affect susceptibility and can be tailored to produce the HIC resistant steels outlined in NACE Publication 8X194.
- Improving steel cleanliness and processing to minimize blistering and HIC damage may still leave the steel susceptible to SOHIC.
- The disadvantage is that an absence of visual blistering may leave a false sense of security that H_2S damage is not active yet subsurface SOHIC damage may be present.
- HIC is often found in so-called “dirty” steels with high levels of inclusions or other internal discontinuities from the steel-making process.

vi) PWHT

- Blistering and HIC damage develop without applied or residual stress so that PWHT will not prevent them from occuring.
- High local stresses or notch-like discontinuities such as shallow sulfide stress cracks can serve as initiation sites for SOHIC. PWHT is highly effective in preventing or eliminating SSC by reduction of both hardness and residual stress.
- SOHIC is driven by localized stresses so that PWHT is also somewhat effective in reducing SOHIC damage.

5.1.2.3.4 *Affected Units or Equipment*

a) Blistering, HIC, SOHIC and SSC damage can occur throughout the refinery wherever there is a wet H_2S environment present.

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

c) Cyanides significantly increase the probability and severity of blistering, HIC and SOHIC damage. This is especially true for the vapor recovery sections of the fluid catalytic cracking and delayed coking units. Typical locations include fractionator overhead drums, fractionation towers, absorber and stripper towers, compressor interstage separators and knockout drums and various heat exchangers, condensers, and coolers. Sour water stripper and amine regenerator overhead systems are especially prone to wet H_2S damage because of generally high ammonia bisulfide concentrations and cyanides.

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

5.1.2.3.5 ***Appearance or Morphology of Damage***

a) All four forms of wet H_2S damage are best illustrated though the pictures and diagrams shown in Figure 5-21 through Figure 5-30.

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

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

5.1.2.3.6 ***Prevention / Mitigation***

a) Effective barriers that protect the surface of the steel from the wet H_2S environment can prevent damage including alloy cladding and coatings.

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

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

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

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

f) Specialized corrosion inhibitors can be used.

5.1.2.3.7 ***Inspection and Monitoring***

a) Process conditions should be evaluated by process engineers and corrosion/materials specialists to identify piping and equipment where conditions are most likely to promote wet H_2S damage. Field sampling of the free water phase should be performed on a periodic or as-needed basis to monitor conditions or changes in conditions, particularly if water washing or polysulfide injection is used.

b) Inspection for wet H_2S damage generally focuses on weld seams and nozzles. Since the consequences can be severe, refineries generally have a procedure to prioritize and execute inspection for this type of damage. General notes on inspection for wet H_2S damage are included below. However, for the development of more detailed inspection plans including methods, coverage and surface preparation, the reader is directed to extensive recommendations on detection and repair outlined in NACE RP0296.

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

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

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

f) AET can be used for monitoring crack growth.

5.1.2.3.8 *Related Mechanisms*

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

b) Amine cracking (see 5.1.2.2) and carbonate cracking (see 5.1.2.5) can also occur in wet H_2S environments, may be similar in appearance, and are sometimes confused with the various forms of wet H_2S damage.

5.1.2.3.9 *References*

1. NACE Standard RP0296, *Guidelines for Detection, Repair and Mitigation of Cracking of Existing Petroleum Refinery Pressure Vessels in Wet* H_2S *Environments*, NACE International, Houston, TX.
2. MPC Report FS-26, *Fitness-For Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service*, Draft 5, October 1995, Materials Properties Council, NY, 1995.
3. G.M. Buchheim, “Ways to Deal With Wet H_2S Cracking Revealed by Study,” *Oil and Gas Journal,* July 9, 1990, pp. 92-96.
4. R.B. Nielson et al, “Corrosion in Refinery Amine Systems,” Paper No. 571, *CORROSION/95*, NACE International, Houston, TX, 1995.
5. NACE Standard RP0472, *Methods and Controls to Prevent in-Service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments,* NACE International, Houston, TX.
6. NACE Publication 8X194, *Materials and Fabrication Practices for New Pressure Vessels used in Wet* H_2S *Refinery Service*, NACE International, Houston, TX, 1994.
7. R.D. Kane, R.J. Horvath, and M.S. Cayard, editors, “Wet H_2S Cracking of Carbon Steels and Weldments,” NACE International, Houston, TX, 1996.
8. NACE Standard MR0103, *Materials Resistant to Sulfide Stress Cracking in Corrosive Petroleum Refining Environments*, NACE International, Houston, TX, 2003.

5.1.3.1 High Temperature Hydrogen Attack (HTHA)

5.1.3.1.1 *Description of Damage*

a) High temperature hydrogen attack results from exposure to hydrogen at elevated temperatures and pressures. The hydrogen reacts with carbides in steel to form methane (CH_4) which cannot diffuse through the steel. The loss of carbide causes an overall loss in strength.

b) Methane pressure builds up, forming bubbles or cavities, microfissures and fissures that may combine to form cracks.

c) Failure can occur when the cracks reduce the load carrying ability of the pressure containing part.

5.1.3.1.2 ***Affected Materials***

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

5.1.3.1.3 ***Critical Factors***

a) For a specific material, HTHA is dependent on temperature, hydrogen partial pressure, time and stress. Service exposure time is cumulative.

b) HTHA is preceded by a period of time when no noticeable change in properties is detectable by normal inspection techniques.

c) The incubation period is the time period during which enough damage has occurred to be measured with available inspection techniques and may vary from hours at very severe conditions to many years.

d) Figure 5-35 contains curves that show a temperature/hydrogen partial pressure safe operating envelope for carbon and low alloy steels. Additional information on HTHA can be found in API RP 941.

e) The curves are reasonably conservative for carbon steel up to about 10,000 psi hydrogen partial pressure.

f) 300 Series SS, as well as 5Cr, 9Cr and 12 Cr alloys, are not susceptible to HTHA at conditions normally seen in refinery units.

5.1.3.1.4 ***Affected Units***

a) Hydroprocessing units, such as hydrotreaters (desulfurizers) and hydrocrackers, catalytic reformers, hydrogen producing units and hydrogen cleanup units, such as pressure swing absorption units, are all susceptible to HTHA.

b) Boiler tubes in very high pressure steam service.

5.1.3.1.5 ***Appearance or Morphology of Damage***

a) HTHA can be confirmed through the use of specialized techniques including metallographic analysis of damaged areas as described below (Figure 5-36).

b) The hydrogen/carbon reaction can cause surface decarburization of steel. If the diffusion of carbon to the surface is limiting, the reaction can result in internal decarburization, methane formation and cracking.

c) In the early stages of HTHA, bubbles/cavities can be detected in samples by a scanning microscope, although it may be difficult to tell the difference between HTHA cavities and creep cavities. Some refinery services expose low alloy steels to both HTHA and creep conditions. Early stages of HTHA can only be confirmed through advanced metallographic analysis of damaged areas (Figure 5-37).

d) In later stages of damage, decarburization and/or fissures can be seen by examining samples under a microscope and may sometimes be seen by in-situ metallography (Figure 5-38).

e) Cracking and fissuring are intergranular and occur adjacent to pearlite (iron carbide) areas in carbon steels.

f) Some blistering may be visible to the naked eye, due to either molecular hydrogen or methane accumulating in laminations in the steel.

5.1.3.1.6 *Prevention/Mitigation*

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

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

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

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

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

5.1.3.1.7 *Inspection and Monitoring*

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

b) Ultrasonic techniques using a combination of velocity ratio and backscatter have been the most successful in finding fissuring and/or serious cracking.

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

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

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

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

5.1.3.1.8 *Related Mechanisms*

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

5.1.3.1.9 *References*

1. API RP 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*, American Petroleum Institute, Washington, D.C.
2. J. Vitovec, F.H., “The Growth Rate of Fissures During Hydrogen Attack of Steels,” API Division of Refining, Vol. 44 {III} 1964, pp. 179-188.
3. Materials Property Council Report FS-26, “Fitness-for Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service,” Draft 5, Materials Properties Council, NY, 1995.